Stabilization of Polymers and Stabilizer Processes

ACS Library
Executive Secretary's Office

A symposium sponsored by
the Division of Industrial
and Engineering Chemistry
at the 153rd Meeting of the
American Chemical Society,
Miami Beach, Fla.,
April 11-13, 1967.

Norbert A. J. Platzer,
Symposium Chairman

ADVANCES IN CHEMISTRY SERIES **85**

AMERICAN CHEMICAL SOCIETY

WASHINGTON, D. C. 1968

Library of Congress Catalog Card 68–59459

PRINTED IN THE UNITED STATES OF AMERICA

Advances in Chemistry Series

Robert F. Gould, *Editor*

AMERICAN CHEMICAL SOCIETY PUBLICATIONS

FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

Synthetic polymers are fabricated into building materials, automotive parts, packaging containers, films, fibers, or surface coatings. For most of these applications they must be stable at processing temperature, withstand outdoor exposure, sunlight and microorganisms, and should be nonflamable. Without stabilization, most polymers deteriorate, discolor, and become brittle. Oxygen attack is accelerated by heat and ultraviolet light and begins at the weak spots of the polymer molecule, generally at the double bonds or tertiary hydrogens on branch points. It proceeds by either an ionic and/or free-radical mechanism and results in oxidation to peroxides and ozonides, followed by cleavage to olefins, alcohols, aldehydes, ketones, or acids, depolymerization or scisson to low molecular weight products, or crosslinking to a three-dimensional structure. Frequently several of these reactions occur simultaneously and interact, causing a series of degradation products. Some of the polymers show additional thermal degradation. For example, poly(vinyl chloride) splits off hydrogen chloride; polyacetals break at their ether bond; and polyamides depolymerize by the interaction of the amino with the carboxyl group. Plasticized vinyls are attacked by microorganisms. The purpose of stabilization is to conserve the original properties of the polymers in different environments.

To prevent degradation and burning, small quantities of chemicals are added to the polymers. Although the ratio of these chemicals to polymers is small, their effect is decisive for the endurance and life of the polymers. 1968's consumption of stabilizers and fire retardants is expected to pass the 350-million pounds mark for plastics and rubbers, as 1967 figures indicate (*see* Table I).

Table I. Domestic Consumption of Stabilizers and Fire Retardants in 1967

	Million Pounds
Thermal stabilizers	59.0
Antioxidants and antiozonants	124.1
Ultraviolet light absorbers	2.0
Fire retardants	129.0
Total	314.1

These chemicals are classified according to their applications. Thermal stabilizers are needed during thermoprocessing of some thermoplastics. Antioxidants, antiozonants, biocides and ultraviolet light absorbers are incorporated for outdoor use of structural plastics and elastomers. Fire retardants are classified into additive and reactive types and are added for the fire protection of flammable plastics. To counteract against the different breakdown reactions, a single stabilizer is often insufficient, and a combination of several stabilizers is necessary and often more effective through synergism. Other stabilizers protect against more than one type of degradation because some of the oxidative breakdown reactions caused by weather, light, heat, or fire are frequently similar and sometimes identical. A novel method of stabilization is effected by building small quantities of metals or comonomers into the polymer molecule.

Thermal Stabilization

The need for stabilization arises during the processing of certain thermoplastics. The temperature required to fuse polymer particles into a plastic product is often close to that of thermal decomposition. It is desirable to separate these temperatures by increasing decomposition temperature, not by decreasing the softening temperature.

Poly(vinyl Chloride). While many thermoplastics suffer from the heat applied during processing, by far the most susceptible is poly(vinyl chloride) (PVC). Therefore, six chapters in this book are concerned with the thermal stabilization of PVC. Its thermal degradation is caused by autocatalytic loss of hydrogen chloride, combined with oxidation, cleavage, and crosslinking. Both ionic molecular and free radical reactions are possible. It is believed that metal salts of inorganic and organic acids, which are acceptors of hydrogen chloride, are typical decelerators of ionic reactions, while antioxidants and hetero-organic compounds, such as dialkyltin derivatives, suppress free radical chain reaction.

Instability of the polymer is responsible for the primary step in decomposition and is attributed either to fragments of initiator or to branched chains or to terminal double bonds. The appearance of branching is the result of reactions of chain transfer through the polymer, while that of unsaturated terminal groups results from reaction of disproportionation and chain transfer through the monomer. During thermal and thermo-oxidative dehydrochlorination of PVC, allyl activation of the chlorine atoms next to the double bonds occurs. In this volume, Klemchuk describes the kinetics of PVC degradation based on experiments with allylic chloride as a model substance. He observed that thermal stabilizers replace the allylic chlorine at a faster ratio than the decomposition rate of the allylic chloride.

Consumption of thermal stabilizers in 1967 amounted to 59 million pounds (*see* Table I). Commercial stabilizers may be classified into four groups: (1) metal salts of inorganic and organic acids; (2) organometallic compounds; (3) epoxides; (4) inhibitors of free radical chain reactions.

Metal salts of inorganic and organic acids (*e.g.*, lead carbonate, calcium, barium, and zinc soaps) act as acceptors of hydrogen chloride. A few of them also decelerate dehydrochlorination by intercepting the zipperlike hydrogen chloride generation. Metals, such as lead, cadmium, or zinc, in which the *d*-layer of the electron shell next to the outer shell is filled, are better decelerators than metals such as calcium or barium, which contain no *d*-electron this shell. Metals, which are acceptors only, initiate frequently oxidative processes resulting in crosslinking and require the addition of inhibitors. Fuchsman deals with the distinction between thermal stabilizers which promote crosslinking and those which retard it.

Lead salts decelerate dehydrochlorination and slow crosslinking. Derivatives of phenols, aromatic hydroxy ketones, and similar compounds have no influence on the rate of dehydrochlorination but prolong the time of initial melt viscosity. Lead sulfate and lead phthalate are low in cost, provide excellent electrical properties, and are used in vinyl cable insulations. Lead stearate is employed in phonograph records. A combination of lead phosphite and lead phthalate is applied for converting plastisols into flexible foams. Lead stabilizers are generally incorporated at concentrations of 3 to 10 p.p.h. Barium and cadmium compounds are used together. Their synergism is caused by a rapid exchange of chlorine from barium to cadmium.

Among the organometallic stabilizers compounds of tetravalent tin are the most effective. They contain a C—Sn bond which can be broken during decomposition of the polymer, forming free radicals. They are used in rigid vinyls, mostly at a concentration of 1-3 p.p.h. Their relatively high cost, however, has limited their use in other vinyl formulations. Dibutyltin lauryl mercaptide and dibutyltin diisooctyl thioglycolate are extremely efficient thermal stabilizers. Weisfeld, Thacker, and Giamundo prefer dibutyltin lauryl mercaptide because it provides the lowest melt viscosity and therefore the best thermoprocessability. Dibutyltin laurate/maleate shows additional lubricating properties. Dioctyltins are less toxic than the dibutyltins and have been accepted in Europe as stabilizers for packaging food, drugs, and cosmetics.

PVC degradation may be measured by the amount of hydrogen chloride generated, by discoloration, or by change of electrical resistivity. In Chapter 4. Novak describes a test apparatus which allows one to measure all three effects simultaneously.

Epoxides can stabilize polymers either by reacting with hydrogen chloride forming chlorohydrin or by inhibiting the radical decomposition of hydroperoxides. Epoxy stabilizers are glycidyl esters condensation products of epichlorohydrin with phenols and aliphatic alcohols, epoxided esters of higher aliphatic acids, and alicyclic epoxyesters of aliphatic and aromatic acids and alcohols. They are used in combination with cadmium stearate and other metallic salts, owing to their synergistic effect. Cadmium salts by themselves give highest initial stability but fail rapidly during longer thermoprocessing. The combination extends the stabilization action. Hopff discusses the preparation and stabilizing effect of epoxides which are nontoxic and serve also as secondary plasticizers. They are added in quantities of 3-10 p.p.h.

The large group of inhibitors of free radical chain reactions are frequently used in combination with metal salts or organometallic stabilizers. They are amines, sulfur- or phosphorus-containing compounds, phenols, alcohols, or chelates. Aromatic phosphites at about 1 p.p.r. chelate have undesirable metal impurities and inhibit oxidative free radical reactions. Some of the more popular are pentaerythritol, sorbitol, melamine, dicyandiamide, and benzoguanamine. Their synergistic effect is utilized in vinyl floors where low cost is imperative.

Internal stabilization is a novel method of enhancing the thermal stability of vinyl polymers. Braun, who proposes this term, reports that metal salts of unsaturated carbonic acids are suitable comonomers acting as internal stabilizers. For example, a copolymer of vinyl chloride with only 0.3 mole % of lead undecylenate has a significantly longer and better thermal stability than externally lead-stabilized PVC.

Other Polymers. Various other polymers frequently require stabilization against thermal or thermo-oxidative degradation. Poly(vinylidene chloride) is stabilized by epoxides and sodium pyrophosphate.

Acetal resins are stabilized twice. They are made from polyformaldehyde in which the terminal hydroxy group is blocked by esterification against the zipperlike thermal destruction. The presence of oxygen accelerates the decomposition reaction and causes oxidation of formaldehyde to formic acid. The addition of 0.9–1.5 p.p.h. of a polyamide, as a formaldehyde acceptor, and of 0.6–1.0 p.p.h. of an antioxidant is used to prevent thermo-oxidative degradation. Thermal degradation of polyamides results in depolymerization caused by the interaction of the free terminal amino and carboxyl groups with the last amide bond of the same molecule. It is accelerated by the water content in the polymer. Polyamides are stabilized against thermal oxidation by adding either a common antioxidant or a copper salt (*e.g.*, copper naphthenate), a halogen or phosphorus compound, or a two- or three-component mixture.

Horowitz discusses organometallic systems of high thermal stability. Coordination polymers of bis(8-hydroxyquinoline) with Mn, Co, Ni, Cu, and Zn show outstanding thermal stability in the sequence cited.

Besides organic polymers, inorganic polymers also are susceptible to thermo-oxidative degradation. Nielsen describes the stabilization of silicone fluids with redox systems of iron and cerium by a free radical mechanism. When stabilized, these fluids show oxidative stability up to 700°F.

Antioxidants and Antiozonants

Almost all commercial polymers are susceptible to the attack of oxygen or traces of ozone in the atmosphere. Oxidation is the major cause of their discoloration, impairment of mechanical properties, and subsequent failure. It is accelerated by heat or sunlight. Antioxidants and antiozonants are added to the polymers to extend their useful temperature ranges and service lives and to allow outdoor application. Their 1967 consumption for various polymers is given in Table II.

Table II. Domestic Consumption of Antioxidants and Antiozonants in 1967

Polymer	*Million Pounds*
Rubber	117.4
Polyethylene	1.9
Polypropylene	2.6
Impact polystyrene	0.7
ABS	1.5
Total	124.1

Unsaturated and Vulcanized Rubbers. Oxidation occurs most readily at polymers with structural double bonds, such as natural rubber, polybutadiene, or polyisoprene. Aromatic amines and sterically hindered phenols are effective antioxidants. From the rubber antioxidants, 96.8 million pounds were amines, and 20 million pounds were phenols. Amines act also as antiozonants whereas phenols are not effective. Furukawa shows that amines have a lower oxidation potential which is a prerequisite for antiozonant action.

Aromatic amines, such as phenyl-β-naphthylamine or condensation products of diphenylamine with acetone condensates, are excellent antioxidants and antiozonants but cause color development. From the sterically hindered phenols, monocyclic phenols, such as 2,6-di-*tert*-butyl-*p*-cresol, are less effective antioxidants but remain white and nontoxic during aging. They are, however, volatile and provide poor protection at elevated processing temperatures. Polycyclic phenols, such as 2,2′-methylene-bis(4-methyl-6-*tert*-butylphenol), are relatively nonvolatile, but become discolored by oxidation to a conjugated system. O'Shea describes a process for using dialkylhydroxybenzyl-*N,N*-dimethyl dithiocarbamates as intermediates in the manufacture of novel non-discoloring polycyclic phenols.

The effectiveness of antioxidants depends substantially on whether raw or cured rubbers are used and how many free impurities and ingredients are present. For example, sulfur reduces the stabilizing power of aromatic amines, whereas dithiocarbamates enhance the stabilizing action.

ABS, impact polystyrene, impact acrylics, and rigid vinyls are generally polyblends with or graft copolymers on unsaturated rubbers, such as polybutadiene or nitrile rubber. They are, therefore, susceptible to oxidation and tend to crosslink with a decrease in elongation, toughness, and elastic properties. They are stabilized by adding monocyclic and polycyclic phenols, with and without thiodipropionate as synergist, and by adding aromatic phosphites.

Saturated Rubbers and Polyolefins. Saturated polyhydrocarbons, such as polyethylene, polypropylene, EVA, ethylene/propylene, and butyl rubber are more resistant to oxidation than unsaturated polymers. Oxidation of polyethylene occurs either at the tertiary hydrogen of the polymer branch points (LDPE) or at the unsaturated terminal points. Under the influence of heat or light, free radicals are formed and react with oxygen to give peroxy radicals. These pull hydrogen atoms from the polymer, producing hydroperoxides, which decompose to hydroxyl, carbonyl, and carboxyl groups, all of which are highly polar and ruin electrical insulating properties. Further decomposition causes scisson, crosslinking and embrittlement. Polypropylene is more susceptible to severe attack than is polyethylene since 17% of the hydrogens are in tertiary position.

Two types of antioxidants are used: One type—amines and phenolics—reacts with the peroxy radicals to form more stable free radicals. The second type—sulfur compounds and phosphites—decomposes the hydroperoxides without formation of free radicals. The effect of sulfur compounds, such as dialkyl dithiocarbamates and alkyl thiols on the hydroperoxide decomposition has been investigated by Marshall.

Thanks to proper stabilization, polypropylene has found outdoor applications as a low cost fiber and engineering material. Phenolic antioxidants, such as methylenebisphenol and thiobisphenol, are highly potent, nonvolatile, and solvent resistant but yellow on exposure to nitrogen oxides, always present in urban atmospheres. 2,6-Didodecyl-*p*-cresol and 2,6-dioctadecyl-*p*-cresol have been found as highly effective, nondiscoloring, and nonvolatile antioxidants. Lappin describes an economic process for the second product.

Commercial antioxidants of monocyclic phenols have only one hydroxy group in the molecule. Pospisil, Taimr, and Kotulak determined the activity of monocyclic dihydrobenzenes. They prepared numerous derivatives of pyrocatechol and hydroquinone and found that their performance as polyproylene stabilizers is significantly better than that of alkylated phenols. According to them, 4-alkyl derivatives of pyrocatechol appear to be the best and pyrocatechol better than hydroquinone which has the advantage of being non-staining.

Polymeric phenolic phosphites represent a new family of polypropylene stabilizers acting through their phenolic group as free radical scavengers and through their phosphite group as hydroperoxide decomposers. They are polymeric reaction products of substitute hydroquinones with phosphorus trichloride, as described by DePaolo and Smith. In contrast to aryl phosphites and phenolic stabilizers, polymeric phenolic phosphites act also as ultraviolet light absorbers. They also provide outstanding heat stability when used in synergism with thiodipropionate.

To evaluate antioxidants for polypropylene, various test methods have been developed. Gordon correlates these methods, and Gysling suggests a modified oven-aging technique and shows antioxidant synergist combinations.

Microbial Stabilizers

Fungi and bacteria do not attack synthetic polymers themselves but their formulated compounds. Their attack on plasticized PVC depends on the type of plasticizer used, residual surfactants, and other ingredients. The attack manifests itself in discolored spots and reduction in physical properties, such as flexibility, elongation, and strength. The purpose of adding biocides is twofold: to control the bacteria and fungi growth on the surface for health reasons and to prevent microbial degradation. Eisenschiml and Bauer describe the phenomena of microbe attack and report on the arsine-epoxy adduct as the most universal microbiocide.

Ultraviolet Light Absorbers

For long, dependable, outdoor service, plastics must be protected not only against oxidation but also against the most damaging portion of sun rays, ultraviolet light. Vinyl polymers, such as polystyrene or poly(methyl methacrylate), do not absorb ultraviolet light directly. They contain small quantities of chromophoric impurities, such as peroxides and ketones, which absorb light and break down the polymers. Other polymers, such as poly(methyl vinyl ketone) or poly(ethylene terephthalate), contain chromophoric ester or keto carbonyl groups. The kinetics of photodegradation in polymers have been studied extensively by Guillet and co-workers, who built chromophoric groups into the backbone and into the side chains of polymers.

Commercially, there are two ways to protect against ultraviolet light, either to pigment the plastic with carbon black or titanium oxide, or to add ultraviolet light absorbers which are colorless. They absorb ultraviolet light and transform it into harmless, longer, infrared wavelength. Some of them, such as the benzophenones, work through a reversible photoenolization. There are six classes of commercial ultraviolet light absorbers: benzophenones, benzotriazoles, salicylates, substituted acrylonitriles, phenyltriazines, and monobenzoates. In addition, the nickel thiophenolates must be mentioned, which provide little ultraviolet light absorption but serve as free radical scavengers and prevent the propagation of photochain degradation. They are used together with ultraviolet light absorbers owing to their synergistic effect.

The major use of ultraviolet light absorbers is in polyolefins, poly(vinyl chloride), polyesters, cellulose esters, and polystyrene, as Table III indicates. Lesser quantities are used in polyamides, acrylics, polyacetals, and polyurethanes.

For polyolefins, 2-hydroxy-4-*n*-octoxybenzophenone, seems to be preferred on a cost-performance basis. In rigid vinyls, 2-hydroxy-4-methoxybenzophenone is more widely used on a commercial basis. The largest quantity of light stabilized plastics is used outdoors, in skylights, automobile and store window glazing, street light globes, stadium seats, carpets, marine ropes, lawn chair webbing, awnings, corrugated sheets, agricultural films, spar varnishes, and surface coatings. Considerable quantities are finding more and more indoor applications for protection against degradation caused by fluorescent lighting, such as in light diffusers, false ceilings, partitions, plastisol-coated floor tiles, lamp shades, and blown bottles. Light diffusers made from light-stabilized polystyrene cost less than those from poly(methyl methacrylate) but are inferior in life. Savides and co-workers show that the light stability of polystyrene can be improved significantly by the combination of an ultraviolet light

Table III. Domestic Consumption of Ultraviolet Light Absorbers in Plastics during 1967

Polymer	*Million Pounds*
Polyolefins	0.7
Poly(vinyl chloride)	0.3
Polyester	0.3
Cellulose esters	0.2
Polystyrene	0.2
Other plastics	0.1
Coatings, etc.	0.2
Total	2.0

absorber and a phenolic antioxidant which acts as a free radical scavenger. This again illustrates the close relationship between oxidation and photodegradation.

Fire Retardants

Burning may be considered another means of oxidation. Non-burning plastics are a must in commercial constructions according to building codes and are often required for automotive, electronic, and electrical applications. From the numerous thermoplastics, only the halogen-containing polymers, polyamides, polycarbonate, poly(phenylene oxide), polysulfone, and polyimides are self-extinguishing. Even these, such as poly(vinyl chloride), may become flammable when plasticized with a flammable plasticizer. Fire control can be the key to volume use of plastics. Polyester panels, urethane foam, and PVC tarpaulins account for nearly 90% of all fire retardants consumed. Consumption in 1967 amounted to 129 million pounds as Table IV indicates. Fire retardants are here classified into four types. From the inorganic fillers, 16 million

Table IV. Domestic Consumption of Rire Retardants in 1967

	Million Pounds
Inorganic Fillers	
Antimony oxide, zinc borate, ammonium phosphate, ammonium bromide, ammonium sulfamate	21
Others	1
Sub-total	22
Additive Types	
Phosphate esters and halogenated esters	50
Chlorinated paraffins	8
Chlorinated polyphenyls, brominated aliphatic esters, acetylene tetrabromide	5
Sub-total	63
Reactive Types	
Chlorendic acid and anhydride	18
Phosphorus containing polyols	7
Others	19
Sub-total	44
Retardant Coatings	
Intumescent and nonintumescent	2
Total	129

pounds of antimony oxide are used in plasticized PVC and 4 million pounds in polyolefins and polyesters. Since antimony oxide must be used in conjunction with a halogen-containing compound, it is necessary to add chlorinated or brominated fire retardants when used with polyolefins and polyesters. Generally, from 3 to 5 p.p.h. of antimony oxide are used with PVC, but 20 p.p.h. of antimony oxide plus 20 p.p.h. of chlorinated wax are used with polyethylene.

The organic fire retardants are generally better fire retardants, but they lower the maximum use temperature of the material. Frequently, a combination of inorganic fillers and organic retardants is used to achieve a synergistic effect.

The volume leaders among fire retardants with 35 million pounds were the three phosphate plasticizers for PVC: tricresyl phosphate, cresyl diphenyl phosphate and triphenyl phosphate. The remaining 6 million pounds were made up of octyl diphenyl phosphate, tributyl phosphate, tri(dibromopropyl) phosphate, tri(dichloropropyl) phosphate and tri(chloroethyl) phosphate. Polymeric phosphorus and phosphorus halogen-containing additives are used in concentrations of 3–25 p.p.h. in polyesters, flexible and rigid polyurethane foam, and phenolics.

In contrast to stabilizers, fire retardants must be added in much higher concentrations, which affect thermal and mechanical properties as well as cost. Sherr and co-workers report that novel derivatives of phosphine oxides, phosphonic acids, phosphinic acid, and phosphonium halides may be used generally in concentrations as low as 2.5–5 p.p.h. to be effective fire retardants in polyethylene and poly(methyl methacrylate).

Chlorinated paraffins, which contain up to 60–70% chlorine, are low in cost and are used as secondary plasticizer in PVC wire and cable insulations. Perchlorobicyclopentadiene has little plasticizing action and is used in polyethylene. Some of the more expensive bromine-containing fire retardants which have been used in the ratio of 5 p.p.h. in polystyrene foam, may be reduced to 0.5 p.p.h. by adding synergists such as peroxides or nitroso compounds. The reaction-type retardants, such as chlorendic acid and anhydride, hydroxy-terminated phosphonated esters, and specific brominated aliphatic esters, are admixed to rigid and flexible polyurethane foams, reinforced polyesters, phenolics, and epoxy resins.

The surface of flammable plastics may be protected by a fire-retardant coating. Intumescent coatings generally contain inorganic salts which will bubble and foam on heating to form a thick nonflammable, multicellular insulative barrier over the plastics surface. These inorganic salts are unstable to moisture, chlorinated paraffin dispersions, and phosphorus-based retardants. Intumescent coatings are applicable for the interior protection of ABS sheets and foam ceiling tiles. Non-intumescent coatings contain halogenated compounds, such as PVC or chlorinated paraffin, in conjunction with antimony oxide. They are less effective fire retardants but more stable and are used for outdoor applications.

Review

On the subject of stabilization and fire-proofing commercial polymers, only one textbook (*1*) and a few summary articles (*2, 3, 4, 5, 6*) exist besides specific publications. It is hoped that this book will show the importance of this area to the industry. The trend is to use plastics more and more outdoors and under severe environments. The achievements of the experts and authors of the following chapters are aimed for this target.

Bibliography

(1) Neiman, M. B., "Aging·and Stabilization of Polymers," translated from the Russian, Consultants Bureau, New York, 1965.
(2) Deanin, R. D., *SPE J.* **22,** 9, 12 (Sept. 1966).
(3) *Mod. Plastics* **44,** 1, 95 (Sept. 1966).
(4) *Mod. Plastics Encyclopedia* **1965, 1966, 1967, 1968.**
(5) *Plastics World* **25,** 2 28 (Feb. 1967).
(6) Wett, T. W., *Chem. Mater.* 13 (March 1965).

Springfield, Mass. NORBERT A. J. PLATZER
January 1968

1

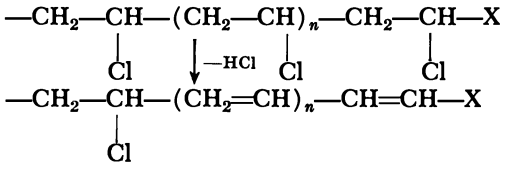
Poly(vinyl chloride) Stabilization Mechanisms

PETER P. KLEMCHUK

Geigy Research Laboratories, Ardsley, N. Y.

Investigation of the kinetics of the reaction of 4-chloro-2-pentene, an allylic chloride model for the unstable moiety of poly(vinyl chloride), with several thermal stabilizers for the polymer has led to a better understanding of the stabilization mechanism. One general feature of the mechanism is complexing of the labile chlorine atom by the metal atom of the stabilizer. A second general feature is substitution of the complexed chlorine atom by a ligand (either carboxylate or mercaptide) bound to the metal. Stabilization requires that the new allylic substituent (ester or sulfide) be more thermally stable than the allylic chlorine. The isolation of products from stabilizer-model compound reactions supports the substitution hypothesis of poly(vinyl chloride) stabilization.

The thermal degradation of poly(vinyl chloride) is now well understood to be caused by the ordered loss of hydrogen chloride, initiated at an unstable site, which results in the formation of long, colored polyene chains:



$$\begin{array}{l} -CH_2-\underset{|}{\underset{Cl}{CH}}-(CH_2-\underset{Cl}{CH})_n-CH_2-\underset{Cl}{CH}-X \\ \qquad\quad \downarrow -HCl \\ -CH_2-\underset{Cl}{CH}-(CH_2{=}CH)_n-CH{=}CH-X \end{array}$$

(X = activating group)

The head-to-tail structure of poly(vinyl chloride) permits the continuous regeneration of an allylic chloride moiety as hydrogen chloride elimination proceeds along a chain. Thus, once initiated, loss of hydrogen chloride may proceed along a polymer chain without abatement.

Allylic chloride (*3*, *6*) and tertiary chloride (*6*) functionalities have been implicated as the unstable sites which initiate dehydrochlorination. Peroxide and hydroperoxide functionalities have also been implicated by some investigators (*11, 12, 13*), and free radical degradation and stabilization mechanisms have been postulated (*10, 13*). The allylic chloride and groups result primarily from chain termination to monomer (*4*). Chain termination by disproportionation may make a small contribution. About 60 terminal allylic chloride groups were estimated to be present among every 100 polymer molecules in one poly(vinyl chloride) sample (*3*). Tertiary chloride groups, estimated in one sample at 20 per polymer molecule, are postulated to arise from chain transfer *via* hydrogen abstraction between a polymer molecule and a growing radical chain (*5*). A study of the thermal decomposition of model compounds led to the following order of increasing stability: tertiary chloride, internal allylic chloride, terminal allylic chloride, secondary chloride (*1, 2*). However, Baum and Wartman (*3*) conclude that hydrogen chloride loss is initiated primarily from terminal unsaturation and that initiation from tertiary chloride is much less important.

Most thermal stabilizers for poly(vinyl chloride) are metal salts of carboxylic acids or mercaptans. The commonly used metals are cadmium, barium, zinc, lead, calcium, and dibutyltin. Originally it was assumed the metal salts act as scavengers for hydrogen chloride. However, Frye and Horst (*7, 8*) found evidence for the introduction of ester groups in the polymer from metal carboxylate stabilizers, which led them to postulate that thermal stabilizers function by substituting the unstable chlorine atoms with the ligands of the stabilizer to yield derivatives which are more thermally stable than the original chloride.

This paper presents the results of a study of the reactions of several thermal stabilizers for poly(vinyl chloride) with an allylic chloride model and a tertiary chloride model. The findings of this study provide considerable insight into the mechanism of stabilizer action.

Experimental

Materials. Chlorobenzene (Matheson) was washed with concentrated sulfuric acid, then with water, dried with anhydrous magnesium sulfate, and distilled.

Dibutyltin dilaurate and dibutyltin maleate, commercial stabilizers Thermolite 12 and Thermolite 13 (Metal and Thermit), were used without further purification. Dibutyltin β-mercaptopropionate (Advastab T 360, Advance Solvents) was recrystallized twice from ethyl acetate. Dibutyltin dichloride (Matheson) was recrystallized twice from *n*-heptane, m.p. 41.0°–43.0°C. The other dibutyltin compounds used were prepared by the reaction of dibutyltin oxide with the carboxylic acid or mercaptan in refluxing toluene with water being retained in a Dean-Stark trap. Filtration of the resulting solution through filter aid, followed by concentration under vacuum to constant weight, gave the desired compounds in virtually quantitative yield. Cadmium 2-ethylhexanoate was prepared in refluxing methanol from the reaction of cadmium oxide and the acid.

Zinc 2-ethylhexanoate was prepared in refluxing toluene from the reaction of 2-ethylhexanoic acid with zinc oxide. The lead salt was prepared in methanol by the reaction of lead acetate with 2-ethylhexanoic acid. The reaction of barium oxide with 2-ethylhexanoic acid in toluene provided the barium salt.

4-CHLORO-2-PENTENE. 1,3-Pentadiene ("Baker"; 100 grams, 1.47 moles) reacted with 60 grams (1.65 moles) of anhydrous hydrogen chloride in 100 ml. of anhydrous ether for three days at ambient temperature. The ethereal solution was washed quickly with water and aqueous sodium bicarbonate and dried quickly with magnesium sulfate. The ether was removed at atmospheric pressure. The colorless concentrate was distilled at 150 mm. in a Nester and Faust spinning band column. 4-Chloro-2-pentene was collected at 55°C. (150 mm.); n_D^{25} 1.4307 [literature value, b.p., 58°C. at 155 mm.; n_D^{20} 1.4328 (9)].

DODECYL 4-PENT-2-ENYL SULFIDE. Dibutyltin oxide (21.37 grams, 0.08589 mole) reacted with 34.7 grams (0.1715 mole) of dodecyl mercaptan in 150 ml. of toluene at reflux for 39 minutes when the evolution of water had ceased. The reaction product was charcoaled, filtered, and concentrated to constant weight at 55°C. and $<$ 1 mm. The yield of colorless dibutyltin bis(dodecylmercaptide) was 54.7 grams (theory 54.53 grams). This mercaptide, 1.5023 grams (0.00494 mole) of dibutyltin dichloride, and 17.96 grams (0.1718 mole) of 4-chloro-2-pentene reacted in 250 ml. chlorobenzene solution for 7.2 hours when analysis of a sample of the reaction product for chloride showed the reaction to be virtually completed.

Distillation in the spinning band column gave chlorobenzene collected at 57°C. (58 mm.). The sulfide was purified by elution from silica gel with *n*-hexane (over-all yield 62% of theory); n_D^{25} 1.4680. The structure of the sulfide was confirmed by NMR and infrared spectroscopy. Analysis: calculated for $C_{17}H_{34}S$: C, 75.48; H, 12.67; S, 11.85; found: C, 75.20; H, 12.45; S, 11.56.

4-PENT-2-ENYL LAURATE. Two chlorobenzene solutions, one 65 ml., the other 70 ml., from virtually completed reactions of 0.086*M* dibutyltin dilaurate with 0.1717*M* 4-chloro-2-pentene were combined and concentrated under vacuum. The resulting liquid concentrate was chromatographed on 240 grams Woelm neutral alumina (3% water added). Elution with *n*-hexane gave 1.99 grams (32%) of 4-pent-2-enyl laurate; n_D^{25} 1.4437. The structure was confirmed by NMR and infrared spectroscopy. Analysis: calculated for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02; found: C, 76.36; H, 11.84.

Kinetic Measurements. All experiments were conducted in a constant temperature oil bath controlled within ±0.1°C. The stabilizer was dissolved in chlorobenzene in a volumetric flask of suitable volume, usually 100 ml., and placed in the bath. After about 7 minutes the volume was adjusted to about 95 ml., and 4-chloro-2-pentene was added from a pipet with swirling; for 100 ml. of solution generally 2.00 ml. (average wt. 1.7958 grams) of chloride was added to give a 0.172*N* solution in chloride. The volume was adjusted quickly to nearly 100 ml. with chlorobenzene, and the contents were mixed thoroughly. Final adjustment to 100 ml. was made when thermal equilibrium was reached.

At suitable intervals 5.00-ml. samples of the reaction product were removed using a pipet which had been preheated to the bath temperature. The reaction was quenched by cooling the samples in an ice bath. The sample was concentrated under vacuum, finally at 50°C. at aspirator vacuum (12 mm.), to remove unreacted 4-chloro-2-pentene which reacts modeartely readily with silver nitrate.

The residue from carboxylate stabilizers was dissolved with acetone and titrated potentiometrically with 0.1*N* silver nitrate in the presence of 100 ml. of water and 5 ml. of concentrated nitric acid.

The residue from mercaptide stabilizers was dissolved with chlorobenzene, and it was allowed to react with 0.4 ml. of 40% peracetic acid for 10–15 minutes. The reaction product was added with acetone rinsing to a solution of 0.50 gram of sodium sulfite in 100 ml. of water. After adding 5 ml. of concentrated nitric acid the chloride ion was titrated potentiometrically with 0.1*N* silver nitrate.

Suitable control experiments had been carried out to establish that dibutyltin dichloride is not lost from the residue at 50°C. and 12 mm. and to establish that the procedure for mercaptide removal (peracetic acid oxidation) did not interfere with the accuracy of the chloride analysis.

Determining Substitution-Elimination Ratios. A 5.00-ml. aliquot of the reaction solution containing dibutyltin stabilizers was concentrated as usual, and the concentrate was titrated in methanol with 0.1*N* potassium hydroxide in methanol. This titration gave total acidity: dibutyltin dichloride, dibutyltin dicarboxylate plus organic acid from the reaction of hydrogen chloride with dibutyltin dicarboxylate. Excess acidity (free organic acid) was calculated by substracting from the meq. of alkali consumed the quantity arising from dibutyltin dichloride and dibutyltin dicarboxylate.

The chloride content of the same aliquot used for total acidity was determined by potentiometric titration with 0.1*N* silver nitrate solution.

$$\%\ \text{Elimination (E)} = \frac{\text{meq. excess acidity}}{\text{meq. Cl}^-}$$

$$\%\ \text{Substitution (S)} = 100 - \text{E} \times 100$$

Substitution elimination ratios for the other metal stabilizers were determined on reaction mixtures which had gone to completion. Aliquots were freed of metal chloride before titration with 0.1*N* sodium hydroxide by filtration (Pb) or extraction with water (Zn, Cd). The titration gave the meq. of excess acidity directly.

Results

Kinetic investigation revealed that thermal stabilizers replace the allylic chlorine at rates which are much faster than the unimolecular decomposition rate of the allylic chloride. This clearly establishes that the stabilizers do not act only as acid acceptors but that they are capable of rapidly replacing labile chlorine atoms with a more stable group, thereby "healing" the polymer and interrupting the zipperlike elimination of hydrogen chloride. It was especially gratifying to find a qualitative agreement between the effectiveness of dibutyltin stabilizers and their rates of reaction with the allylic chloride model.

The rate expression for the reaction of the allylic chloride with dibutyltin stabilizers is considered to have four terms:

$$\frac{-d\mathrm{RCl}}{dt} \quad k_1[\mathrm{RCl}] + k_2[\mathrm{RCl}][\mathrm{Bu_2SnX_2}] + k_3[\mathrm{RCl}][\mathrm{Bu_2SnXCl}] + k_4[\mathrm{RCl}][\mathrm{Bu_2SnCl_2}] \qquad (1)$$

The first term represents the unimolecular decomposition of allylic chloride. The first and fourth terms are responsible for hydrogen chloride elimination and do not result in stabilization. The second and third terms are responsible for stabilization. This work has provided an estimate of the rate constants for dibutyltin dilaurate and dibutyltin bis(monobutyl maleate).

The reaction half-time for 4-chloro-2-pentene, the allylic chloride model, with dibutyltin β-mercaptopropionate is about 1/20 that for 2-chloro-2-methylbutane, a *tert*-chloride model, with the same stabilizer. This result supports the choice of an allylic chloride as the most important unstable functionality of poly(vinyl chloride).

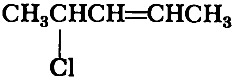
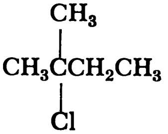
Barium-cadmium synergism is postulated to be caused by a rapid exchange of chlorine from cadmium to barium accompanied by the transfer of stabilizer ligand from barium to cadmium. The importance of this exchange lies in postponing as long as possible the formation of cadmium chloride which, as a strong Lewis acid, is capable of initiating polymer degradation.

Discussion

Allylic Chloride *vs.* *tert*-Chloride Reactivity. There is some question in the literature as to whether the allylic chloride moiety or *tert*-chloride group is more responsible for the thermal instability of poly(vinyl chloride) (*1*, *2*). To shed some light on this problem we compared the relative reactivities at 100°C. in chlorobenzene of 4-chloro-2-pentene and 2-chloro-2-methylbutane with dibutyltin β-mercaptopropionate. Data are summarized in Table I. The half-time for the reaction of the allylic chloride with the stabilizer mercaptide group was less than 15 minutes, whereas the half-time for the *tert*-chloride was nearly 20 times longer. The greater reactivity of the allyl chloride suggests that it is the more important functionality in polymer degradation. However, these results on rates of chlorine substitution are not necessarily an exact measure of thermal instability.

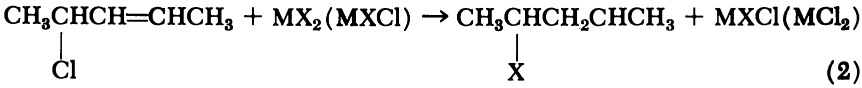
Table I. Allylic Chloride *vs.* *tert*-Chloride

Reaction with $Bu_2Sn(O_2CCH_2CH_2S)$ Stabilizer

Chloride	*Conc.*, M	*Stabilizer Conc.*, M	*Half-time*,[a] *hours*
 $CH_3\underset{Cl}{\underset{\mid}{C}}HCH{=}CHCH_3$	0.172	0.0858	<0.25
 $CH_3\overset{CH_3}{\overset{\mid}{\underset{Cl}{\underset{\mid}{C}}}}CH_2CH_3$	0.161	0.0806	4.8

[a] Mercaptide; chlorobenzene, 100°C.

Product Isolation. Frye and Horst (*7, 8*) postulated that poly(vinyl chloride) stabilization resulted from the replacement of labile chlorine atoms by the ligands of the stabilizer. To test this hypothesis and to confirm that the reaction takes place according to Reaction 2,



$$CH_3\underset{Cl}{\underset{\mid}{C}}HCH{=}CHCH_3 + MX_2(MXCl) \rightarrow CH_3CHCH_2\underset{X}{\underset{\mid}{C}}HCH_3 + MXCl(MCl_2) \qquad (2)$$

products from two reactions of 4-chloro-2-pentene with stabilizers were isolated. From equivalent amounts of the allylic chloride and dibutyltin bis(dodecyl mercaptide), dodecyl-4-pent-2-enyl sulfide was isolated in 62% yield. Dibutyltin dichloride was the other main reaction product. 4-Pent-2-enyl laurate was isolated in 32% yield from the reaction of equivalent amounts of the allylic chloride with dibutyltin dilaurate in the presence of an equivalent of dibutyltin dichloride. These results confirm the Frye-Horst postulate.

Kinetic Results. The reactions were followed by measuring the rate of liberation of chloride ion from the reaction of 4-chloro-2-pentene with stabilizer in chlorobenzene.

The reaction of 4-chloro-2-pentene with dibutyltin dilaurate, one of the first to be studied, provided some interesting observations. A plot of liberated chlorine *vs.* time (Figure 1) shows the reaction to be autocatalytic. Investigation led to the discovery that dibutyltin dichloride, a product of the stabilization reaction, is a catalyst for the reaction (Figure 1). Further investigation revealed that at the outset all the reaction takes place by the unimolecular decomposition of the allylic chloride and that not until species with tin—chlorine bonds are present does this stabilizer undergo reaction with the allylic chloride. The reactive stabilizer in this instance is dibutyltin laurate chloride. Dibutyltin dilaurate does not react with the allylic chloride, and dibutyltin dichloride, which is very reactive, would be expected to catalyze hydrogen chloride elimination and thereby not result in stabilization.

Dibutyltin dilaurate is unique among the stabilizers examined in its inertness toward the allylic chloride. With the exception of dibutyltin bis(dodecylmercaptide), all the other stabilizers studied reacted immediately at different rates. Tables II and III show half-times for the reaction of 0.172*M* 4-chloro-2-pentene with 0.0858*M* metal salts at 100° or 23°C. in chlorobenzene. There is a qualitative correlation between effectiveness as poly(vinyl chloride) stabilizers and the rate of reaction with 4-chloro-2-pentene. Thus, dibutyltin β-mercaptopropionate, one of the best dibutyltin stabilizers for poly(vinyl chloride) was the fastest liberator of chloride, and dibutyltin dilaurate, one of the least effective dibutyltin stabilizers, was the slowest liberator of chloride. The other dibutyltin stabilizers are intermediate in effectiveness. The other metal salts also exhibit qualitative agreement between the rate of chloride liberation and stabilization. Thus, cadmium salts are more effective than lead salts which are more effective than barium salts. Zinc salts are also highly effective for short-term stabilization but the zinc chloride which is formed in the stabilization process soon results in severe polymer degradation.

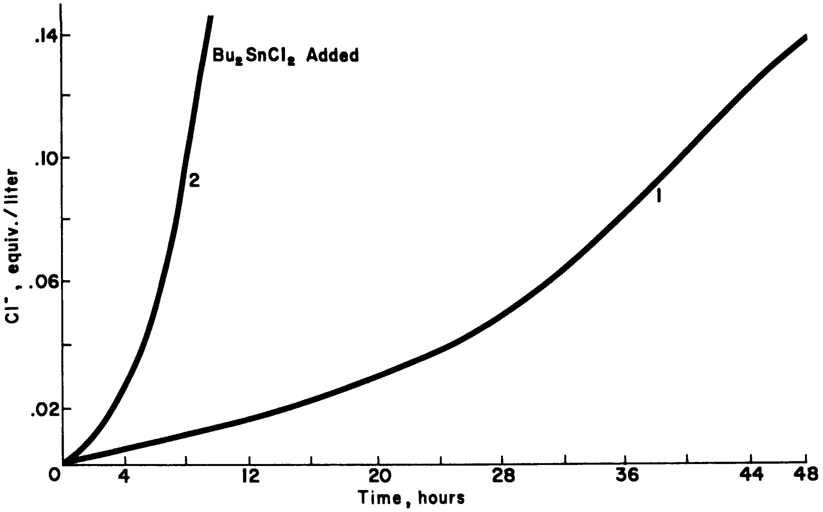


Figure 1. Reaction of dibutyltin dilaurate with 4-chloro-2-pentene at 100°C.

Curve 1: 0.172M halide; 0.0858M stabilizer
Curve 2: 0.172M halide; 0.0858M stabilizer; 0.0858M Bu_2SnCl_2

Table II includes the reaction half-time (6410 minutes) calculated for the unimolecular hydrogen chloride elimination for 4-chloro-2-hexene at 100°C. The data of Baum and Wartman (*3*) were extrapolated to make this calculation. Although our allylic chloride has one carbon atom less and our reaction conditions are not identical with those of Baum and Wartman, we feel justified in using the calculated reaction half-time for a semiquantitative estimate of the unimolecular hydrogen chloride elimination from 4-chloro-2-pentene because the two allylic chlorides are very similar in structure and because we would not expect the difference in solvents to have much effect on the unimolecular reaction rate (Baum and Wartman used di-2-ethylhexyl phthalate as solvent; we used chlorobenzene).

Table II. Reaction Half-times, 100°C.

0.172*M* 4-Chloro-2-pentene and 0.0858*M* Stabilizer

Compound	$t_{1/2}$ *(minutes)*
$Bu_2Sn(O_2CCH_2CH_2S)$[a]	4
$Bu_2Sn(O_2CCH_2CH_2S)$	15 (RS⁻ only)
Bu_2Sn(maleate)	66
$Bu_2Sn(O_2CCH_2CH_2S)$	198
$Bu_2Sn(SC_{12}H_{25})_2$	204
$Bu_2Sn(O_2CCH{=}CHCO_2C_4H_9)_2$	201
$Bu_2Sn(O_2CH{=}CHCO_2C_{12}H_{25})_2$	402
$Bu_2Sn(O_2CC_{11}H_{23})_2$	2270
None	6410

[a] 0.172*M* Stabilizer.

Table III. Reaction Half-times

0.172*M* 4-Chloro-2-pentene and 0.0858*M* Stabilizer

	$t_{1/2}$ *(minutes)*	
Compound	*100°C.*	*23°C.*
Cd(2-ethylhexanoate)$_2$	Inst.[a]	20
Zn(2-ethylhexanoate)$_2$	Inst.	20
Pb(2-ethylhexanoate)$_2$	18	48 hours
Ba(2-ethylhexanoate)$_2$	210	—

[a] Inst. = instantaneous.

Since the estimated half-time for unimolecular elimination of hydrogen chloride from the allylic chloride is considerably greater than the half-times for reaction with stabilizers, the stabilizers do not function only by reacting with liberated hydrogen chloride. Stabilizers function by substituting the labile chlorine atoms with more thermally stable groups, thereby mending the polymer.

The two different functionalities (mercaptide and carboxylate) of dibutyltin β-mercaptopropionate react at different rates with the allylic chloride) stabilization of dibutyltin salts of maleic acid or monoesters

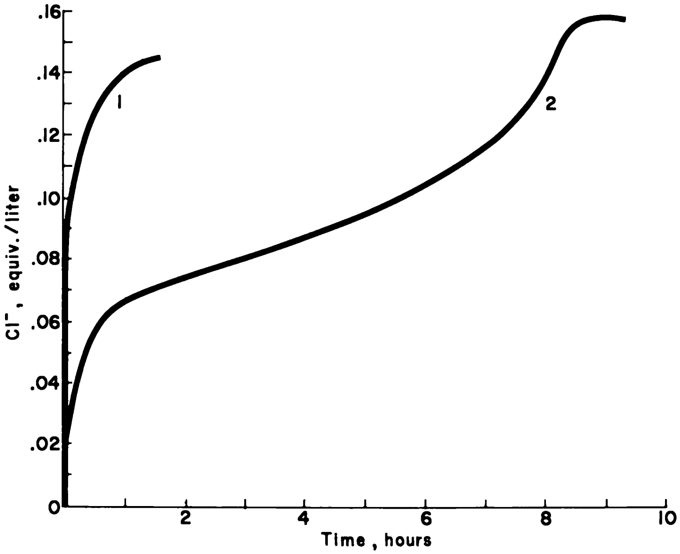


Figure 2. Reaction of dibutyltin β-mercaptopropionate with 4-chloro-2-pentene at 100°C.

Curve 1: 0.172M halide; 0.172M stabilizer
Curve 2: 0.172M halide; 0.0858M stabilizer

the reaction half-time is 4 minutes. With equivalent amounts of reactants the reaction half-time for the mercaptide functionality alone is 15 minutes, whereas the half-time for the two functionalities is 198 minutes.

The data in Table II demonstrate that the effectiveness for poly(vinyl chloride) stabilization of dibutyltin salts of maleic acid or monoesters of maleic acid is caused by a high rate of reaction with allylic chloride moieties. Thus, it is not necessary to postulate, as has been done several times in the literature, that these compounds are effective because they are dieneophiles and therefore capable of disrupting the long chains of unsaturation responsible for color formation. It is gratifying that the performance of the maleate stabilizers is consistent with the Frye-Horst substitution hypothesis.

The behavior of dibutyltin bis(dodecylmercaptide) on reaction with 4-chloro-2-pentene proved interesting (Figure 3). With only the two reactants in chlorobenzene, virtually no reaction took place up to 5 hours. However, the addition of dibutyltin dichloride resulted in a rapid reaction. Furthermore, the addition of a few milligrams of azobisisobutyronitrile eliminated any induction period. This latter consequence is not interpreted to result from a free radical stabilization mechanism, but it is presumed to be caused by free radical-catalyzed hydrogen chloride elimination, resulting (by neutralization with the stabilizer) in the formation

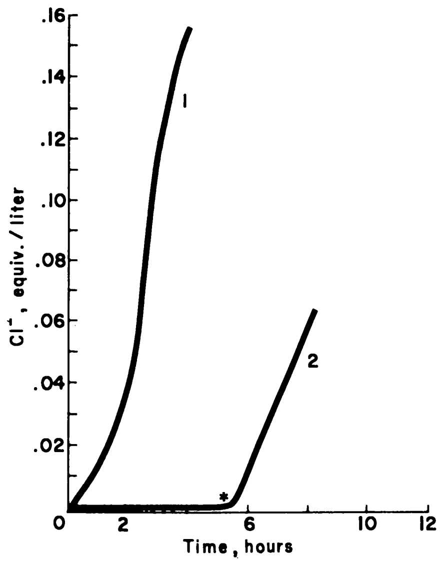


Figure 3. Reaction of dibutyltin dodecylmercaptide with 4-chloro-2-pentene at 100°C.

Curve 1: 0.172N each reactant; catalytic amount of azobisisobutyronitrile
Curve 2: 0.172N each reactant; added Bu_2SnCl_2 to 0.0858N at point marked by asterisk

of dibutyltin dodecylmercaptide chloride. This compound is assumed by analogy with dibutyltin laurate chloride to be much more reactive than the parent stabilizer.

Rate Expressions. More detailed kinetic studies were carried out with dibutyltin dilaurate and dibutyltin bis(monobutyl maleate) at 80°C. to evaluate rate expressions. Elucidation of a rate expression would have been extremely difficult in view of the complexity of the reactions were it not for two simplifying assumptions we made and for the fortuitous straight line plots of allylic chloride concentration *vs.* reaction time which we obtained. We assumed that in a mixture of Bu_2SnX_2, Bu_2SnXCl, and Bu_2CnCl_2 rearrangement of ligands would occur rapidly and that Bu_2SnXCl would be the favored species. Thus, if Bu_2SnX_2 and Bu_2SnCl_2 were combined in equimolar quantities, we assumed that the species Bu_2SnClX would predominate. We also assumed that the rate constant, $k_1 \simeq 2.0 \times 10^{-5}$ min.$^{-1}$, calculated for the unimolecular decomposition of 4-chloro-2-hexene at 80°C. from the data of Baum and Wartman (*3*), would be applicable to 4-chloro-2-pentene.

Attempts had been made to interpret the kinetic data to conform with several mechanisms. These included (1) complexing of RCl with Bu_2SnCl_2, followed by reaction of the complex with Bu_2SnX_2 or Bu_2SnClX; (2) bimolecular reaction of RCl and Bu_2SnX_2 or Bu_2SnCl_2; (3) bimolecular reaction of RCl and Bu_2SnX_2, Bu_2SnXCl, or Bu_2SnCl_2 with an equilibrium among the tin species. None of these mechanisms fit the data until we assumed that Bu_2SnClX was the most favored tin species. With that assumption the data fit a mechanism which included several concomitant reaction paths for RCl:

(1) Unimolecular elimination of HCl
(2) Bimolecular reaction with Bu_2SnX_2
(3) Bimolecular reaction with Bu_2SnXCl
(4) Bimolecular reaction with Bu_2SnCl_2

These concomitant reactions led to Equation 1 for the rate expression. An estimate of k_1 was obtained as explained above from the data of Baum and Wartman.

The data in Table IV, obtained from a reaction at 80°C., gave a straight line with slope -2.65×10^{-5} mole/liter-min. for the plot of RCl concentration *vs.* time. Equation 1 was simplified to Equation 2 by several assumptions. Rapid conversion to Bu_2SnClX was assumed. The slope of the RCl–time plot, $\Delta RCl/\Delta t$, was made equal to $dRCl/dt$, which is justified since the slope is a straight line. The second term of Equation 1, ($k_2[RCl][Bu_2SnX_2]$), was eliminated since it was found that this

$$\frac{2.65 \times 10^{-5}}{[RCl]} - 2.0 \times 10^{-5} = k_3[Bu_2SnXCl] \qquad (2)$$

reaction for 4-chloro-2-pentene and dibutyltin dilaurate was either very slow (much slower than the unimolecular decomposition) or did not take place at all. The fourth term of Equation 1 was eliminated since the assumption that Bu_2SnXCl was the favored species made (Bu_2SnCl_2) very small. The solution of Equation 2 for each set of data in Table IV gave an average value for k_3 of 7.97×10^{-4} liter/mole-min.

Table IV. Reaction of Dibutyltin Dilaurate With 4-Chloro-2-pentene at 80°C.

Time,	*Concentration,*[a] M			
minutes	*RCl*	*Bu_2SnX_2*	*Bu_2SnClX*	*Bu_2SnCl_2*
0	0.1709	0.0647	0.1701	0
60.2	0.1693	0.0632	0.1717	0
121.2	0.1673	0.0612	0.1737	0
243.4	0.1647	0.0585	0.1763	0
365.5	0.1611	0.0549	0.1799	0

[a] Initial Concentrations: 0.1709*M* RCl, 0.1498*M* Bu_2SnX_2, 0.08505*M* Bu_2SnCl_2. Bu_2SnXCl assumed to be favored species.

Table V. Reaction of Dibutyltin Dilaurate With 4-Chloro-2-pentene at 80°C.

Time, minutes	Concentration, M[a]				Rate Constant,[b] k_4 (× 10^3)
	RCl	Bu_2SnX_2	Bu_2SnClX	Bu_2SnCl_2	
0	0.1709	0.000	0.1696	0.0852	
60.0	0.1653	0.000	0.1640	0.0908	4.24
119.8	0.1623	0.000	0.1610	0.0938	4.20
180.0	0.1555	0.000	0.1542	0.1006	4.20
242 5	0.1499	0.000	0.1486	0.1062	4.23
313.0	0.1425	0.000	0.1412	0.1136	4.26
359.6	0.1381	0.000	0.1368	0.1180	4.30
					Av. 4.24

[a] Initially charged 0.1709M RCl, 0.0848M Bu_2SnX_2, 0.1700M Bu_2SnCl_2. Bu_2SnXCl assumed to be favored species.

[b] Calculated assuming $k_3 = 7.97 \times 10^{-4}$ liter/mole-min.

A similar treatment of the data in Table V gave a straight line with $-\Delta RCl/\Delta t = 8.80 \times 10^{-5}$ mole/liter-min. Values of k_4 were calculated from Equation 3. The good agreement among the calculated values of k_4 in Table V supports the mechanism and the assumptions which were made. Further support of the mechanism and assumptions comes from the values, $k_3 = 7.95 \times 10^{-4}$ liter/mole-min. and $k_4 = 4.23 \times 10^{-3}$ liter/mole-min. which were obtained from Equation 4 and the data in

$$\frac{8.80 \times 10^{-5}}{[RCl]} - 2.0 \times 10^{-5} = 7.97 \times 10^{-4}[Bu_2SnClX] + k_4[Bu_2SnCl_2] \tag{3}$$

Table V *via* graphical solution of the series of simultaneous equations.

$$\frac{8.80 \times 10^{-5}}{[RCl]} - 2.0 \times 10^{-5} = k_3[Bu_2SnClX] + k_4[Bu_2SnCl_2] \tag{4}$$

Equation 5 is the rate expression for the reaction of dibutyltin dilaurate with 4-chloro-2-pentene at 80°C.

$$-\frac{dRCl}{dt} = 2.0 \times 10^{-5}[RCl] + 7.97 \times 10^{-4}[RCl][Bu_2SnClX] + 4.24 \times 10^{-3}[RCl][BuSnCl_2] \tag{5}$$

A similar treatment of the data in Figure 4 for several reactions of dibutyltin bis(monobutyl maleate) with 4-chloro-2-pentene gave the rate constants in Table VI. These rate constants were determined by graphical solution of simultaneous equations for each experiment. The agreement among values for k_3 is less satisfying than the results for dibutyltin dilaurate. This may be caused by a lesser relevance of the assumption that Bu_2SnClX is the highly favored tin species or the plots of RCl *vs.* time may not be true straight lines (Figure 4). Equation 6 is the rate expression for dibutyltin bis(monobutyl maleate) at 80°C.

$$-\frac{d\mathrm{RCl}}{dt} = 2.0 \times 10^{-5}[\mathrm{RCl}] + 4.82 \times 10^{-3}[\mathrm{RCl}][\mathrm{Bu_2SnX_2}] + 7.89 \times 10^{-3}[\mathrm{RCl}][\mathrm{Bu_2SnXCl}] + 14.2 \times 10^{-3}[\mathrm{RCl}][\mathrm{Bu_2SnCl_2}] \quad (6)$$

Stabilization Mechanism. The kinetic data show that the reaction of poly(vinyl chloride) stabilizers with the model for poly(vinyl chloride)

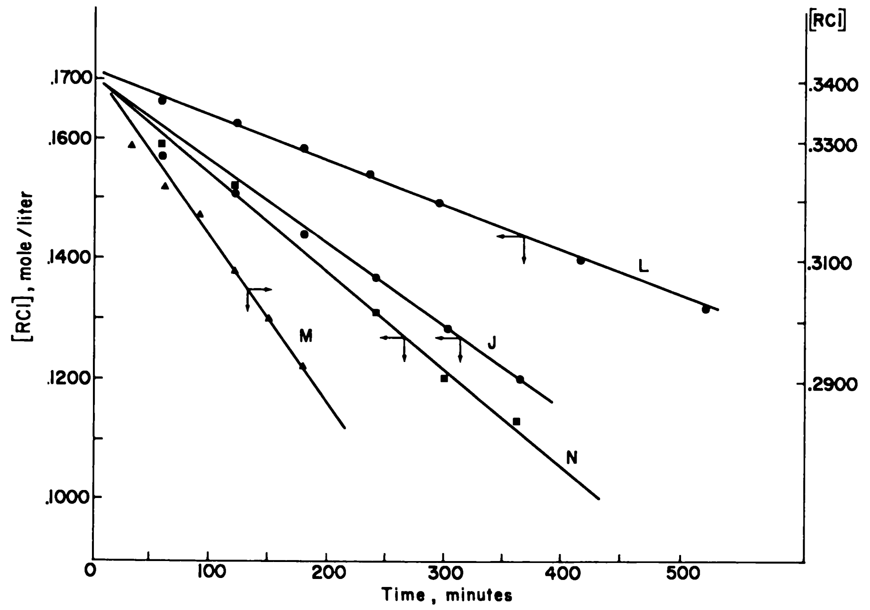


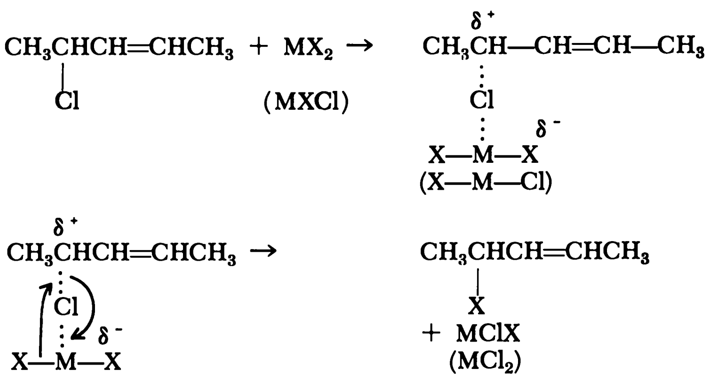
Figure 4. RCl vs. *time for the reaction of 4-chloro-2-pentene with dibutyltin bis(monobutylmaleate) at 80°C. Letters L, J, N, M designate different experiments*

Table VI. Reaction of Dibutyltin Bis(monobutylmaleate) With 4-Chloro-2-pentene at 80°C.

	Concentration Added to Reaction, M				*Rate Constants liter/mole-min. (× 10³)*		
Exp.	*Chloride*	*Stab.*	*Bu_2SnCl_2*	$-\Delta Cl/\Delta t$ *(mole/liter-min.)*	k_2	k_3	k_4
J	0.1709	0.1500	—	1.23×10^{-4}	4.60	9.92	—
L	0.1709	0.0750	—	6.96×10^{-5}	5.11	7.98	—
M	0.3418	0.1501	—	2.53×10^{-4}	4.76	7.42	—
N	0.1709	0.0750	0.0750	1.67×10^{-4}	—	6.25	14.2
					Av. 4.82	7.89	

instability, 4-chloro-2-pentene, is complex, consisting of a series of concomitant reactions with several metal-containing compounds: MX_2, $MXCl$, and MCl_2. The reaction is further complicated by the unimolecular elimination of hydrogen chloride which is negligible in all but a few slow reactions.

In view of the presence of metal atoms in stabilizers and the bimolecular nature of reactions of the allylic chloride with stabilizer, it is reasonable to postulate that the first step in the reaction is complexing of the chlorine atoms by the metal, and the second step is transfer of a ligand from the metal to the allyl chloride with concomitant transfer of chlorine atom to the metal. This is depicted in Reaction 7.



$$\underset{\displaystyle Cl}{CH_3\underset{|}{C}HCH{=}CHCH_3} + \underset{(MXCl)}{MX_2} \rightarrow \begin{array}{l} \overset{\delta^+}{CH_3CH}{-}CH{=}CH{-}CH_3 \\ \;\;\vdots \\ \;\;Cl \\ \;\;\vdots \;\; \delta^- \\ X{-}M{-}X \\ (X{-}M{-}Cl) \end{array} \qquad (7)$$

$$\begin{array}{l} \overset{\delta^+}{CH_3CHCH{=}CHCH_3} \\ \;\;\vdots \\ \;\;Cl \\ \;\;\vdots \;\; \delta^- \\ X{-}M{-}X \end{array} \rightarrow \begin{array}{l} CH_3\underset{\displaystyle X}{\underset{|}{C}H}CH{=}CHCH_3 \\ + MClX \\ \;(MCl_2) \end{array}$$

Another possibility, involving an allylic shift, exists for the exchange of ligand. It is shown in Reaction 8.

$$\begin{array}{l} CH_3CHCH{=}CHCH_3 \\ \;\;\vdots \\ \;\;Cl \\ \;\;\vdots \\ X{-}M{-}X \end{array} \rightarrow \begin{array}{l} CH_3CH{=}CH{-}\underset{\displaystyle X}{\underset{|}{C}H}CH_3 \\ \qquad + MClX \end{array} \qquad (8)$$

Steric considerations would favor Reaction 8 over 7. However, our work does not allow a choice between these two.

Stabilization is postulated to be achieved when a labile chlorine atom is replaced by a ligand of the stabilizer. Consequently, complexing of labile chlorine atoms by MCl_2 or Bu_2SnCl_2 will not lead to stabilization but will lead most likely to elimination of hydrogen chloride, thereby contributing to degradation. Therefore, the species responsible for stabilization are MX_2 and $MXCl$.

At least four features of a stabilizer seem important in determining its effectiveness:

(1) Identity of the metal atom

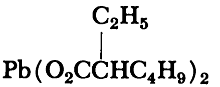
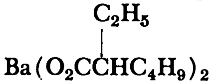
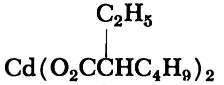
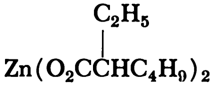
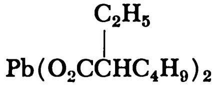
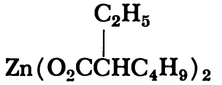
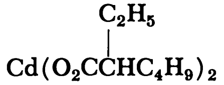
(2) Electron-withdrawing nature of the ligands

(3) Size of the ligands
(4) Nucleophilicity of the ligands

Differences in metals are attributed to differences in complexing ability. The electron-withdrawing nature of the ligand has an influence within narrow limits on the complexing ability of the metal atom. Ligand size will affect the probability and therefore the rate of the stabilizer complexing labile chlorine atoms. Dibutyltin dilaurate is postulated to be of low effectiveness for stabilization because of the large ligands. Dibutyltin β-mercaptopropionate, presumably a highly compact molecule, is one of the most effective tin stabilizers.

Substitution-Elimination Ratios. Estimates of the ratio of substitution to elimination which accompanied several of the reactions with equivalent quantities of allylic chloride and stabilizer were made by analyzing samples of reaction mixtures for excess acidity. Unfortunately,

Table VII. Substitution-Elimination Ratios

Stabilizer	*Temp., °C.*	*% S*	*% E*
 $Pb(O_2C\overset{C_2H_5}{C}HC_4H_9)_2$	100	78	22
$Bu_2Sn(O_2CCH{=}CHCO_2)_2$	100	73, 72	27, 28
$Bu_2Sn(O_2CC_{11}H_{23})_2$	100	59	41
 $Ba(O_2C\overset{C_2H_5}{C}HC_4H_9)_2$	100	42.5	57.5
 $Cd(O_2C\overset{C_2H_5}{C}HC_4H_9)_2$	100	27	73
 $Zn(O_2C\overset{C_2H_5}{C}HC_4H_9)_2$	100	4	96
 $Pb(O_2C\overset{C_2H_5}{C}HC_4H_9)_2$	23	71	29
 $Zn(O_2C\overset{C_2H_5}{C}HC_4H_9)_2$	23	64	36
 $Cd(O_2C\overset{C_2H_5}{C}HC_4H_9)_2$	23	54	46

analytical problems prevented our making these determinations for all stabilizers. This ratio is important because it is a measure of how efficiently a stabilizer functions. Table VII contains the data on this subject.

Cadmium-Barium Synergism. The data in Table VII show that cadmium 2-ethylhexanoate by itself does not provide a high degree of substitution. Furthermore, the reactions with cadmium 2-ethylhexanoate and 4-chloro-2-pentene took place rapidly with immediate, extreme discoloration, suggesting catalysis of side reactions *via* carbonium ion intermediates by cadmium chloride, a strong Lewis acid. However, cadmium salts used in conjunction with barium salts are important stabilizers for poly(vinyl chloride). We, therefore, decided to investigate the nature of cadmium-barium synergism. Unfortunately, analytical difficulties prevented determination of substitution-elimination ratios for these reactions.

Data in Table VIII show that replacement of cadmium by barium retards the rate of discoloration of the reaction mixtures. Finally, when the quantity of barium salt was equivalent to the quantity of allylic chloride, discoloration was prevented entirely. Since discoloration is attributable to the presence of cadmium chloride, the absence of color must have resulted because cadmium chloride was not formed. Since the cadmium salt reacts faster than the barium salt, the formation of CdX_2 and the prevention of discoloration could be achieved by a rapid exchange of ligands between cadmium and barium:

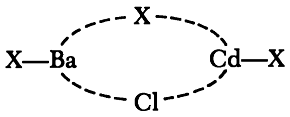
Table VIII. Cadmium-Barium Synergism[a]

Cd/Ba	*Stab./Allylic Cl*	*Time to Discolor at 100°C.*	*% Cl Eliminated in First Hour*
1/0	1/1	Instantaneous	100
3/1	1/1	1 min.	93
1/1	1/1	1 min.	83
1/3	1/1	4 min.	79
1/1	2/1	Colorless	100

[a] Effect of increasing barium stabilizer concentration on rate of discoloration.

$$CdClX + BaX_2 \rightarrow CdX_2 + BaClX$$

Another possible explanation would be the presence of complex metallic compounds such as the following:



Summary

(1) The work reported here shows that the allylic chloride model is a good one for the unstable moiety of poly(vinyl chloride).

(2) Product isolation shows that stabilizers act by replacing labile chlorine atoms with more stable groups. Metal atoms assist in the replacement by complexing the labile chlorine atoms.

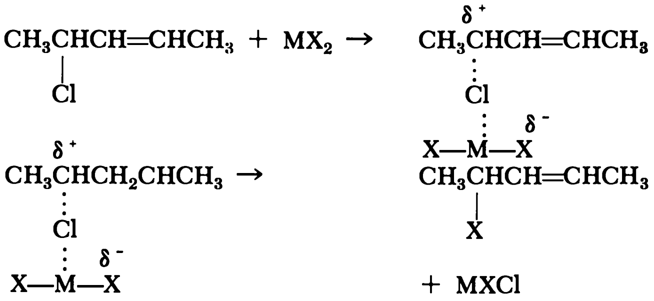
(3) The most effective poly(vinyl chloride) stabilizers exhibited the fastest rates of chloride liberation.

(4) A generalized rate expression for the reaction of allylic chloride (RCl) with metal stabilizers (MX_2) includes terms for the unimolecular elimination of HCl from RCl and for the bimolecular reaction of RCl with all metal containing species.

$$-\frac{dRCl}{dt} = k_1[RCl] + k_2[RCl][MX_2] + k_3[RCl][MXCl] + k_4[RCl][MCl_2]$$

Estimates of the rate constants for dibutyltin dilaurate and for dibutyltin bis(monobutylmaleate) are reported.

(5) Stabilization proceeds *via* ionic mechanisms:



$$\begin{array}{l} CH_3CHCH{=}CHCH_3\\ \ \ \ \ \ \ \ |\\ \ \ \ \ \ \ Cl\end{array} + MX_2 \rightarrow \begin{array}{l}\ \ \ \ \ \ \ \delta^+\\ CH_3CHCH{=}CHCH_3\\ \ \ \ \ \ \ \ \vdots\\ \ \ \ \ \ \ Cl\\ \ \ \ \ \ \ \ \vdots\ \ \delta^-\\ \ \ \ X{-}M{-}X\end{array}$$

$$\begin{array}{l}\ \ \ \ \ \ \ \delta^+\\ CH_3CHCH_2CHCH_3\\ \ \ \ \ \ \ \ \vdots\\ \ \ \ \ \ \ Cl\\ \ \ \ \ \ \ \ \vdots\ \ \delta^-\\ \ \ \ X{-}M{-}X\end{array} \rightarrow \begin{array}{l} CH_3CHCH{=}CHCH_3\\ \ \ \ \ \ \ \ |\\ \ \ \ \ \ \ X\\ \\ + MXCl\end{array}$$

(6) Cadmium-barium synergism is postulated to be caused by a rapid exchange of chloride ions from CdClX to BaX_2 (or BaXCl), thereby postponing as long as possible the formation of deleterious cadmium chloride.

Acknowledgment

The author is indebted to the management of the Geigy Research Laboratories for the opportunity to carry out and publish this research and especially to Martin Dexter, whose questioning, interest, and encouragement prompted the investigation.

Literature Cited

(1) Asahina, M., Onozuka, M., *J. Polymer Sci.* **2A,** 3505 (1964).
(2) *Ibid.,* pp. 3515-3522.
(3) Baum, B., Wartman, L. H., *J. Polymer Sci.* **28,** 537 (1958).
(4) Benough, W. I., Norrish, R. G. W., *Proc. Roy. Soc. (London)* **A 200,** 301 (1950).
(5) Cottman, J. D. Jr., *Ann. N.Y. Acad. Sci.* **57,** 417 (1953).
(6) Drusedow, D., Gibbs, C. F., *Modern Plastics* **30,** 123 (1953).
(7) Frye, A. H., Horst, R. W., *J. Polymer Sci.* **40,** 417 (1959).
(8) *Ibid.,* **45,** 1 (1960).
(9) Henne, A. L., *et al., J. Am. Chem. Soc.* **63,** 3476 (1941).
(10) Kenyon, A. S., *Nat. Bur. Std. Circ.* **525,** 81 (1953).
(11) Sonnerskog, S., *Acta. Chem. Scand.* **13,** 1634 (1959).
(12) *Ibid.,* **14,** 491 (1960).
(13) Winkler, D. E., *J. Polymer Sci.* **35,** 3 (1959).

RECEIVED October 23, 1967.

2

The Control of Thermal Degradation Pathways in Poly(vinyl chloride) by Heat-Stabilizing Additives

CHARLES H. FUCHSMAN

Ferro Chemical, Division of Ferro Corp., Bedford, Ohio 44146

Milled rigid sheets of poly(vinyl chloride) on heating at 185°C. lose weight at a rate which increases with time. By polymer fractionation procedures, it was shown the rate of hydrogen chloride loss increases as the content of tetrahydrofuran-insoluble resin increases. The insoluble resin content accumulates at a rate which depends, in part, on the additive present. This insolubilization reaction is catalyzed by cadmium compounds. The increased dehydrochlorination rate of the insoluble crosslinked resins may result from the susceptibility of the crosslinked structures to oxidation and from the subsequent thermal degradation of the oxidation products. The effects of various common additives on the rates of insolubilization and weight loss are described.

The experimental work reported here was directed to the general problem of the chemical change in poly(vinyl chloride) (PVC) when heated. Commercial experience has shown that the rates of discoloration, the types of discoloration, the rates of hydrogen chloride evolution, and other important evidences of degradation vary not only with time, temperature, and surrounding atmosphere but also with the nature and concentration of "stabilizing" additives. These additives, which vary widely in chemical structure, are selected and combined in many ways to meet particular processing and use requirements. The manufacture, selection, and combination of these additives comprise the art and the science of the stabilizer manufacturer.

The principal reactions which have been studied in thermally degraded poly(vinyl chloride) are: (1) the dehydrochlorination reaction;

(2) the oxidation reaction; (3) change in molecular weight (chain scission and crosslinking).

The dehydrochlorination reaction causes a color change. Marvel and co-workers (*17*, *19*) attributed the discoloration to a conjugated polyene structure. They suggested that random dehydrochlorination to form an olefinic bond would be followed by allylically activated removal of successive hydrogen chloride units to form the polyene structure.

Boyer (*4*) reported the presence of carbonyl groups in degraded vinylidene chloride–vinyl chloride copolymers. Fox and his colleagues (*7*), having found similar evidence in degraded vinyl chloride homopolymer, suggested that these carbonyls, conjugated with olefinic sequences, may explain the observed color intensity. Fox also compared the spectra of degraded poly(vinyl chloride) with conjugated polyunsaturated fatty acids which had been oxidized. The apparent similarity led to the view that the oxidation followed and was facilitated by the dehydrochlorination.

The reverse relationship is implicit in a series of studies by Imoto, Otsu, and Ota (*14*, *15*, *21*) in which the dehydrochlorination rate of the polymer in air was observed to be greater than in nitrogen. Thus, the oxygen caused a reaction which accelerated the rate of hydrogen chloride loss. Therefore, dehydrochlorination was at least in part a result rather than a cause of oxidation.

The oxidation reaction was related, by several investigators, to changes in the carbon chain of the polymer. Scarbrough and co-workers (*25*) observed that discoloration of polymer degrading in nitrogen was often greater than in air and concluded that the carbonyl groups blocked the progressive extension of the polyene chain or that the long chromophoric sequences were broken by chain scission.

That the effect of oxidative degradation on a chain structure is more complex is evident from the work of Druesedow and Gibbs (*6*), who showed that in nitrogen the degrading polymer continually increases in molecular weight until it becomes insoluble, while in air there is a preliminary decline in molecular weight followed by a rapid insolubilization. Thus, it was felt that dehydrochlorination caused crosslinking, and oxidation caused both scission and crosslinking. Scission was also responsible for the oxygen bleaching of color, which is sometimes observed.

In general, crosslinks, by whatever mechanism, were considered to consist of C—C bonds, although there was speculation (*e.g.*, by Rozhdestvenskii (*24*)), that oxygen bridges might also be involved. Razuvaev and co-workers (*23*) have recently proposed a Diels-Alder type of cyclization between neighboring polyene chains as a mechanism of crosslinking.

In an attempt to characterize the resin after degradation in nitrogen, Mikhailov and co-workers (*20*) extracted the solid with cyclohexanone under vacuum in a modified Soxhlet apparatus. They found that while much of the polymer was now insoluble in the solvent, the portion which was soluble was of reduced molecular weight. The more highly degraded the polymer, the smaller was the proportion of the soluble fraction and the lower was the molecular weight of the soluble portion. These observations were related by the authors to simultaneous scission and crosslinking. Thus, scission and crosslinking might occur both in nitrogen and in oxygen, though not necessarily by the same mechanism.

Goto and Fujii (*10*), studying the effects of mechanical shear in poly(vinyl chloride) observed that only the longer chains were broken. Adding radical scavengers (*i.e.*, antioxidants) inhibited the recombination of the fragments, as Furukawa and Kimura (*9*) had shown earlier. Radical initiators (*e.g.*, benzoyl peroxide) promoted rapid crosslinking. The effect of zinc stearate was similar to that of benzoyl peroxide. Both accelerate dehydrochlorination, and both result in extensive crosslinking. Adopting the free radical concept described by Furukawa and Kimura, and later by Arlman (*1*), Goto and Fujii considered that dehydrochlorination progresses through a series of allylic free radicals until it reaches a point where crosslinking occurs. The dehydrochlorination was thus the first step, and crosslinking followed.

Talamini and Pezzin (*26*) also studied the reaction, and while conceding that the influence of oxygen was quite complex, they felt that it involved an interaction of oxygen with the unsaturated groups. Thus, some dehydrochlorination must occur first. Oxygen may then accelerate the process.

Guyot and Benevise (*11*) appear to have been the first to fractionate the polymer after degradation under conditions which simulated commercial processes. The polymer, which had been stabilized with calcium stearate, was processed at 180°C. There was a notable change in molecular weight distribution. The degraded resin had, in addition to 6.5% tetrahydorfuran insolubles, more polymer in the $< 50,000$ MW range, more in the $> 120,000$ MW range, and less in the middle range.

Guyot and Benevise also recorded the chlorine content of the dissolved and reprecipitated polymer obtained from degraded resin samples. Although the degraded sample, as a whole, showed appreciable loss of chlorine, the reprecipitated samples had contents close to that of undehydrochlorinated polymer. According to the authors, this precipitation procedure left in solution small amounts of low molecular weight fragments which did not contain chlorine.

Virtually all previously published opinions on thermally degraded poly(vinyl chloride) regarded the dehydrochlorination process as being in the first instance, a monomolecular process resulting in conjugated polyene structures, and that all oxidation and cross-linking reactions occurred subsequent to and as a consequence of polyene formation. Nevertheless, no investigator reported the isolation of any pure or enriched, soluble fraction of the polymer which was significantly dehydrochlorinated.

The present investigation was initially oriented to the isolation of such fractions as they may occur in the presence of compounds potentially useful as heat stabilizers. Since, as proved to be the case, no such fractions were found, additional observations were made to determine whether such dehydrochlorinated uncrosslinked fractions required by prevailing theory, were likely to exist.

Plan of Investigation

In accordance with existing theory, there should exist at some stage of heat degradation, linear (uncrosslinked) poly(vinyl chloride) molecules in which dehydrochlorination has resulted in the formation of conjugated polyene sequences. Since, according to Marvel, the color formation resulting from this dehydrochlorination is attributable to only a small fraction of the molecules in the system, an extraction procedure using various solvents should yield in one of the resulting fractions a concentration of dehydrochlorinated molecules, which could be identified by intense color and low chlorine content.

Solvent extraction, using Soxhlet equipment, can remove molecules which are not too highly crosslinked. The resulting solution, on admixture with a miscible nonsolvent for polymer, precipitates polymer fractions which can be examined further.

To minimize the possibility of side reactions initiated by light or peroxides during the extraction, the equipment was completely shielded from light by aluminum foil, and all solvents were freshly redistilled before use. Since, as noted below, all samples had been subjected to severe high temperature exposure to air before extraction, the extraction itself was not conducted under conditions of air exclusion.

It should also be possible to observe the effect of various additives in the degradation processes by observing the quantity and type of polymer recovered from the solvent.

Solvent fractionation is usually directed to the separation of polymeric molecules of different molecular weights. For such purposes a graded series of additions of a nonsolvent to the solution has been the means of fractional precipitation. Since we planned to isolate molecules which might be expected to differ also in the degree to which they had undergone dehydrochlorination and oxidation, a different approach was devised. The proposed procedure involved successive extractions of the polymer sample by different solvents. A similar approach had been used by Marvel *et al.* (*18*) in separating chemically different products from the copolymerization of vinyl chloride and vinyl acetate. Marvel used 1-heptyne and phenylacetylene as solvents. The former extracted the low chlorine polymer, the latter the high chlorine polymer.

For this study, chloroform (b.p. 61°C.), butanone (methyl ethyl ketone, b.p. 80°C.), and tetrahydrofuran (b.p. 65°C.) were the solvents selected. Their atmospheric boiling points are low enough not to cause thermal degradation of the polymer. The polymer could be precipitated from solution by adding 2-propanol (b.p. 82°C.). The resulting suspension could be boiled down to remove the bulk of the low boiling solvent. The resulting 2-propanol suspension of polymer was, in the typical case, easily filtered. The choice of a chlorinated solvent, a ketone, and a cyclic ether as extractants should offer some means of separation of chemically different components of degraded polymer.

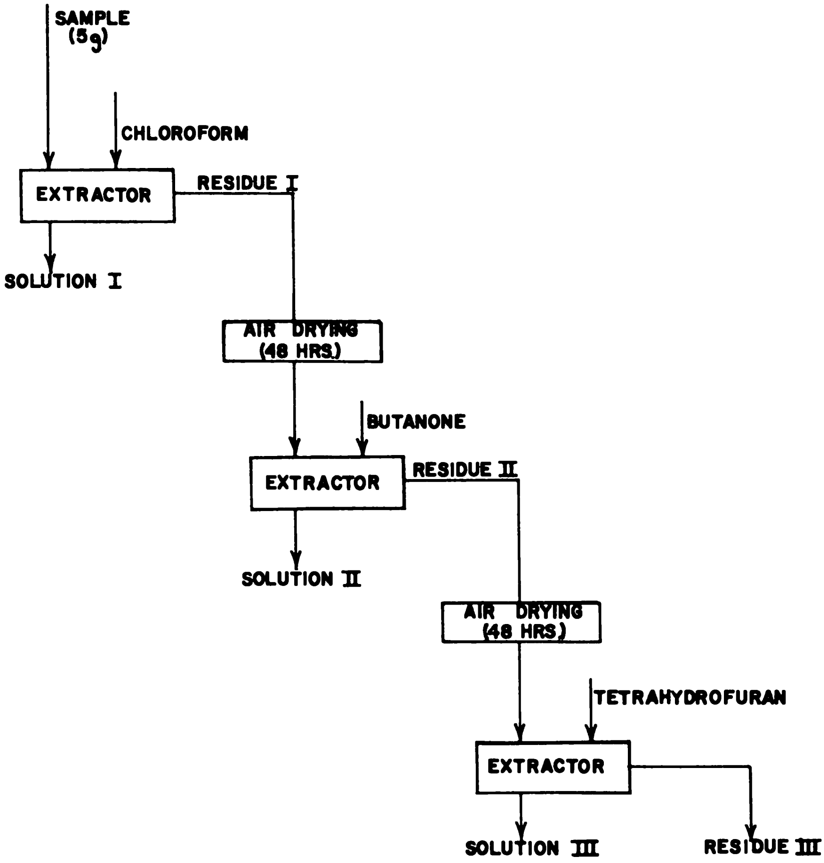


Figure 1. Fractional extraction of PVC samples (complete extraction procedure)

Experimental

Samples were prepared by milling a commercial poly(vinyl chloride) homopolymer (Geon 103EP (B. F. Goodrich Co.)) with 0.5% stearic acid and, typically, 1% of an experimental additive. The milling was carried out on the heated chrome-plated steel rolls of a two-roll mill for 3–5 minutes at 185°C., the time being measured from the beginning of observed fusion of the polymer. The resulting sheet, about 4 mm. thick, was cut into 60-mm. squares and suspended from a rotating wheel in a forced convection oven kept at 185°C. The squares were removed after 1 or 2 hours, depending on the desired degree of heat aging, and were then studied along with other squares which had not been oven heated.

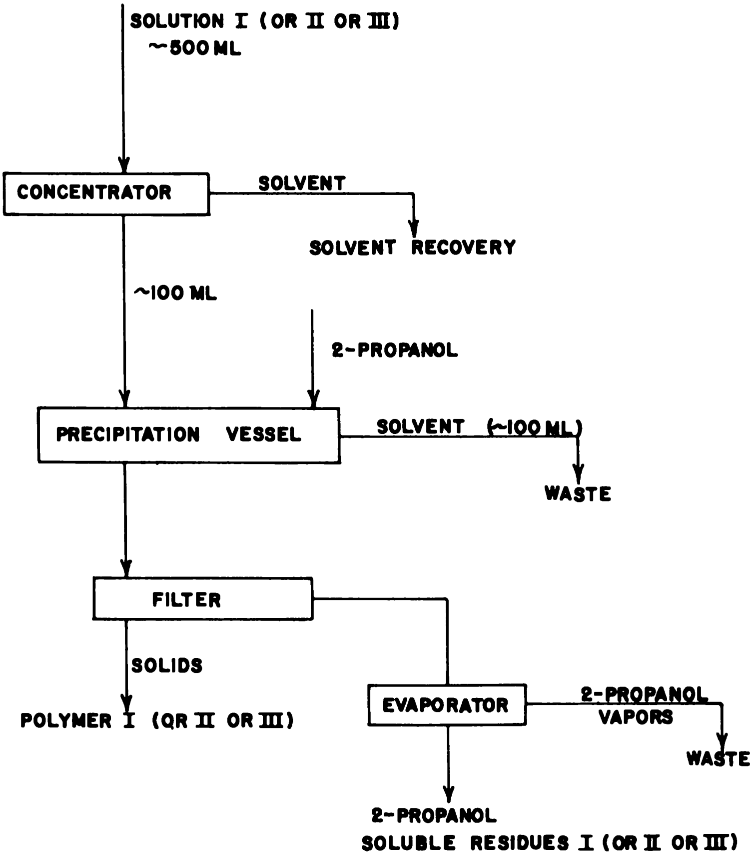


Figure 2. Procedure for recovery of solutes from polymer solutions

For extraction studies the polymer square was cut into strips about 15 mm. wide, and a few strips aggregating 3 to 5 grams in weight were placed in the thimble of a Soxhlet apparatus. The flowsheet is described in Figures 1 and 2.

In a few early experiments, the sample was extracted directly with butanone without preliminary extraction by chloroform. The total quantity of polymer so recovered was equal to that obtainable by extracting with chloroform and with butanone, separately.

Each extraction was conducted for 8 hours. All solvents used were freshly redistilled. To avoid complications resulting from photodegradation, particularly when chloroform was used, the extraction apparatus was entirely shielded from light by aluminum foil. Experience in preliminary experiments demonstrated that little extraction occurred after the first 4 hours and virtually none after 8 hours.

When a sample was to be extracted with butanone after first being extracted with chloroform, the thimble containing the chloroform-insoluble residue was allowed to air dry for about 2 days. The thimble at this point retained no odor of chloroform, and material balances showed that there was virtually no residual chloroform in the polymer.

. The solutions, obtained by these extraction procedures, were concentrated by boiling to about 100 ml. The addition of about 100 ml. of 2-propanol caused precipitation of the polymer. The solution was boiled until the volume was reduced to 75 ml. Fresh 2-propanol was added, and the suspension was reconcentrated whenever a low boiling point suggested the continued presence of the extracting solvent. The suspension, cooled to room temperature, was filtered, washed with fresh 2-propanol, and dried.

The filtrate was evaporated to dryness on the water bath. The fractions were, in individual cases, examined chemically and spectrophotometrically, and their molecular weights were measured by gel-permeation chromatography.

Results

Some preliminary generalizations are useful in reviewing the experimental results.

(1) All oven-aged samples studied were, by commercial criteria, grossly understabilized. That is, after heating for one hour, they were discolored beyond the state of general commercial interest.

(2) Polymer Fraction I ranged from about 0 to about 20% of the weight of the sample and typically was smaller than Fraction II, which ranged from about 2 to about 60%. Fraction III ranged from about 60% in the samples studied.

(3) The 2-propanol-soluble substances (which were not examined in detail in this study), constituted in aggregate about 5% of the weight of the original sample, varying somewhat with the choice of additives and heat history. Infrared spectra of some of these soluble substances give evidence of the presence of ester groups. These substances containd substantially less chlorine than does poly(vinyl chloride).

(4) Polymer Fraction II was almost invariably white. Fractions I and III varied from white to pale yellow, depending on additive and heat history. The 2-propanol-soluble residue after solvent removal was a variable brown in color.

Samples, which had not been subjected to oven-aging contained, typically, 17% of Fraction I, 18% of Fraction II, and about 60% of Fraction III. These values varied only slightly (within about 2%) with

Table I. Polymer Fractions (weight %) in PVC Samples Oven Aged for One Hour at 185°C.[a]

No.	*Additive, 1% of Resin wt.*	*I*	*II*	*III*	*I + II + III*	*THF Insol.*	*Total*
1	DBPC	7	50	39	96	0	96
2	TPP	6	62	28	96	1	97
3	$\frac{1}{2}$ BaSt + $\frac{1}{2}$ TPP	8	50	39	97	2	99
4	$\frac{1}{2}$ E + $\frac{1}{2}$ TPP	9	45	44	98	1	99
5	E	9	52	29	90	5	95
6	DBTL	8	46	46	100	1	101
7	None	6	45	40	91	5	96
8	BaSt	9	40	48	97	1	98
9	BPA	7	46	30	83	12	95
10	Ba–Cd La	3	20	12	35	71	104
11	CdSt	2	5	12[b]	19[b]	74	93[b]

[a] *Legend:*

PVC = poly(vinyl chloride)
THF = tetrahydrofuran
DBPC = 2,6-di-*tert*-butyl-4-methylphenol
TPP = triphenyl phosphite
E = bisphenol A-epichlorohydrin condensate (Shell Epon 828)
DBTL = dibutyltin dilaurate
BaSt = barium stearate
BPA = 4,4′-isopropylidenebisphenol (bisphenol A)
Ba–Cd La = barium–cadmium laurate stabilizer (Ferro 1820, containing 15% Ba, 8% Cd)
CdSt = cadmium stearate

[b] Estimated value. The samples were difficult to filter after the THF extraction.

Table II. Polymer Fractions (weight %) in PVC Samples Oven Aged for Two Hours at 185°C.[a]

No.	*Additive, 1% of Resin wt.*	*I*	*II*	*III*	*I + II + III*	*THF Insol.*	*Total*
1	DBPC	7	40	17	64	36	100
2	TPP	5	45	13	63	36	99
3	$\frac{1}{2}$ BaSt + $\frac{1}{2}$ TPP	4	37	8	49	52	101
4	$\frac{1}{2}$ E + $\frac{1}{2}$ TPP	6	42	10	58	44	102
5	E	7	32	11	50	56	106
6	DBTL	2	39	26	67	32	99
7	None	6	29	12	47	59	106
8	BaSt	6	24	19	49	56	105
9	BPA	3	17	15	35	72	107
10	Ba–Cd La	2	5	5	12	100	112
11	CdSt	0	2	5[b]	7[b]	100	107[b]

[a] Legend as in Table I.

[b] Estimated value.

the nature of additives used. The results are shown in Tables I and II and in Figure 3.

Several important changes occur in the polymer during the first hour of heating.

(1) The chloroform-soluble portion (Polymer Fraction I) decreases from 17 to about 6–9%, or for cadmium-containing additives, to 2–3%. Since the quantity of 2-propanol-soluble material recovered during the chloroform extraction is generally less than the amount by which this fraction has been reduced, it is reasonable to suppose that this reduction of Fraction I has been accomplished by crosslinking. The products of such crosslinking would be found in the higher molecular weight fractions or in the insoluble polymeric residue.

(2) The butanone-soluble, chloroform-insoluble portion, with all non-cadmium-containing additives, increases from 18 to about 40–62%. This increase exceeds that attributable to the crosslinking of Fraction I. Therefore, at least part of this butanone-soluble fraction comes from a previously butanone-insoluble fraction—*i.e.*, from Fraction III. Such a change would imply chain scission. The cadmium stearate-containing sample exhibits a marked reduction in the amount of Fraction II, while a barium-cadmium additive leaves the net amount of Fraction II relatively unchanged. It appears, therefore, that in the presence of cadmium, Fraction II is also reduced in quantity by crosslinking.

(3) The tetrahydrofuran-soluble, butanone-insoluble fraction is reduced in all cases. Where there is no corresponding increase in tetrahydrofuran-insoluble resin, it is necessary to conclude that Fraction III is reduced by scission to lower molecular weight products. Where the tetrahydrofuran-insoluble resin has increased, Fraction III may, in part, have been insolubilized by crosslinking.

After 2 hours of heating, Fraction I has declined further, but only slightly. Fraction II, which was very large after the first hour, has now decreased substantially. The amount of this reduction depends on the additives present. Samples containing 1% of the hindered phenol, the phosphite, the organotin soap, the epoxy resin, or no additive have lost a considerable part of their Fraction II content. Samples containing barium soaps, barium–cadmium soaps, or an unhindered phenol (bisphenol A) have lost an even larger portion of their Fraction II content. The loss in all soluble fractions in the cadmium-containing systems has advanced further toward almost complete insolubilization.

The material balances, which now account for over 100% of most of the samples (Table II), reflect the difficulty in removing the last portion of the solvent from the insoluble fraction. As the insoluble fraction increases, the error attributable to solvent retention becomes more apparent.

The difference between the hindered phenol (DBPC), which retards insolubilization, and the unhindered phenol (BPA), which appears to promote it, is striking. The difference is also striking between a barium soap which promotes crosslinking to a small degree and cadmium stearate which catalyzes crosslinking very strongly. [Although the reader may be tempted to equate crosslinking and hydrogen chloride loss with "instability," most commercial applications are more particularly concerned with color. Cadmium compounds, properly formulated in balanced stabilizers, greatly inhibit discoloration. The mechanism of color inhibition may, in fact, depend on the substitution of crosslinking for polyene formation, a subject on which the author has previously commented (*8*).]

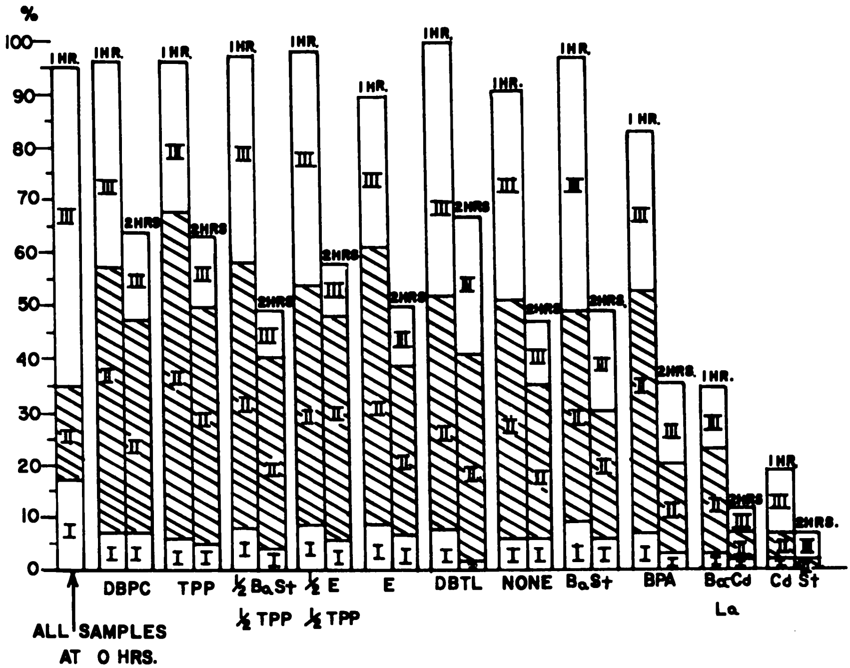


Figure 3. Changes in proportions of soluble poly(vinyl chloride) fractions on heating poly(vinyl chloride) containing 1% of various additives

This additive-dependent insolubilization of the resin may be compared with records of loss in weight of the samples during oven aging as shown in Table III.

In general, the cadmium-containing samples have lost the most weight; the barium stearate and bisphenol A samples have lost somewhat less than the cadmium samples but more than the controls. The rest of the samples are more or less indistinguishable on the basis of weight loss.

The tables show that the increasing amount of insoluble polymer is correlated with the increasing rate of hydrogen chloride loss, judging from the weight loss data. This relationship is shown graphically in Figure 4, in which the abscissa for each experimental point is the arithmetic mean of the amounts of insoluble polymer at the beginning and end of the hour for which the weight loss was measured. The fitted straight line suggests that the contribution of the insoluble polymer to rate of weight loss is probably more than five times as great as the average contribution of all other polymer fractions. The latter is estimated from the *y*-intercept. Since part of the early weight loss probably reflects volatilization of some of the additives or of their decomposition products, the part of the *y*-intercept attributable to dehydrochlorination may be somewhat less than shown, and the relative importance of the insoluble fraction in dehydrochlorination may therefore be even greater.

Table III. Weight Loss of Samples during Heating[a]

	Additive,	*Weight Loss, %*		
No.	*1% of Resin wt.*	*First Hour*	*Second Hour*	*Total*
1	DBPC	0.7	1.3	2.0
2	TPP	0.8	0.9	1.7
3	½ BaSt + ½ TPP	0.8	1.2	2.0
4	½ E + ½ TPP	0.7	1.4	2.1
5	E	0.4	1.9	2.3
6	DBTL	0.6	1.0	1.6
7	None	0.5	1.7	2.2
8	BaSt	0.9	2.6	3.5
9	BPA	1.1	3.3	4.4
10	Ba–Cd La	1.8	3.7	5.5
11	CdSt	3.0	3.7	6.7

[a] Legend as in Table I.

To determine how a strong insolubility promoter like cadmium stearate, and a strong insolubility retarder like 2,6-di-*tert*-butyl-4-methylphenol affects the resin when both are present, a series of one-hour oven-aging tests were run. The results are given in Table IV. Even at very low cadmium concentration the insolubilization effect is great and is only slightly altered by adding the hindered phenol.

To help establish that the polymer fractions were substantially unaltered components of the sample to be extracted, the following relationships were verified on the polymer fraction samples after isolation.

(1) Tetrahydrofuran was a solvent for Fractions I, II, and III.

(2) Butanone was a solvent for Fractions I and II, but appeared to dissolve minor portions of III.

(3) Chloroform was a solvent for Fraction I but not for II and III.

(4) When butanone was used as an extractant without preliminary use of chloroform, the polymer recovered was equal to the combined weights of I and II extracted separately from an equivalent sample. This was verified for many individual samples, using various additives.

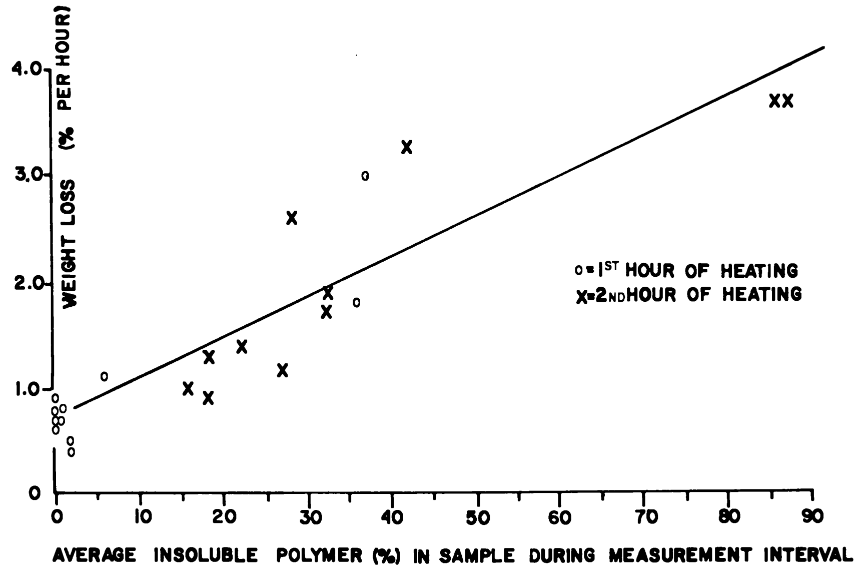


Figure 4. Weight loss of heated PVC in relation to insoluble polymer content

Thus, each of the fractions had a real identity consistent with its observed solvent extraction behavior.

The chlorine content of Polymer Fractions I, II, and III was determined by gravimetric analysis and found in all cases to be within 1% of the value for undegraded poly(vinyl chloride). (Since it was difficult to remove the last traces of solvent, the actual chlorine content of the polymers was probably even closer to the theoretical value.) The chlorine content of the insoluble residue was much lower. Thus, the insoluble residue of samples obtained from the experiments illustrated by Table III contained typically only 46–49% Cl.

Table IV. Polymer Fraction in PVC Heated for One Hour in the Presence of Cadmium Stearate and 2,6-Di-*tert*-butyl-4-methylphenol

Additives, %		*% of Original Sample Weight*		
CdSt	*DBPC*	*Fraction I*	*Fraction II*	*Fraction III*
0.1	0.0	5	9	21
0.2	0.0	3	9	13
0.4	0.0	2	5	14
0.1	1.0	4	12	17
0.2	1.0	1	11	17[a]
0.4	1.0	1	7	18
0.0	1.0	7	50	39[b]

[a] Estimated.
[b] Data from an earlier test presented here for comparison.

Polymer Fractions I and II were investigated for molecular weight distribution, with the results (showing the range of variations over all the samples so analyzed) given in Table V. (The analyses and interpretations were obtained from ArRo Laboratories, Joliet, Ill. Tetrahydrofuran was the solvent used in the column separation.)

Table V. Molecular Weight of Polymer Fractions

	Polymer Fraction II	*Polymer Fraction I*
$\overline{M}_n$	49,000–62,200	19,100–25,600
$\overline{M}_w$	103,500–118,400	33,800–46,400
$\overline{M}_w/\overline{M}_n$	1.76–2.19	1.78–1.84

The ratio of molecular weights(M_{II}/M_I) is approximately 3, and this was confirmed by independent viscosity observations.

Polymer Fraction III was generally higher in molecular weight than Fractions I and II, but it was more variable, more dependent on the heat history of the sample and, in some cases, on the physical limitations of the extraction apparatus. Typically, the molecular weights in Fraction III were about 50% higher than in Fraction II. The presence of minor amounts of low molecular weight components tended to raise the $\overline{M}_w/\overline{M}_n$ ratio of this fraction to about 3. There was also evidence in highly crosslinked samples that a small amount of extremely high molecular weight polymer soluble in tetrahydrofuran was unable to pass through the pores of the particular Soxhlet thimble used in these experiments.

Discussion

None of the polymer fractions precipitated by 2-propanol showed significant dehydrochlorination. That is, all the analyses for chlorine differed from the theoretical value by 1% or less, and this difference could be attributed at least in part to the last traces of solvent, which are hard to remove. By contrast the chlorine analyses of the insoluble residues gave evidence of extensive dehydrochlorination, even after correction was made for possible retention of solvent. The 2-propanol-soluble fractures were generally too small in quantity to contribute significantly to the over-all loss of hydrogen chloride.

It is therefore possible to consider that the most of the polymer which has undergone dehydrochlorination is to be found in the insoluble residue. One may then inquire whether the insolubilization was a consequence or a cause of hydrogen chloride loss.

If the dehydrochlorination preceded the insolubilization, then the whole process of chlorine loss and subsequent crosslinking would have to occur rapidly since at no time does there appear to be any soluble non-crosslinked polymer which is markedly low in chlorine. (One may except the 2-propanol-soluble low molecular weight substances as unlikely to be the principal intermediate in the formation of the high molecular weight insoluble residue).

When dehydrochlorination generally precedes crosslinking and insolubilization, one may postulate the sequence: undegraded polymer → dehydrochlorinated polymer → insoluble polymer. The dehydrochlorination rate should thus be greater when there is more undegraded polymer. The reverse relationship is, however, observed (*see* Figure 4). The rate of hydrogen chloride loss increases as the total amount of relatively undegraded polymer decreases, and as the amount of insoluble polymer increases.

The alternate sequence is: undegraded polymer → crosslinked and insoluble polymer → dehydrochlorinated insoluble polymer. Here a small hydrogen chloride loss would be expected to occur during crosslinking. Most of the hydrogen chloride loss would however be attributable to the subsequent reactions of the crosslinked polymer. Such a sequence can be rationalized.

The principal chemical change on crosslinking is the creation of new tertiary carbons. Since tertiary carbons already exist at branch points in the polymer before heat aging, as shown by Cotman (*5*), it may be of value to point out the fundamental change which crosslinking brings about.

Bengough and Norrish (*2*) interpreted data on the kinetics of the polymerization of vinyl chloride as evidence that chain transfer, reactivating "dead" polymer, was a common process. Cotman, drawing on some prior work by Kenyon (*16*), concluded that the establishment of the free-radical site in a previously "dead" polymer must occur by radical abstraction of a hydrogen atom and not of a chlorine atom. This left undecided whether the hydrogen must come from the CH_2 group or the CHCl group. Cotman devoted more consideration to the latter possibility than to the former, and in this respect he has been followed by those who cite his work. Although no experimental data were adduced, Cotman's choice appears to be entirely reasonable since partial delocalization of the 3*p* electrons on the chlorine atom would impart some stability to the Cl–C· structure which is not obtainable from H–C· structures (*see* Figure 5). The addition of monomer to the Cl–C· site creates the *tert*-chlorine structure.

However, the new tertiary carbon site is quite different when crosslinking occurs by dehydrochlorination. When chlorine is removed from a CHCl group, the resultant tertiary carbon bears a hydrogen. The

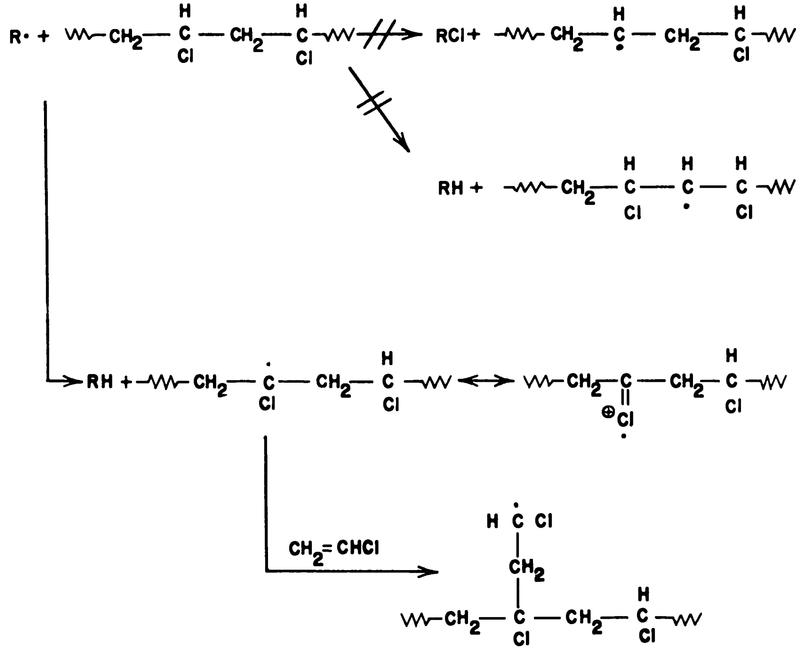


Figure 5. Formation of tertiary chlorine sites in the polymerization process

second tertiary carbon may also bear hydrogen (if crosslinking occurs with a methylene group). Thus, at least one and possibly two tertiary hydrogen sites are formed (*see* Figure 6).

The difference in the reactions of the two types of tertiary structures is significant.

(1) Tertiary alkyl chlorides are easily dehydrochlorinated by base (*via* the E2, or bimolecular elimination reaction mechanism), but the environment of the degrading resin is not basic. Loss of hydrogen chloride to yield an olefin can occur principally by the E1, or monomolecular elimination reaction. This is a slow reaction because, in the rate-determining step, the C—Cl bond is broken to form two separated oppositely charged particles. The reaction rate is not assisted by the acid present.

(2) The tertiary hydrogen structure is readily attacked by oxygen to form hydroperoxides. The thermal decomposition of a tertiary hydroperoxide results in a variety of products, including tertiary alcohols. Tertiary alcohols are easily dehydrated in an acid medium to yield olefins. The hydroxyl group is rapidly protonated by available hydrogen chloride to form an oxonium structure. Water is then lost by an E1 mechanism. The reaction is facilitated by the circumstance that water is a neutral molecule, and hence there is no strong electrostatic attraction to be overcome in the physical separation of the water from the positively charged carbon atom. Since protonation is required to prepare the structure for

the elimination step, the reaction is acid catalyzed and is thus favored by the environment of the degrading resin (*see* Figure 7).

Thus, the initiation of double bond formation in poly(vinyl chloride) seems to be a simple consequence of crosslinking. The crosslinking step appears to be ionic in mechanism. Bengough and Sharpe (3), working with poly(vinyl chloride) in ethyl benzoate solution, concluded that "crosslinking occurs *via* intermolecular condensation with the elimination of HCl and not by a free radical process." The study was concerned with the early stages of crosslinking which resulted, in their experiments, in gel formation.

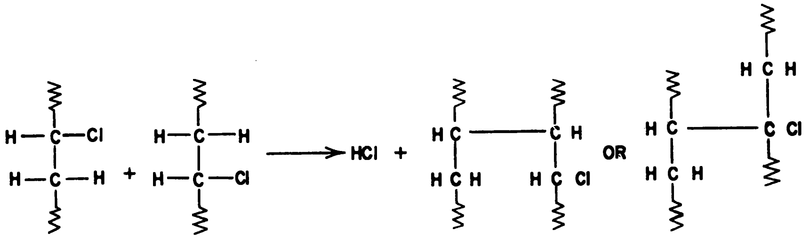


Figure 6. Formation of tertiary hydrogen sites by crosslinking

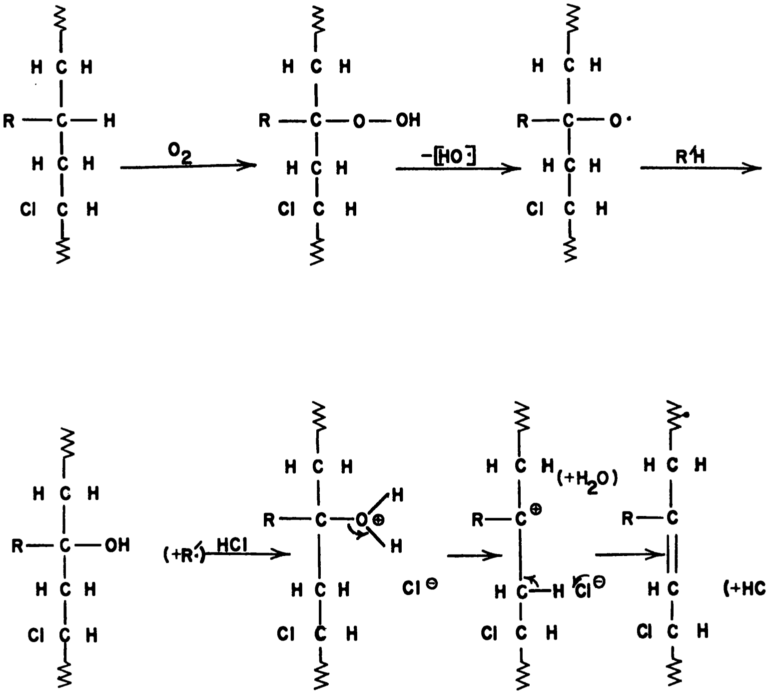


Figure 7. Formation of olefin by oxidation and elimination reactions

The rapid increase in the rate of formation of the insoluble fraction when cadmium is present suggests that crosslinking may occur in an ionic mechanism in this solvent-free system, too.

The effect of metal compounds on HCl evolution has been noted by many authors. Thus, Hartmann (*12, 13*) pointed out that lead and dibutyltin compounds did not affect dehydrochlorination rate, but ferric salts and zinc chloride accelerated it. Rafikov and co-workers (*22*) reported that lead and calcium soaps promoted crosslinking. These investigators do not seem to have considered the hypothesis that dehydrochlorination is accelerated as a consequence of crosslinking.

To the extent to which mechanisms have been proposed to account for the catalytic effect of some metal salts in dehydrochlorination (*e.g.*, by Troitskaya and Troitskii (*27*)), the removal of H and Cl from adjacent carbon atoms on the same chain is generally postulated. Such mechanisms, with little modification, could as easily explain crosslinking. Crosslinking will, of course, occur without metal catalysts, but the rate is much slower.

At this point the partial reaction scheme consists of a crosslinking step (possibly ionic) which establishes a hydrogen-bearing tertitary carbon. Oxidation occurs at this point which may lead to double-bond formation.

Once the double bond is formed, further dehydrochlorination proceeds more readily. The activation energy for allylic propagation is lower than that required to form new isolated double bonds. Since, however, isolated double bonds are probably formed as a consequence of crosslinking and subsequent oxidation, the dehydrochlorination proceeds predominantly in the crosslinked (*i.e.*, the insoluble) fraction of the degrading mass. The more highly crosslinked systems (*i.e.*, those formed in the presence of cadmium compounds) have higher rates of weight loss and thus presumably higher dehydrochlorination rates.

During the first hour of heating, the rate of weight loss exhibits no clear dependence on choice of additive in the non-cadmium systems. During the second hour of heating, there is more crosslinking and more dehydrochlorination, but it is evident that these reactions are not simply continuations of what was observed during the first hour. At this stage, hindered phenols can retard crosslinking. An unhindered phenol (bisphenol A) does not. Crosslinking, thus, has become a reaction over which an antioxidant has some control.

This change can be attributed to the fact that the composition of the system during the second hour has changed markedly from what it was earlier. It is now, in a sense, a network-reinforced plastic, in which the network consists of crosslinked partly dehydrochlorinated polymer, and the interstices are filled with relatively undegraded polymer.

The dehydrochlorination has brought into being a high concentration of double bonds. Free radical addition to double bonds is therefore increasingly probable. By hydrogen abstraction reactions in the presence of oxygen, free radical sites can be established in the previously undehydrochlorinated molecule. During the second hour of heating there are enough double bonds to make likely the addition of the free radical so formed to the insoluble crosslinked double-bonded polymer. The quantity of insoluble polymer is thus increased.

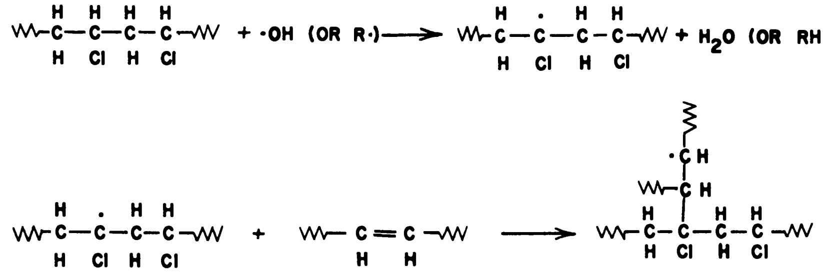


Figure 8. Crosslinking by addition to olefinic double bond

The carbon of the olefinic group at which the addition reaction occurs becomes again a tertiary carbon bearing a hydrogen, and the oxidative degradation is again initiated (*see* Figure 8).

The antioxidant (a hindered phenol or, to a smaller extent, a phosphite) can retard this latter stage free radical crosslinking by any of several mechanisms, or by a combination of them.

(1) The antioxidant may retard the attack of oxygen at the original crosslinking site and thus preclude the sequence which leads ultimately to the polyene structures required for the later free radical crosslinking reaction.

(2) The antioxidant may retard the allylically propagated free radical dehydrochlorination along the chain. By so doing, it decreases the number of sites available for later free radical crosslinking.

(3) The antioxidant may lose a hydrogen atom to an attacking free radical and thus render it less capable of adding to an olefinic double bond.

Conclusions

Milled rigid sheets of poly(vinyl chloride) on oven aging at 185°C. undergo a slow initial dehydrochlorination which, if continued long enough, results in the formation of a tetrahydrofuran-insoluble fraction. This insoluble polymer dehydrochlorinates much more rapidly than the soluble polymer fractions.

The early dehydrochlorination probably results, at least in part, from a crosslinking reaction. This reaction is catalyzed by cadmium-containing additives and is probably ionic in character.

The acceleration of dehydrochlorination in the crosslinked insoluble fraction is probably attributable to oxidation at the tertiary carbon formed by crosslinking, and to the subsequent ease of acid-catalyzed thermal decomposition to yield olefinic structures. The oxidation and the subsequent propagation of polyene structures are free radical in nature and are therefore inhibited to some extent by antioxidants.

Acknowledgment

I am gratefuly to Margaret Acela for her assistance in the laboratory work and to Ferro Chemical Division, Ferro Corp., for making possible this investigation and the publication of these results.

Literature Cited

(1) Arlman, E. J., *J. Polymer Sci.* **12,** 547 (1954).
(2) Bengough, W. I., Norrish, R. G. W., *Proc. Roy. Soc. (London)* **A200,** 301 (1950).
(3) Bengough, W. I., Sharpe, H. M., *Makromol. Chem.* **66,** 45 (1963).
(4) Boyer, R. F., *J. Phys. Colloid Chem.* **51,** 80 (1947).
(5) Cotman, J. D., *Ann. N.Y. Acad. Sci.* **57,** 417 (1953).
(6) Druesedow, D., Gibbs, C. F., *Natl. Bur. Std. Circ.* **525,** 95 (1953).
(7) Fox, V. W., Hendricks, J. G., Ratti, H. J., *Ind. Eng. Chem.* **41,** 1774 (1949).
(8) Fuchsman, C. H., *SPE J.* **15,** 787 (1959).
(9) Furukawa, J., Kimura, T., *J. Chem. Soc. Japan, Ind. Chem. Sect.* **55,** 133 (1952).
(10) Goto, K., Fujii, H., *Chem. High Polymers (Tokyo)* **14,** 644 (1957).
(11) Guyot, A., Benevise, J. P., *Ind. Plastiques Mod. (Paris)* **13** (5), 37 (1961).
(12) Hartmann, A., *Kolloid Z.* **139,** 146 (1954).
(13) *Ibid.,* **149,** 67 (1956).
(14) Imoto, M., Ota, M., *J. Chem. Soc. Japan, Ind. Chem. Sect.* **54,** 470 (1951).
(15) Imoto, M., Otsu, T., *J. Inst. Polytechnics, Osaka City Univ. Ser. C* **4** (2), 269 (1953).
(16) Kenyon, A. S., *J. Am. Chem. Soc.* **74,** 3372 (1952).
(17) Marvel, C. S., Horning, E. C., "Organic Chemistry, An Advanced Treatise," H. Gilman *et al.*, Eds., Chap. 8, p. 754, Wiley, New York, 1943.
(18) Marvel, C. S., Jones, G. D., Mastin, T. W., Schertz, G. L., *J. Am. Chem. Soc.* **64,** 2356 (1942).
(19) Marvel, C. S., Sample, J. H., Roy, M. F., *J. Am. Chem. Soc.* **61,** 3241 (1939).
(20) Mikhailov, N. V., Tokareva, L. G., Klimenkov, V. S., *Kolloid Z.* **18,** 578 (1956).
(21) Ota, M., *J. Chem. Soc. Japan, Ind. Chem. Sect.* **55,** 31 (1952).
(22) Rafikov, M. N., Razinskaya, I. N., Popova, Z. V., Shtarkman, B. P., *Tr. po Khim. i Khim. Tekhnol.* **1963** (2), 303.

(23) Razuvaev, G. A., Troitskaya, L. S., Myakov, V. N., Troitskii, B. B., *Dokl. Akad. Nauk SSSR* **170** (6), 1342 (1966).
(24) Rozhdestvenskii, V. A., *Khim. Prom.* **1954,** 350.
(25) Scarbrough, A. L., Kellner, W. L., Rizzo, P. W., *Natl. Bur. Std. Circ.* **525,** 95 (1953).
(26) Talamini, G., Pezzin, G., *Makromol. Chem.* **39,** 26 (1960).
(27) Troitskaya, L. S., Troitskii, B. B., *Plast. Massy.* **1966** (7), 46.

RECEIVED April 14, 1967.

3

Effect of Stabilizers on the Melt Rheology of Poly(vinyl chloride)

L. B. WEISFELD, G. A. THACKER, and L. GIAMUNDO

Advance Division, Carlisle Chemical Works, Inc., New Brunswick, N. J. 08903

Rheological studies using the Brabender plastograph show that the magnitude of the torque plateau generated by molten, unplasticized poly(vinyl chloride) depends greatly on the nature of the metal or organometallic stabilizer incorporated. These effects are related to the extrusion rates and dynamic processing liability of the resin compound. It is proposed that the apparent increase in viscosity is caused by the propensity of the metal atom of the stabilizer to satisfy its vacant d-*orbital requirements with the* p-*electrons of the pendent substituents on the polymer chain, thereby setting up secondary crosslink structures and increasing the dynamic liability of the compound. Low melt viscosities engendered by organotin mercaptides are explained by intramolecular* $d\pi$–$p\pi$ *orbital fulfillment.*

Since a wide variety of thermoplastic materials are fairly stable at processing temperatures, the incorporation into them of low molecular weight adjuvants, notably stabilizers and antioxidants, is almost superfluous. No one will say that such adjuvants are unnecessary, but in many cases the benefits are related mainly to end use and the retardation of aging effects. Poly(vinyl chloride) (PVC), however, is perhaps the most liable of the commercial thermoplastics. Processing of PVC is hardly possible without using stabilizers, and most practical innovations in PVC applications have been foreshadowed by advances in stabilizer technology.

In the early history of PVC, application was confined almost entirely to highly plasticized and flexible compositions, and the thermal processing liability of such formulations was practically the only question. Minimal mechanical shear work was applied to the polymer itself. Concomitant with the growth of the industry was the discovery that certain metal soaps and combinations effectively retarded thermal degradation during processing. It was sufficient, for the most part, to determine the efficacy of a stabilizer system for any particular PVC formulation by a relatively simple "oven test," whereby PVC films were incubated in a circulating air oven for varying periods of time, and the rate of color development was noted.

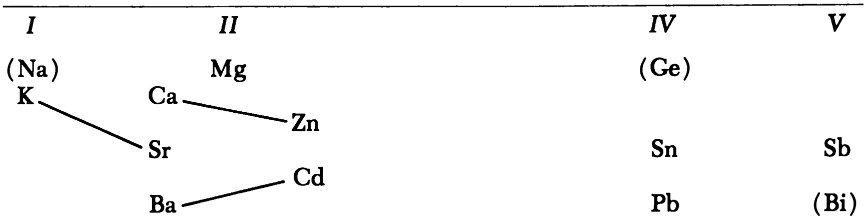
With the discovery of the organotin mercaptide stabilizers came the realization that much more could be demanded of the processing latitude for PVC. Plasticizer levels dropped, and rigorous extrusion techniques became practical, leading eventually to the production of clear and rigid PVC articles. Today, the most interesting and rapidly growing area of PVC application technology is in rigid products (bottles, pipes, building materials). Much more is demanded of a stabilizer than its simple thermal response. The "oven tests" are no longer sufficient and, indeed, scarcely correlate with the phenomena obtained in the extruder. A critical distinction exists between the "static" and "dynamic" thermal liability of PVC.

It is not the purpose of this paper to review or expound on the well-documented stabilization mechanisms for PVC. Nor will we consider the other well known auxilliaries to PVC stabilization such as phosphites, epoxies, and hindered phenols. Rather, attention will be paid to only the primary metallic and organometallic stabilizers, the principle elements illustrated in Table I. The metal soap derivatives of the Group II elements invariably are not used singly, but in Subgroup A-B couples.

Table I. Elements of Metallic (or Organometallic) Stabilizers of Interest in Stabilizing Poly(vinyl chloride)

Periodic Arrangement of Stabilizer Elements

Group



I	*II*		*IV*	*V*
(Na)	Mg		(Ge)	
K	Ca			
		Zn		
	Sr		Sn	Sb
		Cd		
	Ba		Pb	(Bi)

Aside from lead compounds, the elements currently used in most applications are barium, cadmium, calcium, zinc, and tin—*e.g.*, the calcium–zinc soap systems for nontoxic (food contact) applications, the general purpose barium–cadmium soap stabilizers, and the organotin stabilizers. The objective of this paper is to consider the rheological consequences of using these materials in rigid PVC and to provide a possible explanation for this behavior.

Experimental

The Brabender plastograph was used for these investigations with a 120-mm. chamber, roller heads, oil heated, and ram charged. A typical plastograph curve, with its important characteristics, is illustrated in Figure 1. The time to decomposition of rigid PVC is usually noted by an upward inflection at the end of the curve, where crosslinking ostensibly occurs. This inflection is coincident with the evolution of HCl, detected by Congo Red paper. More important for current considerations, the minimum torque plateau preceding decomposition provides an estimate of the effect of the stabilizer component on the melt viscosity of the compound, all other compound factors being equivalent.

Two types of resin were investigated: PVC homopolymer (Opalon 630) and copolymer (Diamond CR-80). The stabilizer systems used are indicated in Table II. The organotin series of stabilizers proceeds from

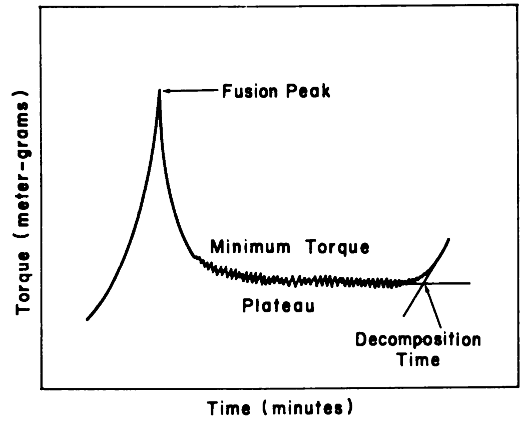


Figure 1. Typical Brabender plastograph curve

Table II. Stabilizers Used in Dynamic Stability Studies

Stabilizer	*Identity*
$Bu_2Sn(SCH_2COOR)_2$	Dibutyltin bis(isooctyl acetomercaptide)
$Bu_2Sn(SR)_2$	Dibutyltin bis(lauryl mercaptide)
$Bu_2Sn(SCH_2CH_2COO)$	Dibutyltin mercaptopropionate
$Bu_2Sn(OCOCH{=}CHCOOR)_2$	Dibutyltin bis(isooctyl maleate)
BC-1	14% Ba, 7% Cd carboxylates
BC-2	7% Ba, 11% Cd carboxylates
CZ-1	1% Ca, 1% Zn carboxylates
CZ-2	1% Ca, 2% Zn carboxylates

those with only tin-carbon and tin-sulfur bonds, through one with tin-carbon, tin-sulfur and tin-oxygen bonds, to finally a tin-carbon, all tin-oxygen bond species. Formulated compounds were "dry blended" in a laboratory Henschel mixer. In addition to the stabilizers and amounts noted in Table III, the homopolymer was compounded with 1.0 p.h.r. (per 100 parts of resin) of epoxidized soya oil and 0.25 p.h.r. glyceryl monostearate. No additional adjuvants were used with the copolymer resin. Sixty grams of each compound were rammed into the plastograph chamber, and those of the homopolymer were sheared at 175°C. jacket temperature and 40 r.p.m. Copolymer compounds were sheared at 180°C., 35 r.p.m. The results for homopolymer are shown in Table III and those for copolymer in Table IV.

Table III. Plastograph Results for PVC Homopolymer with Various Stabilizers[a]

Stabilizer	*Concentration, % per 100 resin*	*Minimum Torque, meter-grams*	*Decomposition, minutes*	*Stock Temperature, °F.*
$Bu_2Sn(SCH_2COOR)_2$	2.0	2350	18.8	395
$Bu_2Sn(SR)_2$	2.0	2200	12.6	400
$Bu_2Sn(SCH_2CH_2COO)$	1.0	2400	9.9	400
$Bu_2Sn(OCOCH{=}CHCOOR)_2$	2.1	2650	4.8	405
BC-1	2.0	2600	7.5	390
BC-2	2.0	3100	17.4	395
CZ-1	2.0	2800	6.3	390
CZ-2	2.0	2700	5.0	390
None	—	2750	4.5	410

[a] Resin, Opalon 630, 100.0 p.h.r., with 1.0 p.h.r. epoxidized soya oil and 0.25 p.h.r. glyceryl monostearate. Sheared at 175°C., 40 r.p.m.

Table IV. Plastograph Results for PVC Copolymer with Various Stabilizers[a]

Stabilizer	*Concentration, % per 100 resin*	*Minimum Torque, meter-grams*	*Decomposition, minutes*	*Stock Temperature, °F.*
$Bu_2Sn(SCH_2COOR)_2$	2.0	420	17.5	375
$Bu_2Sn(SR)_2$	2.0	500	14.6	375
$Bu_2Sn(SCH_2CH_2COO)$	2.0	590	10.5	375
$Bu_2Sn(OCOCH{=}CHCOOR)_2$	2.0	600	11.5	374
BC-1	3.0	610	7.7	370
BC-2	3.0	600	7.5	370
CZ-1	2.0	900	1.8	375
CZ-2	2.0	900	3.3	365
None	—	620	9.3	375

[a] Resin, Diamond CR-80, 100.0 p.h.r. Sheared at 180°C., 35 r.p.m.

Discussion

The lowest melt viscosities are provided by the organotin mercaptides, as are the longest stabilization periods. As tin-oxygen bonds replace the tin-sulfur bonds, the melt viscosities increase and the stabilization times diminish. These phenomena cannot be explained on the basis of simple plasticization or "internal lubricity" since no structural correlations are apparent. For example, the dibutyltin bis(isooctyl maleate) and dibutyltin bis(isooctyl thioglycolate) are liquids of approximately the same viscosity and molecular weight, and yet they provide opposing melt viscosity behavior. Further, the magnitude of increase in melt viscosity for homopolymer between these two stabilizers (13%) is smaller than that for copolymer (43%). The barium–cadmium stabilizers and the calcium–zinc system also provide high melt viscosities, for the most part exceeding that for the organotin carboxylate.

A probable explanation for these effects resides in a recognition of the vacant *d*-orbital requirements of the metal (organometal) stabilizers. The increase in melt viscosity may be the product of an intermolecular chain association through the vacant *d*-orbitals of the organotin carboxylates, which have a hexacoordinate aptitude, or those of the Group II metals, which have a tetracoordinate aptitude for the most part. Thus, the vacant orbital requirements are satisfied through coordination with the *p*-electrons of pendent substituents on the polymer chain, setting up secondary crosslinks in the polymer network, as shown in Figure 2. The situation would probably be further aggravated in copolymer (vinyl acetate) systems because of the greater basicity of oxygen over chlorine. Such a configuration as shown in Figure 2 has been considered previously in explaining the mechanism of stabilization afforded by organotin com-

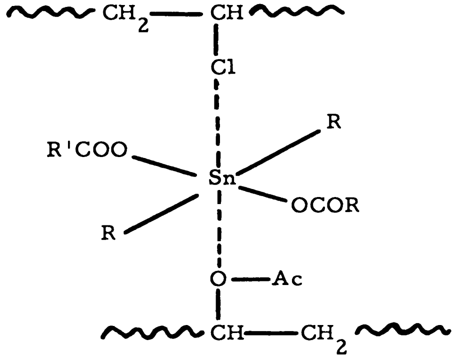


Figure 2. Probable configuration of a secondary crosslink in a PVC-PVAc melt

pounds and other metal salts (2). However, it was invoked without considering the consequences of dynamic liability.

Attention is drawn to the feature of 17.4 minutes of apparent stabilization provided by BC-2 in homopolymer (Table III). This is inordinately long and demonstrates that torque plateaus under consideration do not necessarily correspond with stabilization times. For that matter, BC-2 is unique in that it contains an organic auxilliary stabilizer which, although it apparently increases the "decomposition" time, does not otherwise diminish the polymer bonding aptitudes of the metal-containing stabilizer.

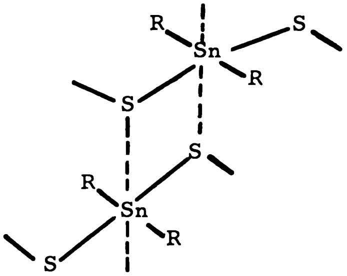


Figure 3. Possible route to orbital requirement satisfaction within the organotin mercaptide series

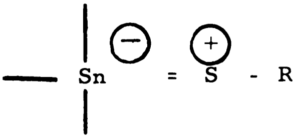
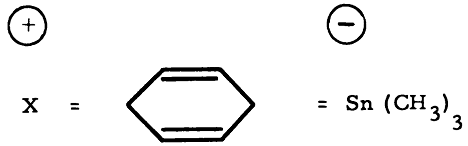


Figure 4. Representation d_π-p_π *overlap between tin and sulfur*

With the organotin mercaptides, the lowest melt viscosities are manifest. This can be explained by the ability of sulfur to expand its octet, or more correctly, by the ability of sulfur pi electrons to overlap the vacant tin *d*-orbitals. Oxygen has a much lower aptitude for such. One possible polymeric configuration for organotin mercaptides is shown in Figure 3. In lieu of this, it is more probable that significant d_π-p_π bonding occurs intramolecularly between tin and sulfur (Figure 4). Such has been suggested for certain trimethylphenyltin derivatives (3), where electric dipole measurements indicate that structures such as that in Figure 5 contribute to the ground state of molecules wherein strongly



Journal of Organometallic Chemistry

Figure 5. Electric dipole representation of trimethylphenyltin derivative

electron-releasing substituents are attached para to the $Sn(CH_3)_3$ group. It has even been suggested that double bond character between Sn—C or Sn—halogen exists in the series $(CH_3)_nSnX_{4-n}$ where X is Cl, Br, and I through PMR spectra and electric moment studies (*4*). The existence of such double bond character between tin and sulfur would obviate the necessity of using pendent pi-electron rich substituents on polymer chains for satisfying orbital requirements. That such requirements are fulfilled by sulfur next to tin is consistent with the foregoing observations.

The factors which cause an increase in melt viscosity of molten, unplasticized PVC are also responsible for the gelation of solutions of homo- and/or copolymer (*1*). For that matter, an analogous explanation is envoked, and it has been shown that displacement of simple ligands on the metal soaps by chelating types of ligands—*i.e.*, those which possess pi-electron rich substituents adjacent to the principal point of attachment, will reverse gelation.

In summary, care must be exercised in choosing stabilizers for rigid PVC extrusion, and attention must be paid to the effect of such a stabilizer on the melt viscosity of the resin. By using a bonding type of stabilizer, not only may the melt viscosity be increased beyond practical extrusion rates, but the dynamic liability of compound is increased. Magnifying these effects are increased extruder residence time and a curtailment of regrind possibilities. For all these reasons and the foregoing considerations, the organotin mercaptides are, today, the most versatile and useful stabilizers for rigid PVC processing.

Literature Cited

(1) Burger, C. A., U. S. Patent **3,259,597** (July 5, 1966).
(2) Frye, A. H., Horst, R. W., Paliobagis, M. A., *Am. Chem. Soc., Div. Polymer Chem., Preprints* **4** (1) 260 (1963).
(3) Huang, H. H., Hui, K. M., *J. Organomet. Chem.* **6,** 504 (1966).
(4) van den Berghe, E. V., van der Kelen, G. P., *J. Organomet. Chem.* **6,** 515 (1966).

RECEIVED February 6, 1967.

4

Determination of the Stability of PVC Compounds Against High Temperature

JINDŘICH NOVAK

Research Institute for Rubber and Plastics Technology,
Gottwaldov, Czechoslovakia

Two apparatuses are described for determinating darkening, electrical resistance decrease, and dehydrochlorination of PVC compounds. The rate of degradation can be followed on the foil or paste-like pure polymer (eventually on its compounds), heated in oxygen or an inert atmosphere. The time dependence of these changes serves as a guide for solving the stability problem and for examining the PVC destruction mechanism. The apparatus used to detect escaping HCl can also be used to evaluate heat destruction of the polyolefin according to the proposed ISO Recommendation. The equipment, which is based on the conductometric principle, can be installed easily in any kind of machine or apparatus where the polymer is exposed permanently to high temperature.

Degradation of a polymer can be evaluated by its rate of decomposition. This consists of dehydrochlorination, change in color, electrical resistance, viscosity, solubility, specific weight, and infrared spectrum. The factors influencing the rate of destruction are:

(1) Properties of the macromolecule concerning chlorine distribution, chain branching, presence of the double bond, primary oxy groups, and partially polymerized residues of initiating and emulsifying agents.

(2) Compound admixtures.

(3) Trace impurities of compounds ingredients.

(4) Oxygen effects.

(5) Participation of the products of degradation and stabilization.

Darkening is attributed to the presence of a polyene structure exceeding seven conjugated bonds which results from dehydrochlorination. It is known that the discoloration of PVC is not directly related to the released HCl either from a time or a quantitative point of view. In their studies Dyson *et al.* did not find sufficient evidence to claim that color change was induced by polyenes. Instead, they assumed that color changes lead to colored compounds of fulvene type (2).

The study of this effect in our laboratory proved that high active carbon black, when mixed in low concentrations with polyethylene, colored the polyethylene to ruby and brown shades. Using surface-active agents to enhance its despersion, PVC compounds could also be colored to similar shades. To prepare a reference color chart, glass standards containing different amounts of carbon proved convenient.

The first product of the PVC pyrolysis is basically HCl, the skeleton C_nH_n remains from the macromolecule. Continuing the pyrolysis at higher temperature, aliphatic and aromatic hydrocarbons are found in the volatile products, most of which are of higher hydrogen content than the formula indicates. In addition, a small quantity of free hydrogen and traces of water have been observed (5). These products arise from the dehydrogenation and carbonization of the residue. If we follow the degradation by the conductiometric method described below, we can apply an equivalency principle with regard to the effect of temperature or time under heat stress on the degradation. Therefore, even at temperatures below 200°C. chemisms of destruction similar to that mentioned above is to be expected. However, the rate of the process is substantially lower. The darkening of polymer can be caused by the initiation of carbonization, which at high temperatures undoubtedly takes place.

We did not succeed in isolating the presumed colloidal carbon from a degraded PVC solution either by electrolysis or by means of an ultracentrifuge. With highly viscous solutions and maximum carbon activity this task would have been a great problem.

The PVC compound represents a solid dispersion of the individual ingredients rather than a solution. The interaction of the ingredients cannot be evaluated merely on the basis of analogous chemical processes. In a solid, dispersion chemical processes depend on melting point, polarity, viscosity, and surface activity. Inactive substances may alter the reactivity by changing these properties (4). Owing to these complex relations, the possibility of success in analyzing these substances is relatively low. The lack of knowledge of the thermal decomposition is felt even more when stabilizers are added. The formulation for stabilizing PVC cannot yet be computed but must be found empirically.

For this reason an apparatus for determining thermal stability on the basis of electrical resistance change (3) was designed, and an automatic device for exposing PVC strip specimens to a gradient increase of heating time at the test temperature was built.

Conductivity Method

The change in electrical resistance of heated PVC has been used to measure degradation. The method can be used to measure small polymer specimens, to evaluate colored to black compounds, and to express the stability directly by a numerical time value.

The apparatus consists of cylindrical heated electrodes with the test specimen between them. To prevent the specimen from sticking to the electrodes, the contact surfaces were covered by aluminum foils. In the given time intervals, ranging from 3 to 10 minutes, the resistance of the heated specimen was measured. The values obtained were converted to conductivity and plotted on a logarithmic coordinate system. The point of the curve where a rapid increase in conductivity sets in was taken as the stability value (*see* Figure 1). Conventional electrical resistance decrease as compared with the value obtained after heating the sample for 5 minutes at a given test temperature was proposed as a criterion during the discussion of this method at the International Standard Organization. In this proposal the device used has been simplified as much as possible, thus making it available to everyone. Our apparatus consists essentially of a metal plate on which the sample is placed and loaded with a weight of about 500 grams. Both the plate and weight are used as electrodes and are connected to an ohmmeter. The unit is heated in a circulating air drier.

Conductivity measurements were carried out at several test temperatures on a series of compounds with various polymers and stabilizers.

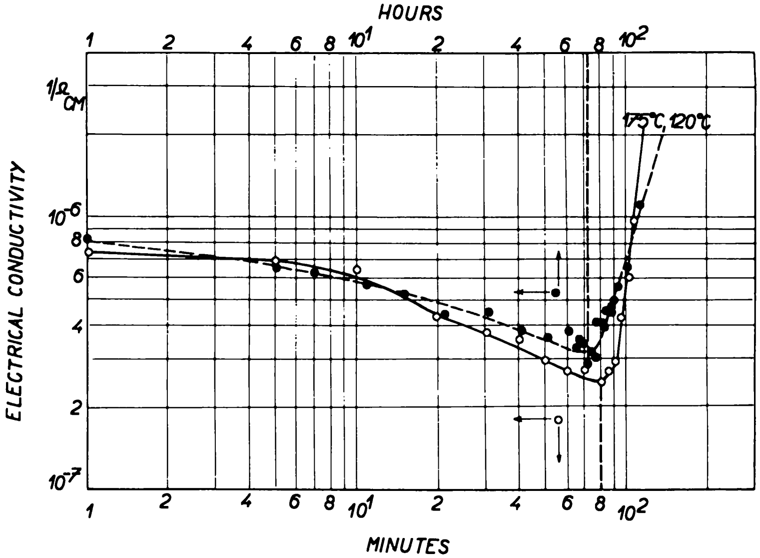


Figure 1. Determination of the stability of PVC compounds on the basis of conductance change. Time at test temperature of 120°C. expressed in hours; at 175°C. in minutes

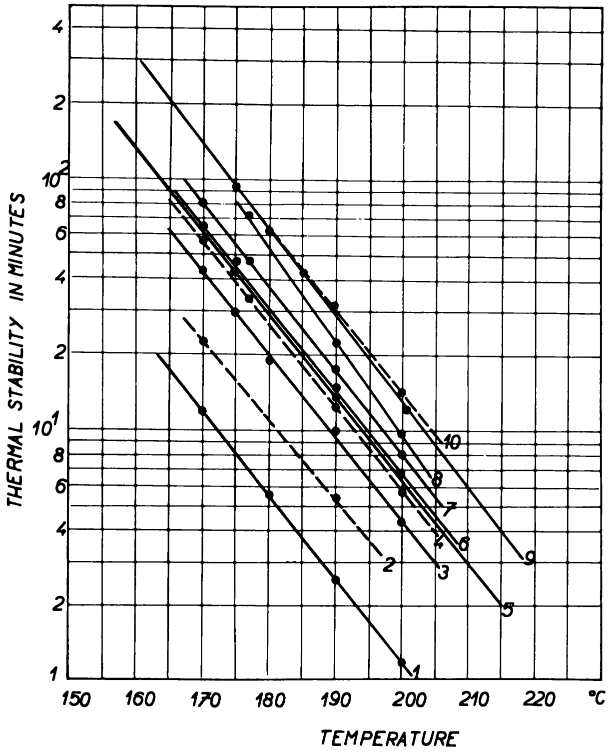


Figure 2. Dependence of heat stability on test temperature in Compounds 1–10

A plot of temperature *vs.* measured stability on a logarithmic scale gives parallel straight lines for the individual compounds (Figure 2). This illustrates the heat effect at any temperature and corresponding time and allows one to construct a nomogram for converting the stability at one temperature to that at another (Figure 3). It is also possible to convert the values according to:

$$\log S_1 = \log S_2 + \frac{T_2 - T_1}{30}$$

where S_1 is the desired stability at temperature T_1 in a compound, whose stability at temperature T_2 may be estimated as S_2 minutes. In this way the stability values corresponding to lower temperatures may be obtained, and no long term measurements need to be carried out.

An improved apparatus was designed to allow simultaneous detection of hydrogen chloride generation. It consists of a titanium block maintained at a given temperature (Figure 4). Six test tube-shaped cavities are within this block, their upper and lower ends provided with gas ducts for conveying the hydrogen chloride generated by absorption.

Each of the cavities is occupied by one pair of cylindrical electrodes from metallic titanium, connected to the cavity cap. After unlocking the plug, the electrodes can be drawn out of the heated space, and a PVC specimen is placed between them. The electrode material is hydrogen chloride

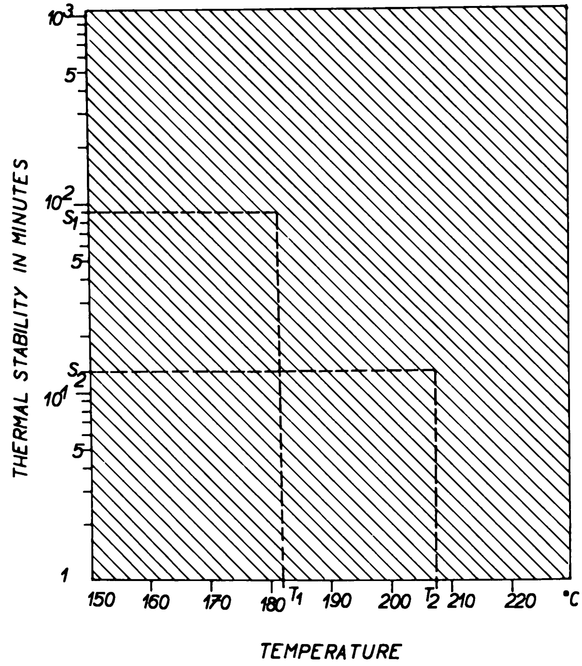


Figure 3. Nomogram for converting the stability found at one test temperature to another

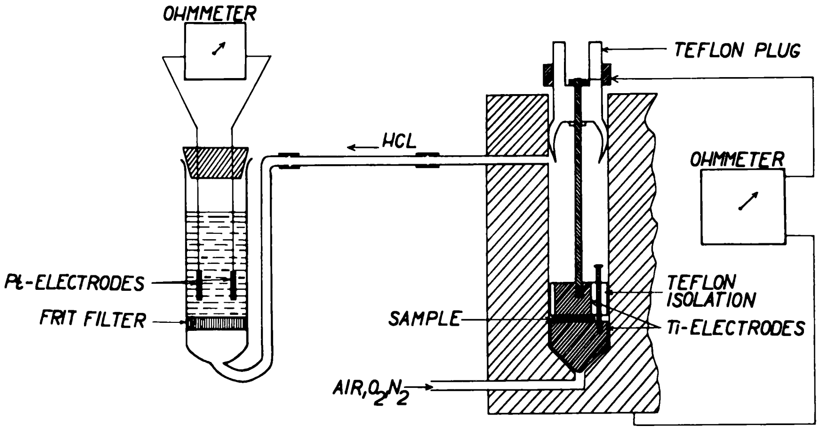


Figure 4. Conductometric layout

resistant, making it unnecessary to protect the electrodes with aluminum foils.

Three electrode types are used. The first is a partly smooth surface to allow minimum contact with the test atmosphere. The second is corrugated to enhance the contact and facilitate HCl escape. The third is hollow on the bottom for placing powdered materials and has a corresponding projection on the upper part (Figure 5). PVC materials in the shape of powder and paste foils can be evaluated in the apparatus when using the corresponding electrodes. Heat degradation may be carried out in various atmospheres. The hydrogen chloride generated is conveyed by an inert gas and absorbed in redistilled water where the change in electrical resistance is measured between platinum electrodes. In this way, both the change in electrical resistance and the rate of hydrogen chloride generation can be studied simultaneously.

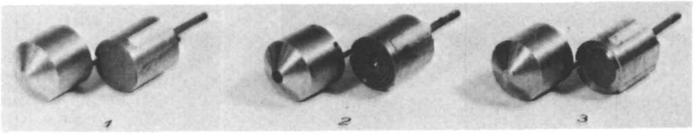


Figure 5. Titanium electrodes

1: Smooth surface
2: Corrugated surfaces
3: For loose materials

Automatic Device for Evaluating the Thermal Stability on the Basis of Color Change

To determine the color change of PVC materials, another device has been built and tested, as shown in Figure 6. The basic apparatus is a

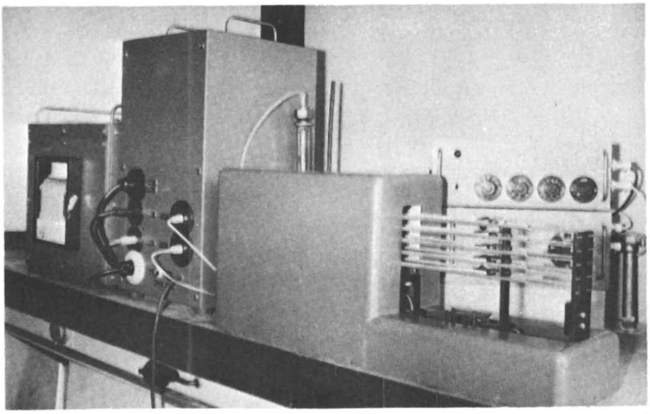


Figure 6. Automatic device for exposing strip test pieces to elevated temperature

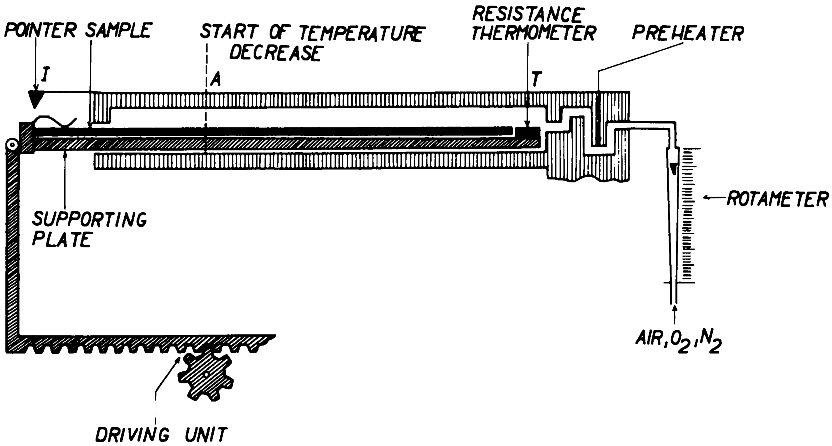


Figure 7. Automatic device outlay

tunnel maintained at a temperature between 120° and 220°C. It is divided into five stages, with gas inlets at their back sides for preheated gas. There the thermal degradation occurs. On the front side of each stage a slot is provided through which the specimen is shifted, and gas may pass freely outward (*see* Figure 7). Specimens of 40 × 250 × 0.5 mm. are cut in such a way that the expected contraction at elevated temperatures takes place longitudinally. With the traveling mechanism shut off, the specimens are fastened to glass supports and are inserted in the preheated apparatus. Now, a time relay is actuated. As soon as the specimen has reached the set test temperature, the relay engages the traveling mechanism, moving the specimens out of the heated area. The specimens inserted reach the test temperature within 7–10 minutes. During this preiod, their dimensional stabilization is accomplished also.

The degradation time is set according to thermal conditions. It is carried out by means of a platinum resistance thermometer which has been fastened to the inside of the specimen-supporting plate provided with a ruler. The supporting plate is inserted in the apparatus in such a way that the outer ends of the specimens are located at the index mark I. This mark is kept stationary for 10 minutes and then drawn out by the travel mechanism at a constant rate of 2 mm./min. As soon as the recorded temperature begins to decrease, the distance of the thermometer from the index IA is read off the scale. Point A represents the border of the heated area. In Figure 8, the tunnel temperature is represented by the curve C_A. The temperature course at the internal end of the specimen during one operation is shown in curve C_B. To determine the temperature at A, the platinum thermometer is inserted in the tunnel up to the depth IA. It is allowed to heat up again for 10 minutes and is drawn out in the same manner as before. At A the temperature corresponds to the curve C_D. Here, the sample is heated to the test temperature T_1; only and while leaving the heated zone it is cooled again. It is possible to correlate the thermal degradation occurring at A to the given test

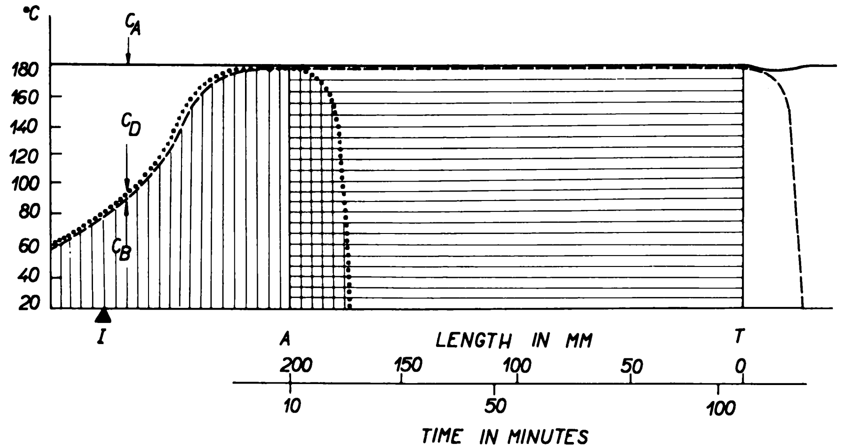


Figure 8. Temperature course

C_A: *Within the device*
C_B: *At internal specimen end*
C_D: *At the point corresponding to the distance* $\overline{IA}$ *from the external end of specimen*

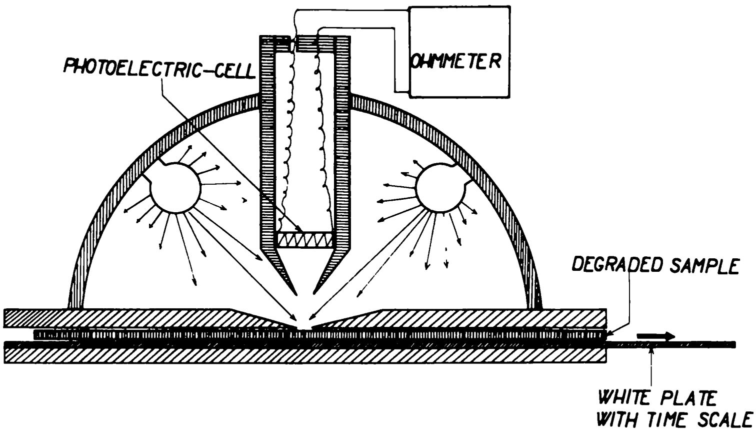


Figure 9. Device for evaluating color change by photoresistance apparatus

temperature using the heat stability-test-temperature relation which has been determined by the conductivity method. Region C_D is to be divided into an arbitrary number of time intervals S_2 with average temperatures, T_2. It is based on S_1 at temperature T_1 computed for specific segments. The sum of the resulting values of all segments gives an approximate time during which it would be necessary to maintain the material at temperature T_1 to obtain the same degree of degradation. Should the thermal degradation value converted to temperature T_1 be equal to 10 minutes, for example, the specimen must be applied with its point A to the corresponding number on the time scale. From this point, as mentioned before, the course of the heat stress of the sample exposed is linear. The color change caused by degradation is then followed continuously. This is preferable to another test method, which permits evaluation only of step changes of color during selected time intervals. By a single operation a color change corresponding to a heating period of up to 100 minutes can be determined.

With highly stable specimens the exposure must be repeated several times, and the time scale reading must be multiplied by the same factor. Should the approximate stability be known, it is possible to extend the exposure time, correspondingly.

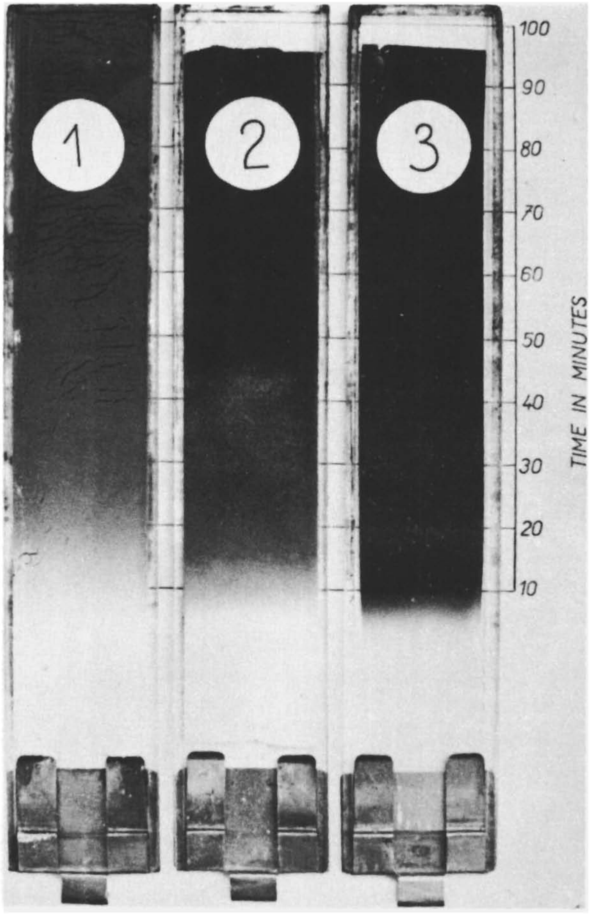


Figure 10. Exposed specimens of the same unstabilized domestic emulsive polymer (1, powder; 2, paste; 3, foil)

The specimens exposed my be evaluated visually, comparing them with reference materials or with a standard. They may be cut lengthwise into three strips and may serve as short term evidence of the stability of the tested PVC compound. To measure color change, a simple device has been used as a provisional arrangement, as illustrated in Figure 9. It consists of a photoelectric cell mounted in a travelling tube. Opposite the tube, a 2-mm. wide slot is provided, beneath which moves the degraded test specimen. Slot lighting is effected from two sides at an angle

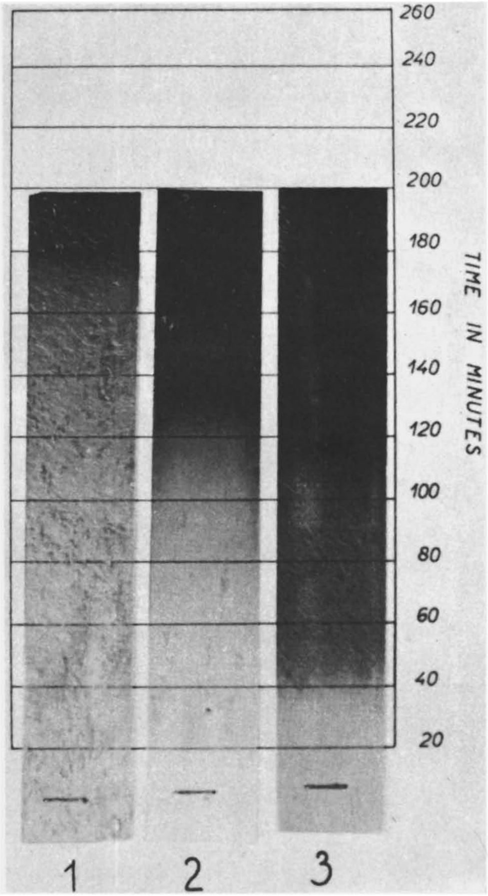


Figure 11. Exposed PVC compound specimens

1: PVC Halvic 223 2% Mellitte 131

2: PVC Halvic 223 2% PP 554 Orgatine domestic

3: PVC Halvic 223 2% PP 554 + epoxide CHS 110 of 45°. The sample to be exposed is fixed on a white supporting plate provided with a time scale. At the beginning, a white reference surface is provided, a black one being situated at the end of the scale. By shifting the specimen, a change in the photoelectric cell resistance is induced, whose values are picked up for individual heat stress times by an ohmmeter. The change in resistance represents a criterion of darkening of the sample tested, depending on the heating time. For materials featuring a rapid color change, the numerical value of stability can be read off

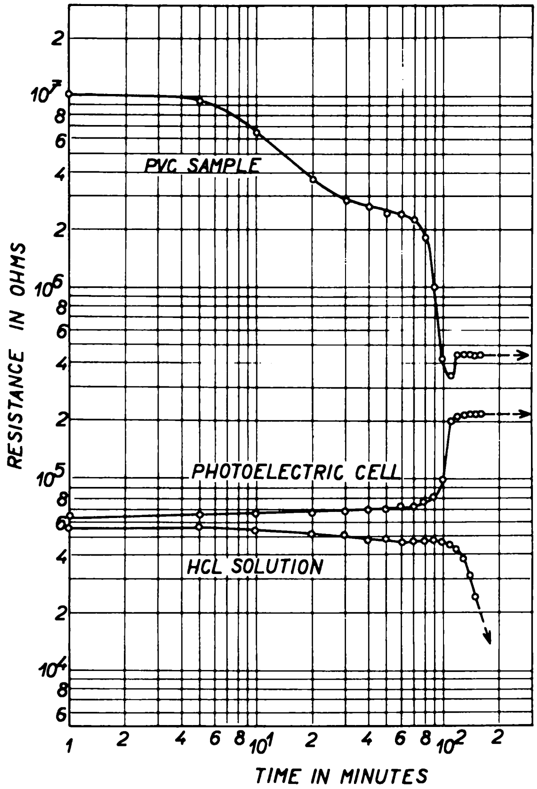


Figure 12. Variation in electrical resistance

1: Specimen during the test
2: Degraded specimen measured in photometer
3: Solution with hydrogen chloride absorbed

from the fast resistance increase either directly or from the point of intersection of tangent lines leading to the initial and ascending parts of the curve. In this way, the color change of PVC materials in the form of a powder or paste foil can be determined (Figure 10).

Figure 11 shows examples of commercial PVC compounds with different stabilizers which have been exposed at 180°C. A comparison of Samples 2 and 3 shows a negative influence of low molecular epoxide resin on the performance of the organostannic stabilizer used. All three tests were carried out in air and are compared in Figure 12.

The slope of the electrical resistance shows the following phenomena. Initially a slight decrease and, in compounds containing some organostannic stabilizers, even increase takes place followed by a rapid decrease which slows down again until it stops completely. While the rapid decrease of electrical resistance stops, the rate of generated hydrogen chloride continues to increase. This may be explained by the fact that hydrogen chloride is first absorbed by the PVC mass and only thereafter escapes outside of the sample. This explanation is further supported by experiments carried out in our laboratory (*1*). During these experiments a decrease in specific weight or an increase in volume of the degrading specimen has been noted and explained by the formation of microvacuoles by hydrogen chloride absorbed. The sudden decrease of an insulation resistance of heated PVC compound also shows the increase in viscosity. This has been noticed during the flow measurement of the compounds with an extrusion plastometer, whose piston was equipped with measuring electrodes arranged in a manner which enabled simultaneous measurement of thermal stability.

The use of color change as a criterion proved suitable for plasticized light-colored compounds. The color change is less noticeable in powdered or sintered microporous materials. A decrease in resistivity may be explained either through a loss of hydrogen chloride or by the stopping of the reaction with an acid acceptor. In fabricated plasticized specimens the escape of free hydrogen chloride is more delayed than in powdered ones, owing to the fact that the resistance decrease in these cases is faster. When determining the critical point of hydrogen chloride generation, longer cycles are observed in shaped specimens than in powdered ones.

Literature Cited

(1) Cervinka, T., Research Institute for Rubber and Plastics Technology, Gottwaldov, Czechoslovakia, unpublished data.
(2) Dyson, G. M., *Plastics* **28,** 128 (1961).
(3) Novak, J., *Kunststoffe* **8,** 712 (1961).
(4) *Ibid.,* **12,** 833 (1965).
(5) Straus, Achhammer, Stromberg, S. *Pol. Sci.* **1959,** 355.

RECEIVED April 10, 1967.

Polyepoxides as Stabilizers for Poly(vinyl chloride)

HEINRICH HOPFF

Swiss Federal Institute of Technology, Zurich 6, Switzerland

The mechanism of the thermal degradation of PVC is not completely understood, but it is generally accepted that the major effect is the splitting off from the polymer of hydrogen chloride, which results in the formation of highly chromophoric conjugated double bonds and coloration. Therefore, HCl-absorbing reagents have proved to be effective stabilizers for chlorine-containing polymers. Epoxy compounds, especially polyepoxides, have found practical application because of the high reactivity of the epoxy group with HCl. A number of new polyepoxides containing aromatic rings have been prepared, and their stabilizing effect has been determined, whereby dibutyltin laurate was used as standard. The epoxidized unsaturated oils can be used as stabilizing plasticizers and show good compatibility with the resinous compounds.

Both heat and light will degrade poly(vinyl chloride) (PVC) with elimination of HCl and formation of chromophoric double bonds. These bonds are highly reactive and decrease the mechanical properties of the polymer by oxidation and crosslinking. Although the full mechanism of all reactions involved in this process is not known, the major effect is the splitting off of hydrogen chloride. For that reason, acceptors for this acid were generally used to stabilize PVC. Wartman (*7*) has examined a number of metal salts of organic acids, but he could not find a general relationship with the rate of decomposition. Arlman (*1*) has proved that no catalytic effect of HCl exists and that added HCl does not increase the rate of decomposition. In the presence of lead stabilizers the decomposition is independent of HCl. Arlman could show that iron salts induce oxidation by radical formation. For that reason, benzoyl peroxide (1%)

doubles the rate of decomposition, and diazoaminobenzene increases it 30-fold. For radical formation Arlman gives the following scheme.

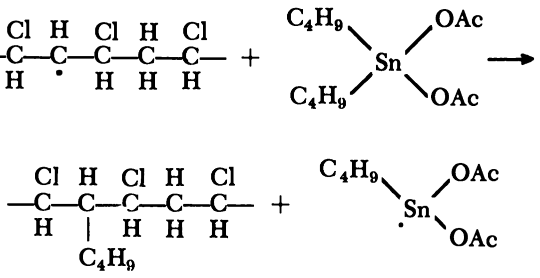
For the mechanism of the reaction it is supposed that the thermal initiation consists in splitting off the end group:

$$\begin{array}{c}
RCH_2{-}CHCl{-}CH_2{-}CHCl{-}CH_2{-}CHCl \\
\downarrow \\
R\cdot + \underset{\cdot}{C}H_2{-}CHCl{-}CH_2{-}CHCl{-}CH_2{-}CHCl
\end{array}$$

after which propagation might proceed as follows:

$$\begin{array}{l}
\underset{\cdot}{C}H_2{-}CH{=}CH{-}CHCl \sim \\
\quad\quad \downarrow\uparrow \\
CH_2{=}CH{-}\underset{\cdot}{C}H{-}CHCl{-}CH_2 \sim \\
\quad\quad \downarrow \\
CH_2{=}CH{-}\underset{\cdot}{C}H{-}CH{=}CH{-}CHCl \sim \\
\quad\quad \downarrow\uparrow \\
CH_2{=}CH{-}CH{=}CH{-}\underset{\cdot}{C}H{-}CHCl{-}CH_2{-} \sim
\end{array}$$

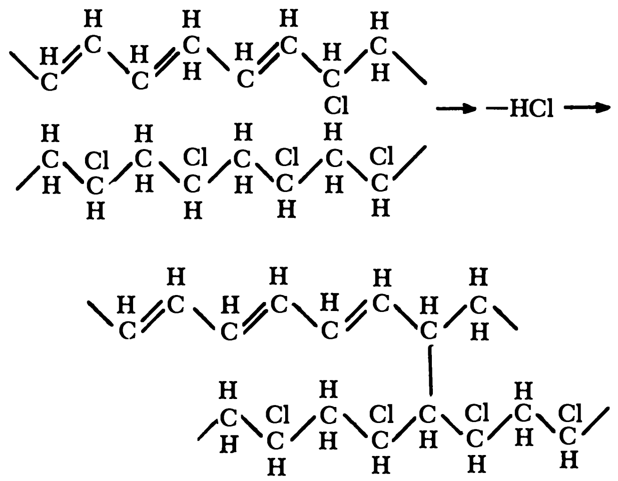
Marvel and Horning (*6*) suggested an allyl (zipper) mechanism. More is known about the mechanism of PVC stabilization with tin compounds as Kenyon (*5*) has shown. In this case, it could be proved with C_{14}-labelled dibutyltin diacetate, that only the butyl groups react with the radicals, and the rest adds on the HCl.



There seem to be different kinds of HCl eliminations, and Fuchsman (*4*) designates them as paradehydrochlorination (double bond formation) and diadehydrochlorination, whereby no double bonds are formed (crosslinking) (*see* top of p. 59).

The problem is complex. Commercial types of PVC show great differences in their behavior, depending on the method of production, additives, and impurities.

The practical demands for a good PVC stabilizer are manifold. The stabilizer should be efficient in small amounts and not only be effective at high temperatures but also in the presence of light. It should not give any color and should be miscible with PVC to give products with



the same refractive indexes. It should have an agreeable odor, be nontoxic, not decrease the good electrical properties and working conditions of the polymer. Of course, PVC's good mechanical properties must be maintained, and last but not least, the price of the stabilizer should be low.

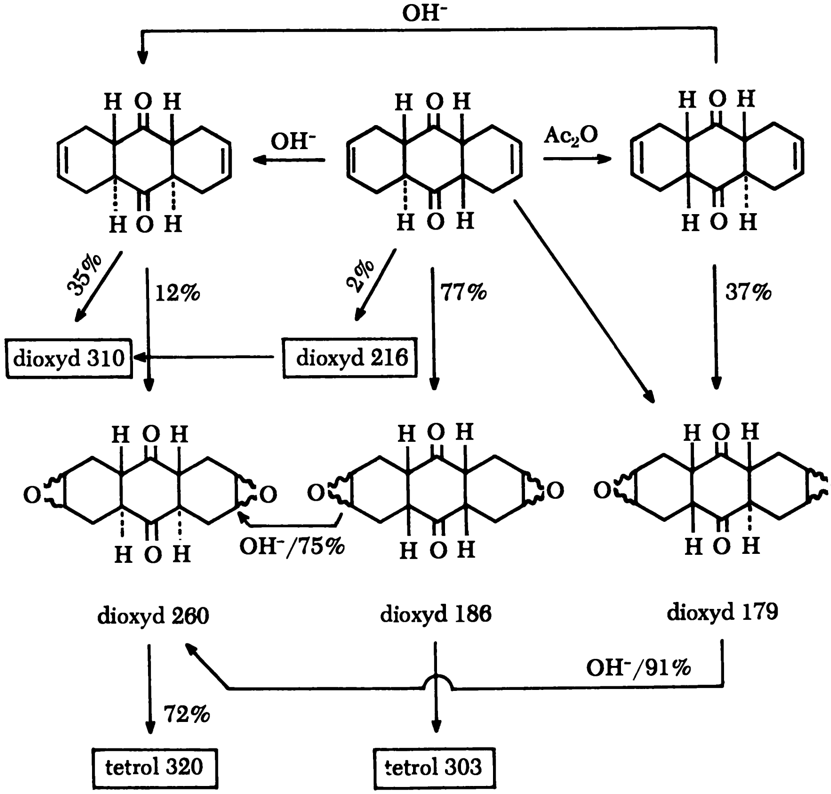
From this standpoint, the epoxy compounds seemed promising and are practically used on a large scale, very often with other compounds. The mechanism of their effect is certainly caused somewhat by their ability to add HCl and form chlorohydrins, but other effects will play a part too, especially the presence of oxygen.

The first type of epoxy product (phenoxypropene oxide) from sodium phenolate and epichlorohydrin was used in 1932 by IG Farbenindustrie but showed too high a volatility. Corresponding derivatives of alkylphenols gave excellent results. The condensation product of diisobutylphenol was used under the name, stabilizer DBG. The epoxides do not form insoluble metal chlorides like lead compounds.

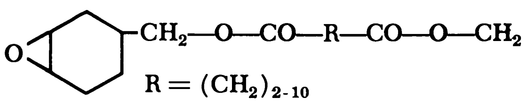
As the tendency to bind HCl increases with the number of the epoxy groups, many polyepoxides have been studied as stabilizers for PVC. Most of these products were obtained by reaction of polyhydroxy compounds with epichlorohydrin, for example, diphenylolpropane, 4,4′-dihydroxybenzophenone, hydroquinone. Diglycidyl esters of dicarboxylic acids can be prepared from epichlorohydrin and alkali salts of dicarboxylic acids. All these products have the epoxy group in ether linkage. Another category contains the epoxy group in direct bonding with aromatic rings. In our laboratory the following products have been prepared:

(1) Diepoxides of aromatic hydrocarbons: 1,4-diepoxyethylbenzene, 4,4′-di(epoxyethyl)diphenyl, 4,4′-di(epoxyethyl)diphenylether, and 1,3-5-tri(epoxyethyl)benzene.

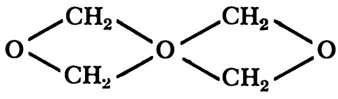
(2) Diepoxides from Diels-Alder addition products of quinone with two molecules of butadiene, which exist as several isomers (f.p., 179°, 186°, 216°, 260°, and 320°C.



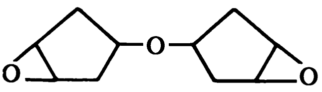
The structure of the diepoxides was proved by saponification to the corresponding tetrahydroxy compounds (tetrol 303 and 320). Many other types with similar structure are known—*e.g.*,



USP 2.750.395



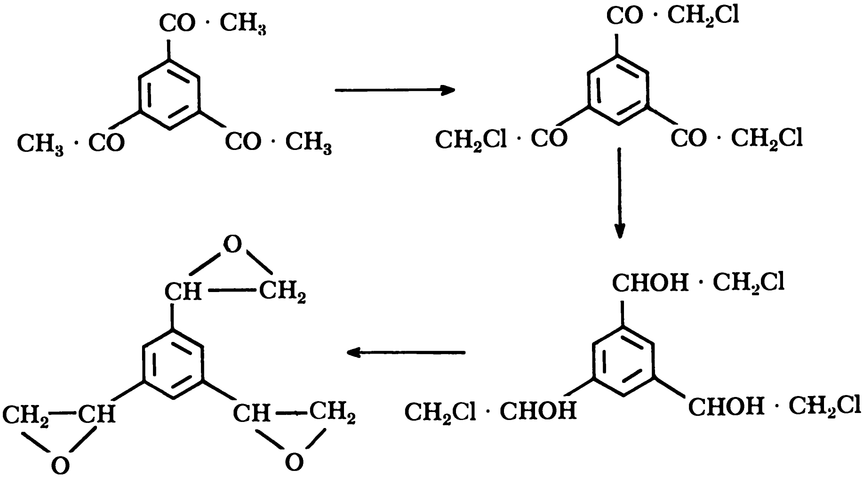
DRP 931.130



USP 2.739.161

To synthesize the new polyepoxides, two different methods can be considered: (1) epoxidation of the corresponding vinyl-compounds; (2) chlorination of the corresponding acetyl compounds, reduction to the corresponding carbinols, and elimination of HCl by potassium hydroxide.

1,4-Diepoxyethylbenzene was first prepared by Everett and Kon (3) as a liquid which evidently was not pure because analysis showed a difference of 4% in the carbon content. Our product was a white crystalline mass with melting point 79°C. and boiling point 95°C. at 0.06 mm. Catalytic hydrogenation gave the theoretical absorption. The stabilizing effect in PVC mixtures was about 30% of dibutyltin laurate—*i.e.*, 3.3 times more of the stabilizer is necessary to obtain the same discoloration as dibutyltin laurate in a plasticized mixture of PVC with 30% dioctylphthalate at 200°C. for 20 minutes. 1,3,5-Triacetylbenzene was prepared by the two methods mentioned above.

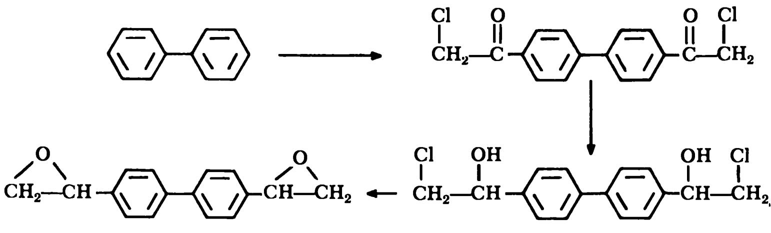


Epoxidation of the trivinylbenzene gave only a poor yield because of polymerization. Chlorination of 1,3,5-triacetylbenzene in chloroform gave the chloroketone in 80% yield and 96% of the chlorohydrin by Meerwein-Ponndorf reduction. The chlorhydrin could be separated into two isomers, one of which melts at 146°C. The other racemic product was not obtained in crystalline form. By treatment with potassium hydroxide, both chlorohydrins gave the corresponding epoxides, one melting at 81.5°, the other at 64°C. The triepoxides as well as the trichlorohydrins have three asymmetric centers; four optical isomers exist, which form two pairs of antipodes. Two racemic forms are possible: *ddd-lll* and *dld-ldl*. The two isomers mentioned above should correspond to these pairs. The stabilizing effect in PVC is about half that of dibutyltin laurate.

Another interesting triepoxide has been prepared recently from 1,3,4-trivinylcyclohexane (2). Its stabilizing effect on PVC has not yet been tested.

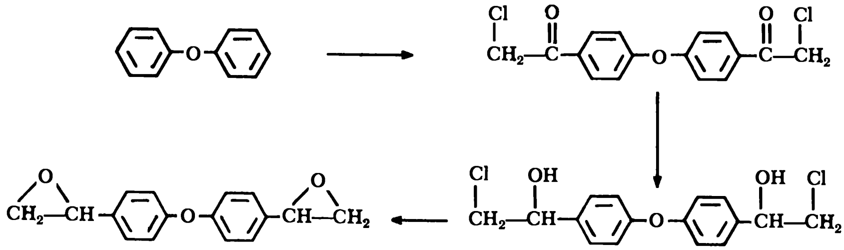
4,4′-Di(epoxyethyl)diphenyl was obtained from diphenyl by Friedel-Crafts reaction with chloracetyl chloride. Meerwein-Ponndorf reduction gave the dichlorohydrin, and treatment with alcoholic potassium hydroxide gave 97% of the theoretical yield of diepoxide, (f.p., 161°C.). The stabilizing effect was about one-fourth that of dibutyltin laurate.

4,4′-Di(epoxyethyl)diphenyl



4,4′-Di(epoxyethyl)diphenyl ether was prepared by the same method (f.p., 93°–94°C.) The stabilizing effect was about one-fourth that of dibutyltin laurate.

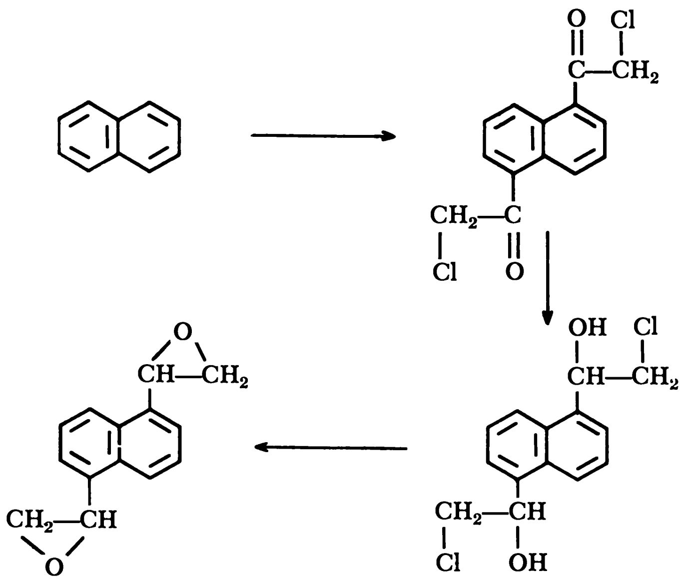
4,4′-Di(epoxyethyl)diphenylether



1,5-Di(epoxyethyl)naphthalene was prepared according its formula (f.p., 74.5°–75°C.) The stabilizing effect was about one-fourth that of dibutyltin laurate. All these polyepoxides form white leaflets.

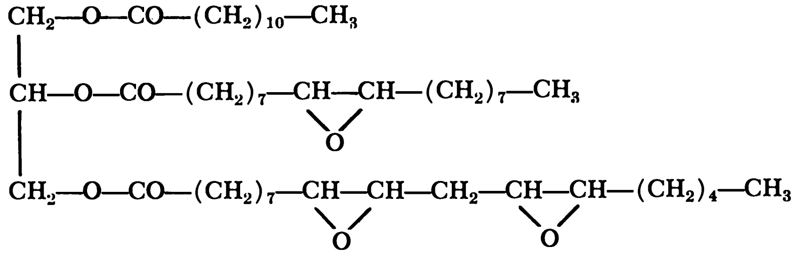
The practical stability tests of these epoxides showed that there is a relationship between the number of epoxide groups and the stabilizing effect, but this behavior does not occur in all cases. Thus, for example, the epoxides of the Diels-Alder adducts of butadiene are not as effective as the diepoxides of diphenyl. The best effects were obtained with 1,3,5-triepoxyethylbenzene (*ca.* half the effect of dibutyltin laurate). Unfortunately, the stability of this product on storage is not satisfactory. After four weeks standing at normal temperature a considerable part of the

1,5-Di(epoxyethyl)naphthalene



product was completely insoluble in ethanol. The diepoxides from diphenylether were more stable. Storage at lower temperature increases the stability considerably.

The importance of polyepoxides is increased by the fact that epoxides of unsaturated oils (linseed or soybean oil) can be used as stabilizing plasticizers. The general structure of such products is shown below.



Epoxy-plasticizers of this type are used commercially—*e.g.*, Paraplex resins of Rohm and Haas and the epoxy plasticizer D 81 of Henkel International GmbH, Düsseldorf).

The Abrac A (Bush Roake Allen Ltd., London) belong to this class. In addition to their stabilizing properties, all these products have a strong plasticizing action, thus making possible a reduction in the quantity of other plasticizers used. Besides low volatility they show a low tendency

Table I. Epoxystearate as a Plasticizer for Vinylite VYRD[a]

	Exposed for 264 hours		*Aged*	
Plasticizer	*Loss of Tensile Strength, %*	*Loss of Elongation, %*	*Loss of Tensile Strength, %*	*Loss of Elongation, %*
Butyl epoxystearate	38	60	22	18
Epoxidized diacetomonoolein	20	35	19	10
Epoxidized soybean oil	4	0	10	0
Dioctylphthalate	32	60	24	24

[a] Change in mechanical properties by 264 hours exposure to the atmosphere and 264 hours aging at 140°C. in the presence of air.

to migration, good resistance to mineral oil, water, and detergent solutions. The epoxy content is normally higher than 6%. Aluminum and zinc compounds, when used as the sole stabilizers, have a tendency to form chlorides, which may act as catalysts to decompose PVC. With the epoxidized plasticizers this disadvantage does not exist. Combination of zinc or calcium compounds with epoxidized oils show a synergistic effect, which permits a reduction in the amount of the expensive tin stabilizers. The increase in heat stability of epoxy plasticizers is often combined with a better light stability (Table I).

Literature Cited

(1) Arlman, J., *J. Polymer Sci.* **12,** 543 (1954).
(2) Derichs, F., Schade, W., Glossauer, O., Franke, W., *Ann. Chem.* **687,** 116 (1965).
(3) Everett, J. L., Kon, G. A. R., *J. Chem. Soc.* **1950,** 3131.
(4) Fuchsman, C. H., *SPE J.* **9,** 787 (1959).
(5) Kenyon, A. S., *Natl. Bur. Std. Circ.* **S25** (1953).
(6) Marvel, S., Horning, E. C., "Organic Chemistry," Wiley, New York, 1943.
(7) Wartman, L. H., *Ind. Eng. Chem.* **47,** 1013 (1955).

RECEIVED April 19, 1967.

Published on June 1, 1968 on http://pubs.acs.org | doi: 10.1021/ba-1968-0085.ch005

6

Internal Stabilization of Poly(vinyl chloride)

DIETRICH BRAUN

Deutsches Kunststoff-Institut, Darmstadt, West Germany

The poor thermal stability of poly(vinyl chloride) requires processing in the presence of heat stabilizers. Numerous low molecular inorganic and organic compounds are suitable for this purpose. Another stabilization method, which has not yet been utilized, consists of copolymerizing vinyl chloride with comonomers to improve the stability of the resulting copolymers. Most halogen-free comonomers, such as diethyl fumarate or isobutylene, which prevent zipperlike dehydrochlorination, do not serve the purpose because the resulting copolymers are generally less stable than pure poly(vinyl chloride). However, metal salts of unsaturated carboxylic acids are suitable comonomers for enhancing the thermal stability of vinyl polymers. They have been used to determine the factors responsible for the improved heat stability of vinyl copolymers. Since these stabilizers are bonded into the polymer chain, it has been suggested that this method be called "internal stabilization," analogous to "internal plasticization."

Compared with other thermoplastics, poly(vinyl chloride) (PVC) is relatively unstable against the action of light and heat. Even at temperatures as low as 100°C. PVC splits off noticeable amounts of hydrogen chloride. This degradation accelerates with increasing temperature and is troublesome in processing PVC at the required elevated temperatures because of the corroding action of the liberated hydrochloric acid; in practical applications of PVC as plastic the discoloration accompanying degradation is equally undesirable.

Because of its thermal instability, commercial PVC requires the addition of stabilizing agents which retard as much as possible dehydrochlorination and thus also prevent discoloration during processing. There are many compounds which act as "stabilizers." The most effective are those used commercially because practically no PVC is processed without stabilizers.

The stabilizers which have found practical application are nearly exclusively low molecular compounds which, in addition to an optimum stabilizing effect, meet certain requirements regarding their color, toxicity, and compatibility with the polymer and with other additives. Disadvantages of low molecular stabilizers are, for instance, their extractibility with certain solvents and the possibility of their migration from the polymer. Furthermore, there is as yet no universally applicable stabilizer, but, depending on the type of PVC and its prospective use, the most suitable stabilizer must be selected more or less by trial and error in each case. To circumvent these handicaps, attempts were made to produce modified vinyl chloride polymers which are thermally so stable that subsequent stabilization would be more or less superfluous. To achieve this, several theoretical possibilities may be deduced from the presumed structure of PVC and the processes accompanying thermal degradation. One could attempt to lower the glass transition temperature to such an extent that processing becomes possible in a temperature range in which the polymer is thermally stable. It is also conceivable that discoloration during PVC processing may be avoided by preventing the formation of long polyene sequences absorbing in the visual range. Chemical incorporation of stabilizers in the polymer chains to prevent degradation under the usual processing conditions constitutes another possibility. The extent to which these considerations may be of practical value for stabilizing PVC are discussed in this paper.

Lowering the Glass Transition Temperature by External or Internal Plasticization

When PVC is processed in the presence of plasticizers, the thermal sensitivity of the polymer is not as high as it is in the absence of plasticizers; however, the stabilizing effect of plasticizers alone is by no means sufficient to retard degradation to the desired extent in the temperature range of 150° to 200°C., which is still required even for plasticized PVC.

Internal plasticization of PVC has not solved this problem either. In this case, monomer units which lower the forces of interaction between the polymer chains are built into the PVC by copolymerization, thus allowing somewhat lower temperatures for processing as are required for rigid PVC. However, most of the monomers suitable for copolymerization with vinyl chloride have an adverse effect on the thermal stability of the resulting PVC; therefore, additional admixing of stabilizers is generally indispensable. In addition, the mechanical properties of the polymer are also affected by copolymerization. Hence, lowering the glass transition temperature of PVC by either external or internal plasticization does not offer a satisfactory method for avoiding thermal degradation of PVC under processing conditions.

Preventing Discoloration during Dehydrochlorination

Discoloration of PVC is intimately connected with dehydrochlorination, which causes the formation of polyene sequences of different length in the polymer chains. About 20 years ago Boyer (*3*) pointed out that a visually detectable discoloration is to be expected when the polyene sequences formed in a polymer contain at least five to seven conjugated double bonds. This is in good agreement with later investigations on the light absorption of low molecular polyenes (*11*). According to these investigations there is a connection between the number, *n*, of conjugated bounds and the wavelength, λ, of the absorption maximum:

$$\lambda = k\sqrt{n} + k' \qquad (1)$$

Dehydrochlorinated PVC exhibits in the visual and ultraviolet range about 10 to 12 distinct, though only weakly resolved absorption maxima which can be considered as being caused by the overlapping of the individual spectra of polyene sequences of different length.

Several investigations have shown that these absorption maxima may be assigned to polyene sequences of definite length using Equation 1. Furthermore, the following relation holds:

$$\epsilon_n = \epsilon_g \cdot n \qquad (2)$$

i.e., the extinction coefficient ϵ_n of the main band of a polyene is directly proportional to the number of conjugated double bonds, *n*. It can be shown (*6*) that by using these equations and by knowing the degree of dehydrochlorination, the relative frequency H'_n of the different polyene sequences in degraded PVC can be obtained. H'_n is hence a measure of the extent to which the different polyene sequences are present in the degraded polymer. H'_n is given by

$$H'_n = \frac{\log I_0/I}{d \cdot n \cdot x \cdot c_p}$$

where $\log I_0/I$ is the extinction of the solution of degraded polymer at the absorption maximum of the polyene sequence having *n* double bonds; *d* is the thickness of the liquid layer (cm.); *x* is the degradation conversion (amount of split-off hydrogen chloride to amount of hydrogen chloride originally present in the polymer); c_p is the concentration of the dissolved polymer (grams/liter); for copolymers $c_p \cdot f$ should be used, where *f* is the weight fraction of vinyl chloride in the copolymer.

In degrading pure PVC, relatively short polyene sequences containing up to about 10–12 conjugated double bonds are formed primarily. The share of longer polyene sequences is small, the upper limit being about 25–30 conjugated double bonds.

Upon incorporating halogen-free, thermally stable monomer units into the PVC chains, the possible length of the polyene sequences is lowered since the number of conjugated double bonds cannot grow beyond the number of vinyl chloride monomer units between two halogen-free monomer units. By knowing the copolymerization parameters, the average length of the vinyl chloride sequences can be calculated (2). Particularly short sequences of vinyl chloride units can be obtained even at high concentrations of vinyl chloride in the monomer mixture when using comonomers which add easily to the growing vinyl chloride chain ends but, at the same time, have a small copolymerization ratio r_1. Some examples of this are shown in Table I. Although only the average length of the vinyl chloride sequences can be obtained from these calculations, they do show that by using suitably composed monomer mixtures the vinyl chloride sequences can indeed be shortened. This is confirmed by the color of the partially dehydrochlorinated products. Figure 1 shows the absorption spectra of degraded pure PVC and of copolymers of vinyl chloride and diethyl fumarate, isobutylene, and vinyl isobutyl ether. The degree of dehydrochlorination is of the same magnitude in all these samples. The degraded copolymers exhibit distinctly lower absorptions in the visual range above 400 mμ than does pure PVC from which approximately the same amount of hydrogen chloride has been split off. To the human eye, therefore, the copolymers appear much lighter in color than does pure PVC degraded to the same extent, giving an impression of greater stability.

Upon calculating the share of each polyene sequence length in the polymer, one obtains a frequency distribution as shown in Figure 2. Compared with degraded homopolymeric vinyl chloride, the degraded copolymers contain a larger amount of short polyene sequences. While, after dehydrochlorination to about 0.6%, there are in the homopolymer about four times as many polyene sequences having three conjugated double bonds than there are sequences having 10 double bonds, the copolymer, containing, for instance, 9 mole % diethyl fumarate monomer units, has about seven times as many sequences of three double bonds than it has sequences of 10. Accordingly, the copolymers exhibit considerably less discoloration than does regular PVC dehydrochlorinated to the same extent. Therefore, it is possible to repress discoloration of PVC during processing by incorporating suitable comonomers in its chains.

Table I. Compositions and Average Sequence Lengths of Vinyl Chloride (M_1) Copolymers[a]

	Monomer Reactivity Ratios		*Composition, mole % of*				*Average Sequence Length*	
			Monomer Mixture,		*Copolymer*			
Comonomer, M_2	r_1	r_2	M_1	M_2	m_1	m_2	n_1	n_2
Isobutylene (60°C.)	2.0	0.08	90	10	95	5	19	1
			81	19	90	10	9.5	1
			62	38	80	20	4	1
Vinyl isobutyl ether (50°C.)	2.0	0.02	90	10	95	5	19	1
			72	28	85	15	6	1
			52	48	75	25	3	1
Diethyl fumarate (60°C.)	0.12	0.47	99.3	0.7	95	5	18	1
			98.5	1.5	90	10	9	1
			97.6	2.4	85	15	6	1
			96.3	3.7	80	20	4	1
Vinyl acetate (68°C.)	2.1	0.3	90.5	9.5	95	5	21	1
			81	19	90	10	10	1
			72	28	85	15	6	1
			56	44	75	25	4	1

[a] Composition calculated according to $n_1 = (r_1M_1 + M_2)/M_1$ and $n_2 = (r_2M_2 + M_1)/M_1$.

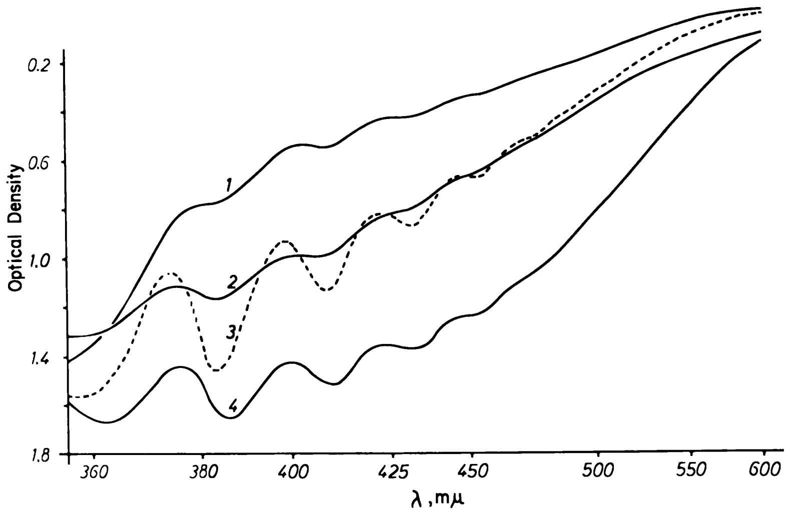


Figure 1. Absorption spectra and degradation conversions (%) of copolymers of vinyl chloride (VC) after degradation at 180°C. under nitrogen

1: VC and 9 mole % diethyl fumarate (≅1.03%)
2: VC and 17.2 mole % vinyl isobutyl ether (≃0.96%)
3: VC and 15 mole % isobutylene (≃2.24%)
4: VC and PVC (≃0.99%)

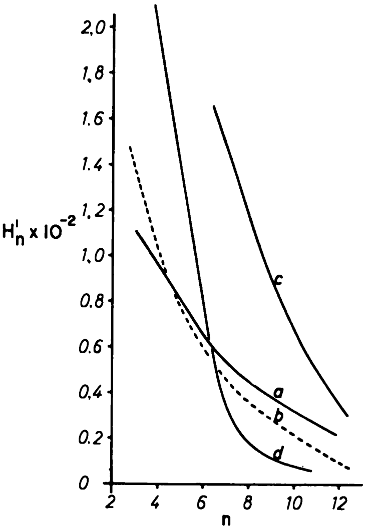
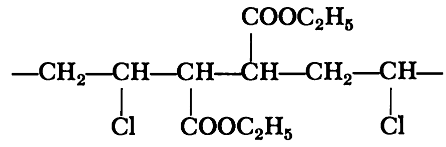


Figure 2. Frequency distributions of polyene sequences in PVC and degraded copolymers

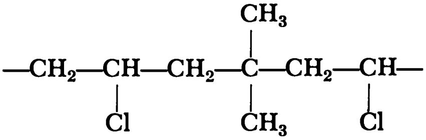
a: PVC
b: VC and 9 mole % diethyl fumarate
c: VC and 17.2 mole % vinyl isobutyl ether
d: VC and 15 mole % isobutylene
For degradation conversions and conditions see *Figure 1*

However, as the data in Table I show, the share of halogen-free comonomer units must be relatively high if sufficiently short sequences of vinyl chloride units are to be formed in the polymer chains. In that case, however, the properties of the polymer change markedly, resulting in a considerable restriction of the applicability of the polymer compared with regular PVC. A further limitation arises from the already noted fact that copolymers are thermally less stable than is PVC obtained by homopolymerization. This is especially true for copolymers of vinyl chloride and halogen-containing monomers, as we recently showed with vinyl bromide and 2-chloropropene as comonomers (*5*). Brighton (*7*) found that the rate of dehydrochlorination of copolymers of vinyl chloride/vinylidene chloride increases with the concentration of vinylidene chloride units in the chains. Also halogen-free comonomers also usually increase the rate of dehydrochlorination. Thus, Thinius and Schlimper (*15*) observed that the thermal stability of copolymers of vinyl chloride and vinyl acetate decreases with increasing content of vinyl acetate monomer units. In this case thermal instability is undoubtedly enhanced by the fact that vinyl acetate readily splits off acetic acid at elevated temperatures so that the polymer chains contain potentially more labile sites than does homo-PVC. According to our investigations (*14*), the copolymers of vinyl chloride with diethyl fumarate, as well as those with isobutylene or vinyl isobutyl ether as comonomers, dehydrochlorinate faster than does PVC. Figure 3 shows the initial rates of dehydrochlorination of copolymers of vinyl chloride and diethyl fumarate, isobutylene, and vinyl isobutyl ether. Possibly, the ester groups of the isolated comonomer units



$$\text{—}CH_2\text{—}\underset{\displaystyle Cl}{CH}\text{—}\underset{\displaystyle COOC_2H_5}{CH}\text{—}\overset{\displaystyle COOC_2H_5}{CH}\text{—}CH_2\text{—}\underset{\displaystyle Cl}{CH}\text{—}$$

as well as the methyl groups of the isobutylene monomer units



$$\text{—}CH_2\text{—}\underset{\displaystyle Cl}{CH}\text{—}CH_2\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{—}CH_2\text{—}\underset{\displaystyle Cl}{CH}\text{—}$$

enhance dehydrochlorination. It is, however, still not clear whether these substituents weaken the neighboring bonds, or whether the more rapid dehydrochlorination is a result of internal plasticization by the comonomer units. Thus, even though discoloration of a copolymer can be retarded during dehydrochlorination by having the length of its vinyl chloride sequences restricted, this benefit is cancelled by the concomitant acceleration of degradation. Hence, genuine stabilization cannot be achieved in this way.

Internal Stabilization

To stabilize PVC against the action of heat, it is necessary to prevent dehydrochlorination. If one does, nevertheless, intend to forego the use of stabilizers for the initially discussed reasons, one must use comonomers which not only restrict the length of the polyene sequences but which, at the same time, check the process of dehydrochlorination.

There have been various attempts to obtain stable copolymers of vinyl chloride by using comonomers from which the desired stabilizing effect was to be expected on the basis of their structure. [We suggested some time ago that in analogy to internal plasticization, this method of stabilizing a polymer be called "internal stabilization" (*4*).]

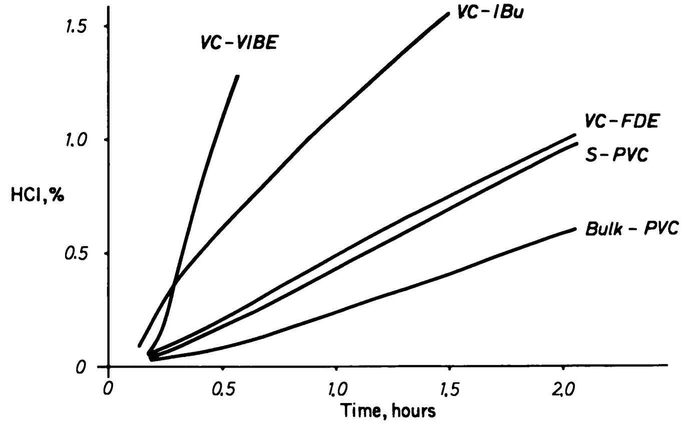


Figure 3. Dehydrochlorination of suspension PVC and bulk PVC and copolymers of Figure 1. Degradation at 180°C. under nitrogen

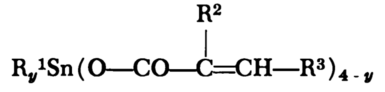
Legend: VC = vinyl chloride; FDE = diethyl fumarate; IBu = isobutylene; VIBE = vinyl isobutyl ether

The earliest stabilizers comprised alkali salts of inorganic and organic acids. Perhaps the first example of inner stabilization is contained in a patent of the IG-Farben (9). According to this patent, vinyl chloride polymers of enhanced heat and light stability are obtained when polymerizing vinyl chloride or a mixture of vinyl chloride with other polymerizable compounds in the presence of small amounts (up to a few %) of unsaturated carboxylic acids or their amides; the polymers are subsequently treated with alkali or strongly alkaline compounds. Some suitable comonomers are acrylic or methacrylic acid or their substituted products, as well as maleic acid and other unsaturated acids or mixtures of such acids, provided that they are copolymerizable with vinyl chloride. By subsequent treatment with solutions of sodium hydroxide, ammonia, or sodium carbonate salts are presumably formed which bind split-off hydrogen chloride and thereby exercise a certain stabilizing effect. This process was used commercially for several years. Its advantage was that PVC of constant alkali content could be produced. PVC prepared in the conventional manner, however, contained varying amounts of alkali, depending upon particle size and structure of the polymer, after it had been washed with soda solution, so that the effects of prestabilization obtained by this treatment differed widely.

Another popular class of heat stabilizers for PVC consists of the alkali earth metal salts of carboxylic acids. An Italian patent issued in 1940 suggested conducting the polymerization of vinyl chloride in the presence of metal salts of unsaturated mono- or polybasic carboxylic acids (*12*). Metals used in this connection are the alkali earth metals, aluminum, and lead. Apparently, the effect of stabilization by this process also arises from an incorporation of stabilizing groups in the polymer chains by copolymerization. Later experiments have shown, however, that useful stabilization can be obtained only in certain cases by this method (*see below*).

The stabilizing effect of organotin compounds can also be used for internal stabilization. In this respect, a French patent of 1957 suggests copolymerization of vinyl chloride with small amounts of a vinyltin compound (*e.g.*, the vinyldiethyl laurate of tin), which considerably improves the thermal stability over homopolymeric vinyl chloride (*8*). An American patent of 1959 suggests two types of organotin compounds as stabilizers (*13*):

(1) Hydrocarbontin esters of α, β-unsaturated acids having the general formula



$$R_y^1Sn(O—CO—\overset{\overset{\displaystyle R^2}{|}}{C}=CH—R^3)_{4-y}$$

where R^1 and R^3 are monovalent hydrocarbon radicals such as alkyl, aryl, cycloalkyl, and aralkyl, preferably having no more than 20 carbon atoms; R^2 is selected from the class consisting of hydrogen and lower alkyl radicals, preferably having no more than six carbon atoms, and y is an integer from 1 to 3.

(2) Organovinyltin compounds having the general formula

$$(CH_2=CH)_nR_aR_n'R_c''SnX_{4-(n+a+b+c)}$$

where R, R′, and R″ are aryl, aralkyl, or alkyl groups, X is an anion including halogen, alkoxy, aryloxy, thiocarboxylate, and carboxylate groups, n is an integer from 1 to 4, and a, b, c are integers from 0 to 3, totaling not more than 3.

Copolymerization of vinyl chloride with metal salts of unsaturated carboxylic acids has been investigated more closely. By radical copolymerization in methanol solution of vinyl chloride and lead acrylate small amounts of lead acrylate can be inserted into the copolymer chains. However, only about one-third to one-half of the lead salt originally present in the monomer mixture is incorporated in the chains. Moreover, the thermal stability of the resulting polymer shows only a relatively small improvement over that of homopolymeric vinyl chloride (*1*) (*see* Figure 4). Although the rate of dehydrochlorination is distinctly lowered with increasing lead content in the polymers, there is no induction period at the onset of thermal treatment. Therefore, one cannot speak of true stabilization in this case.

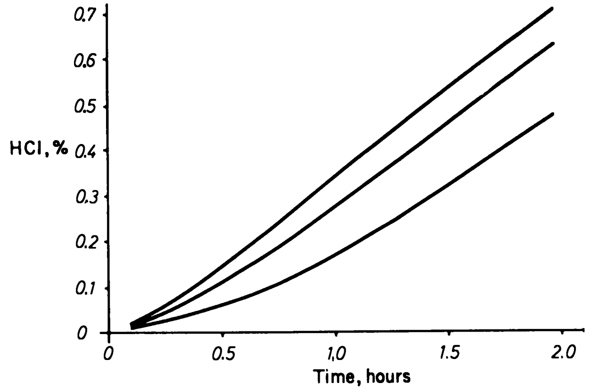


Figure 4. Dehydrochlorination of copolymers of vinyl chloride and lead acrylate at 170°C. under nitrogen. Values on curves designate initial amounts of lead acrylate (wt. %) in monomer mixtures used to prepare copolymers

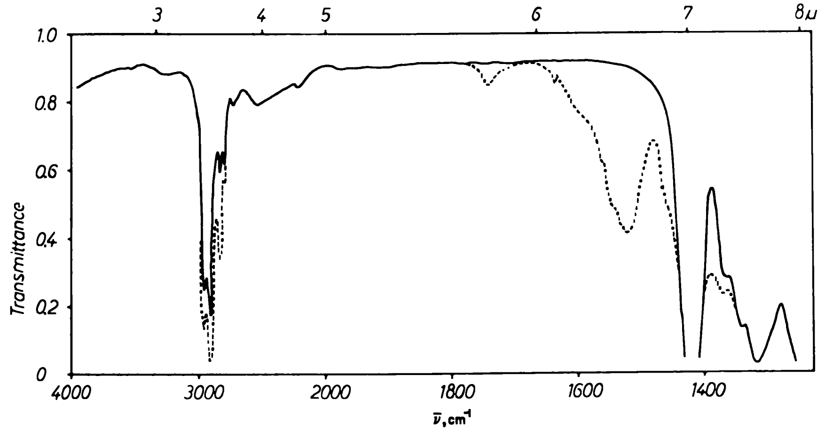
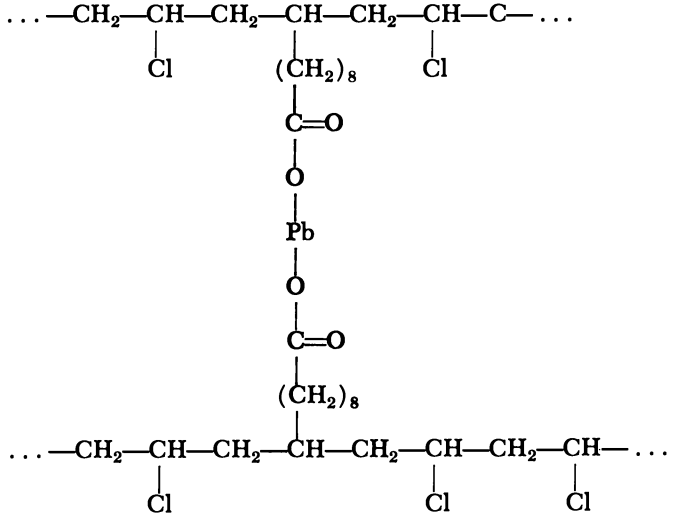


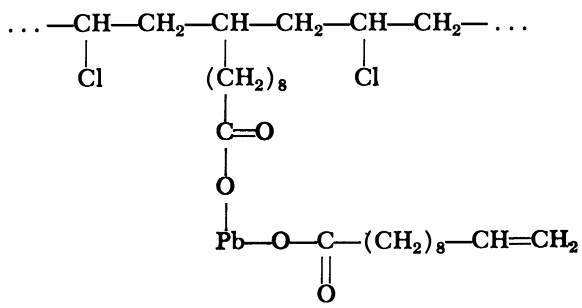
Figure 5. Infrared spectra of PVC (——) and of copolymer of vinyl chloride and 0.5 mole % lead undecylenate (- - -). Spectra are of polymer films

Considerably better results are obtained with copolymers of vinyl chloride and lead undecylenate. The lead salt of undecylenic acid, $(CH_2{=}CH{-}(CH_2)_8{-}COO)_2Pb$, can be copolymerized by free radicals in bulk or in methanol solution. The composition of the resulting polymer has been determined by infrared spectroscopy (*4*). Figure 5 shows an infrared spectrum of a film of homopolymeric PVC and of a copolymer obtained from vinyl chloride and lead undecylenate. At wavenumbers

2920, 2850, 1730, and 1520 cm.$^{-1}$ the copolymer exhibits a marked, while at 1640 cm.$^{-1}$ only a weak increase in absorption over that of PVC. The enhanced absorptions at 2920 and at 2850 cm.$^{-1}$ are to be attributed to the increase in CH_2 groups with increasing lead salt content in the copolymer; these absorption bands are caused by the asymmetric and symmetric CH_2 valence oscillations. The band at 1640 cm.$^{-1}$ is that of the valence oscillation of the C=C double bond. The bands at 1730 and 1520 cm.$^{-1}$ are to be assigned to the C=O valence oscillation of the incorporated lead salt, as confirmed by measurements on pure lead undecylenate. The content of lead salt monomer units in the copolymer was determined by comparing its absorption with the absorptions of different mixtures of PVC and lead undecylenate.

The band at 1640 cm.$^{-1}$ is undoubtedly caused by those lead salt monomer units which are incorporated in the polymer *via* only one of their vinyl groups.





Since the absolute extinction depends on the thickness of the film, the extinctions at the characteristic bands mentioned before were taken relative to the extinction at 830 cm.$^{-1}$ to have a measure for the content of lead salt in the copolymer, independent of the dimension of the measured sample. The intensity of the band at 830 cm.$^{-1}$ is of the same order of magnitude as are the intensities of the characteristic band of the lead compound. Furthermore, the absorption at 830 cm.$^{-1}$ is independent of the concentration of the lead salt since it is caused by the rocking oscillation of the PVC CH_2-groups and does not interfere with the corresponding oscillation of lead undecylenate at 725 cm.$^{-1}$.

Evaluation of the spectra of the copolymers indicates that, depending on the content in the monomer mixture, only 40 to 70% of the lead salt is incorporated in the copolymer. In the copolymers obtained by polymerization in methanol solution, practically all lead undecylenate monomer units are incorporated in the chains *via* both their vinyl groups. Copolymers prepared in bulk, on the other hand, do still contain a noticeable amount of free vinyl groups.

Because of the low content (up to about 1 mole %) of lead undecylenate monomer units in the copolymers, and because of the relatively low molecular weights of the copolymers (30,000–40,000) they do not contain crosslinked, insoluble portions.

All copolymers were purified carefully from unreacted lead undecylenate by extraction with suitable solvents. Figure 6 shows the results of dehydrochlorination of some samples at 170°C. As can be seen, the rate of dehydrochlorination is not only distinctly lower compared with that of PVC, but there is, initially, also a certain period during which no hydrogen chloride is evolved. Although the sample, prepared with 6 wt. % lead salt in the monomer mixture, contains only about 0.3 mole % lead salt in the polymer, it exhibits a remarkable thermal stability; at 170°C. almost no dehydrochlorination occurs within the first 2 hours. This is, therefore, a genuine case of internal stabilization, which finds expression also in the color of the polymer. Discoloration of the samples is substantially less than that of unstabilized PVC; the polymer containing 1 mole % lead salt is still nearly colorless after 2 hours of heat treatment.

Evaluation of the absorption spectra shows that the frequency of polyene sequences consisting of 10 or more double bonds is noticeably smaller in the copolymers than in PVC of approximately equal degree of degradation (Figure 7). Under the applied degradation conditions, PVC contains, for example, three times as many polyene sequences with four conjugated double bonds than sequences having 12 conjugated double bonds; in the copolymer of vinyl chloride and 0.2 mole % lead undecylenate this ratio is about 5 to 1. From the frequency distribution also it is evident that by incorporating stabilizing groups in the polymer chains, shorter polyene sequences are formed during degradation of the copolymers than of homopolymeric vinyl chloride, which explains the less intense discoloration of the copolymers.

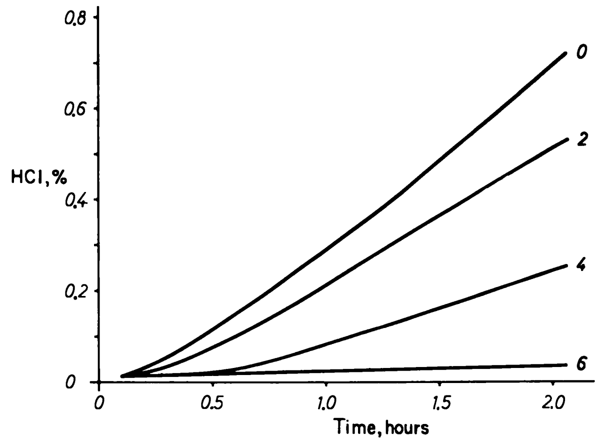


Figure 6. Dehydrochlorination of copolymers of vinyl chloride and lead undecylenate at 170°C. under nitrogen. Values on curves designate the amounts (wt. %) of lead salt in monomer mixtures used to prepare copolymers

For comparison we also investigated copolymers of vinyl chloride and undecylenic acid salts of metals other than lead. The compositions of the copolymers were determined by infrared spectroscopy from the extinction ratios of the symmetric CH_2 valence oscillation at 2850 $cm.^{-1}$ and the CH_2 rocking oscillation at 830 $cm.^{-1}$. Table II shows the compositions of the copolymers and the amounts of hydrogen chloride split off during the heat treatment at 170°C. In Figure 8 dehydrochlorination is shown as a function of time. The copolymer containing barium undecylenate possesses good initial stability, while cadmium and, above all, zinc undecylenate monomer units impart no stabilizing effect on the polymer. Compared with the barium salt, calcium salt monomer units effect lesser initial but greater long-time stabilization of the polymer. Remember, however, that the amounts of comonomer units in these polymers are quite different, so that any comparison can only be qualitative. Nevertheless, the copolymer containing lead undecylenate has an extraordinary stability, which is clearly superior to that of the other copolymers, despite its low stabilizer content.

The causes responsible for the stabilizing action of carboxylic acid salts are not yet completely clear. Some years ago Frye and Horst (*10*) were able to show that, upon heating a mixture of PVC and metal salts

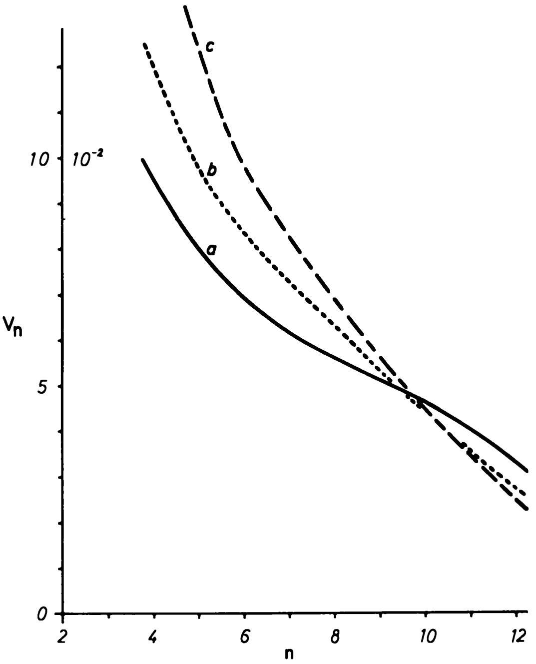


Figure 7. Frequency distributions and degradation conversions (%) of polyene sequences after degradation for 2 hr. at 180°C. under nitrogen

a: PVC (0.71%)
b: VC and 0.2 mole % lead undecylenate (0.42%)
c: VC and 0.8 mole % lead acrylate (0.52%)

Table II. Composition and Stability of Copolymers from Vinyl Chloride and 2 wt. % of Undecylenic Acid Salts[a]

Cation	*Amount of Salt Incorporated in Copolymer, wt. %*	*Dehydrochlorination at 170°C.*	
		hrs.	*%*
Pb	0.8	1.15	0.26
Ba	2.5	0.76	0.65
Ca	1.4	1.15	0.59
Cd	0.8	0.24	0.61
Zn	0.7	0.08	1.22

[a] Copolymerization at 60°C. in methanol with AIBN.

of 2-ethylhexanoic acid, an absorption band at 5.75 μ (1740 cm.$^{-1}$) is observed, which occurs neither in the spectra of pure PVC nor in those of barium, cadmium, or zinc salts. This new band can be attributed to

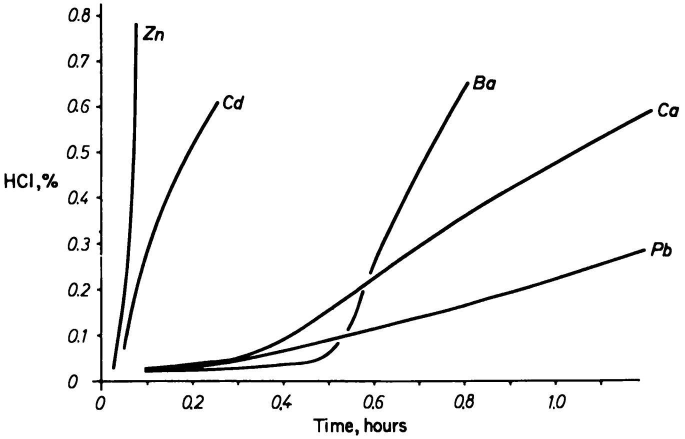
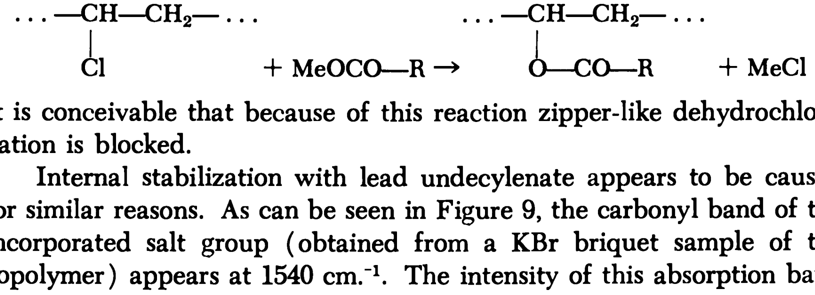


Figure 8. Dehydrochlorination of copolymers of vinyl chloride and undecylenic acid salts (2 wt. % in monomer mixtures used for preparation) at 170°C. under nitrogen

the carbonyl stretching frequency of esters of aliphatic carboxylic acids, so that one may assume that at certain points of the PVC chains chlorine atoms are replaced by ester groups:



$$\begin{array}{l}\ldots\text{—CH—CH}_2\text{—}\ldots\\ \quad\ \ |\\ \quad\ \text{Cl}\end{array} + \text{MeOCO—R} \rightarrow \begin{array}{l}\ldots\text{—CH—CH}_2\text{—}\ldots\\ \quad\ \ |\\ \quad\ \text{O—CO—R}\end{array} + \text{MeCl}$$

It is conceivable that because of this reaction zipper-like dehydrochlorination is blocked.

Internal stabilization with lead undecylenate appears to be caused for similar reasons. As can be seen in Figure 9, the carbonyl band of the incorporated salt group (obtained from a KBr briquet sample of the copolymer) appears at 1540 cm.$^{-1}$. The intensity of this absorption band decreases with time of heat treatment. At the same time a band appears at 1730 cm.$^{-1}$ which, in analogy to the investigations of Frye and Horst (*10*), is to be attributed to formation of ester groups in the polymers. Accordingly, there seems to be no basic difference between the stabilizing action of admixed and of chemically incorporated lead salts of aliphatic carboxylic acids.

It is remarkable, however, that comonomer units of lead undecylenate have a substantially greater stabilizing effect than those of lead acrylate, which may possibly arise from the greater mobility of the relatively long lead-containing side chains at the polymer backbone. This leads to the conclusion that in internal stabilization of PVC it will be advantageous if the stabilizing groups are not too close to the main chains. It is still not clear whether the lead salt groups react with labile

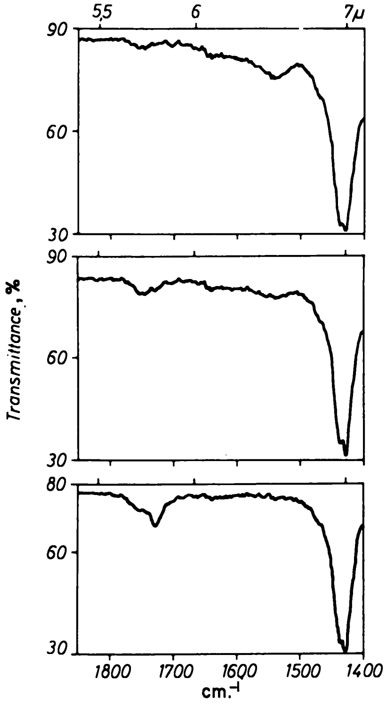


Figure 9. Infrared spectra of copolymer of vinyl chloride and 0.3 mole % lead undecylenate before and after heat treatment (KBr briquet sample)

Top: Before heating
Middle: After heating for 1 hr. at 160°C.
Bottom: After heating for 2.5 hr. at 160°C.

chloride of the PVC chains or whether they prevent zipper-like dehydrochlorination by adding to double bonds initially formed during degradation. In conclusion one may say that genuine internal stabilization can be obtained only by introducing into the polymer chains groups which retard or prevent dehydrochlorination. So far, the choice of suitable comonomers is still limited. Copolymers of substantially improved thermal stability can, however, be prepared.

Besides the initially mentioned advantages of internal stabilization, there are some disadvantages: Preparation of suitable copolymers is more difficult and more complicated than homopolymerization of vinyl chloride. With increasing comonomer content internal plasticization of the polymer chains becomes noticeable, which in turn may restrict the range of application of the polymer. It is, therefore, not yet safe to predict whether the evident advantages of internal stabilization can be utilized successfully on such an inexpensive plastic as PVC. It might be conceivable, however, that bulk polymerization of vinyl chloride, as it has come in technical use during the past years, may be used to prepare internally stabilized PVC. It will, therefore, probably be rewarding to study further the still insufficiently investigated possibilities of internal stabilization of PVC.

Literature Cited

(1) Agha-Ebrahim, G., unpublished results.
(2) Alfrey Jr., T., Goldfinger, G., *J. Chem. Phys.* **12**, 205 (1944).
(3) Boyer, R. F., *J. Phys. Colloid Chem.* **51**, 80 (1947).
(4) Braun, D., Agha-Ebrahim, G., Langbein, G., *Kunststoffe* **54**, 147 (1964).
(5) Braun, D., Thallmaier, M., *J. Polymer Sci.* **6**, 235 (1962).
(6) Braun, D., Thallmaier, M., *Makromol. Chem.* **99**, 59 (1966).
(7) Brighton, C. A., *Brit. Plastics* **28**, 62 (1955).
(8) Evieux, E. A., French Patent **1166281**.
(9) Fikentscher, H., Franke, W., German Patent **663220** (Oct. 19, 1935).
(10) Frye, A. H., Horst, R. W., *J. Polymer Sci.* **40**, 419 (1959).
(11) Hausser, W. W., Kuhn, R., *Z. Physik. Chem.* **B 29**, 363, 371, 378, 384, 391 (1935).
(12) Italian Patent **381013** (Feb. 2, 1940).
(13) Mack, G. P., U. S. Patent **3,069,394** (Oct. 16, 1959).
(14) Thallmaier, M., Braun, D., unpublished results.
(15) Thinius, K., Schlimper, R., *Plaste Kautschuk* **9**, 165 (1962).

RECEIVED April 3, 1967.

7

Metallo-organic Systems with High Thermal Stability

EMANUEL HOROWITZ

National Bureau of Standards, Washington, D. C. 20234

When 8-hydroxyquinoline and derivatives of bis(8-hydroxyquinoline) react with metal ions, coordination complexes and polymers are formed, respectively, which exhibit improved thermal stability. This paper reviews the reaction of first-row transition metal ions with such ligands and their effect on the stabilization of these organic molecules. For the polymers containing divalent Mn, Co, Ni, Cu, or Zn the decomposition temperature is related to the periodic properties of the metal as well as the composition of the ligand to which the metal is coordinated. Trivalent chromium produces a crosslinked polymer when it reacts with bis(8-hydroxy-5-quinolyl)methane, and the thermogram for this polymer is also reported.

The stabilization of organic molecules by their reaction with metal ions to form coordination compounds and polymers has been known for some time, although the reasons for this behavior have not been understood completely. More than 30 years ago Dent and Linstead (*8*) reported that Cu(II)-phthalocyanine (Figure 1, I), could be heated at 580°C., at low pressure under nitrogen, without decomposition. The complex of Cu(II)ethylenediamineacetylacetone (Figure 1, II), was studied by Combes (*7*) and later by Morgan and Smith (*22*), who reported that it decomposed slowly at red heat; however, Bailar (*1*) states that the ligand is decomposed at moderate temperatures while the complex is stable at least to 380°C.

Organic molecules can be stabilized with respect to hydrolysis and oxidation by coordinating them with metal ions. Thus, hydrolysis of salicylaldehyde-glycine Schiff base occurs with relative ease compared with the low rate of hydrolysis of the Cu(II) complex (Figure 1, III). The resistance to chemical attack has been attributed to stabilization upon coordination (*12*). Drinkard (*9*) reports that ethylenediamine is oxidized almost immediately on coming in contact with boiling concentrated nitric acid, but the Co(III)tris(ethylenediamine) complex (Figure 1, IV), can be boiled in the acid for prolonged periods without decomposition. This surprising resistance is extremely interesting and merits further study, particularly when one considers that the molecular weight of the compound is only 239 and that the C—C bonds in the ligand are exposed and should be susceptible to attack.

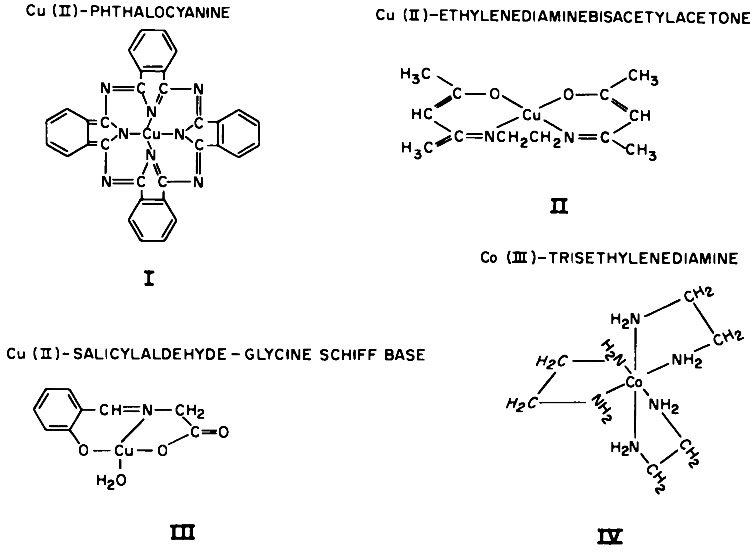

Cu (II)-PHTHALOCYANINE
I
Cu (II)-ETHYLENEDIAMINEBISACETYLACETONE
II
Cu (II)-SALICYLALDEHYDE-GLYCINE SCHIFF BASE
III
Co (III)-TRISETHYLENEDIAMINE
IV

Figure 1. Structure of some coordination compounds

When bis-multifunctional organic ligands react with metal ions to yield coordination polymers, stable systems are also produced which have interesting properties. Marvel and Martin (*19*) have prepared a coordination polymer containing beryllium acetate-succinate units which exhibits some plasticity and is stable until heated above 450°C. However, it apparently disproportionates on prolonged storage at room temperature. Based on the high thermal stability reported for the phthalocyanine complex (*8*), Marvel and co-workers (*20, 21*) prepared phthalocyanine coordination polymers but found them to be only moderately stable; some decomposed at about 350°C. Drinkard and Bailar (*11*) synthesized a Cu(II)phthalocyanine polymer with a molecular weight of about 4000, but it also lacked high thermal stability. Naphtharizin polymers with divalent, first-row transition metals have been evaluated for thermal stability by Bottei and Gerace (*4*), and based on static heating they found the polymers stable to about 350°C. They ranked the polymers in order of their stability as follows: Ni $>$ Zn $>$ Co $>$ Cu.

The work described here supports the view that the chemical combination of metal ions with organic molecules leads to coordination complexes and polymers with enhanced stability with respect to weight loss, thermal degradation, or oxidation. Bis(8-hydroxyquinoline) derivatives were used to prepare a series of coordination polymers containing first-row transition metals, and the thermal stabilities of the polymers were evaluated. The influence of the structure of the organic molecule and the role of the metal are discussed.

Published on June 1, 1968 on http://pubs.acs.org | doi: 10.1021/ba-1968-0085.ch007

Coordination Polymer Synthesis

When a bis-bifunctional ligand like bis(8-hydroxy-5-quinolyl)methane (Figure 2, V), reacts with a divalent metal ion having a coordination number 4, linear polymers are expected. Thus, as shown at the top of Figure 2, two hydrogens are lost from the OH groups on the ligand, and unpaired electrons on oxygen and the ring nitrogen are donated to empty orbitals in the metal ion to form chemical bonds. Theoretically, metallo-organic polymers of this type should be flexible and soluble in organic solvents, but thus far only insoluble, highly colored powders have been recovered as products of the polymerization reaction. The polymers remained insoluble even when heated at elevated temperatures in a wide variety of organic solvents. The coordination polymers were purified by prolonged extraction with *N,N*-dimethylformamide, followed by extraction with ethyl alcohol. The products (*13, 14, 15*) were then dried *in vacuo*. If the same ligand (V) reacts with a metal ion having a coordination number 6, as in Figure 2 (II), a highly crosslinked polymer (VI) is obtained which is also insoluble.

When a stoichiometric amount of chromic ion was added to a boiling *N,N*-dimethylformamide solution of bis(8-hydroxy-5-quinolyl)methane, the chromium coordination polymer precipitated immediately. Elemental analysis: analyzed for $[Cr_2(C_{19}H_{12}N_2O_2)_3 \cdot 2H_2O]_n$.

Calculated, %: C, 65.8; H, 3.87; N, 8.07; Sr, 9.99. Found, %: C, 63.5; H, 4.10; N, 7.78; Cr, 10.6.

As shown schematically in Figure 2 the stereochemistry at the metal-ligand site may be planar (Ib), tetrahedral (Ic), or octahedral (IIb), depending on the valance state of the metal ion and the distribution of electrons in the orbitals of the metal ions.

Thermal Stability

The weight loss of samples heated at a rate of 2.5°C./minute at 10^{-3} to 10^{-5} torr was automatically recorded as a function of temperature (*13,*

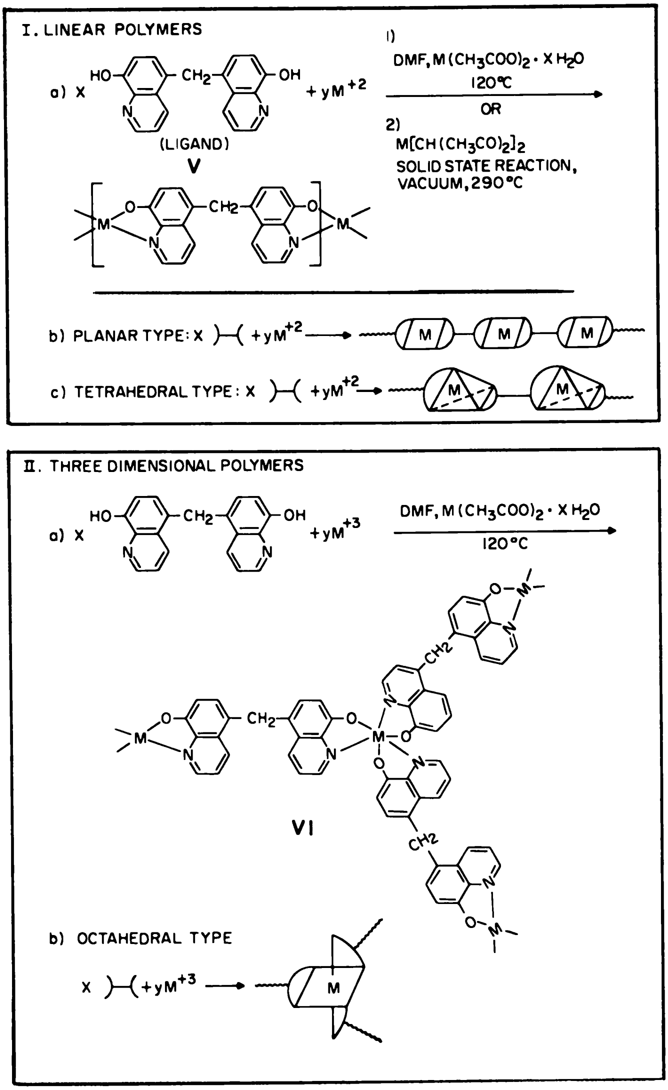
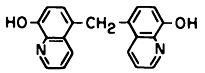


Figure 2. Synthesis of bis(8-hydroxy-5-quinolyl)methane coordination polymers

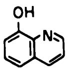
14, 15), using thermogravimetric analysis. As has been pointed out (*13*), meaningful results of the effect of temperature on these systems can be obtained when the thermal process is separated from the oxidative process by operating *in vacuo*.

Discussion

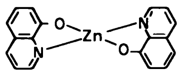
Some results of the thermogravimetric analyses for 8-hydroxyquinoline (VII), bis(8-hydroxy-5-quinolyl)methane (V), the nonpolymeric Zn-bis(8-hydroxyquinoline) (VIII) and the Zn-bis(8-hydroxy-5-quinolyl)-methane coordination polymer (IX) are given in Figure 3. While the different organic compounds and metallo-organic systems are compared with respect to weight loss it should be remembered that only for the coordination polymer are we dealing with decomposition involving bond cleavage. For 8-hydroxyquinoline (VII), the melting point in air and the approximate sublimation temperature at 10^{-5} torr are also indicated for comparative purposes.



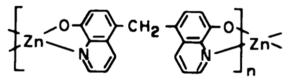
V



VII



VIII



IX

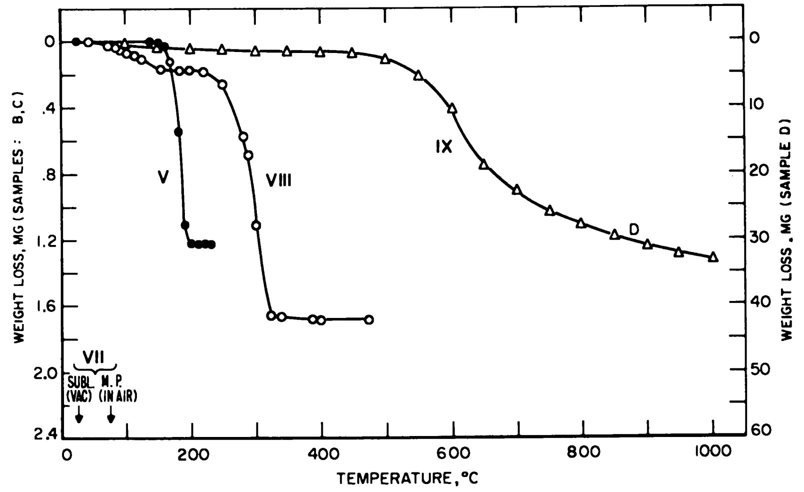


Figure 3. Thermograms of ligands and metallo-organic products

The least stable of the series with respect to weight loss is the organic ligand 8-hydroxyquinoline (VII) which begins to lose weight rapidly at approximately 25°C. in *vacuo*. Virtually 100% of the sample is volatilized at this temperature. Curve VIII of Figure 3 shows the increased thermal stability that results on forming the zinc complex of 8-hydroxyquinoline (VIII). The nonpolymeric zinc complex starts its accelerated weight loss at approximately 265°C., and the rapid volatilization ends abruptly at 325°C. when almost the entire sample was volatilized. In this case no residue remains on continued heating because the zinc complex does not decompose *in vacuo* at these temperatures but sublimes intact. For Curve VIII, the initial weight loss which begins at about 60°C. and ends at 155°C. amounts to 9.4% and is accounted for by the dehydration of zinc 8-hydroxyquinolate dihydrate.

Bis(8-hydroxy-5-quinolyl)methane (V), which is highly aromatic and has a molecular weight of 302.3, undergoes rapid weight loss at about 165°C. (Figure 3). When the thermogram for this ligand is compared with the one for the Zn-bis(8-hydroxy-5-quinolyl)methane polymer (Figure 3, IX), one can judge the significant stabilization with respect to weight loss that has occurred after coordination. The zinc coordination polymer is the most stable member of the group and does not begin to lose weight until the temperature has reached about 520°C.

Table I gives the molecular weights of the systems studied and the temperatures from the thermograms which correspond to initiation of accelerated weight loss (T_1), 50% weight loss (T_2), and 100% weight loss (T_3).

Table I. Thermal Stability Data of Organic Ligands and Their Zinc Coordination Compounds *in vacuo*

Ligand and Coordination Compound	*MW*	*Temperature,*[b] *°C.*		
		T_1	T_2	T_3
VII. 8-Hydroxyquinoline	141.15	~25	~25	~25
VIII. Zn(II)-bis(8-hydroxyquinolate)	208.50	265	300	325
V. Bis(8-hydroxy-5-quinolyl)methane	302.31	165	185	200
IX. Zn(II)-bis(8-hydroxy-5-quinolyl)methane polymer	—	520	740	1000[c]

[a] For structures, *see* Figure 3.

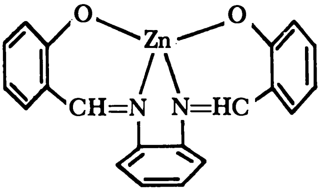
[b] T_1 at start of accelerated weight loss; T_2, at 50% weight loss; T_3 at 100% weight loss.

[c] After 8 hours at 1000°C.

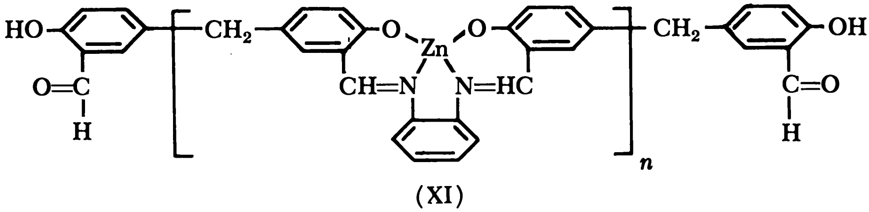
The more stable of the two organic ligands is completely volatilized below 200°C., and even the zinc complex is fully sublimed at 325°C. On the other hand, the zinc coordination polymer has only lost 68% by weight at 1000°C. and must be heated at this elevated temperature for about 8 hours before it is essentially completely volatilized. The zinc polymer is unique in this respect because the metallic zinc formed on thermal degradation is volatile at 1000°C. *in vacuo,* while the metallic residues remaining after decomposition of the other coordination polymers are not volatile under these conditions.

While reports in the literature (*13, 14, 15, 16, 23*) invariably stress the connection between coordination and enhanced stability, Block (*3*) cites some interesting examples in which coordination does not improve the thermal stability of the ligand. He discusses the work on acetylacetone (*5*), which when heated for several hours at 265°C. in a sealed, evacuated glass tube, degrades very little as judged by the amount of volatile products generated. On the other hand, the coordination compounds of Cu(II), Ni(II), Co(II), and Mn(III) decompose appreciably at this temperature. This is in line with the results of Berg and Truemper (*2*), who found that the acetylacetonate complexes of Ni(II) and Cu(II) decompose in air at 230°C.

Another case in which the thermal stability of the coordination polymer is reported to be lower than that of the monomeric coordination compound is worth mentioning. Marvel and Tarköy (*18*) examined the thermal stability of the nonpolymeric Zn-salicylaldehyde-*o*-phenylenediamine compound (X), which they reported was stable when heated in air at 250°C., losing less than 5% by weight after 24 hours. The related Schiff base coordination polymer (XI) was less stable and decreased in weight by 12% after only 3 hours in air at 250°C.



(X)



(XI)

The stability sequence for these divalent metal coordination polymers was reported to be: Fe > Ni > Zn > Co > Cu. Thus, it is evident that different thermal stability sequences will be developed when different experimental conditions and criteria are employed.

In an earlier study (*13, 14, 15*), we examined the thermal behavior *in vacuo* of some Mn, Co, Ni, and Cu divalent, first-row transition metal coordination polymers, using the procedure previously described. These included coordination polymers containing the same transition metals but different derivatives of bis(8-hydroxyquinoline) so that the effect of the ligand on the thermal stability of these systems could also be judged. The critical temperatures (initiation of accelerated weight loss) for these systems are given in Table II.

Table II. Thermal Stabilities of Divalent First-Row Transition Metal Coordination Complexes and Polymers

Temperature at Start of Accelerated Weight Loss, °C.

Ligand[b]	*Mn*	*Co*	*Ni*	*Cu*	*Zn*
VII	355[a]	280[a]	250[a]	200[a]	265
V	—	510	460	420	510
XII	440	425	420	365	425
XIII	470	415	380	350	430

[a] Data of Charles and Langer (*6*).

[b] VII: 8-Hydroxyquinoline
V: Bis(8-hydroxy-5-quinolyl)methane
XII: 5,5′-[*p*-phenylene-bis(methylidynenitrilo)]di-8-quinolinol
XIII: 5,5′-[methylene-bis(*p*-phenylenenitrilomethylidyne)]di-8-quinolinol

The temperature at the start of accelerated weight loss is plotted *vs.* the atomic number of the central metal in Figure 4 for the coordination compounds and polymers containing the following four ligands: 8-hydroxyquinoline (VII), bis(8-hydroxy-5-quinolyl)methane (V), 5,5′-[*p*-phenylene-bis(methylidynenitrilo)]di-8-quinolinol (XII), and 5,5′-[methylene-bis(*p*-phenylenenenitrilomethylidyne)]di-8-quinolinol (XIII). These plots show that the thermal stability of the coordination compounds and polymers depends on the central metal. Generally, the thermal stability decreases linearly from Mn to Cu and then increases with Zn. Similarly shaped curves are obtained when one plots such periodic properties of the metal as ionic radius *vs.* the atomic number. The nature of the ligand also governs the thermal stability, and for the polymers the ligand (V) with the —CH_2— bridge is more stable than either of the other two with considerably longer bridging groups. Thermal stabilization of about 150°–200°C. is evident when one compares the temperatures at the start of accelerated weight loss for the nonpolymeric metal complexes (which undergo sublimation) with those of the coordination polymers containing similar metals (which undergo decomposition). For the polymers, experimental data support the view that at the critical temperature (T_1) the metal—ligand bonds are ruptured, and organic degradation products of the polymer are volatilized.

Until now we have been dealing with metals of coordination number 4 which normally lead to linear type polymers. When trivalent chromium

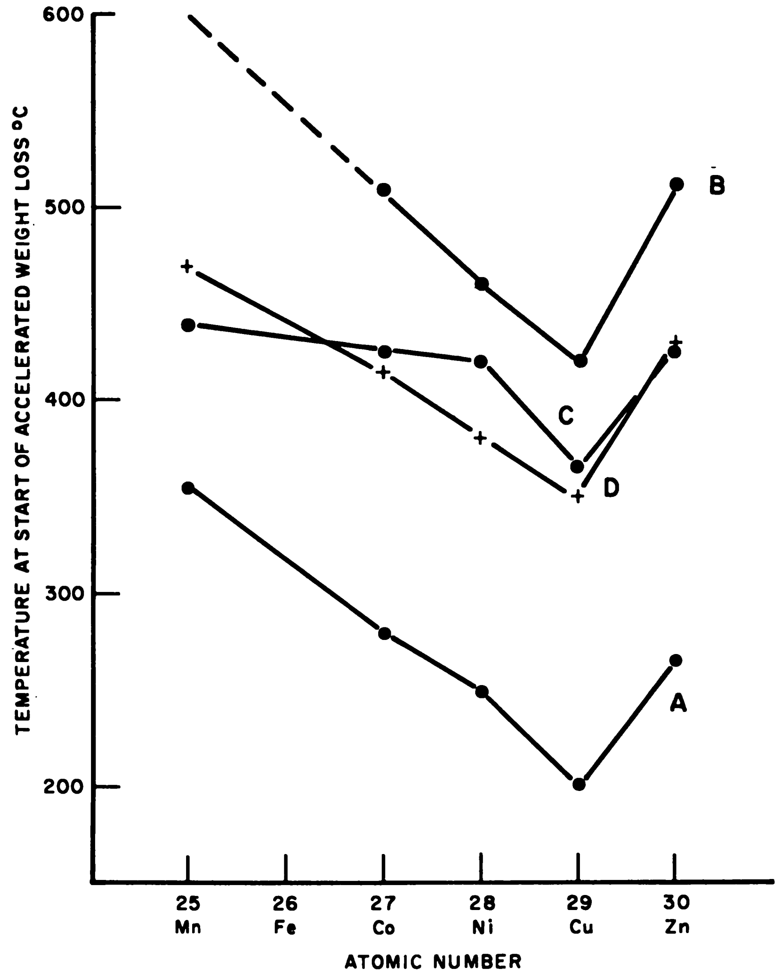


Figure 4. Dependence of the accelerated weight loss temperature on the coordinated metal and the ligand

A: 8-Hydroxyquinolate complexes
B: Bis(8-hydroxy-5-quinolyl)methane polymers (—CH_2—; 5,5′ bridge)
C: 5,5′-[p-phenylenebis(methylidynenitrilo)] di-8-quinolinol polymers (—N=CH—C_6H_5—CH=N—; 5,5′ bridge)
D: 5,5′-[Methylenebis(p-phenylenenitrilomethylidyne)] di-8-quinolinol polymers (—CH=N—C_6H_5—CH_2—C_6H_5—N=CH—; 5,5′ bridge)

(coordination number 6) reacts with the bifunctional ligand, bis(8-hydroxy-5-quinolyl)methane (V), one obtains a highly crosslinked coordination polymer similar to that shown in Figure 2 II (VI). This polymer was also heated *in vacuo* at 2.5°C./minute, and the recorded percent weight loss curve is shown in Figure 5. No weight loss is recorded for this polymer until the temperature reaches about 200°C.; between 200° and 500°C. approximately 8%, by weight, is volatilized. This may reflect the loss of water which is often very difficult to remove from coordination compounds, even when they are vacuum dried at a relatively high temperature, or, it may represent low molecular weight products. The chromium coordination polymer had been dried *in vacuo* over P_2O_5 at 140°C. for 20 hours. The next deflection point in this thermogram occurs at approximately 500°C. and may signify the onset of polymer decomposition. At 675°C., after 27% of the polymer has been volatilized, there is another change in slope in the thermogram, the weight loss becoming more gradual. Even after 16 hours at 870°C. the cumulative weight loss of the sample amounted to only 36% by weight.

The highly crosslinked, three-dimensional network structure of the Cr(III) coordination polymer is considerably more stable at elevated temperatures than the Zn(II) polymer or the other transition metal polymers which have been studied. For example, while the Cr(III) sample sustains a loss in weight of about 30% at 850°C., the Zn(II) coordination polymer loses 60% under similar conditions.

The foregoing are examples of polymers formed during coordination reactions. It is possible to stabilize preformed organic polymers provided they are synthesized to have functional groups so positioned strategically as side chains that these can react with metal ions to form coordinated structures. Such an example is shown in Figure 6 where polymer XIV, prepared from salicylaldehyde and butylene mercaptan, reacts with a divalent, first-row transition metal having a coordination number 4 to yield a stable metallo-organic system (XV). Here the electron pairs on both sulfur and oxygen are bonded to empty orbitals in the metal through a metallization process. Some of the polymers formed through this mechanism have been studied by Drinkard (*10*) who found the zinc polymer to be more stable than the copper polymer. In the example given earlier in which the Schiff-base salicylaldehyde-*o*-phenylenediamine polymer reacted with Zn^{2+} to give a coordination polymer, no comparison was made of the relative heat stabilities of the two systems; however, it is expected that the metal-containing polymer would have the greater stability when evaluated under the conditions described for the 8-hydroxyquinoline polymers.

The coordination polymers of 8-hydroxyquinoline derivatives are not only stabilized with respect to temperature, but a preliminary study (*24*) has disclosed that these polymers are also highly resistant to thermal oxidation. When samples were heated at 190°C. in a sealed system in an air atmosphere, very little oxidation occurred, even after several days,

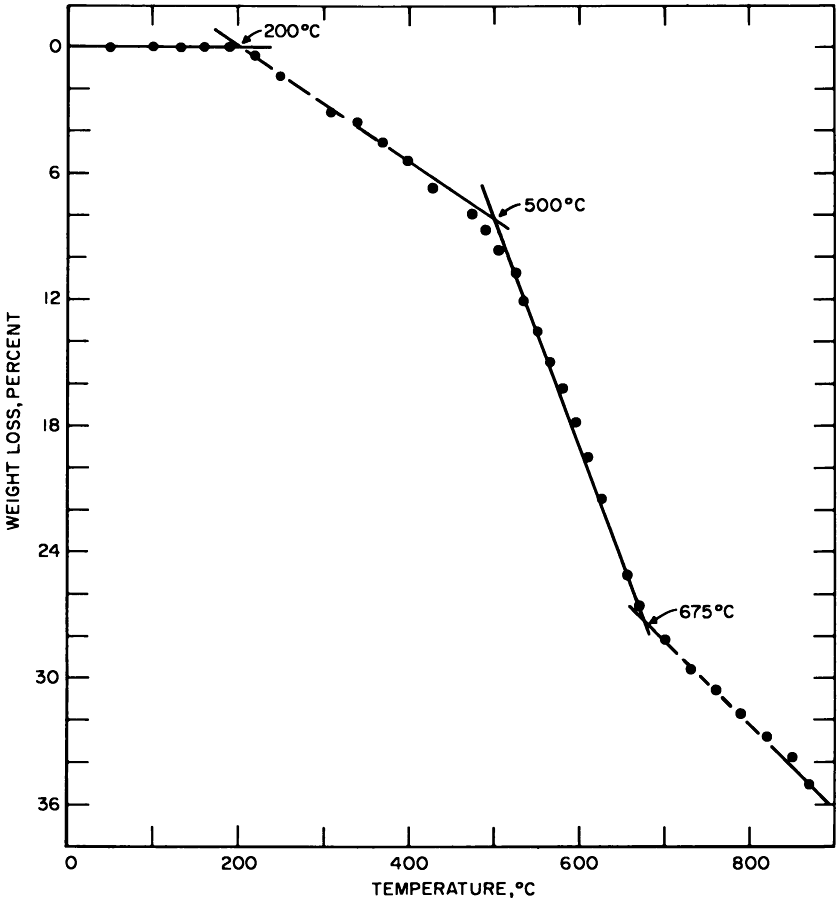
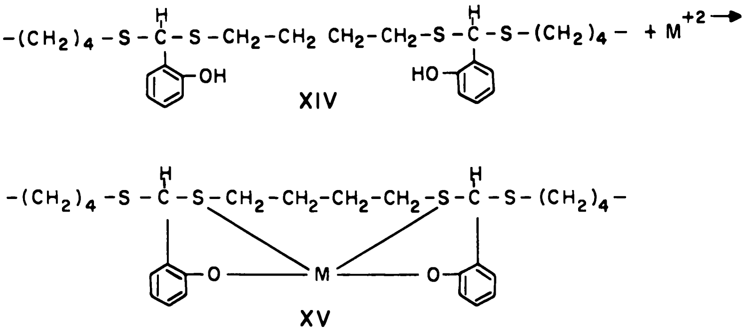


Figure 5. Thermogram for Cr(III)-bis(8-hydroxy-5-quinolyl)methane coordination polymer

as measured by the oxygen content of the atmosphere surrounding the sample. On the other hand, under similar conditions virtually all the oxygen reacted with a polyethylene sample within 30 minutes when it was subjected to the same treatment. Another interesting aspect of this study is that the stability to thermal oxidation of the divalent, first-row transition metal coordination polymers is also governed by the metal, but the trend in stability appears to be reversed from that observed for the thermal degradation process studied *in vacuo*. Under thermal oxidative conditions, the coordination polymers can be arranged in the following stability order: Mn < Co < Ni < Cu > Zn. It will be recalled that the thermal stability order *in vacuo* is: Mn > Co > Ni > Cu < Zn.

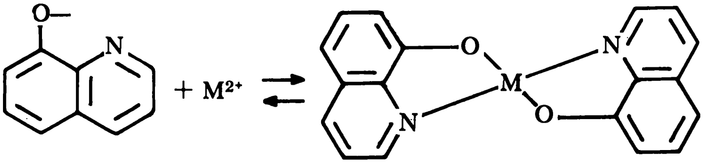


XIV

XV

Figure 6. Preformed organic polymers combine with metal ions to produce coordination polymers

With regard to stabilization, perhaps the most thoroughly investigated aspect of metallo-organic chemistry is the evaluation of stability constants. For the present discussion, a stability constant can be considered as analogous to the reciprocal of the dissociation constants of acids and bases. Thus, if L represents the 8-hydroxyquinoline anion and ML_2 the metal complex, then:

(1) 2 

$$2\,L^- + M^{2+} \rightleftharpoons ML_2 \tag{2}$$

The stability of the complex is expressed by the over-all stability constant K_2, where

$$K_2 = \frac{[ML_2]}{[M^{2+}]\,[L^-]^2} \tag{3}$$

Malley and Mellor (*17*) have shown that for a given ligand the stability constants depend on the central metal. For convenience the values of the constants are frequently quoted on a logarithmic scale. Thus, for 8-hydroxyquinoline, the logarithmic stability constants, log K_2, of some divalent, first-row transition metal oxinates are:

Fe(18.8 V) Co(20.5 V) Ni(22.0 V) Cu(29.0 V) Zn(20.8 V).

The trend is the same as that indicated by the preliminary study on oxidation. When these stability constants are plotted *vs.* the atomic number of the metal or some other related periodic property, a plot is obtained which is just the reverse of that presented for the thermal decomposition data. This shows that while it may be possible to stabilize organic molecules and preformed organic polymers through reactions with metals, certain properties (*e.g.*, thermal stability) will be enhanced, but other properties may not be improved as dramatically or may even be impaired. Thus, for particular applications, coordination polymers may need to be specially tailored so that they meet the requirements of the user.

Acknowledgments

The author acknowledges the assistance of Max Tryon and John Maurey of the Polymer Characterization Section.

Literature Cited

(1) Bailar, J. C., Jr., "Preparative Inorganic Reactions," W. L. Jolly, Ed., Vol. 1, p. 8, Interscience, New York, 1964.
(2) Berg, E. W., Truemper, J. T., *Anal. Chim. Acta* **32,** 245 (1965).
(3) Block, B. P., "Inorganic Polymers," F. G. A. Stone, W. A. G. Graham, Eds., p. 488, Academic, New York, 1962.
(4) Bottei, R. S., Gerace, P. L., *J. Inorg. Nucl. Chem.* **23,** 245 (1961).
(5) Charles, R. G., Hickam, W. M., Von Hoene, J., *J. Phys. Chem.* **63,** 2084 (1959).
(6) Charles, R. G., Langer, A., *J. Phys. Chem.* **63,** 603 (1959).
(7) Combes, A., *Compt. Rend.* **108,** 1252 (1889).
(8) Dent, C. E., Linstead, R. P., *J. Chem. Soc.* **1934,** 1027.
(9) Drinkard, W. C., Jr., Ph.D. Thesis, University of Illinois, 1956.
(10) Drinkard, W. C., Jr., *WADC Tech. Rept.* **59-427,** 367 (Jan. 1960).
(11) Drinkard, W. C., Jr., Bailar, J. C., Jr., *J. Am. Chem. Soc.* **81,** 4795 (1959).
(12) Eichhorn, G. L., Marchand, N. D., *J. Am. Chem. Soc.* **78,** 2688 (1956).
(13) Horowitz, E., Perros, T. P., *J. Inorg. Nucl. Chem.* **26,** 139 (1964).
(14) Horowitz, E., Perros, T. P., *J. Res. Natl. Bur. Std.* **69A,** 53 (1965).
(15) Horowitz, E., Tryon, M., Christensen, R. G., Perros, T. P., *J. Appl. Polymer Sci.* **9,** 2321 (1965).
(16) Kenney, C. N., *Chem. Ind. (London)* **1960,** 880.
(17) Maley, L. E., Mellor, D. P., *Australian J. Sci. Res.* **2A,** 92 (1949).
(18) Marvel, C. S., Tarköy, N., *J. Am. Chem. Soc.* **79,** 6000 (1957).
(19) Marvel, C. S., Martin, M. M., *J. Am. Chem. Soc.* **80,** 619 (1958).
(20) *Ibid.*, p. 6600.
(21) Marvel, C. S., Rassweiler, J. H., *J. Am. Chem. Soc.* **80,** 1197 (1958).
(22) Morgan, G. T., Smith, J. D. M., *J. Chem. Soc.* **1926,** 912.
(23) Sowerby, D. B., Audrieth, L. F., *J. Chem. Educ.* **37,** 134 (1960).
(24) Tryon, M., Horowitz, E., unpublished results.

RECEIVED June 13, 1967.

8

Oxidative Stabilization of Silicone Fluids

J. M. NIELSEN

Silicone Products Department, General Electric Co., Waterford, N. Y. 12188

Certain cerium and iron compounds, when properly incorporated by preoxidation, are excellent antioxidants for dimethyl silicone fluids (DMS) and methylphenylsilicone fluids (MPS). The useful life of these stabilized fluids depends on the temperature, on the concentration and dispersion of the redox metal moieties, and on the conditions of aeration—better aeration providing the longer useful life with inhibited DMS. A mechanism of stabilization by the redox metals has been proposed to account for the observed data.

The useful life of silicone fluids in air is limited as the temperature increases by the oxidative instability of the hydrocarbon substituents on the siloxane backbone of the polymers: $R_3Si—O—(R_2Si—O—)_x—SiR_3$ (*11, 32*). If R includes alkyl groups (other than methyl) (*11*) or alkenyl groups (*35*), oxygen attack can occur readily below 150°C. If R is methyl (DMS), the attack of oxygen on the $—CH_3$ groups begins to occur in air above 150°C. (*3, 35*), and at a slow rate at 200°C., the rate increasing with increasing temperature (Figure 1). If R includes both phenyl (ϕ) and methyl (Me) groups (MPS), improved oxidative stability is generally obtained in proportion to the ϕ/Me ratio (*1, 2, 6, 7, 9, 11, 28, 36, 38*) (*see also* Figure 5). The oxidative removal of hydrocarbon substituents from a silicone fluid leaves the original polymer backbone essentially intact, but crosslinking occurs at the oxidation sites, giving increased molecular weight and eventually gelling the fluid (*cf. 11, 22, 23*). [Present evidence indicates that structure is also important in oxidative stabilization—*e.g.*, $—OSi\phi Me—O—Si\phi Me—$ appears more oxidatively stable than $—OSi\phi_2—O—SiMe_2—$. It has been reported (*34*) that $R_3Si(OSi\phi Me)_xOsiR_3$ in air at 350°C. gives 50% longer life when R is ϕ than when R is Me, and that $\phi_2MeSi—$ chain stopper behaved nearly like $\phi_3Si—$. It has also been reported (*28*) that no appreciable oxidation occurs below 225°C. in a methylphenylsilicone fluid with $\phi/Me \geqslant 0.4$, that it is the methyl groups which undergo most of the oxidation, and that it is probably the terminal methyl groups which are most readily oxidized in this system. Gas-phase comparative oxidation of various siloxane structures has been reported (*11*). The stabilizing effects of phenyl groups and siloxane structure have been discussed (*1, 2, 11, 32*).]

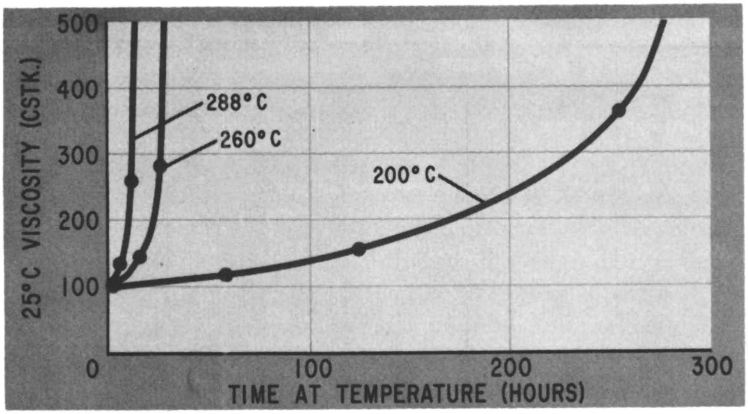
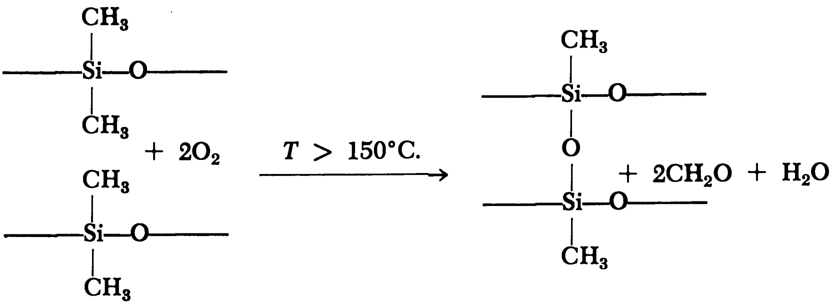


Figure 1. Oxidation of DMS at various temperatures

Oxidation of Silicone Fluids

A simplified representation of the oxidation of dimethylsilicone (DMS) in air is shown below.



$$\begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ CH_3 \\ CH_3 \\ | \\ -Si-O- \\ | \\ CH_3 \end{array} + 2O_2 \xrightarrow{T > 150^\circ C.} \begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ O \\ | \\ -Si-O- \\ | \\ CH_3 \end{array} + 2CH_2O + H_2O$$

Other oxidation products, in addition to those above, have been reported for the oxidation of DMS (*1, 2, 16, 22, 23, 28, 35*): formic acid, carbon dioxide, carbon monoxide, silanols (≡Si—OH), cyclic siloxanes, hydrogen, and methanol. Analogously, acetaldehyde and acetic acid are reported as the oxidation products from diethyl silicone at 160°–190°C. (*18*).

Carbon monoxide has been reported from oxidations carried out above 350°C. (*1, 2, 16*), but it was not found as an oxidation product of DMS below 300°C. (*35*). It is probable that CO and H_2 can arise either from the air oxidation of formaldehyde (*12, 17, 37*) or by a direct decomposition of a peroxide radical $\equiv SiCH_2OO\cdot$ to CO and H_2 as proposed by Kuzminskii (*22*).

Silanols produced by oxidation can condense to form siloxane linkages plus water, and they can also provide a low energy path for siloxane rearrangements (*cf.* *22, 23, 24, 25*).

Cyclic siloxanes form more rapidly from DMS at higher temperatures because of increased rates of thermal rearrangement of the polysiloxane structure (*1, 2, 16, 26, 29*).

Methanol has been detected in the products of oxidation of DMS at 430°C. (*16*) and in the products of oxidation of hexamethyldisiloxane at 300°C. (*22*).

Improvement of the oxidative stability of silicone fluids is needed to extend their usefulness. It was recognized early (*30*) that some improvement could be obtained by using conventional hydrocarbon antioxidants—the aromatic amines and phenols. Such can be useful with DMS and MPS and are especially useful with alkyl (C_nH_{2n+1}, $n > 1$) silicone fluids which are more comparable with alkanes in susceptibility to oxidation as *n* increases.

Incorporation of Redox Metal Antioxidants in Silicone Fluids

A new area of study was opened by Elliot's discovery (*14*) that certain metal soaps, particularly the 2-ethylhexanoate soaps, could greatly prolong the fluid life of dimethylsilicone (DMS) and methylphenylsilicone (MPS) fluids above 250°C. The metals found effective are transition elements capable of giving a one-electron redox system: $M^{x+1} + e^{-1} \rightleftarrows M^x$, for example, where M is Fe, Cu, Co, Ni, Ce, Mn, etc. (*9, 14, 19, 20, 33*). However, the tendency for systems containing these redox metal antioxidants to form excessive amounts of haze and sludge in storage and/or during use was an obstacle to their practical application. An inhibitor was required that could be dispersed readily in a silicone fluid and that would remain stable for long periods when the fluid was subjected to various thermal and oxidative conditions. In addition, the redox metal could not be deleterious to the important properties of the silicone fluid (*9, 29*).

From such criteria our present experience has indicated the choice of cerium or iron antioxidants as the most feasible candidates to use in DMS and MPS fluids (*6, 7, 9*). Future study, of course, may indicate the importance of other metals, such as manganese (*21*). The oxidative stability of alkylsilicones can also be improved with redox inhibitors; for example, it is reported (*27*) that the oxidative stability of diethylsilicone at 170°C. is improved by addition of 0.2% of a copper or chromium chelate.

The most successful method of incorporating stabilized iron or cerium into silicone fluids has been by a preoxidation process with DMS or MPS which requires the heating of a mixture of silicone fluid and an appropriate compound or complex of the redox metal to 200°–300°C., while bubbling air into the mixture (*4, 5, 6, 7, 8, 9, 10, 13, 19, 20, 31*). Such processing has been carried out mainly with iron soaps (*4, 13, 31*), with substituted ferrocenes (*5, 13*), and with special cerium complexes (*6, 7, 8, 9, 10, 19, 20*). A minimum aeration rate of one volume of air per minute per volume of fluid has been recommended (*9*). Changes in fluid properties are usually minor during the preoxidation, but fluid weight losses and viscosity increases can become excessive in prolonged processing. (*6, 7, 9*).

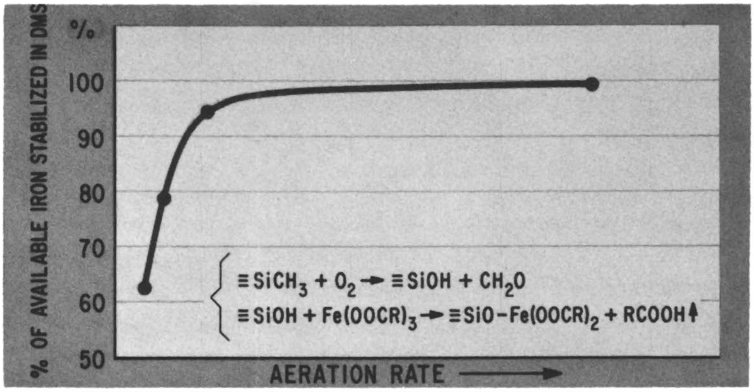


Figure 2. Iron stabilization vs. *aeration rate*

It has been suggested that preoxidation achieves stabilization of cerium in a silicone polymer by formation of Ce—O—Si structures (*6, 7*). This formation of M—O—Si structures can also be inferred from the preoxidation of iron soaps in DMS fluid. The data indicate that the level of stabilized iron that can be attained in DMS fluid in the preoxidation process is independent of the aeration rate at high rates of air flow, but directly dependent on aeration at low air flow rates, keeping other variables constant, such as the level of ferric soap used, the time and temperature of processing (Figure 2). Indicative also is the processing requirement that preoxidation be carried out above 200°C., a temperature at which the oxidation rate of methyl groups in DMS begins to become significant. It is interpreted from this data that iron is stabilized at sites on the polymer created by oxidation, probably by Fe—O—Si bond formation. It is usually necessary to filter a pre-oxidized DMS fluid to remove some redox metal-containing material that was not stabilized in the polymer during processing.

The state of dispersion and structure of the redox metal moiety in the silicone fluid are highly important to oxidative stability (*6, 7*). A low level of well-dispersed iron can give better stabilization than a higher level of less well dispersed iron (*see* Figure 3). Filtered fluids containing colloidal agglomerates of iron are much less effective in resisting oxidative damage than those fluids of the same iron level in which the iron is more nearly molecularly dispersed. Also, fluids with poorly dispersed iron have a greater tendency for haze and sludge formation.

In general, DMS fluids which are properly stabilized with iron or cerium antioxidant have a useful fluid life in air of thousands of hours at or below 500°F. (260°C.) and hundreds of hours at 550°F. (288°C.) as measured by testing 40-gram samples in 150-ml. beakers in a rotating shelf, air circulating oven (Table I). These long fluid lives are in contrast to the relatively short gelation times of the non-inhibited fluids tested under the same conditions.

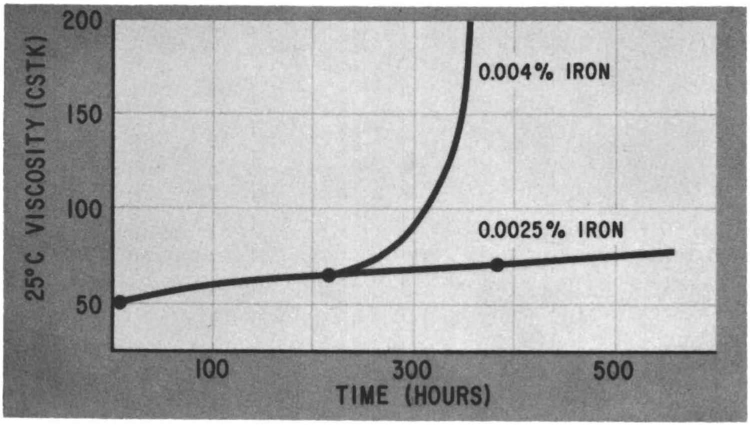


Figure 3. 550°F.-oven tests of filtered DMS (50) fluid inhibited with Fe of varying dispersion

When the iron level in a silicone fluid is increased, iron dispersion being held constant, the time to gelation can be lengthened (Figure 4); however, a point of diminishing returns is reached where negligible improvement results from increasing the antioxidant level. There is a minimum rate of oxidation damage for a DMS fluid under given oxidation conditions that cannot be improved by increasing the level of redox metal antioxidant. As indicated in Table II, at higher temperatures of operation,

Table I. Gelation Time of DMS (100) in Air, with and without Iron

Temperature		*Hours to Gelation*	
°F.	*°C.*	*DMS(100)*	*DMS(100) + Iron*
400	204	270	>>2000
500	260	36	>2000
550	288	14	>800
600	316	5	>100
625	330	3	18-20
650	343	2	9-11

higher levels of well-dispersed iron are required for the oxidative stabilization of DMS fluid in air, but excessively high levels of redox antioxidant can decrease fluid life (*6, 7, 13, 14, 19, 20*) and can increase the tendency for haze and sludge formation. From the study of the oxidative stability of thin films of methyl- and phenyl-containing silicone fluids (MPS fluids) above 300°C., Baker *et al.* (*6, 7, 8, 10*) have recommended that about 0.025% of cerium (*see also 19, 20*) be incorporated in the fluid for oxidative stabilization. The redox metal level—about 1.8×10^{-3} gram atom of Ce/kg. of fluid—is about the same order as that recommended for iron in DMS fluids in Table II.

Oxidative Stability vs. *Aeration Conditions*

It has been observed (a) that aeration plays an important role in prolonging the life of a redox metal stabilized silicone fluid by sweeping away any partially oxidized volatiles to prevent their return to the bulk fluid; (b) that aeration is needed to keep some redox antioxidants from

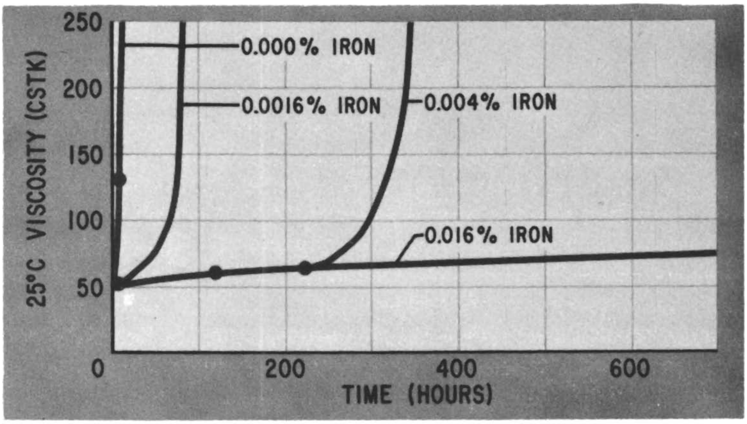


Figure 4. 550°F.-oven tests of DMS (50) with various levels of iron by dilution

dropping out of solution; (c) that the surface-to-volume ratio during fluid testing is important in determining fluid life—a greater exposure to air providing a longer fluid life (*6, 7, 9*). Table III illustrates the effect of surface to volume both on the life of DMS (1000) (*cf. 9*) and of DMS (1000) inhibited with iron. [This inhibited fluid is not highly stabilized as indicated by the short gelation time (168 hours) for the 40-gram sample.] The gelation time of the DMS fluid is inversely proportional to the surface-to-volume ratio, while the inhibited fluid exhibits either a direct or an inverse proportionality depending on the magnitude of the surface-to-volume ratio. [Other test variables, such as fluid viscosity, effective iron level, air circulation, and test temperature, are important in this relationship. These were held constant in obtaining the illustrative data reported in Table III.] When the surface-to-volume ratio is low, the fluid life of iron-inhibited DMS becomes more like that of the non-inhibited fluid. The change of fluid life of redox metal-inhibited silicone fluids under conditions of restricted oxygen availability or with a change in the surface-to-volume ratio has been widely observed in testing and in the practical use of such fluids. Control of aeration is a fundamental key to the practical use and understanding of these systems.

Table II. Guidelines for Incorporating Iron Soap Antioxidant Into DMS Fluids by a Preoxidation Process

Max. Temperature for Use		*Minimum Level of Dispersed Iron*	
°F.	*°C.*	*gram atom Fe/kg.*	*% Fe*
400	204	1.8×10^{-4}	0.001
500	260	3.6×10^{-4}	0.002
550	288	1.1×10^{-3}	0.006
600	316	2.7×10^{-3}	0.015

Table III. Oxidative Life of DMS (1000) with and without Iron Antioxidant at 550°F.

150 ml. Beaker, grams Sample Wt./	*Relative Surface/Volume*	*Time to Gelation, Hours*	
		DMS(1000)	*DMS(1000) + Iron*
15	6.66	4	697
30	3.33	—	479
40	2.50	8	168
50	2.00	—	48, 37
60	1.67	—	37
75	1.33	15	73

Proposed Mechanism of Inhibition of Oxidation of DMS Fluids

The following three postulates have proved useful in interpreting the available data on the inhibition of oxidation of silicone fluids by redox metals.

(I) The oxidation of DMS fluid occurs by a free radical, branching chain reaction which is initiated by oxygen attack on methyl groups (*22, 23, 25, 35, 39*).

Initiation

$$\equiv SiCH_3 + O_2 \rightarrow \equiv SiCH_2\cdot + \cdot OOH \text{ and/or} \qquad (1)$$

$$\equiv SiCH_3 + O_2 \rightarrow [\equiv SiCH_2OOH]\cdot \rightarrow \equiv Si\cdot + \cdot OH + CH_2O \qquad (2)$$

Propagation

$$\equiv SiCH_2\cdot + O_2 \rightarrow \equiv SiCH_2OO\cdot \qquad (1a)$$

$$\equiv SiCH_2OO\cdot \rightarrow \equiv SiO\cdot + CH_2O \qquad (1b)$$

$$\equiv Si\cdot + O_2 \rightarrow SiOO\cdot \qquad (2)$$

$$\begin{array}{lllll} & & \cdot OOH & & HOOH \\ & & \cdot OH & & HOH \\ \equiv SiCH_3 & + & \equiv SiO\cdot & \rightarrow & \equiv SiOH + \equiv SiCH_2\cdot \qquad (3) \\ & & \equiv SiOO\cdot & & \equiv SiOOH \\ & & \equiv SiCH_2OO\cdot & & \equiv SiCH_2OOH \end{array}$$

Chain Branching

$$\equiv SiCH_2OOH \rightarrow \equiv Si\cdot + \cdot OH + CH_2O \qquad (4b)$$

$$\equiv SiOOH \rightarrow \equiv SiO\cdot + \cdot OH \text{ or } \equiv Si\cdot + \cdot OOH \qquad (4a)$$

$$HOOH \rightarrow 2\ \cdot OH \qquad (4c)$$

Kuzminskii (*22*) suggests that chain branching in the free radical reaction occurs through further oxidation of formaldehyde,

$$CH_2O + O_2 \rightarrow \cdot CHO + \cdot OOH.$$

Termination

$$\equiv Si\cdot + \cdot OH \rightarrow \equiv SiOH \qquad (1)$$

$$\equiv Si\cdot + \cdot OSi\equiv \rightarrow \equiv Si{-}O{-}Si\equiv \qquad (2)$$

$$X\cdot + \cdot Y \rightarrow XY \qquad (3)$$

Termination Reactions 1 and 2 are favored; the other possible reaction, 3, gives material which is thermally or oxidatively unstable, resulting in new free radicals (*e.g.*, the formation of $\equiv SiCH_2OH$ by termination Reaction 3 would give a material subject to further attack by oxygen, perhaps to $\equiv SiCH(OH)OOH$, which then could rearrange to $\equiv Si\cdot + \cdot OH + HCOOH$). Any silanols formed can condense to water and siloxanes.

(II) M^{x+1} can destroy free radicals, being reduced to M^x in the process. The reduction of a redox metal by a free radical can be illustrated as follows: $M^{x+1} + A\cdot \rightarrow M^x + A^{+1}$, where $A\cdot$ is $\equiv Si\cdot$ and $\equiv SiCH_2\cdot$. As long as sufficient M^{x+1} is available in the system in a well dispersed state, free radical chain reactions are quickly terminated by the destruction of these radicals; thus, the rate of oxidative damage is controlled at about the rate of attack of oxygen on methyl groups in the initiation step. M^x is not considered effective in destroying free radicals.

(III) In a hot system M^x can react rapidly with oxygen to regenerate M^{x+1}. The low level of redox metal used to stabilize silicone fluids requires the regeneration of the inhibiting species to continue the stabilization for prolonged periods. This regeneration can be illustrated as follows:

$$2M^x + O \rightarrow 2M^{x+1} + O^{2-}$$

(This reaction also supplies the anions to balance the cations formed in the destruction of free radicals). As long as this reaction recycles the redox metal and keeps the concentration of M^{x+1} on a par with the generation of free radicals by oxygen, a low level of redox inhibitor can protect a methylsilicone against the rapid gelation rate of the unprotected fluid. Under these conditions a DMS fluid would rise slowly in viscosity over a prolonged fluid life. If free radical generation outstrips the availability of M^{x+1}, the rate of viscosity rise accelerates rapidly as the diverging free radical chain reaction propagates to cause gelation.

To regenerate M^{x+1} fast enough to keep up with free radical generation, a minimum level of oxygen must be available for the fluid conditions. Present experience indicates that levels of oxygen which are too low to regenerate effectively M^{x+1} can still be effective in attacking the methyl groups of the polymer. High levels of air undoubtedly increase the rate of attack of oxygen on the methyl groups of the silicone fluid, but they also allow regeneration of M^{x+1} which prevents catastrophic rates of oxidation from occurring. The availability of oxygen in a fluid depends upon the following factors:

(1) The oxygen content of the atmosphere in contact with the fluid.

(2) The dispersion of the oxygen into the fluid:
    The surface/volume ratio and the geometry of the container
    Fluid viscosity
    Fluid agitation and circulation
    Solubility and diffusion rate of oxygen in the fluid
    Temperature.

Under conditions of high oxygen availability (with adequate inhibitor concentration for the temperature conditions) the DMS fluid has a very long life compared with that of the non-inhibited fluid. Such conditions will occur most favorably with (1) thin films of fluid, (2) low viscosity fluid, (3) agitated fluid, (4) aerated fluid (air bubbled through the fluid), (5) good air circulation, (6) an appreciable level of oxygen in the atmosphere, etc. As the oxygen level in the fluid is reduced, a point is reached where the methyl groups and M^x compete for the available oxygen. As the M^x begins to lose this competition, the rate of oxidation accelerates because of a deficiency of M^{x+1}. Free radicals then accumulate still faster, using up more of the oygen; the viscosity rises, making it more difficult to disperse further oxygen into the fluid, the inhibitor level drops still further, allowing further acceleration of oxidation. These cascading effects lead rapidly to gelation.

The low level of redox metal used for antioxidant protection of silicone fluids requires avoidance of inhibitor loss from solution. Materials used with these fluids must be free of interactions which could excessively remove inhibitor from solution or which could provide a source of easy free radical generation to overwhelm the inhibitor.

Certain fluids show the effects of the redox system more plainly. For example, an iron inhibited methylsilicone fluid which also contains tetrachlorophenyl groups maintains a homogeneous solution when heated with aeration, but under oxygen-deficient conditions it can become hazy on heating. When 40 grams of this fluid in a 150-ml. beaker are heated in air at 500°–550°F. until just gelled, there can be observed a 1-cm. thick top layer that is a clear, brown-colored, homogeneous gel; below this is hazy gel. This clear layer represents the depth to which oxygen can diffuse into the gel at a sufficient concentration under the test conditions to regenerate Fe^{3+} and thus prevent haze formation by separation of Fe^{2+}. (Oxygen apparently penetrates a fluid more readily than a soft gel since the fluid sample was homogeneous before gelation).

The effective stabilization of diethylsilicone fluid by redox inhibitors at 170°C. (27), but not at 260°C. (*13*), fits the theory since the presence of (CH_2) groups in this material means an easier formation and propagation of free radicals (*15, 39, 40, 41, 42*). Under conditions which allow prolonged stabilization of DMS fluid by a redox inhibitor, a diethylsilicone fluid is quickly gelled when the redox inhibitor is overwhelmed by the faster rate of generation of free radicals from (CH_2) groups. It is expected that silicone fluids with higher alkyl groups than ethyl will have still less stabilization by the redox inhibitors.

The redox metal stabilization of silicone resins and rubber also fits the theory. Comparatively massive levels of red iron oxide (Fe_2O_3) (about 3% based on silicone or 0.5 gram atom of iron/kg. of DMS gum) are used in certain rubber formulations to prolong the useful life of silicone rubber at high temperature. These massive levels of iron are required not only because of the lack of homogeneity of the system but also because of the difficulty of diffusing sufficient oxygen into the rubber structure to regenerate Fe^{3+}. In resin coatings soluble redox inhibitors at low levels are useful in prolonging resin life by reducing the rate of embrittlement above 400°F. Since resin coatings are usually very thin, oxygen can still diffuse into the solid structure at an adequate rate to regenerate M^{x+1} to keep the oxidation rate under control.

An example of theoretical interest of the air aging of an Fe_2O_3 inhibited silicone rubber slab at high temperature has been reported by a co-worker. After an appropriate aging period a cross section of this rubber slab was examined; five distinct layers were observed: a red, rubbery center section; an off-white, stiffened, but rubbery, layer on either side of the center; and red, brittle outside layers. Oxygen had not penetrated the center section to a significant degree, and this section remained unchanged. The whitish layers had been attacked by oxygen increasing the crosslinking; the iron had partially protected the polymer, being reduced to Fe^{2+} (loss of red color), but insufficient oxygen diffused into the structure to regenerate Fe^{3+}. The exterior red layers had sufficient oxygen to maintain iron in the Fe^{3+} state, but the oxidative conditions were too severe to prevent embrittlement of the polymer by oxidation of methyl groups.

Comparative Oxidation of Redox Metal Inhibited DMS and MPS Fluids

The response of DMS or MPS fluids to oxidative stabilization by redox metal antioxidants is quite different and is temperature dependent (*6, 7, 38*). At temperatures above 700°F. in air, an inhibited DMS fluid has a fluid life no longer than the DMS fluid itself, while above 700°F. in air MPS fluids can still show some redox antioxidant improvement. At temperatures below 600°F. in well-aerated systems, DMS fluids show a much greater improvement in fluid life upon proper incorporation of redox inhibitors than do MPS fluids. Our work has indicated that in a rotating shelf, air circulating oven test at 550°F., using 40-gram samples in 150-ml. beakers, the higher the phenyl content of a MPS fluid, the less the improvement in oxidative stabilization with iron antioxidant. In fact, Figure 5 seems to indicate that the phenyl group is the oxidative weak link in such tests. Further interesting effects are observed when com-

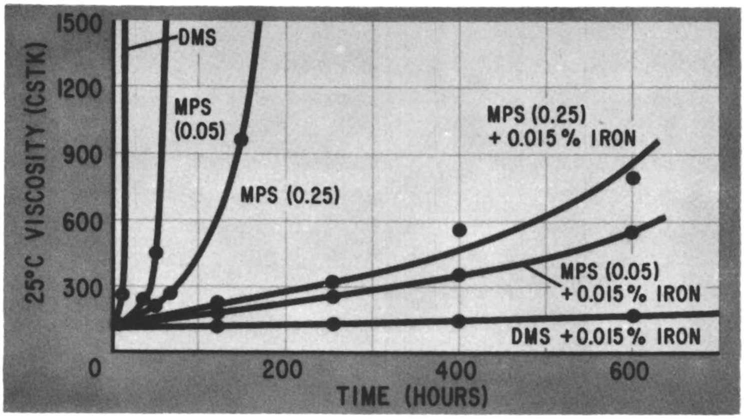


Figure 5. Oxidative stability of DMS and MPS fluids with and without Fe at 550°F.

parative rates of viscosity increase at different temperatures of iron-inhibited DMS and MPS fluids (about 0.015% Fe) are examined (Figure 6). The rate data obtained show the effective stabilization of DMS by iron up to about 600°F., but above this temperature a rapid increase in the rate of oxidation occurs. [Curves of viscosity *vs.* time were obtained similar to Figure 5. The comparative rates were obtained from time intervals in the early, nearly linear portions of these curves. The fluid viscosities at zero time were not used in the rate data.] Inhibited MPS fluids also experience this acceleration of oxidation rate at about 600°F., but above 600°F. the phenyl-containing fluids have less catastrophic rates of oxidation than DMS fluid, and the higher phenyl contents improve fluid life.

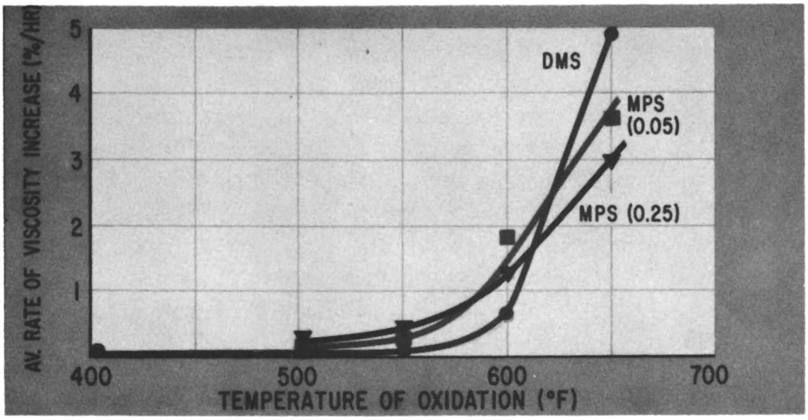


Figure 6. Comparative, early oxidation rates of Fe-inhibited 100-cst. DMS and MPS fluids

In contrast to the faster rate of oxidation of inhibited, phenyl-containing fluids in well-aerated systems below 600°F., when systems of restricted aeration are used for testing, the inhibited MPS fluids can show a distinct advantage. Table IV indicates the test results of heating 40-gram samples of iron- or cerium-inhibited fluids in 150-ml. beakers at 550°F. for an appropriate time. Half of the beakers (for contrast) were covered with a closely fitting aluminum foil cap to restrict aeration. The tabulated viscosity and weight loss data indicate the importance of phenyl content in stabilizing poorly aerated systems. Under conditions of low oxygen availability, the redox inhibitors are not very effective since M^{x+1} is not readily regenerated. It is then that the antioxidant property of the phenyl group is the deciding factor (*1, 2*). This fact is emphasized in Table IV which includes test data from a non-inhibited sample of MPS fluid (0.25 ϕ/Me ratio). The higher viscosity of the

Table IV. Comparative Testing of 100-cst. Fluids Containing Iron or Cerium at 550°F.[a]

A. 0.011% Cerium and 0.013% Iron for 305 Hours

	25°C. Viscosity of Fluids After Testing, cst.			
Fluid	*0.011% Cerium*		*0.013% Iron*	
(φ/Me Ratio)	*Covered Beaker*[b]	*Open Beaker*	*Covered Beaker*[b]	*Open Beaker*
DMS (0.00)	gelled[c]	131	103[c]	142
MPS (0.05)	gelled[c]	418	1203	247
MPS (0.25)	583	805	333	299

B. 0.011% Cerium for 168 Hours

	Covered Beaker Test[b]		*Open Beaker Test*	
	25°C. Visc., cst.	*Wt. Loss, %*	*25°C. Visc., cstk.*	*Wt. Loss, %*
DMS (0.00)	gelled[c]	13.8	126	16.8
MPS (0.05)	845	11.9	194	20.8
MPS (0.25)	237	8.2	340	30.9
C. 0.013% Iron for 94 Hours				
DMS (0.00)	102[c]	5.1	128	14.5
MPS (0.05)	190	8.2	191	15.4
MPS (0.25)	164	4.0	210	17.3
MPS (0.25) No Inhibitor	128	6.0	500	19.0

[a] 40-Gram samples/150 ml. beakers placed on a rotating shelf in an air circulating oven.
[b] Beaker covered with aluminum foil to restrict air circulation. The foil was carefully conformed to the walls of the top half of the beaker.
[c] Deposition of amorphous silicon-containing solid on the interior walls of the beaker above the fluid (or gel) level (*6, 7*).

iron-containing MPS (0.25) fluid as compared with the non-inhibited fluid may be caused by an acceleration of hydroperoxide degradation by iron (*15*). The apparent anomaly of low viscosity, inhibited DMS fluids in some of the covered beaker tests is believed caused by exhaustion of available oxygen by vapor phase oxidation of volatile cyclic siloxanes, forming gel on the beaker walls but protecting the bulk fluid.

Summary

Certain cerium and iron compounds can be useful as antioxidants when properly incorporated into DMS and MPS fluids by preoxidation. The conditions of fluid use determine the level of redox metal required (usually about 0.2 to 3.0 × 10^{-3} gram atoms/kg.) and the silicone to be used. The role of the redox metal inhibitor is to control the rate of oxidation of methyl groups, and a mechanism has been proposed to account for the stabilizing effect.

In general, inhibited DMS fluid is best used below 600°F. and under good aeration conditions; inhibited MPS fluids (ϕ/Me $>$ 0.05) are favored where temperatures rise above 600°F. and when conditions of poor aeration prevail.

Literature Cited

(1) Andrianov, K. A., Sokolov, N. N., *Khim. Prom.* **1955**, 329; *CA* **50**, 7499 (1956).

(2) Andrianov, K. A., Sokolov, N. N., *Elektrichestvo* **1956**, 31; *CA* **50**, 16171 (1956).

(3) Atkins, D. C., Murphy, C. M., Saunders, C. E., *Ind. Eng. Chem.* **39**, 1395 (1947).

(4) Awe, R. W., Schiefer, H. M., *U. S. Patent* **3,002,927** (1961).

(5) Awe, R. W., Schiefer, H. M., *U. S. Patent* **3,002,989** (1961).

(6) Baker, H. R., Kagarise, R. E., O'Rear, J. G., Sniegoski, P. J., *J. Chem. Eng. Data* **11**, 110 (1966).

(7) Baker, H. R., Kagarise, R. E., O'Rear, J. G., Sniegoski, P. J., *U. S. Naval Res. Lab. Rept.* **6156** (1965).

(8) Baker, H. R., O'Rear, J. G., *U. S. Patent* **3,267,036** (1966).

(9) Baker, H. R., Singleterry, C. R., *J. Chem. Eng. Data* **6**, 146 (1961).

(10) Baker, H. R., Singleterry, C. R., Ravner, H., *U. S. Patent* **3,008,901** (1961).

(11) Bazant, V., Chvalovski, B., Rathousky, J., "Organosilicon Compounds," Vol. 1, pp. 321-322, Academic, New York, 1965.

(12) Bone, W. A., Gardner, J. B., *Proc. Roy. Soc. (London)* **A154**, 297 (1936); *CA* **30**, 4461 (1936).

(13) Brown, E. D. Jr., Holdstock, N. G., Nielsen, J. M., *Wright Air Develop. Center Rept.* **56-168**, Part III, 55-77 (1958).

(14) Elliot, J. R., *U. S. Patent* **2,445,567** (1948).

(15) Frank, C. E., *Chem. Rev.* **46**, 155 (1950).

(16) Hardman, B. B., *General Electric Co. Rept.* R65ChSD-120 (1965).

(17) Horner, E. C. A., Style, D. W. G., *Trans. Faraday Soc.* **50**, 1197, 1201 (1955).

(18) Hyde, J. F., DeLong, R. C., *J. Am. Chem. Soc.* **63**, 1194 (1941).

(19) Kobzova, R. I. *et al.*, *Plast. Massy* **8**, 31 (1966); *CA* **65**, 18769 (1966).

(20) Kobzova, R. I. *et al.*, *Plast. Massy* **9**, 35 (1965); *CA* **63**, 18415 (1965).

(21) Kobzova, R. I. *et al.*, *Khim. Tekhnol. Topliv Masel* **4**, 47 (1966).

(22) Kuzminskii, A. S. *et al.*, *Intern. Symp. Organosilicon Chem., Sci. Commun., Prague, 1965*, 362-370.

(23) Kuzminskii, A. S. *et al.*, *Vyscokomol. Soed.* **3**, 1054 (1961); *CA* **56**, 2540 (1962).

(24) Kuzminskii, A. S., Goldovskii, E. A., *Dokl. Akad. Nauk. SSR* **149**, 606 (1963).

(25) Kuzminskii, A. S., Goldovskii, E. A., *Chem. Prum.* **13**, 377 (1963); *CA* **59**, 12998 (1963).

(26) Lewis, C. W., *J. Polymer Sci.* **37**, 425 (1959).

(27) Lipovetz, I., Borbely, A., *Periodica Polytech.* **2**, 259 (1958); *CA* **54**, 4438 (1960).

(28) Murphy, C. M., Saunders, C. E., Smith, D. C., *Ind. Eng. Chem.* **42**, 2462 (1950).

(29) Murphy, C. M., Ravner, H., Kagarise, R. E., *U. S. Naval Res. Lab. Rept.* **6383** (1966).

(30) McGregor, R. R., Leathen, V., Leathen, R., *U. S. Patents* **2,389,804–7** (1945).

(31) Nielsen, J. M., *U. S. Patent* **3,009,877** (1961).

(32) Noll, W., "Chemie Und Technologie Der Silicone," pp. 273-275, Verlag Chemie, Weinheim, 1960.

(33) Piccoli, W. A., *U. S. Patent* **2,979,482** (1961).

(34) Sabolevskii, M. V. *et al., Plast. Massy* **1962,** 13; *CA* **57,** 4841 (1962).

(35) Scala, L. C., Hickam, W. W., *Ind. Eng. Chem.* **50,** 1583 (1958).

(36) Scala, L. C., *J. Appl. Polymer Sci.* **2,** 297 (1959).

(37) Scheer, M. P., *J. Chem. Phys.* **23,** 1357 (1955).

(38) Schiefer, H. M., Awe, R. W., Whipple, C. L., *J. Chem. Eng. Data* **6,** 155 (1961).

(39) Scott, G., "Atmospheric Oxidation and Antioxidants," Elsevier, New York, 1965.

(40) Stewart, R., "Oxidation Mechanisms," Benjamin, New York, 1964.

(41) Tipper, C. F. H., *Quart. Rev.* **11,** 313 (1957).

(42) Waters, W. A., "Mechanism of Oxidation of Organic Compounds," Methuen, London, 1964.

RECEIVED March 17, 1967.

9

Mechanism of Antioxidation and Antiozonization of Amines for Rubber

JUNJI FURUKAWA, SHINZO YAMASHITA, and TEIZO KOTANI

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University,
Kyoto, Japan

Antioxidizing or antiozonizing effects of amine derivatives on oxidative degradation of vulcanized rubbers were evaluated by several methods: (a) the relative ability of amine to protect rubber solution aginst viscosity lowering owing to the action of oxygen or ozone, (b) the rate of reaction of amine with oxygen radical initiated by azobisisobutyronitrile, (c) the protecting effect of amine on the oxygen-Tetralin reaction, and (d) the amount of ozone consumed by amine in rubber solution. Good stabilizers were found to be those amines having some adequate oxidation potentials, which are about 0.4 volt for antioxidant and 0.25 volt for antiozonant. The radical and nucleophilic reactivity indices based on the frontier electron theory were concluded to be good measures of the antioxidizing and antiozonizing actions of the amines.

A number of amines and phenols are known to be effective stabilizers for rubber (*2, 20*). They are capable of protecting unsaturated polymers from the attack of oxygen and ozone, but the effects of the stabilizers on antioxidation and antiozonization are not always the same —*e.g.*, *N,N′*-diphenyl-*p*-phenylenediamine (A) is an antioxidant, whereas *N,N′*-phenylcyclohexyl-*p*-phenylenediamine (B) is an antiozonant.

A

B

In this work, the activities of amines as antioxidants and antiozonants are discussed in relation to their chemical structures. As a possible mechanism it is believed that the antioxidant acts as a scavenger of peroxy radical, a reducing agent for peroxide or a hydroperoxide decomposer in the following chain reaction:

$$\text{Initiator} \rightarrow \text{R}\cdot \qquad (1)$$

$$\text{R}\cdot + \text{O}_2 \rightarrow \text{ROO}\cdot \qquad (2)$$

$$\text{ROO}\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}\cdot \qquad (3)$$

$$\text{ROO}\cdot + \text{ZH} \rightarrow \text{ROOH} + \text{Z}\cdot \qquad (4)$$

(Scavenging peroxy radical)

$$\text{ROOH} \rightarrow \text{RO}\cdot + \cdot\text{OH} \qquad (5)$$

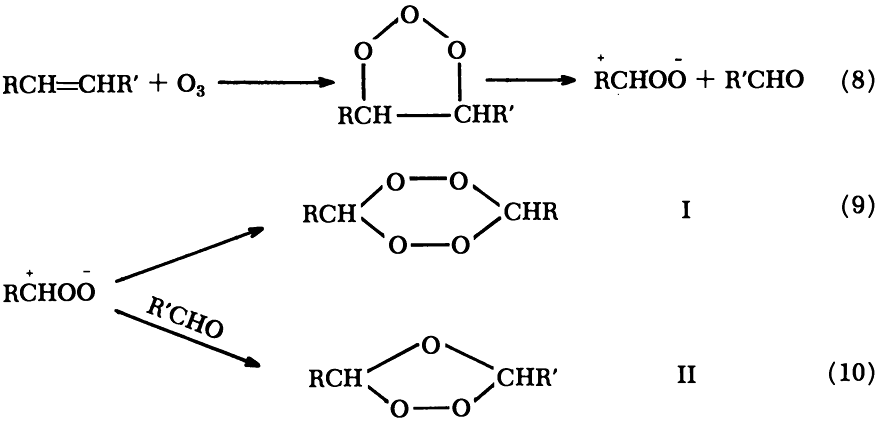
$$\text{RO}\cdot\ (\text{or HO}\cdot) + \text{ZH} \rightarrow \text{ROH}\ (\text{or H}_2\text{O}) + \text{Z}\cdot \qquad (6)$$

(Reducing alkoxy or hydroxy radical)

$$\text{ROOH} + \text{Z}' \rightarrow \text{ROH} + \text{Z}'\text{—O}\cdot \qquad (7)$$

(Decomposing hydroperoxide)

On the other hand, the reaction of ozone with rubber is very rapid and proceeds by a scheme other than chain mechanism. A direct attack of ozone on olefinic double bond brings about cyclic or polyperoxide (I), or isoozonide (II) (*1, 5*).



Antiozonant is regarded as a scavenger for ozone (*11, 21*) or its reaction product (*4*). Amine may react with ozone more rapidly than does rubber to give rise to amine-*N*-oxide (*12*). A nucleophilic attack of pyridine on ozone was also proposed by Slomp and Johnson (*22*).

As a measure of the activity of antioxidants and antiozonants, oxidation potential has been used (*3, 15, 16, 19*). Compounds having an oxidation potential lower than 0.44 volt seem to be effective as antiozonants (*20*), whereas good antioxidants are known to have the potentials between 0.7 and 0.9 volt (*16*). The Hückel molecular orbital calculations seem useful for analyzing the correlation between the oxidation potential of antioxidants and their chemical structures. In fact, Fueno *et al.* (6) have shown that the oxidation potentials of a number of phenolic compounds are linearly correlated with the heights of the calculated highest molecular orbitals to be occupied by π-electrons. They have further shown how the antioxidizing actions of a series of a limited number of phenols may eventually be correlated with the heights of the highest occupied π-levels, and consequently with the oxidation potentials. However, in view of the frontier electron theory of organic reactions developed by Fukui *et al.* (7, 8), the energy levels alone may not always be a measure of reactivity in a more general case.

This paper shows that Fukui's theory is plausible for interpreting the presence of the optimum oxidation potentials for amines to be effective as antioxidants or antiozonants.

Experimental and Results

Amines as Antioxidants or Antiozonants for Rubber (*13*). Oxidative degradation of vulcanized rubber is evaluated from the depression in the tensile properties during aging in the Geer oven.

Rubbers were compounded with the ingredients and vulcanized as shown in Table I. The vulcanizates were cut off from the sheet with JIS (Japanese Industrial Standard) No. 3 dumbbell cutter to prepare the samples for heat aging. Styrene-butadiene rubber (SBR), *cis*-polybutadiene (BR), and butyl rubber (IIR) vulcanizates were aged in the Geer oven at 100°C. for 48 hours. Natural rubber (NR) was aged at 100°C. for 36 hours.

Table I. Recipe for Vulcanizing Rubber

Cure Temp., °C.	*143*	*143*	*147*	*147*
	Weight Parts			
	NR[a]	*BR*[b]	*SBR*[c]	*IIR*[d]
Rubber	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Sulfur	2.5	1.5	2.5	2
Accelerator CZ[e]	1	1	1.5	—
Accelerator TMTD[f]	—	—	—	1.5
Accelerator M[g]	—	—	—	0.5
HAF black[h]	30	30	30	—
Amine	0.008 mole/100 grams of rubber			

[a] Pale crepe #1
[b] BR-01 (JSR)
[c] JSR-1502
[d] Polysar #301
[e] *N*-Cyclohexylbenzothiazyl-2-sulfenamide
[f] Tetramethylthiuramdisulfide
[g] 2-Mercaptobenzothiazole
[h] Philblack O

The amine derivatives used are listed in Table II together with their oxidation half-wave potentials. The ratio of the tensile strength of aged (TS) to unaged $(TS)_0$ rubber is used as a measure of the degree of oxidative degradation (*see* Figures 5–8).

Table II. Amine Derivatives and Their Oxidation Potentials

No.[b]	*Amine Derivative*	*Oxidation Half-Wave Potential (SCE)*
1	Aniline	0.65[a]
2	*p*-Methoxyaniline	0.47
3	*p*-Hydroxyaniline	0.45
4	*p*-Phenylaniline	0.65[a]
5	*N*-Methylaniline	0.75[a]
6	*N*,*N*-Dimethylaniline	—
7	Dicyclohexylamine	0.70
8	Diphenylamine	0.62[a]
9	Di-*p*-tolylamine	—
10	*p*-Hydroxydiphenylamine	0.58
11	*N*-Phenyl-β-naphthylamine	0.54
12	*p*-Phenylenediamine	0.18
13	*N*-Phenyl-*p*-phenylenediamine	0.22
14	*N*-Phenyl-*N′*-cyclohexyl-*p*-phenylenediamine	0.24
15	*N*-*p*-Methoxyphenyl-*N′*-cyclohexyl-*p*-phenylenediamine	0.20
16	*N*-Phenyl-*N′*-isopropyl-*p*-phenylenediamine	0.26
17	*N*,*N′*-Diphenyl-*p*-phenylenediamine	0.35
18	*N*-*p*-Methoxyphenyl-*p*-phenylenediamine	0.20
19	*N*,*N′*-Di-*o*-nitrophenyl-*p*-phenylenediamine	0.84
20	*N*,*N′*-Di-*o*-tolyl-*p*-phenylenediamine	0.33
21	*N*,*N′*-Di-*p*-tolyl-*p*-phenylenediamine	0.30
22	*N*,*N′*-Diphenyltriphenylenediamine	0.35
23	*N*,*N′*-Di-β-naphthyl-*p*-phenylenediamine	0.40
24	Benzidine	0.18
25	*N*,*N′*-Dicyclohexylbenzidine	0.45
26	*N*,*N′*-Diphenylbenzidine	0.48
27	2,2,4-Trimethyl-1,2-dihydroquinoline	0.47
28	6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	0.33

[a] Decomposition potential.
[b] These numbers identify the compounds in Figures 1-13.

Vulcanized rubber was ozonized as follows. Natural rubber was compounded with the ingredients shown in Table III and cured at 141°C. for 13 minutes. The vulcanizates were cut off from the sheets with JIS No. 1 dumbbell cutter to obtain the specimens for the ozone crack test. The test pieces were exposed to an oxygen atmosphere containing 0.01% ozone under an elongation of 50%, and a time, t_c, required for the initial crack formation was measured.

Table III. Recipe for Vulcanization

	Weight Parts
Natural rubber	100
Zinc oxide	5
Sulfur	3
Stearic acid	1
Hexamethylenetetramine	0.4
2-Mercaptobenzothiazole	0.4
Amine	0.004 mole

Oxidation potentials of the amines were measured by a conventional polarograph. The sample solutions consisted of 16 ml. of dioxane, 2 ml. of water, 2 ml. of methanol, and 5 × 10^{-5} mole of the amine together with 0.04 mole/liter of lithium chloride. The measurements were carried out at 12°C. by using a positive electrode of platinum.

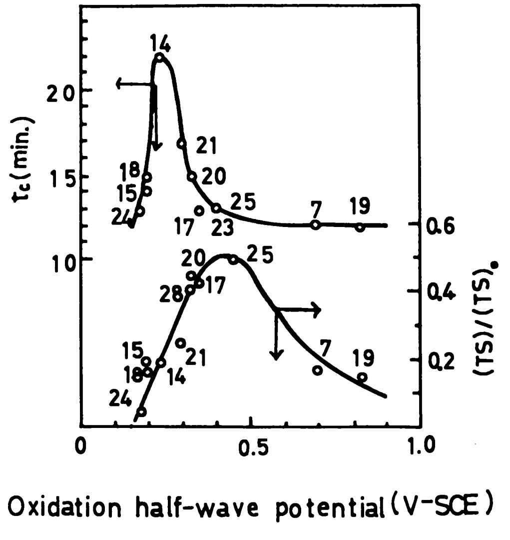


Figure 1. Correlation between the relative tensile strength $(TS)/(TS)_0$ *or the time for the crack formation of NR gum vulcanizates,* t_c *and the oxidation potential of the amine used (see Table II)*

Figure 1 shows the correlation between the relative tensile strength $(TS)/(TS)_0$ or the time, t_c, for the crack formation of NR gum vulcanizates and the oxidation potential of the amines employed as the stabilizer. The antioxidant or antiozonant activity of amine first increases with increasing oxidation potential and reaches a maximum at about 0.4 or 0.25 volt, beyond which the ability decreases with the increase in the potential.

These results lead us to conclude that some amines are effective as both antioxidants and antiozonants for rubber, and their efficiencies depend on their oxidation potentials. The optimum potentials of amines exist at about 0.4 volt for antioxidants and 0.25 volt for antiozonants.

Reactivities of Amines in Homogeneous Systems (*14, 17*). The decrease in the tensile properties of the vulcanized rubber during aging may be attributed to the degradation of the rubber molecule by oxidation. This may be supported by the experimental result in the oxidation of rubber solution.

Thus, the reactivities of the amines in homogeneous systems were investigated. The protecting ability of the amine against viscosity lowering of rubber solution by oxygen or ozone and the reactivity of amine with ozone or the radical originated from the reaction of azobisisobutyronitrile with oxygen are reported here. These results are compared with their radical and nucleophilic reactivity indices.

SBR (JSR 1502) was purified by dissolving rubber in benzene and precipitating it with a mixture of acetone and methanol (1:1), followed by drying. One gram of purified rubber was dissolved in 100 ml. of *o*-dichlorobenzene and added with 1×10^{-4} mole amine. Oxygen (0.5 liter/min.) was introduced into the solution at 100°C. for 5 hours. Two milliliters of the solution were diluted with 10 ml. of *o*-dichlorobenzene, and the viscosity was measured at 30°C. The viscosity lowering of a 1% rubber solution is illustrated in Table IV. The result indicates that *N,N'*-diaryl-*p*-phenylenediamines protect rubber effectively from degradation by oxygen.

Table IV. Effect of Amine on the Ratio of Viscosity of Treated[a] (η) and Untreated (η_0) SBR Solution

No.	*Amine Derivative*	η/η_0
	None	0.656
8	Diphenylamine	0.915
11	*N*-Phenyl-β-naphthylamine	0.931
12	*p*-Phenylenediamine	0.890
13	*N*-Phenyl-p-phenylenediamine	0.944
14	*N*-Phenyl-*N'*-cyclohexyl-*p*-phenylenediamine	0.896
17	*N,N'*-Diphenyl-*p*-phenylenediamine	0.934
23	*N,N'*-Di-β-naphthyl-*p*-phenylenediamine	0.988
26	*N,N'*-Diphenylbenzidine	0.919
27	2,2,4-Trimethyl-1,2-dihydroquinoline	0.912
28	6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	0.913

[a] Treated with oxygen.

The absorption of oxygen and ozone in solution of Tetralin or rubber was also carried out. A 200-ml. long-necked flask was charged with oxygen. A 30-ml. portion of monochlorobenzene containing azobisisobutyronitrile (5×10^{-3} mole) was poured into the flask at 62.5 ± 0.02°C.

One-fifth mole of Tetralin and 20 ml. of the solution containing 2 × 10^{-4} mole of amine were added to the above solution. Under vigorous stirring, the oxygen absorption was measured by using a gas buret connected to the flask.

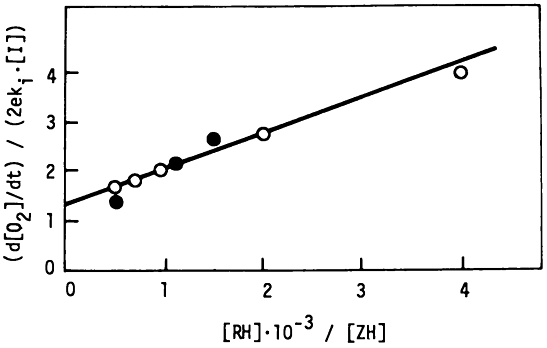


Figure 2. Linear relationship between oxidation rate and Tetralin [RH]/phenyl-β-naphthylamine [ZH] ratio

○: *[RH], 2 × 10^{-1} mole; [ZH], variable*
●: *[ZH], 2 × 10^{-4} mole; [RH], variable*

A constant rate of absorption was observed (Figure 2). The efficiency of amine for terminating chain reactive oxidation is calculated according to the following reaction proposed by Hammond *et al.* (9), in which the rate constant of initiation k_i was taken to be 8.16 × 10^{-4} mole/min. from the rate of evolution of nitrogen in a simple decomposition of azobisisobutyronitrile in chlorobenzene at 62.5°C., and the efficiency e of initiator was taken to be 0.58 (*10*).

$$d[O_2]/dt = 2ek_i[I]\{1 + (k_p/k_t)(RH/ZH)\}$$

where [I], [RH], and [ZH] denote the concentrations of initiator, Tetralin and amine. The results are summarized in Table V. Amines having larger k_t/k_p have a higher reactivity toward peroxy radical and seem to be more effective as radical acceptors in the oxidative degradation of rubber.

The protecting action of amine against ozonization of rubber molecule in solution was also evaluated by its viscosity measurement in a way similar to that used for oxidation. Purified SBR was dissolved in *o*-dichlorobenzene to give 2% rubber solution. A 50-ml. solution was mixed with 50 ml. of *o*-dichlorobenzene containing 1 × 10^{-3} mole amine. Oxygen, containing 1.05% ozone, was introduced into the solution for 4 minutes at a rate of 250 ml./min. at 30°C. Relative viscosities of the rubber solution treated and untreated with ozone were measured at 30°C. by the Ostwald viscometer. The results are given in Table VI.

Table V. Effect of Amine Derivatives on Oxygen Absorption of Tetralin Initiated with AIBN

28	*Amine Derivative*	$d(O_2)/dt \times (10^7)$ *(mole/min.)*	$\log \frac{k_t}{10 \times k_p}$
No.	*N*-Phenyl-*N'*-cyclohexyl-*p*-phenylenediamine	52.6	0.79
1	*N*-Phenyl-*N'*-isopropyl-*p*-phenylenediamine	55.2	1.55
2	*N,N'*-Diphenyl-*p*-phenylenediamine	50.4	0.76
4	*N,N'*-Di-β-naphthyl-*p*-phenylenediamine	49.3	0.91
5	Benzidine	236.2	0.85
7	*N,N'*-Diphenylbenzidine	80.2	1.68
8	6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	51.6	1.95
11	Aniline	812.9	2.95
14	*p*-Methoxyaniline	181.6	2.78
16	*p*-Phenylaniline	879.6	3.19
17	*N*-Methylaniline	629.5	3.37
23	Dicyclohexylamine	712.9	1.40
24	Diphenylamine	146.2	2.16
26	*N*-Phenyl-β-naphthylamine	100.8	3.04

Table VI. Effect of Amine on the Ratio of Viscosity of Treated[a] (η) and Untreated (η_0) SBR Solution

No.	*Amine Derivative*	η/η_0
1	Aniline	0.733
2	*p*-Methoxyaniline	0.810
4	*p*-Phenylaniline	0.734
6	*N,N*-Dimethylaniline	0.746
8	Diphenylamine	0.768
9	Di-*p*-Tolylamine	0.830
13	*N*-Phenyl-*p*-phenylenediamine	0.886
14	*N*-Phenyl-*N'*-cyclohexyl-*p*-phenylenediamine	0.920
17	*N,N'*-Diphenyl-*p*-phenylenediamine	0.914
28	6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	0.916

[a] Treated with ozonized Oxygen.

The rate of reaction of ozone with amine was determined during the ozonization of rubber solution, where the reaction between ozone and rubber also proceeded concurrently. The extent of the reaction of rubber with ozone was calculated from the change in unsaturation of the rubber determined by the Wijs reagent. For example, SBR (Japan Synthetic Rubber, JSR 1502), purified by precipitation with acetone from benzene solution, was dissolved in carbon tetrachloride to give a 5% rubber solution. The rubber solution (20 ml.) was added with 80 ml. of carbon tetrachloride containing 1×10^{-3} mole of amine derivatives. Oxygen, containing 0.89% ozone, was introduced into the solution at 30°C. for 3 minutes at the rate of 550–560 ml./min. Under these conditions, all ozone present in the oxygen stream was absorbed completely by the solution. After the reaction, about 1000 ml. of acetone containing a small amount of hydrochloric acid were added to the solution. The precipitated rubber was dissolved again in 100 ml. of carbon tetrachloride. Ten ml. of the Wijs reagent (0.0138*N*) were added to 10 ml. of the rubber solution to determine the degree of the unsaturation of rubber. The ratio of ozone consumed by amine to the total ozone consumed was estimated from the degree of the unsaturation of rubber. The results are listed in Table VII.

Table VII. Ratio (*R*) of Ozone Consumed by Amine to Total Ozone Consumed by SBR–Amine System

No.	*Amine Derivative*	*R*
1	Aniline	0.135
3	*p*-Hydroxyaniline	0.216
4	*p*-Phenylaniline	0.865
8	Diphenylamine	0.815
9	Di-*p*-tolylamine	0.845
12	*p*-Phenylenediamine	0.800
13	*N*-Phenyl-*p*-phenylenediamine	0.848
14	*N*-Phenyl-*N'*-cyclohexyl-*p*-phenylenediamine	1.000
17	*N,N'*-Diphenyl-*p*-phenylenediamine	0.973
20	*N,N'*-Di-*o*-tolyl-*p*-phenylenediamine	1.000
27	2,2,4-Trimethyl-1,2-dihydroquinoline	0.846

Discussion

Oxidation potentials are recognized to be correlated with the highest occupied levels of electrons, which may be evaluated according to the Hückel molecular orbital calculation. In this paper the calculations were carried out with the following values (*18*) as the Coulomb parameters.

—NH—	$\alpha + 2\beta$
$—NHCH_3$	$\alpha + 1.8\beta$
$—NHC_6H_{11}$	$\alpha + 1.5\beta$

As is shown in Figure 3 the highest occupied energy level is found to parallel well the oxidation potential in aniline and *p*-phenylenediamine derivatives. To elucidate the existence of the optimum oxidation potentials for antioxidation and antiozonization, the reactivity indices S^r and S^n for radical and nucleophilic reactions have been used. These are:

$$S^n = 2 \sum_i^{\mathrm{occ}} (C^2{}_i/\lambda_i) \tag{11}$$

$$S^r = \sum_i^{\mathrm{occ}} (C^2{}_i/\lambda_i) + \sum_i^{\mathrm{unocc}} (C^2{}_i/\lambda_i) \tag{12}$$

where, $\sum_i^{\mathrm{occ}}$, $\sum_i^{\mathrm{unocc}}$, C_i^2, and λ_i are the summations of occupied and unoccupied orbitals, electron density on the nitrogen atom, and the level of the molecular orbital, respectively.

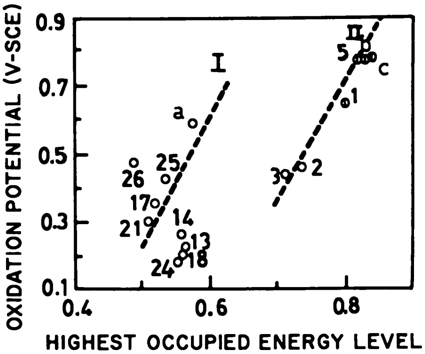


Figure 3. Relation between the oxidation potential and the highest occupied energy level of amine

(I): p-*Phenylene and benzidine derivatives*
(II): Aniline derivatives
○: *Oxidation half-wave potential*
⦶: *Decomposition potential*
a: N-p-*nitrophenyl*-p-*phenylenediamine*
b: p-*Chloroaniline*
c: p-*Aminobenzoic acid*

The relationships of oxidation potential to radical reactivity index S^r and nucleophilic reactivity index S^n illustrated in Figure 4 are very similar to those with antioxidation and antiozonization, where the maximum values were observed at 0.4 and 0.25 volt. Therefore, antioxidation seems to proceed by a radical mechanism in contrast to the nucleophilic type of antiozonization. Indeed, the antioxidation effect of amines toward NR, SBR, BR, and IIR is well correlated with radical reactivity as shown in Figures 5–8. The protection of SBR solution by amines from oxidative degradation and the termination of chain reaction in the oxygen–Tetralin system are also shown as functions of S^r in Figures 9 and 10.

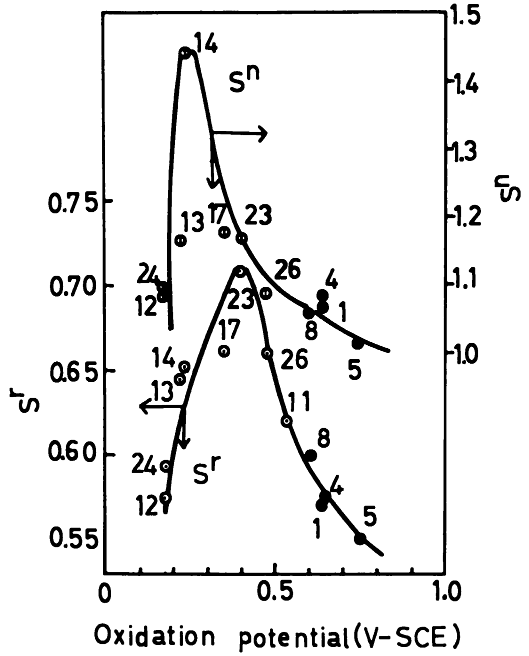


Figure 4. Relation of oxidation potential of amine with its radical reactivity index S^r and nucleophilic reactivity index S^n

○, ⦶: *Oxidation half-wave potential*
●: *Decomposition potential*

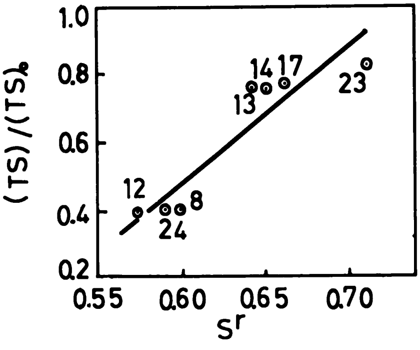


Figure 5. Relative tensile strength of NR-black vulcanizate, $(TS)/(TS)_0$ vs. the radical reactivity index of the amine compounded, S^r. Aging condition: 100°C. for 36 hours

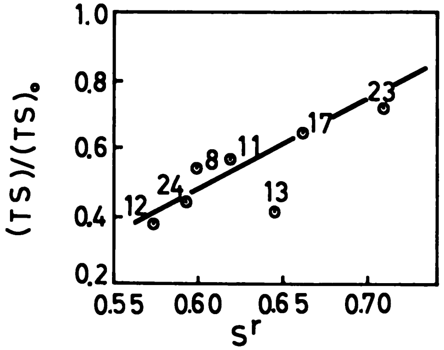


Figure 6. Relative tensile strength of SBR-black vulcanizate, (TS)/(TS)$_0$ vs. *the radical reactivity index of the amine compounded,* S^r. *Aging condition: 100°C. for 48 hours*

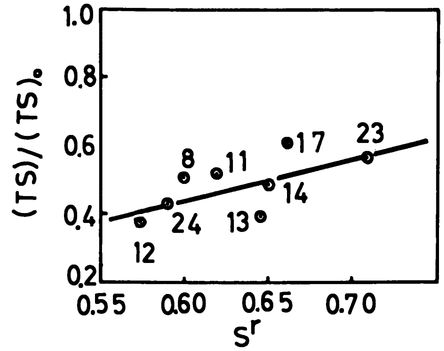


Figure 7. Relative tensile strength of BR-black vulcanizate, (TS)/(TS)$_0$ vs. *the radical reactivity index of the amine compounded,* S^r. *Aging condition: 100°C. for 48 hours*

On the other hand, antiozonization for the NR vulcanizate in Figure 11 and SBR solution in Figure 12 seems to be correlated better with the nucleophilic index S^n than with the radical index S^r. The direct reactivity of amines toward ozone is also associated with S^n as shown in Figure 13.

Conclusion

The antioxidizing effect of amine on oxidative degradation of vulcanized rubber is evaluated from the following measurements:

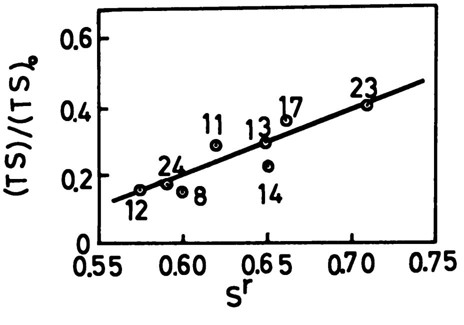


Figure 8. Relative tensile strength of IIR gum vulcanizate, $(TS)/(TS)_0$ vs. *the radical reactivity index of the amine compounded,* S^r. *Aging condition: 100°C. for 48 hours*

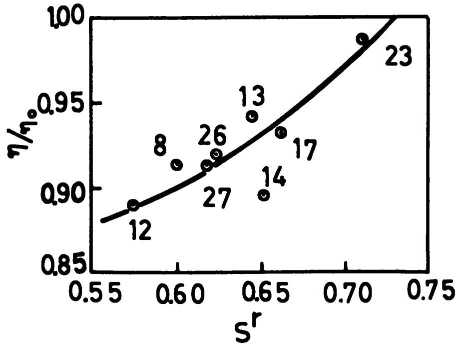


Figure 9. Correlation between the viscosity lowering of SBR by oxygen, η/η_0 *and the radical reactivity index of the amine employed,* S^r *(see Table IV)*

(a) Relative protecting ability of amine against the viscosity lowering of rubber solution by oxygen.

(b) The rate of reaction of amine with oxygen radical initiated by the azobisisobutyronitrile.

(c) The protecting effect of amine on the oxygen–Tetralin reaction.

To evaluate amine as a chemical antiozonant, the following measurements are available:

(a) Relative protecting ability of amine on viscosity lowering of rubber solution by ozone.

(b) The amount of ozone consumed by amine in rubber solution.

It is now possible to see some of the connections between these stabilizing abilities of amine and its oxidation potential measured by

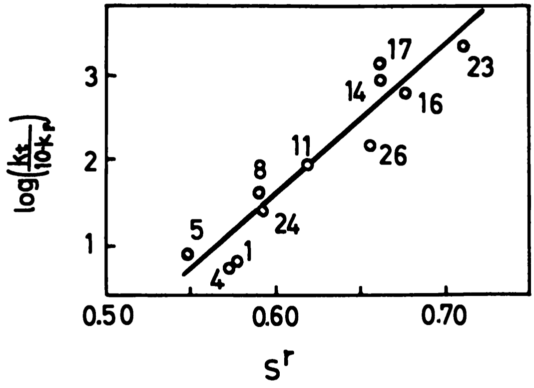


Figure 10. Value of k_t/k_p *in oxygen absorption of Tetralin* vs. *the radical reactivity index of the amine employed (see Table V)*

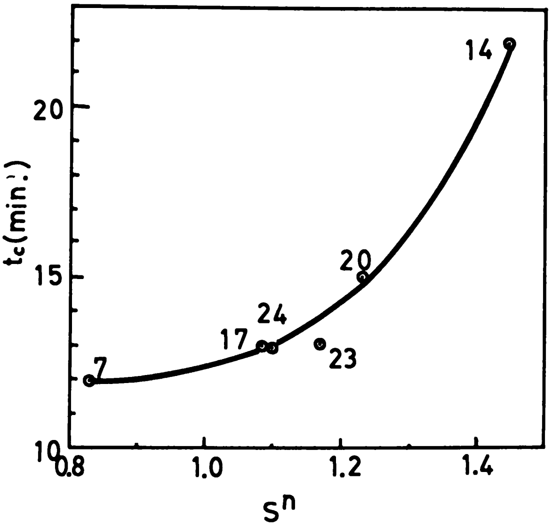


Figure 11. Correlation between the time, t_c*, for the crack formation of NR gum vulcanizate and the nucleophilic reactivity index of the amine compounded,* S^n *(see Figure 1)*

polarography. Good stabilizers seem to have definite oxidation potentials —*i.e.*, about 0.4 volt for antioxidant and about 0.25 volt for antiozonant.

The reactivity indices of amine derivatives based on the frontier electron theory show that there are maximum activities at 0.25 and 0.4

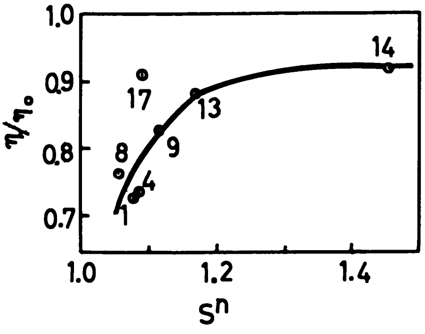


Figure 12. Correlation between the viscosity lowering of SBR by ozone, η/η_0 and the nucleophilic reactivity index of the amine employed, S^n *(see Table VI)*

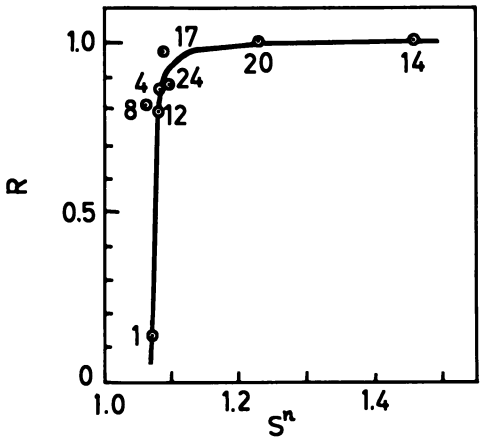


Figure 13. Correlation between the nucleophilic reactivity index of amine, S^n *and the ratio of ozone consumed by the amine to the total ozone consumed by SBR and the amine, R (see Table VII)*

volt for nucleophilic and radical reactions. The radical and nucleophilic reactivities are concluded to be good measures of the actions of the amines as antioxidants and aniozonants.

Literature Cited

(1) Bailey, P. S., *Chem. Rev.* 58, 925 (1958).
(2) Bevilacqua, E. M., "Autoxidation and Antioxidants," W. O. Lundberg, Ed., Vol. 2, Interscience, New York, 1962.

(3) Bolland, J. L., Have, P. T., *Discussions Faraday Soc.* **2,** 252 (1947).
(4) Braden, M., Gent, A. N., *J. Appl. Polymer Sci.* **6,** 449 (1962).
(5) Criegee, R., *Ber.* **88,** 1878 (1955).
(6) Fueno, T., Ree, T., Eyring, H., *J. Phys. Chem.* **63,** 1940 (1959).
(7) Fukui, K., Yonezawa, T., Nagata, C., Shingu, H., *J. Chem. Phys.* **22,** 1433 (1954).
(8) Fukui, K., Yonezawa, T., Shingu, H., *J. Chem. Phys.* **20,** 722 (1952).
(9) Hammond, G. S., Boozer, C. E., Hamilton, C. E., Sen, J. N., *J. Am. Chem. Soc.* **77,** 3238 (1955).
(10) Hammond, G. S., Sen, J. N., Boozer, C. E., *J. Am. Chem. Soc.* **77,** 3244 (1955).
(11) Hoffman, A. E., *Rubber Age* **83,** 509 (1958).
(12) Horner, L., Schaefer, H., Ludwig, W., *Ber.* **91,** 75 (1958).
(13) Kotani, T., Yamashita, S., Furukawa, J., *J. Soc. Rubber Ind., Japan* **35,** 441 (1963).
(14) Kotani, T., Yamashita, S., Furukawa, J., to be published.
(15) Lloyd, W. G., Zimmerman, R. G., Dietzler, A. J., *Ind. Eng. Chem., Prod. Res. Develop.* **5,** 326 (1966).
(16) Lowry, C. D., Egloff, G., Morrell, J. C., Dryer, C. G., *Ind. Eng. Chem.* **25,** 806 (1933).
(17) Nakamura, T., Furukawa, J., Yamashita, S., to be published.
(18) Orgel, L. E., Cottrell, T. L., Dick, W., Sutton, L. E., *Trans. Faraday Soc.* **47,** 113 (1951).
(19) Penketh, G. E., *J. Appl. Chem.* **7,** 512 (1957).
(20) Scott, G., "Atmospheric Oxidation and Antioxidants," Elsevier, New York, 1965.
(21) Shaw, R. F., Ossefort, Z. T., *Rubber World* **130,** 636 (1954).
(22) Slomp, G., Johnson, J. L., *J. Am. Chem. Soc.* **80,** 915 (1958).

RECEIVED April 19, 1967.

10

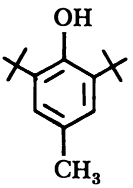
Dialkylhydroxybenzyl-*N*,*N*-Dimethyl Dithiocarbamates as Intermediates in the Preparation of Phenolic Polymer Stabilizers

FRANCIS X. O'SHEA

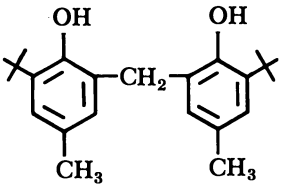
UniRoyal Chemical, Naugatuck, Conn. 06771

*3,5-Dialkyl-4-hydroxybenzyl-*N,N*-dimethyl dithiocarbamates, readily prepared by reaction of 2,6-dialkylphenols with formaldehyde, dimethylamine, and carbon disulfide, serve as useful intermediates in preparing substituted, sterically hindered phenols which are effective polymer stabilizers. These intermediates react with nucleophiles—alcohols, mercaptans, and amines—in the presence of sodium hydroxide to replace the dithiocarbamate group. The reaction apparently proceeds by generation of a transient 2,6-dialkylquinonemethide intermediate and its subsequent reaction with the nucleophile. 2-Hydroxy-3,5-dialkylbenzyl-*N,N*-dimethyl dithiocarbamates and 2-hydroxy-3,5-dialkylbenzyl 2-benzothiazolyl sulfides, prepared from 2,4-dialkylphenols, undergo similar nucleophilic reactions to give isomeric compounds through 4,6-dialkylquinone methide intermediates. The products derived from reaction of these latter intermediates with dimercaptans are particularly effective polymer stabilizers.*

Sterically hindered phenols are used widely today as effective nondiscoloring, nonstaining antioxidants for hydrocarbon systems, particularly rubbers and plastics. These compounds may be grouped in two broad classifications—monocyclic phenols represented by a compound such as 2,6-di-*tert*-butyl-4-methylphenol (I) and polycyclic phenols such as 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) (II). (Throughout this chapter, X represents *tert*-butyl).



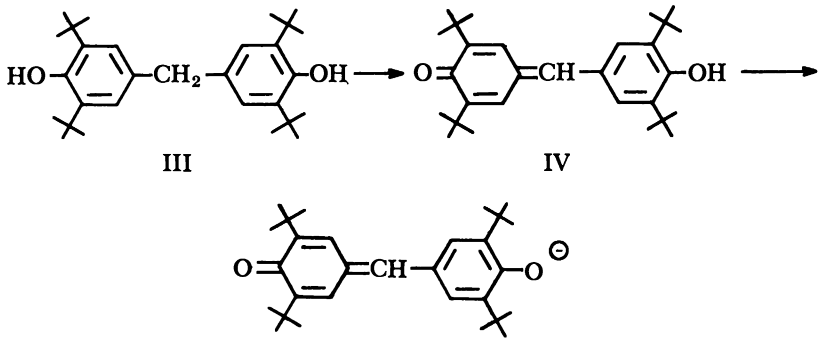
I



II

Monocyclic phenols generally afford excellent nondiscoloring properties and good activity against aging at ambient temperature. These compounds are volatile, however, and generally provide poor protection at elevated temperatures.

The polycyclic phenols, being somewhat more effective and relatively nonvolatile, afford good protection at both ambient and elevated temperatures. This improvement in activity, however, is generally accompanied by a sacrifice in color. For methylenebisphenols the discoloration may be caused by oxidation products of the antioxidant in which a highly conjugated system is developed. For example, Kharasch and Joshi (7) found that a purple color developed when oxygen was bubbled through an alkaline alcoholic solution of 4,4′-methylenebis(2,6-di-*tert*-butylphenol), III, a commercial antioxidant. They showed that this color was caused by the anion, V, of a quinonemethide type oxidation product, IV, of the phenol.

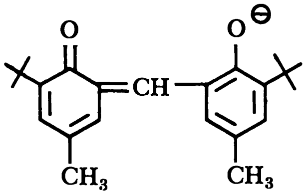


III IV

V

They synthesized IV independently and found it to be bright yellow. We have found that rubber samples containing 4,4′-methylenebis(2,6-di-*tert*-butylphenol) tend to turn yellow on aging and that, in some cases, films laid from high pH latexes have turned purple on heat aging.

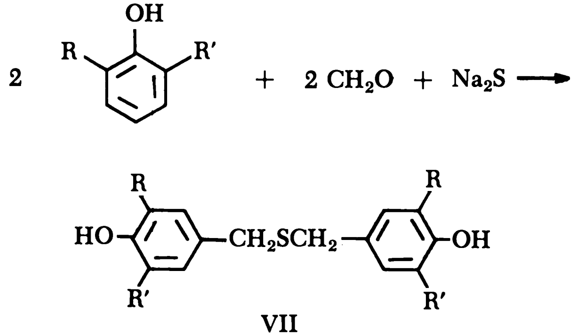
It is also known that 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) II, tends to give a pink discoloration in certain latex film systems. Once again, the possibility of oxidation of this material and subsequent ionization to produce the ion VI may account for this discoloration.



VI

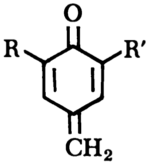
Several years ago we set out to synthesize new nondiscoloring phenolic antioxidants with the objective of combining the excellent color of monocyclic phenols with the activity of polycyclic phenols. We hoped to accomplish this by preparing polycyclic phenols in which the linkages between rings were designed so as to prevent the development of conjugation between the rings. Initially, we had two secondary objectives: (1) to investigate the use of recently available 2,6-dialkylphenols as starting materials, and (2) to investigate the effect of sulfur atoms on antioxidant activity by incorporating sulfur in the linkages.

The first series of compounds to be developed in our program were bis(3,5-dialkyl-4-hydroxybenzyl)sulfides, VII. Compounds of this type were prepared by a unique reaction of 2,6-dialkylphenols with formaldehyde and sodium sulfide which we have reported (*13*, *18*).



VII

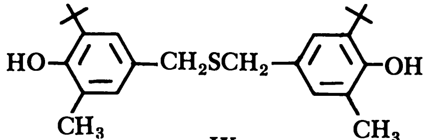
At that time we postulated a mechanism involving methylolation of the phenol followed by dehydration to produce a transient quinonemethide intermediate, VIII. Nucleophilic attack on such an intermediate by



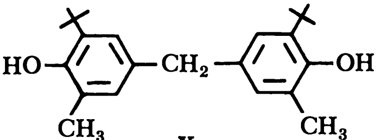
VIII

sulfide ion would, in two steps, generate the product. The existence of quinonemethide intermediates is well substantiated in the literature (*3, 5, 9*). The reaction of nucleophiles with compounds capable of generating quinonemethide intermediates has also been described by Gardner (*4, 10*) and others (*1, 2, 6, 9, 23, 24*).

When this reaction was carried out on 2,6-di-*tert*-butylphenol, bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfide was produced in 90% yield. However, 2-methyl-6-*tert*-butylphenol gave only a 64% yield of the expected sulfide compound, IX, along with a 26% yield of 4,4′-methylenebis(2-methyl-6-*tert*-butyl phenol), X.



IX

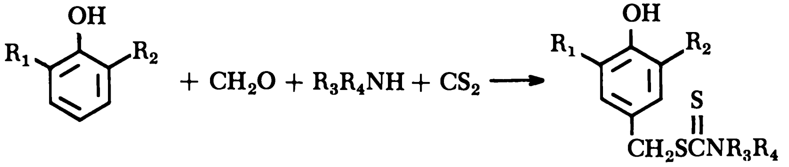


X

The by-product in this reaction apparently arises from reaction of the quinonemethide intermediate with the as yet unreacted parent phenol. Since initial evaluations showed bis(3-methyl-4-hydroxy-5-*tert*-butylbenzyl)sulfide, IX, to be a promising antioxidant, we sought an improved method for its synthesis.

An obvious way to avoid methylenebisphenol formation would be to generate the quinonemethide in the absence of any unreacted parent phenol. Therefore, a suitable intermediate was sought. The preparation of chloromethyl and hydroxymethyl intermediates was ruled out as being difficult to achieve in good yields by the methods then known. The use of Mannich base methiodides (*4*) was considered uneconomical. Our answer came in the form of an intermediate which had been prepared for another purpose.

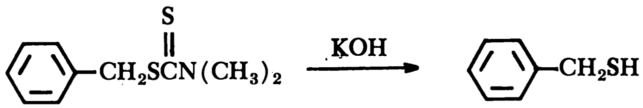
Turner (*25*) has shown that 2,6-di-*tert*-butylphenol and 2-methyl-6-*tert*-butylphenol will react with formaldehyde and a dialkylamine in excess carbon disulfide to produce 3,5-dialkyl-4-hydroxybenzyl-*N,N*-dialkyldithiocarbamates, XI.



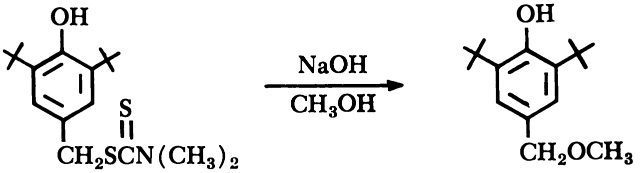
XI

We have also applied this reaction to 2,6-dialkylphenols including less hindered phenols such as 2,6-dimethylphenol. For all compounds studied the reaction takes place under very mild conditions—*e.g.*, in refluxing methanol. The yields of such compounds are generally in excess of 90%.

Kulka (*8*) has reported that benzyl-*N*,*N*-dimethyldithiocarbamate can be hydrolyzed with alkali to benzyl mercaptan.

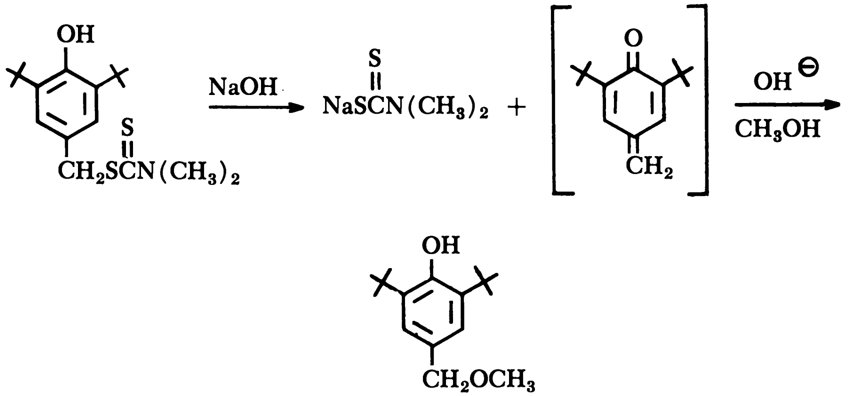


When we attempted to hydrolyze 3,5-di-*tert*-butyl-4-hydroxybenzyl-*N*,*N*-dimethyldithiocarbamate with sodium hydroxide in methanol, the reaction produced 3,5-di-*tert*-butyl-4-hydroxybenzyl methyl ether, XII, instead of the corresponding benzyl mercaptan.

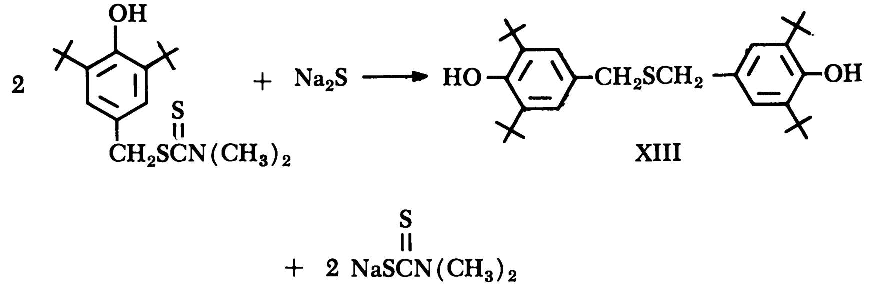


XII

It is reasonable to postulate the formation of the product through the quinonemethide intermediate.



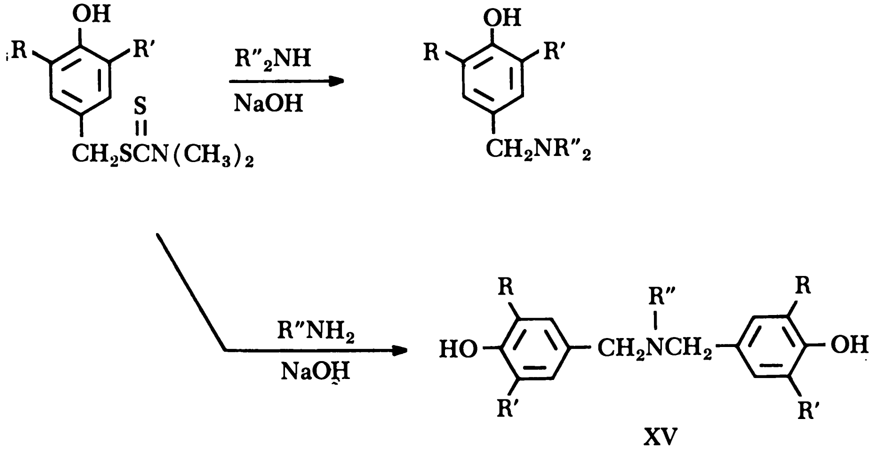
Since these dithiocarbamates appeared to be suitable compounds for generating quinonemethide intermediates, we investigated their reaction with sodium sulfide. It was found that 3,5-di-*tert*-butyl-4-hydroxybenzyl-*N*,*N*-dimethyldithiocarbamate reacts with sodium sulfide to produce bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfide, XIII, in essentially quantitative yield (*20*).



XIII

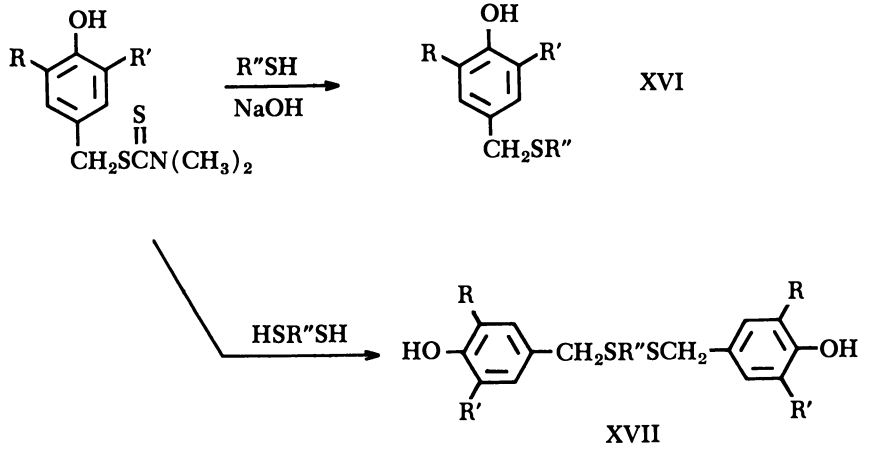
This reaction sequence was applied to 2-methyl-6-*tert*-butylphenol, and it was found that bis(3-methyl-4-hydroxy-5-*tert*-butylbenzyl)sulfide can be produced in an over-all yield greater than 90% in pilot-plant scale reactions. Since the reaction mother liquor, after removal of the product, contains sodium dimethyldithiocarbamate, it can be recycled and neutralized, thus regenerating carbon disulfide and dimethylamine for reuse in preparing the intermediate. In essence, therefore, the over-all reaction consumes only 2,6-dialkylphenol, formaldehyde, and sodium sulfide. The scope of this reaction sequence was demonstrated by preparing bis(3,5-dialkyl-4-hydroxybenzyl)sulfides from a number of phenols ranging from 2,6-dimethylphenol to 2,6-di-*tert*-butylphenol (*20*).

The ease with which the dithiocarbamate intermediates can be prepared prompted further study of their utilization in preparing potential antioxidants by reaction with other nucleophiles. In addition to their reaction with alcohols to produce 3,5-dialkyl-4-hydroxybenzyl alkyl ethers (*22*) we found that the intermediates react with secondary amines to give 3,5-dialkyl-4-hydroxybenzylamines, XIV, and with primary amines to give bis(3,5-dialkyl-4-hydroxybenzyl)amines, XV, (*19*).



XV

Although the compounds in which R″ is alkyl can be prepared more readily by the simple Mannich reaction, this sequence is useful for nitrogen compounds such as aromatic amines, hydrazines, and hydroxylamine which do not ordinarily enter into the Mannich reaction. These intermediates react cleanly with mercaptans (*21*) and with dimercaptans (*17*) to produce compounds of the type XVI and XVII.



XVI

XVII

The latter compounds, para-linked bisphenols derived from dimercaptans, have proved to be of particular interest since they exhibit excellent antioxidant activity along with very good nondiscoloring properties. For example, Table I shows the results of a screening test in *cis*-polyisoprene in which films of the rubber containing 1% of the antioxidants were deposited from solution on salt plates and aged at 130°C. in a circulating air oven. Stability of the films is determined by the time to development of a carbonyl band in the infrared spectra. The results show a significant advantage in activity for 1,2-bis(3,5-di-*tert*-butyl-4-hydroxybenzylthio)-ethane over 4,4′-methylenebis(2,6-di-*tert*-butylphenol) and 2,6-di-*tert*-butyl-4-methylphenol.

Of the three antioxidants 2,6-di-*tert*-butyl-4-methylphenol was the least effective discoloring agent after one-hour oven aging at 130°C. and

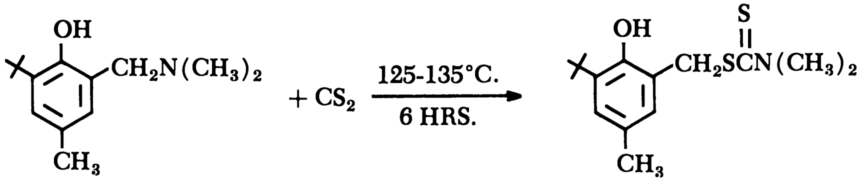
Table I. Aging of *cis*-Polyisoprene

Antioxidant	*Time to Carbonyl Development, hours*
2,6-Di-*tert*-butyl-4-methylphenol	0.5
4,4′-Methylenebis(2,6-di-*tert*-butylphenol	4
1,2-Bis(3,5-di-*tert*-butyl-4-hydroxybenzylthio)ethane	9

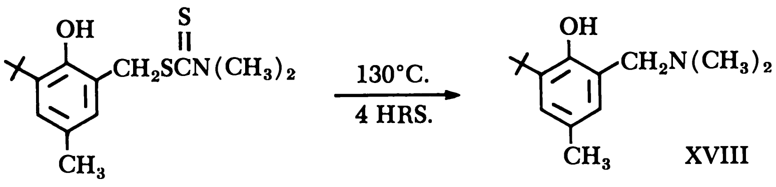
8-hour sunlamp aging of bulk samples of the rubber. 4,4′-Methylenebis-(2,6-di-*tert*-butylphenol) was the most effective discoloring agent, imparting a yellow color in both tests. 1,2-Bis(3,5-di-*tert*-butyl-4-hydroxybenzylthio)ethane was intermediate in discoloration properties, being significantly better than the methylenebis compound.

Since compounds of the type XVII have shown comparable activity in a number of systems including *cis*-polybutadiene, styrene–butadiene rubber, and ethylene–propylene rubber, they have some commercial promise, and development work on these compounds is continuing. Nevertheless, they are not completely nondiscoloring, and in certain applications, particularly carboxylated styrene–butadiene latex films, yellow discoloration caused by the antioxidant is a serious drawback. We therefore turned our attention to ortho-linked compounds derived from 2,4-dialkylphenols.

Unfortunately, Mannich bases derived from 2,4-dialkylphenols do not react readily with carbon disulfide. Under forcing conditions—*e.g.*, in a high boiling solvent with slow addition of carbon disulfide or under pressure in an autoclave—dithiocarbamates are formed but in poorer conversions than from 2,6-dialkylphenols.



The poor conversion may be accounted for, at least in part, by the apparent reversibility of this reaction. This was demonstrated by heating 2-hydroxy-3-*tert*-butyl-5-methylbenzyl-*N*,*N*-dimethyl dithiocarbamate in diethylene glycol dimethyl ether whereupon the Mannich base XVIII was formed.

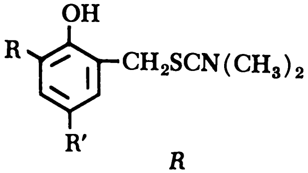


XVIII

Despite this difficulty, dithiocarbamate intermediates were prepared from a variety of 2,4-dialkylphenols. These compounds are described in Table II.

It was demonstrated (*20*) that these intermediates react with sodium sulfide in a manner analogous to the dithiocarbamates derived from 2,6-

Table II. Dithiocarbamate Intermediates

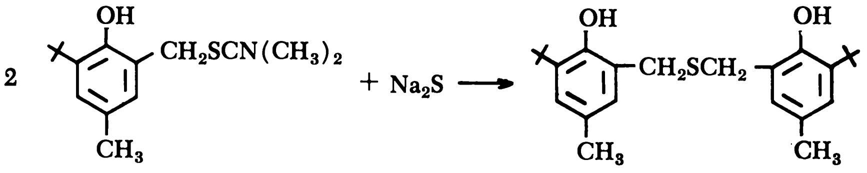


R	*R′*	*m.p., °C.*	*% Yield*[a]
$—CH_3$	$—CH_3$	127–128	22
$—C(CH_3)_3$	$—CH_3$	97–98	55
$—C(CH_3)_3$	$—C(CH_3)_3$	208–209	50
$—C_8H_{17}$[b]	$—CH_3$	111–112	48
$—C(CH_3)_2\phi$[c]	$—CH_3$	114–116	47
$—CH_3$	$—C(CH_3)_3$	109–111	82
$—CH_3$	$—C(CH_3)_2\phi$[c]	131–133	34

[a] Based on intermediate Mannich base.

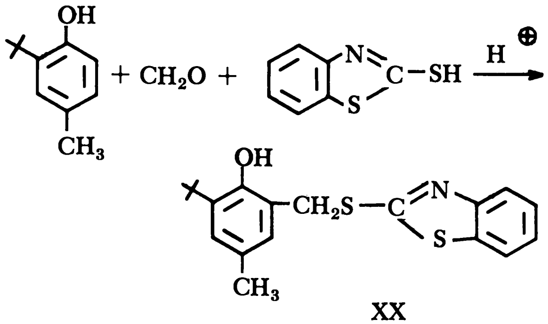
[b] 2,2,4,4-Tetramethylbutyl.

dialkylphenols. For example, 2-hydroxy-3-*tert*-butyl-5-methylbenzyl-*N*,*N*-dimethyldithiocarbamate was converted to bis(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)sulfide, XIX, in 93% yield.



XIX

Another useful class of intermediates in this series was found to be the 2-hydroxy-3,5-dialkylbenzyl 2-benzothiazolyl sulfides, some of which are described in Table III. John Bill of our laboratories had previously found that 2-*tert*-butyl-*p*-cresol will react with formaldehyde and mercaptobenzothiazole under acid conditions to produce 2-hydroxy-3-*tert*-butyl-5-methylbenzyl 2-benzothiazolyl sulfide, XX, in 70% yield.



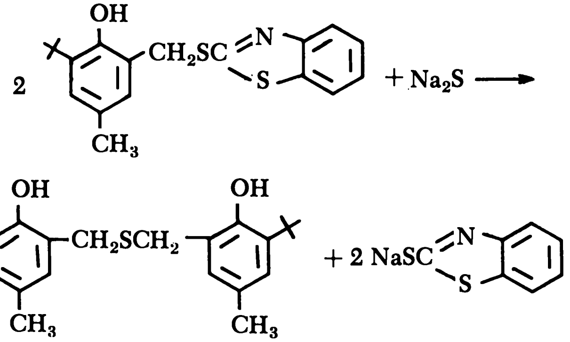
XX

Prepared from 2,4-Dialkylphenols

Calculated				*Found*			
C	*H*	*N*	*S*	*C*	*H*	*N*	*S*
56.43	6.71	5.49	25.11	56.65	6.84	5.72	24.94
60.56	7.79	4.71	21.56	60.70	7.70	4.60	21.68
63.67	8.61	4.13	18.89	63.87	8.51	3.95	19.22
64.54	8.84	3.96	18.14	64.62	8.75	3.88	18.15
66.81	7.01	3.90	17.84	66.82	7.01	3.80	18.04
60.56	7.79	4.71	21.56	60.70	7.71	4.82	21.53
66.81	7.01	3.90	17.84	66.69	7.29	3.70	17.77

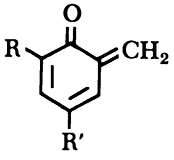
[c] α,α-Dimethylbenzyl.

Since this compound contains a sequence of atoms quite similar to the dithiocarbamate, we postulated that it could react in the same way. This was demonstrated (*14*) by the reaction of XX with sodium sulfide to produce bis(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)sulfide in 94% yield.



After isolating the product, the mercaptobenzothiazole can be recovered in such reactions by acidification of the mother liquor.

Both of these types of intermediates react with nucleophiles in reactions which presumably proceed through an *o*-quinonemethide intermediate of the type XXI.



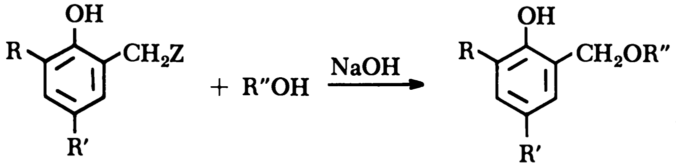
XXI

Table III. 2-Hydroxy-3,5-dialkylbenzyl

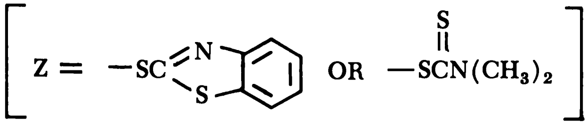
R	*R′*	*m.p.*, °*C.*	% *Yield*
$—C(CH_3)_3$	$—CH_3$	164–165	72
$—C(CH_3)_3$	$—C(CH_3)_3$	153–154	28
$—C_8H_{17}$[a]	$—CH_3$	102–103	83
$—C(CH_3)_2\phi$[b]	$—CH_3$	141–143	33

[a] 2,2,4,4-Tetramethylbutyl.

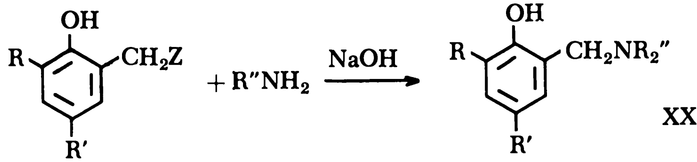
For example, they react with alcohols (*15, 22*) to produce 2-hydroxy-3,5-dialkylbenzyl alkyl ethers, XXII.



XXII

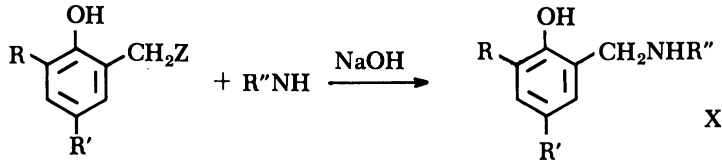


They react with secondary amines (*11, 19*) to produce hydroxybenzylamines of the type XXIII.



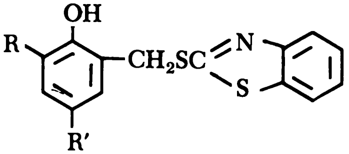
XXIII

Reaction with primary amines proceeds differently from the 2,6-dialkylphenol case, generally stopping at the 1:1 adduct, XXIV.



XXIV

2-Benzothiazolyl Sulfides

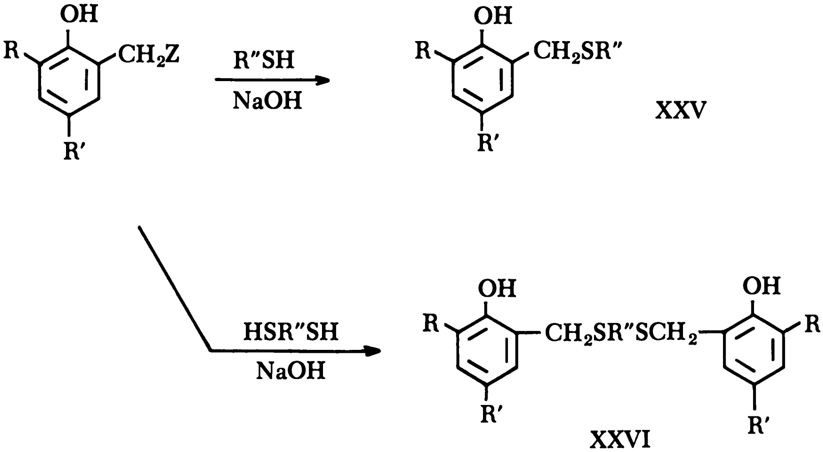


Calculated				*Found*			
C	*H*	*N*	*S*	*C*	*H*	*N*	*S*
66.43	6.16	4.08	18.67	66.65	6.14	4.06	18.56
68.53	7.06	3.63	16.63	68.54	6.93	3.83	16.68
69.13	7.31	3.51	16.05	69.10	7.28	3.79	16.24
71.07	5.72	3.45	15.81	71.36	5.66	3.44	15.85

[b] α,α-Dimethylbenzyl.

This is probably because intramolecular hydrogen bonding with the phenolic hydroxyl in the 1:1 adduct reduces the nucleophilic character of the amine nitrogen sufficiently to render it unreactive in a second step.

Reaction with mercaptans and dimercaptans (*12, 16, 21*) proceeds normally to produce the 2-hydroxybenzyl thioether compounds XXV and XXVI.



XXV

XXVI

Of all the compounds prepared in this work, these latter compounds, the ortho-linked compounds derived from dimercaptans, come the closest to realizing our objective of structures with the activity of a bisphenol and the nondiscoloring characteristics of a monocyclic phenol. For example, Table IV shows some results in *cis*-polybutadiene which demonstrate that a compound of the type XXVI is superior as a heat stabilizer to both 2,6-di-*tert*-butyl-4-methylphenol and 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol) in both activity and color. Screening results in *cis*-

Table IV. *cis*-Polybutadiene Aged for 150 Hours at 100°C.

Antioxidant	*% Gel*	*Mooney Viscosity*[a]	*Color Rating*
2,6-Di-*tert*-butyl-4-methylphenol (0.9 parts)	60	60	2
2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol (0.5 parts)	33	50	3
β,β′-Bis(2-hydroxy-3-*tert*-butyl-5-methylbenzylthio) diethyl ether (0.5 parts)	nil	37	1

[a] Unaged Mooney viscosity was 33.

polyisoprene using the carbonyl development test previously described are shown in Table V and again demonstrate the superiority in activity of these new compounds. After one-hour oven aging at 130°C. and 8-hour sunlamp aging of bulk samples of the rubber, β,β′-bis(2-hydroxy-3-*tert*-butyl-5-methylbenzylthio) diethyl ether was found to be equivalent to 2,6-di-*tert*-butyl-4-methylphenol in nondiscoloring characteristics and far superior to 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol) which turned the rubber yellow-brown.

These ortho-linked compounds have also shown considerable promise in emulsion and solution SBR and are particularly valuable in carboxylated SBR latex films combining good activity with excellent color—*i.e.*, no pinking. The results of resinification tests on films laid from carboxylated SBR latex shown in Table VI demonstrate that the polycyclic nature of these compounds contributes significantly to their stabilizing activity, monocyclic compounds of similar structure being markedly poorer in activity.

Although having excellent color in most systems, the antioxidant activity of these compounds in certain systems such as polypropylene and ethylene–propylene rubber has been only fair. Possibly intramolecular hydrogen bonding between the phenolic hydroxyl and the benzylic sulfur

Table V. Polyisoprene Heat Aged at 130°C.

Antioxidant, 1%	*Time for Carbonyl Development, hours*
2,6-Di-*tert*-butyl-4-methylphenol	0.5
2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol)	3
β,β′-Bis(2-hydroxy-3-*tert*-butyl-5-methylbenzylthio) diethyl ether	10

Table VI Carboxylated SBR Latex Films Aged at 270°F.

Antioxidant	*Time to Resinify, hours*
2-Hydroxy-3-*tert*-butyl-5-methylbenzyl β-hydroxyethyl sulfide	44
β,β'-Bis(2-hydroxy-3-*tert*-butyl-5-methylbenzylthio) diethyl ether	587

atom affects hydrogen abstraction processes in these systems. The generally poor level of activity found for othro-linked compounds containing benzylic oxygen or nitrogen atoms may be the result of the stronger hydrogen bonding expected. Therefore, although our original goal has been accomplished to a large extent in this work, we believe that the optimum result has yet to be achieved. Perhaps further work on bisphenol linkages will afford greater improvements in this area.

Literature Cited

(1) Atkinson, R. O., *J. Chem. Soc.* **1954,** 1329.
(2) Fields, D. L., Miller, J. B., Reynolds, D. D., *J. Org. Chem.* **30,** 3962 (1965).
(3) Filar, L. J., Winstein, S., *Tetrahedron Letters* **25,** 9 (1960).
(4) Gardner, P. D., Rafsanjani, H. S., Rand, L., *J. Am. Chem. Soc.* **81,** 3364 (1959).
(5) Gardner, P. D., Sarrafizadeh, H., Brandon, R. & R. L., *J. Am. Chem. Soc.* **81,** 5515 (1959).
(6) Hellman, H., Pohlmann, J. L. W., *Ann.* **642,** 40 (1961).
(7) Kharasch, M. S., Joshi, B. S., *J. Org. Chem.* **22,** 1435 (1957).
(8) Kulka, M., *Can. J. Chem.* **34,** 1093 (1956).
(9) McClure, J. D., *J. Org. Chem.* **27,** 2365 (1962).
(10) Merijan, A., Gardner, P. D., *J. Org. Chem.* **30,** 3965 (1965).
(11) O'Shea, F. X., U. S. Patent **3,219,701** (Nov. 23, 1965).
(12) *Ibid.,* **3,260,757** (July 12, 1966).
(13) *Ibid.,* **3,272,869** (Sept. 13, 1966).
(14) *Ibid.,* **3,281,473** (Oct. 25, 1966).
(15) *Ibid.,* **3,291,841** (Dec. 13, 1966).
(16) *Ibid.,* **3,299,147** (Jan. 17, 1967).
(17) *Ibid.,* **3,310,587** (March 21, 1967).
(18) O'Shea, F. X., Root, F. B., "Abstracts of Papers," 140th Meeting, ACS, Sept. 1961, 49Q.
(19) O'Shea, F. X., Root, F. B., U. S. Patent **3,219,700** (Nov. 23, 1965).
(20) *Ibid.,* **3,260,756** (July 12, 1966).
(21) *Ibid.,* **3,260,758** (July 12, 1966).
(22) *Ibid.,* **3,291,842** (Dec. 13, 1966).
(23) Poppelsdorf, F., Holt, S. J., *J. Chem. Soc.* **1954,** 4094.
(24) Smith, L. I., Horner, Jr., J. W., *J. Am. Chem. Soc.* **60,** 676 (1938).
(25) Turner, J. M., U. S. Patent **3,117,947** (Jan. 14, 1964).

RECEIVED November 30, 1966.

11

Hydroperoxide Decomposition by Some Sulfur Compounds

BRIAN A. MARSHALL

Research Laboratories, Imperial Chemical Industries, Plastics Division,
Welwyn Garden City, Hertfordshire, England

The kinetics of the decomposition of Tetralin and tert-*butyl hydroperoxides by dilauryl thiodipropionate were determined in the temperature range 30°-90°C. The reaction had an induction period which was eliminated by acetic acid but not by dilauryl sulfinyldipropionate. The rate equation*

$$d/[\text{Hydroperoxide}]/dt =$$

$$k_2/[\text{Hydroperoxide}]/[\text{Sulfur compound}]$$

was obtained in the initial stages of the reaction, but at least 20 moles of hydroperoxide were eventually decomposed per mole of sulfur compound. It is proposed that a complex is formed during the induction period, which decomposes according to the above rate equation. It is postulated that the catalytic nature of the over-all reaction is caused by an acid-induced decomposition of the hydroperoxide by a species formed from the sulfur compound.

The oxidation of polyolefins under the influence of heat or light is usually regarded as involving a free radical chain mechanism having the following main reactions (3):

$$\begin{array}{lcll}
\text{RH} & \rightarrow & \text{R}^{\cdot} & \text{Initiation} \quad (1) \\
\text{R}^{\cdot} + \text{O}_2 & \rightarrow & \text{ROO}^{\cdot} & \left.\right\} \text{Propagation} \quad (2) \\
\text{ROO}^{\cdot} + \text{RH} & \rightarrow & \text{ROOH} + \text{R}^{\cdot} & \quad (3) \\
\text{ROOH} & \rightarrow & \text{RO}^{\cdot} + {}^{\cdot}\text{OH} & \text{Chain branching} \quad (4) \\
2\text{ROO}^{\cdot} & \rightarrow & \text{Inert products} & \text{Termination} \quad (5)
\end{array}$$

The oxidation can be inhibited by using stabilizers which fall into two main categories: those which react with the peroxy radicals, ROO$^\cdot$, to form more stable free radicals which are less capable of continuing the oxidation chain,

$$\text{ROO}^\cdot + \text{IH} \rightarrow \text{ROOH} + \underset{\text{(stable)}}{\text{I}^\cdot} \qquad (6)$$

and those which decompose the hydroperoxides without the formation of free radicals. Phenolic and amine type stabilizers are examples of the first class, and sulfur compounds and phosphites are examples of hydroperoxide decomposers.

The object of this work was to gain some insight into the mechanism by which sulfur compounds function as stabilizers by studying the kinetics of the decomposition of hydroperoxides in the presence of dilauryl thiodipropionate—one of the most widely used sulfur compounds in the stabilization of polyolefins.

Tetralin hydroperoxide and *tert*-butyl hydroperoxide were selected for this work, both of which could be prepared readily in a pure state.

Experimental

Materials. HYDROPEROXIDES. Tetralin hydroperoxide was prepared by passing air through technical Tetralin at 60°C. for 16 hours (*6*). The hydroperoxide was purified by recrystallization from 40°–60°C. petroleum spirit to constant melting point, 53°–54°C.

tert-Butyl hydroperoxide (Laporte Chemicals, Ltd.) was purified by extraction with cold 15% potassium hydroxide solution. The residue was saturated with ammonium chloride, and the hydroperoxide was dried, initially with anhydrous sodium sulfate and then overnight with anhydrous calcium sulfate. It was distilled at 20 mm. pressure, in a nitrogen atmosphere, through an 18-inch silvered column packed with multiturn glass helices; b.p., 41°C. Both hydroperoxides assayed iodometrically as better than 98% pure.

DILAURYL THIODIPROPIONATE (DLTP). DLTP (American Cyanamid) m.p., 39°C. was used without further purification. A series of experiments in which recrystallized material was used gave identical results to experiments in which the commercial sample was used.

All other materials were of AnalaR quality; toluene and chlorobenzene were dried over anhydrous sodium sulfate before use.

Determination of the Hydroperoxide. Glacial acetic acid (30 ml.) containing 0.0005% ferric chloride hexahydrate and 5 ml. saturated potassium iodide solution was added to an aliquot of the hydroperoxide solution which had been flushed with nitrogen. The mixture was stored in the dark for 10 minutes, diluted with water (50 ml.), and the liberated iodine was titrated with sodium thiosulfate solution using starch as indicator.

Kinetic Procedure. In a typical experiment 0.82 gram Tetralin hydroperoxide (5×10^{-3} mole) and 0.3214 gram dilauryl thiodipropionate

(0.624×10^{-3} mole) were dissolved in 100 ml. chlorobenzene; 10 ml. aliquots were transferred to glass tubes fitted with ground glass stoppers, and the tube and contents were thermostatted. Tubes were withdrawn at various times, and the hydroperoxide content was determined. No difference in the results was observed if the tubes and contents were flushed with nitrogen before thermostatting. The decomposition of the hydroperoxide solution containing no sulfur compound was taken into account in calculating the hydroperoxide content of the reaction solutions. This correction was usually negligible.

Results

Tetralin Hydroperoxide. STOICHIOMETRY OF THE REACTION. Initial kinetic experiments at 30°, 40°, and 50°C. in toluene solution showed that at least 25 moles of Tetralin hydroperoxide could be decomposed by 1 mole of dilauryl thiodiproprionate. For experimental reasons the bulk of the kinetic data was obtained in the temperature region 70°–90°C. using chlorobenzene as solvent.

Solutions containing 2.5×10^{-2} mole/liter of Tetralin hydroperoxide and 1.0×10^{-3} mole/liter of various stabilizers were allow to react in chlorobenzene solution at 70°C. The percentage hydroperoxide remaining after 24 and 100 hours is shown in Table I.

It is clear from these results that the reaction between Tetralin hydroperoxide and many sulfur compounds is not a simple one, inasmuch as at least 20 moles of hydroperoxide were decomposed by 1 mole of the

Table I. Percentage of Hydroperoxide Decomposed in Chlorobenzene Solutions Containing Tetralin Hydroperoxide (2.5×10^{-2} mole/liter) and Various Stabilizers (0.1×10^{-2} mole/liter) at 70°C.

Stabilizer	*Hydroperoxide Decomposed, %* *After 24 Hours*	 *After 100 Hours*
None	12.2	10.0
Dilauryl thiodipropionate	96.5	—
Distearyl thiodipropionate	99.5	—
Dilauryl sulfinyldipropionate	98.7	—
Di-*tert*-dodecyl sulfide	98.2	—
Di-*tert*-dodecyl disulfide	98.7	—
n-Octadecyl mercaptan	97.2	—
Di-*n*-octadecyl sulfone	12.2	14.0
Tetramethyl thiuram disulfide	94.7	—
Zinc dinonyl dithiocarbamate	98.7	—
4,4′-thiobis(3-methyl-6-*tert*-butylphenol)	5.5	4.2
1,1,3-tris(2′-methyl-5′-*tert*-butyl-4′-hydroxyphenyl)butane	3.0	3.5

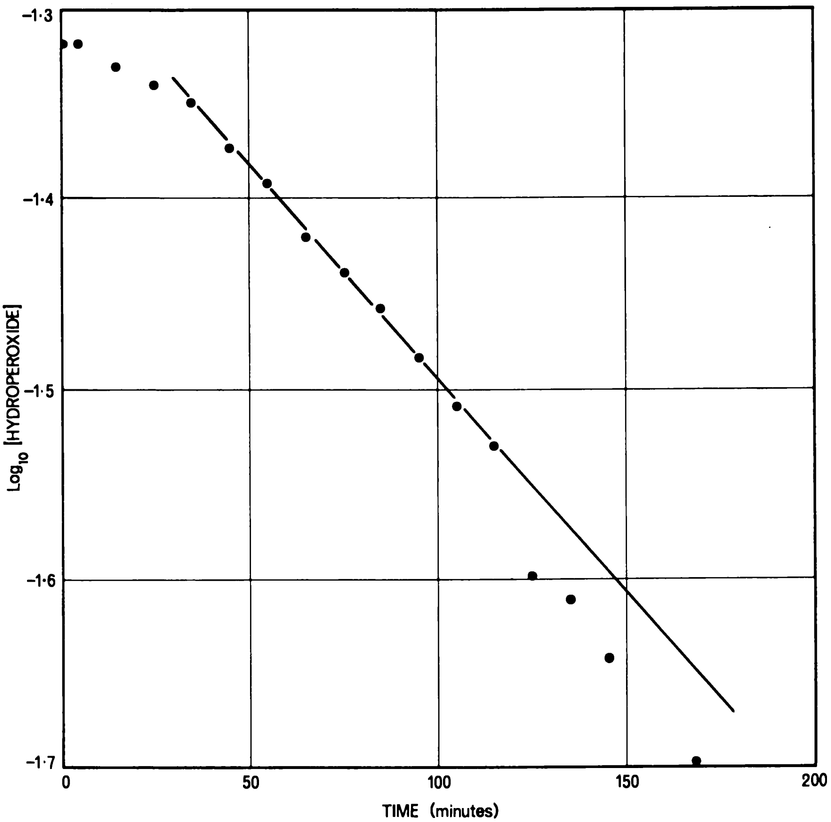


Figure 1. First-order plot for the decomposition of Tetralin hydroperoxide (4.8 × 10^{-2}M) by dilauryl thiodipropionate (2.47 × 10^{-2}M) at 80°C.

sulfur compound. Neither of the two phenolic antioxidants decomposed the hydroperoxide; in fact they retarded the free radical, thermally induced decomposition. The failure of the sulfur-bridged bisphenol to decompose the hydroperoxide is surprising in that it might be expected to react as both a chain stopper and a hydroperoxide decomposer. It is also noteworthy that whereas dilauryl sulfinyldipropionate decomposed the hydroperoxide readily, di-*n*-octadecyl sulfone was ineffective.

PRODUCTS OF THE REACTION. A solution containing 5 × 10^{-2} mole/liter hydroperoxide and 2 × 10^{-2} mole/liter dilauryl thiodipropionate was allowed to react at 70°C. until no hydroperoxide remained. A brown resinous precipitate was formed which was filtered, washed, and dried *in vacuo*. The infrared spectrum of the solid revealed the presence of —O—SO_2— groups and the presence of an ortho-substituted aromatic compound, but no further details of its constitution could be obtained. This precipitate was not formed in the kinetic experiments which had a

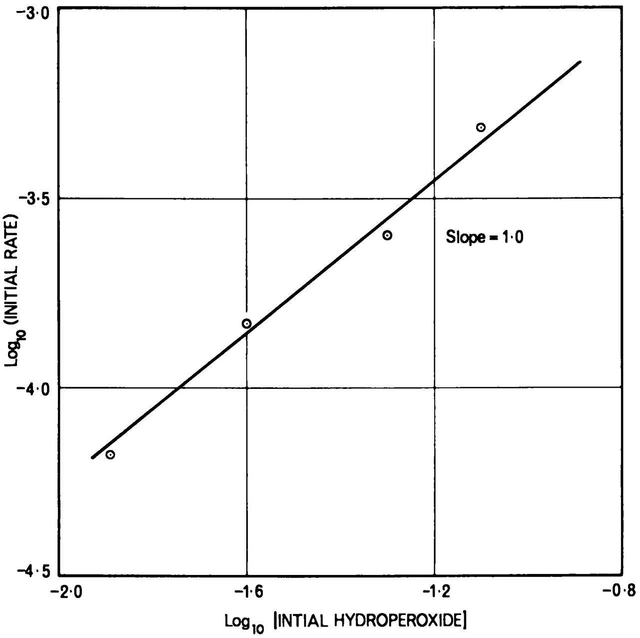


Figure 2. Order of reaction with respect to Tetralin hydroperoxide at 80°C.

maximum duration of 6 hours. The filtrate was analyzed by vapor phase chromatography on a column packed with 20% w/w silicone gum rubber, SE 30, on 60-80 mesh C22 firebrick, at 180°C. using nitrogen as carrier gas. Comparison with the retention times of the pure compounds showed that α-tetralol was the major product and that no trace of α-tetralone was present. Several small unidentified peaks at long retention times were observed.

KINETIC ORDER OF THE REACTION. The decomposition of the hydroperoxide had an initial slow reaction or induction period followed by a faster main reaction. The induction period was unaffected by the addition of dilauryl sulfinyl dipropionate or by carrying out the reaction in an atmosphere of nitrogen but was eliminated by the addition of acetic acid. The length of the induction period decreased as the initial concentration of both hydroperoxide or sulfur compound increased.

A first-order plot of $\log_{10}$ [Hydroperoxide] *vs.* time (Figure 1) was linear, at least until the amount of hydroperoxide decomposed approached a value equal to the initial concentration of sulfur compound. After this point the rate of decomposition increased. Confirmation that the reaction was first order with respect to hydroperoxide was obtained by measuring the initial slopes of the rates of decomposition of varying amounts of hydroperoxide by a fixed amount of dilauryl thiodipropionate (Figure 2). The order of the reaction with respect to the sulfur compound, determined by the initial slopes method, was also unity (Figure 3).

That the reaction was first order with respect to both reactants was confirmed at 70°, 80°, and 90°C. in chlorobenzene solution and at 30°, 40°, and 50°C. in toluene solution.

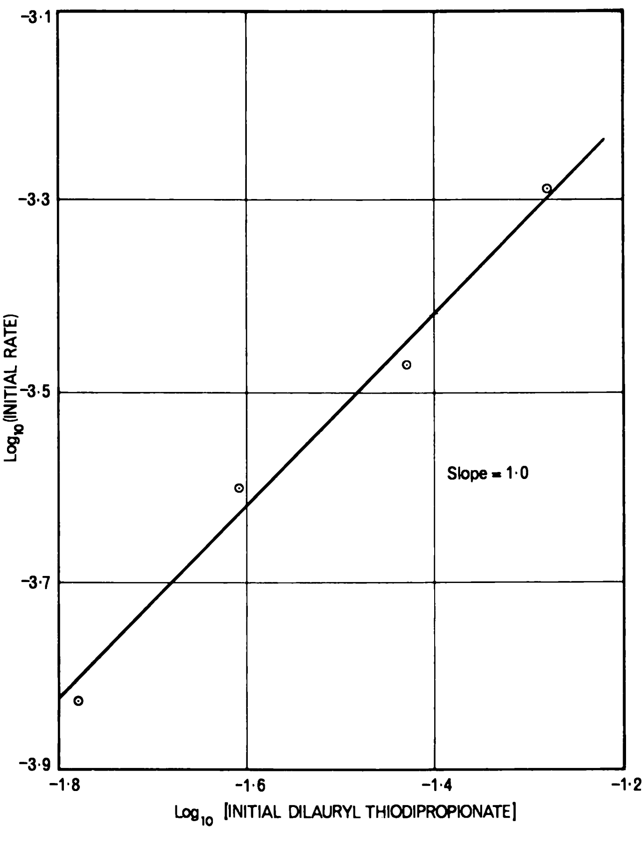


Figure 3. Order of reaction with respect to dilauryl thiodipropionate at 80°C.

EFFECT OF DILAURYL SULFINYLDIPROPIONATE (DLTP SULFOXIDE). The addition of dilauryl sulfinyl dipropionate to a solution containing Tetralin hydroperoxide and dialuryl thiodipropionate had little effect on the length of the induction period, but the rate of the subsequent reaction was increased. Comparison of the rate of decomposition of the hydroperoxide (5.0×10^{-2} mole/liter) by dilauryl thiodipropionate (1.60×10^{-2} mole/liter) or dilauryl sulfinyl dipropionate (1.60×10^{-2} mole/liter)

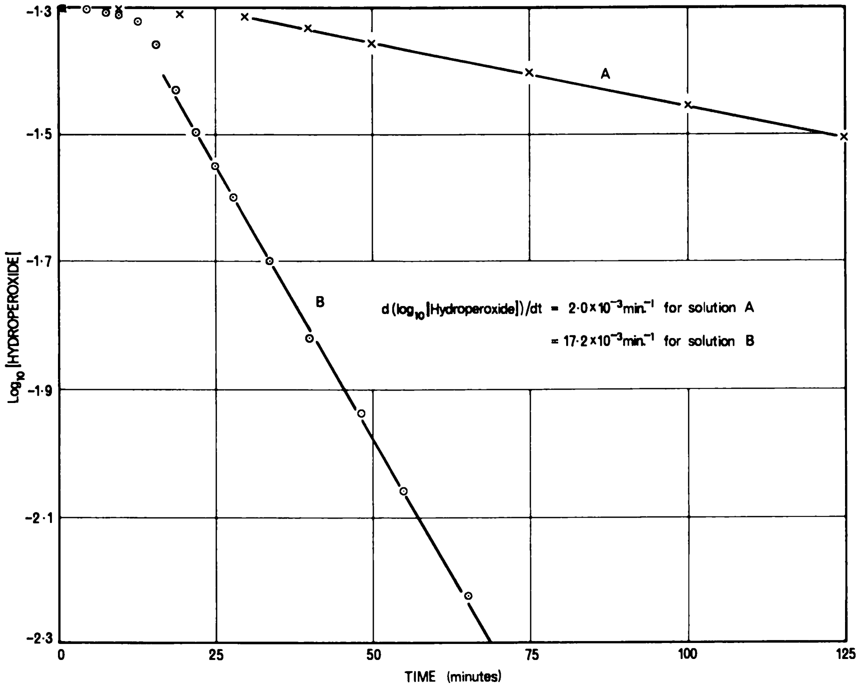


Figure 4. Decomposition of Tetralin hydroperoxide (5.0 × 10^{-2}M) by (A) dilauryl thiodipropionate (1.6 × 10^{-2}M) and by (B) dilauryl sulfinyldipropionate (1.6 × 10^{-2}M)

showed that the rate of decomposition $d[\log_{10}$ hydroperoxide$]/dt$, was 8.6 times faster with the sulfoxide (Figure 4).

Effect of Acetic Acid. Addition of acetic acid (35 × 10^{-2} mole/liter) to a solution containing Tetralin hydroperoxide (2.0 × 10^{-2} mole/liter) and dilauryl thiodipropionate (2.5 × 10^{-2} mole/liter) not only eliminated the 60-minute induction period but substantially increased the rate of reaction (Figure 5). The over-all rate equation in the presence of acetic acid at 70°C., determined by the initial slopes method was

$$d[\text{hydroperoxide}]/dt = k^1[\text{HOAc}]^{0.5}[\text{hydroperoxide}]^{0.9}[\text{DLTP}]^{0.8} \quad \text{(I)}$$

Effect of a Phenolic Antioxidant. The rate of decomposition of a solution containing the hydroperoxide (5.0 × 10^{-2} mole/liter) dilauryl thiodipropionate (2.5 × 10^{-2} mole/liter) and 1,1,3-tris(2′-methyl-5′-*tert*-butyl-4′-hydroxyphenyl)butane (2.5 × 10^{-2} mole/liter) at 80°C. was identical with that containing no phenolic compound. In addition no formation of polymer was observed when solutions of Tetralin hydroperoxide and dilauryl thiodipropionate were allowed to react at 70°C. in sealed tubes in the presence of inhibitor-free acrylonitrile in nitrogen atmosphere. Free radicals initiate the polymerization of acrylonitrile under these conditions to give an insoluble polymer. From these experiments it was concluded that the reaction was non-radical in nature.

ACTIVATION ENERGY. An Arrhenius plot of the second-order rate constants calculated according to the equation

$$d[\text{hydroperoxide}]/dt = k_2[\text{hydroperoxide}]\,[\text{DLTP}] \qquad \text{(II)}$$

for the reaction at 70°, 80°, and 90°C. (Table II) gave a value for the activation energy of the reaction of 12.0 ± 1.0 kcal./mole.

DECOMPOSITION BY DISTEARYL THIODIPROPIONATE. The rate of decomposition at 80°C. of Tetralin hydroperoxide by distearyl thiodipropionate was very similar to the rate with dilauryl thiodipropionate although the induction period was longer (Figure 6).

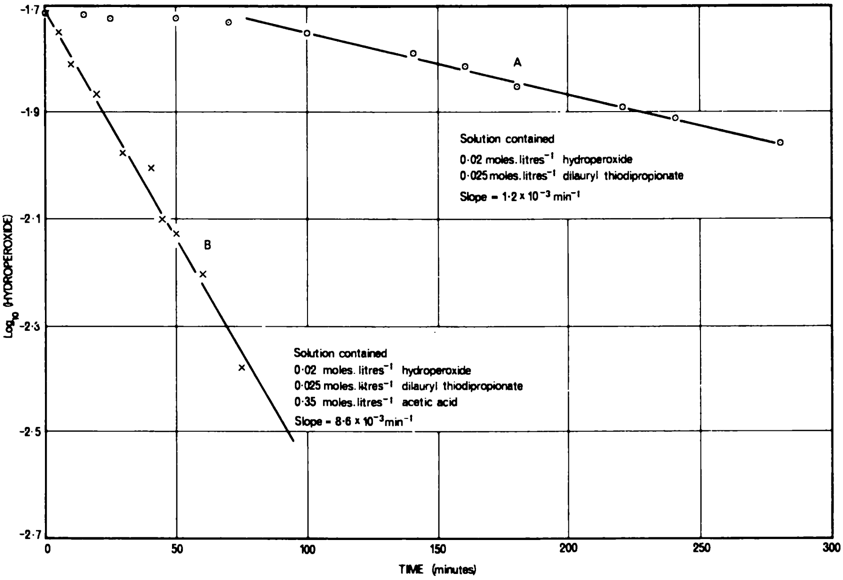


Figure 5. Decomposition of Tetralin hydroperoxide by dilauryl thiodipropionate in the presence of acetic acid at 70°C.

Table II. Second-Order Rate Constants for the Decomposition of Tetralin Hydroperoxide by Dilauryl Thiodipropionate in Chlorobenzene

Temperature, °C.	k_2, *liter/mole/min.*
70	0.10
80	0.16
90	0.28

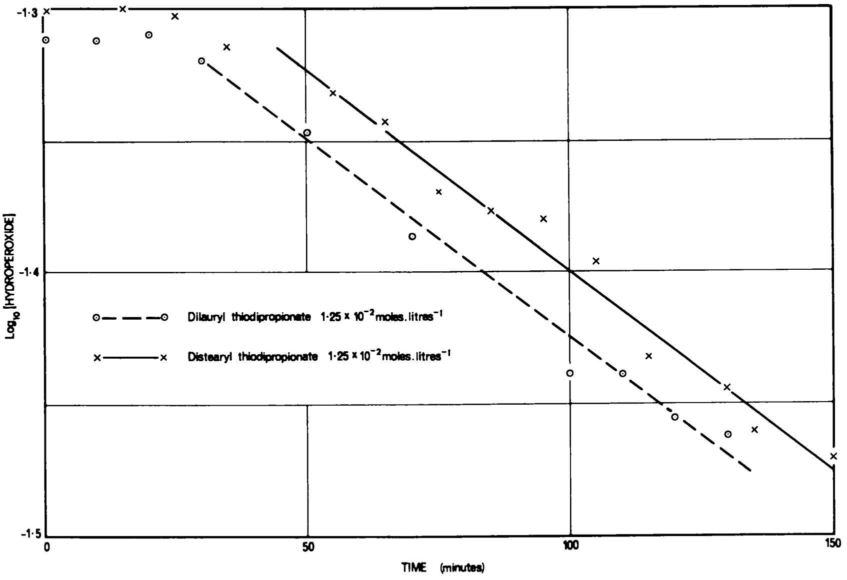


Figure 6. Decomposition of Tetralin hydroperoxide (5.0 × 10^{-2}M) at 80°C. by dilauryl thiodipropionate and distearyl thiodipropionate

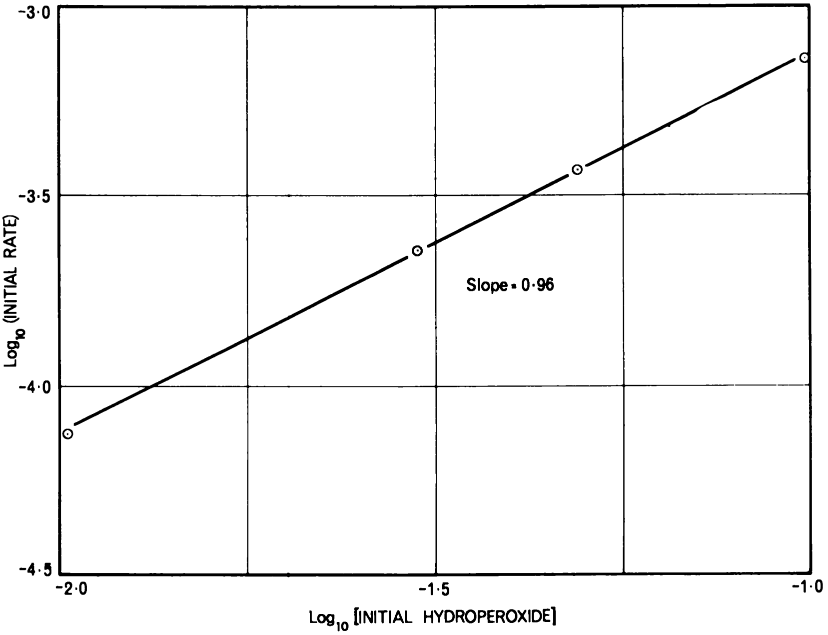


Figure 7. Order of reaction with respect to tert-*butyl hydroperoxide at 80°C.*

***tert*-Butyl Hydroperoxide.** The kinetic features of the decomposition of *tert*-butyl hydroperoxide by dilauryl thiodipropionate in chlorobenzene at 70°, 80°, and 90°C. were the same as those with Tetralin hydroperoxide. There was a slow initial reaction or induction period, followed by a faster reaction which was first order with respect to both hydroperoxide and dilauryl thiodipropionate (Figures 7 and 8). The activation energy for the main reaction derived from an Arrhenius plot of the second-order rate constants $k_2{}^1$ (Table III) obtained from the expression

$$d[\text{hydroperoxide}]/dt = k_2{}^1[\text{hydroperoxide}][\text{DLTP}] \qquad \text{(III)}$$

was 16.0 ± 1.5 kcal./mole. The extent of reaction was such that at least 20 moles of *tert*-butyl hydroperoxide were decomposed by 1 mole of sulfur compound.

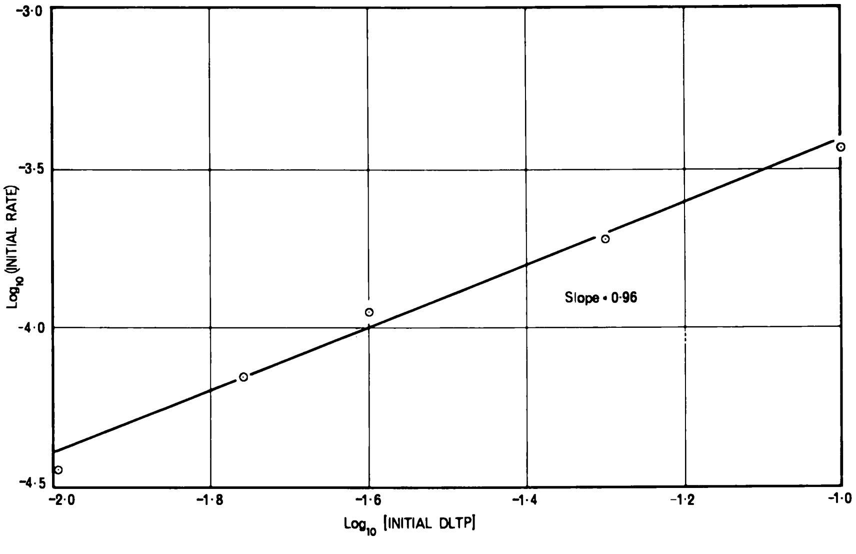


Figure 8. Order of reaction with respect to dilauryl thiodipropionate at 80°C.

Table III. Second-Order Rate Constants for the Decomposition of *tert*-Butyl Hydroperoxide by Dilauryl Thiodipropionate in Chlorobenzene

Temperature, °C.	$k_2{}^1$, *liter/mole/min.*
70	0.063
80	0.11
90	0.23

A solution containing 5.0×10^{-2} mole/liter *tert*-butyl hydroperoxide and 2.5×10^{-2} mole/liter dilauryl thiodipropionate was allowed to react at 80°C. until no hydroperoxide remained. A slight precipitate was obtained which could not be identified. Vapor phase chromatography of the residual solution at 100°C. on a column containing 20% w/w di-*n*-decyl phthalate on 60–80 mesh C22 firebrick gave *tert*-butyl alcohol as the main identifiable product.

Discussion

Although the kinetic expression obtained in this work for the initial stages of the main reaction

$$-d[\text{hydroperoxide}]/dt = k_2[\text{hydroperoxide}]\,[\text{DLTP}] \qquad \text{(II)}$$

indicates that the rate-determining step might be

$$\text{ROOH} + \text{R}_2{}^1\text{S} \xrightarrow{k_7} \text{ROH} + \text{R}_2{}^1\text{SO} \qquad (7)$$

which agrees with the formation of α-tetralol and *tert*-butyl alcohol, the existence of an induction period and the unexpected stoichiometry of the over-all reaction show that this explanation is insufficient.

An induction period suggests the formation of a complex, which then decomposes, or the formation of an active species responsible for the decomposition of the hydroperoxide, while the fact that at least 20 moles hydroperoxide are decomposed by 1 mole of dilauryl thiodipropionate also indicates the formation of an active species or the existence of several consecutive reactions. A mechanism in which DLTP itself is regenerated and is the sole decomposing agent seems improbable, and the formation of products containing $—\text{O}—\text{SO}_2—$ groupings is evidence that DLTP is converted into a variety of products during the reaction. The theory that sulfur-containing stabilizers are only the precursors of the effective peroxide decomposers has been suggested by Hawkins and Sautter (*4*). It is unlikely that dilauryl sulfinyl dipropionate is the active species in this work, or else the induction period should be eliminated by adding the sulfoxide. Rather it seems that in the initial stages of the main reaction the following over-all reactions occur

$$\text{ROOH} + \text{R}_2{}^1\text{S} \xrightarrow{k_7} \text{ROH} + \text{R}_2{}^1\text{SO} \qquad (7)$$

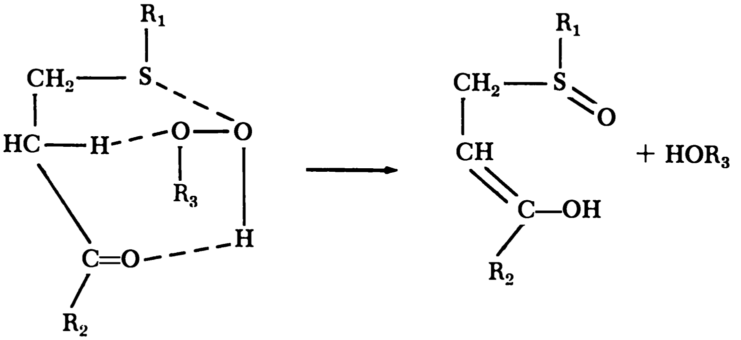
$$\text{ROOH} + \text{R}_2{}^1\text{SO} \xrightarrow{k_8} \text{ROH} + \text{R}_2{}^1\text{SO}_2 \qquad (8)$$

The rate constant k_8 is 8.6 times greater than k_7 (Figure 4), so that in the initial stages of the main reaction the rate equation corresponds to Equation II where $k_2 = k_7$.

Considering the induction period and the initial stages of the main reaction only, it seems possible that during the induction period a complex is formed which involves the hydroperoxide and sulfur compound.

$$\mathrm{ROOH} + \mathrm{R_2{}^1} \rightleftharpoons \mathrm{Complex} \rightarrow \mathrm{ROH} + \mathrm{R_2{}^1SO} \qquad (9)$$

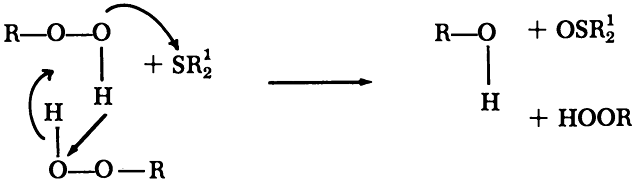
When the rate of formation of the complex equals its rate of decomposition, then the rate equation will correspond to Equation II. The mechanism of the complex formation may involve the type proposed by Scott (*7*) for the decomposition of hydroperoxides by β-ketosulfides,



(10)

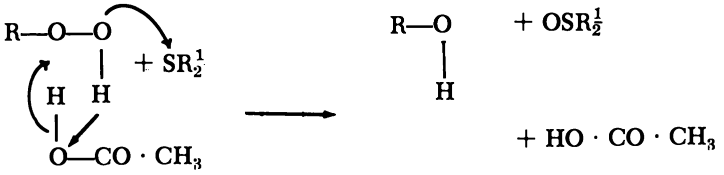
Presumably the sulfoxide can form a similar complex, and Bateman *et al.* (*1*) have proposed strong complex formation between sulfoxides and squalene hydroperoxide.

Bateman and Hargrave (*2*), who studied the decomposition of *tert*-butyl hydroperoxide by a dialkyl sulfide at 50°C., found that in benzene solution the reaction was second order with respect to hydroperoxide and first order with respect to sulfide. They proposed Reaction 11 to account for this.



(11)

The apparent disagreement between these results and the present work is explicable if complex formation of the type proposed by Scott is correct. With DLTP, which contains a β-keto grouping, a complex corresponding to A is possible, leading to a reaction order of unity with respect to both reactants, while for the dialkyl sulfides such complex formation is not possible, and the alternative complex proposed by Bateman and Hargrave occurs. The fact that acetic acid not only increases the rate of reaction but also eliminates the induction period can be explained by the reaction scheme proposed by Bateman and Hargrave (2),



(12)

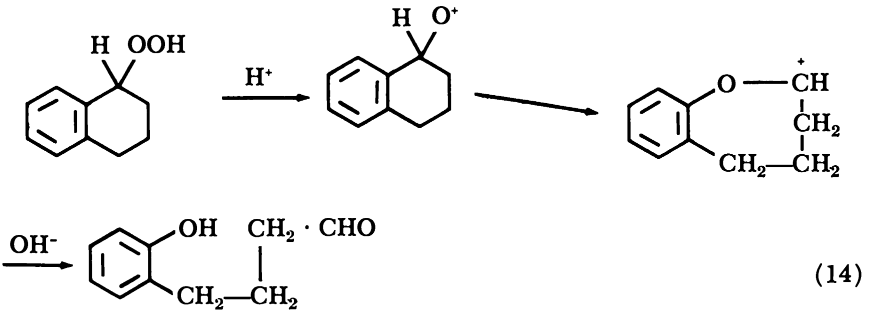
where the formation of a complex is no longer necessary. The fact that the rate equation for the decomposition in the presence of acetic acid contains the term $[\mathrm{HOAc}]^{0.5}$ may be caused by the existence of acetic acid as the dimer in most organic solvents,

$$2\mathrm{HOAc} \rightleftharpoons (\mathrm{HOAc})_2 \tag{13}$$

so that the concentration of HOAc available for Reaction 12 will be proportional to the square root of the added acetic acid. In acid solution if both Reactions 9 and 12 occur simultaneously, the kinetic equation may not be simple and fractional orders for both hydroperoxide and sulfur compound will occur (Equation I).

The mechanism proposed so far takes account of the induction period and initial stages of the reaction only, and it is difficult to see how it can account for the large amount of hydroperoxide decomposed by the sulfur compound. However, Tetralin hydroperoxide is decomposed catalytically by acids (5). Although in the absence of dilauryl thiodipropionate the decomposition of Tetralin hydroperoxide in the presence of acetic acid at 70°C. was very slow, if the acid species is a much stronger acid than acetic—*e.g.*, a sulfonic acid as seems likely from the nature of the products of the reaction, the rate of acid-induced decomposition may be comparable with the rate of decomposition by the sulfur compound. Some evidence that acid-induced decomposition does occur at some stage in the over-all reaction is found in the presence of an ortho substituted aromatic compound in the solid product of the reaction. The acid catalyzed decomposition of Tetralin hydroperoxide follows the path of Reaction 14 (5) to give γ-(*o*-hydroxyphenyl)butyraldehyde. This forms a brown resin which is mainly the aldol of this aldehyde (*cf.*, the resin obtained in this work).

Thus, a possible reaction mechanism which would account for the induction period, the initial kinetic features of the reaction, and the large amount of hydroperoxide eventually decomposed is that during the induction period a complex is formed which decomposes to form the sulfoxide (Reaction 9). The sulfoxide can be converted to the sulfone by a similar mechanism, and the initial stage of the reaction will follow the rate ex-



(14)

pression, Equation II. Concurrently either the sulfoxide or sulfone is converted to an acid species which can then both catalyze the decomposition according to Reaction 12 and induce the decomposition of the hydroperoxide according to Reaction 14. The induced decomposition would lead both to a deviation from the kinetic expression, Equation II, and to the decomposition of a large amount of hydroperoxide per mole of dilauryl thiodipropionate.

Instead of either an acid-induced decomposition or acid-catalyzed sulfur compound—hydroperoxide decomposition reaction occurring—formation of alternative active species which catalytically decompose the hydroperoxide is possible, such as SO_2, as suggested by Hawkins and Sautter (*4*). However, under conditions of this work where vigorous drying of solvents was not used, SO_2 could be converted into the acid which would then induce the acid-catalyzed decomposition of the peroxide.

Table IV. Oven Life of Polypropylene Containing 0.25% 1,1,3-Tris(2′-methyl-5′-*tert*-butyl-4′-hydroxyphenyl)butane and 0.25% Sulfur Compound at 140°C.

Sulfur Compound	*Time to Embrittlement of 0.02-inch Thick Polypropylene Sample, hours*
Dilauryl thiodipropionate	800
Distearyl thiodipropionate	1000

The similar rate of decomposition of Tetralin hydroperoxide by distearyl and dilauryl thiodipropionate at 80°C. is of interest when compared with the former's better antioxidant properties in polypropylene at 140°C. Tests showed that the stearyl compound was superior to the lauryl compound as a synergist, in the presence of a phenolic antioxidant, in delaying the embrittlement of polypropylene sheet in an air oven at 140°C. (Table IV).

The sulfur compounds are regarded as peroxide-decomposing stabilizers (3), and it might have been expected, on the basis of the kinetic work, that the efficiency of the lauryl and stearyl compounds would be similar in polypropylene. However, at 140°C. in the polymer the volatility of the antioxidant probably becomes important, so that the less volatile stearyl compound is the better stabilizer. In addition, the nature of the hydroperoxide in polypropylene may also affect the reaction mechanism. Although the rates of decomposition of Tetralin hydroperoxide by dilauryl and distearyl thiodipropionates may not relate directly to their efficiency as stabilizers for the polymer at 80°, the result does show a possible source of error in extrapolating the stability of polymers from high temperatures—*e.g.*, 140°C. to the 60°–80°C. range, where the relative effectiveness of two stabilizers may be altered significantly.

Acknowledgments

The author thanks D. R. Mosely for assistance with the experimental work, V. J. Zichy for the infrared spectra determinations, A. R. Jeffs for the vapor phase chromatographic analysis, D. G. Corbin for the purification of *tert*-butyl hydroperoxide, and R. J. Hurlock for the preparation of dilauryl sulfinyl dipropionate.

Literature Cited

(1) Bateman, L., Cain, M. E., Colclough, T., Cuneen, J. I., *J. Chem. Soc.* **1962,** 3570.
(2) Bateman, L., Hargrave, K. R., *Proc. Roy. Soc. (London)* A **224,** 389, 399 (1954).
(3) Hawkins, W. L., *Oxidation Combust. Rev.* **1,** 169 (1965).
(4) Hawkins, W. L., Sautter, H., *Chem. Ind.* **1962,** 1825.
(5) Kharasch, M. S., Burt, J. G., *J. Org. Chem.* **16,** 150 (1951).
(6) Robertson, A., Waters, W. A., *J. Chem. Soc.* **1948,** 1584.
(7) Scott, G., "Atmospheric Oxidation and Antioxidants," p. 191, Elsevier, New York, 1965.

RECEIVED March 27, 1967.

12

Antioxidants Derived from Alkylation of Phenols with Alpha Olefins

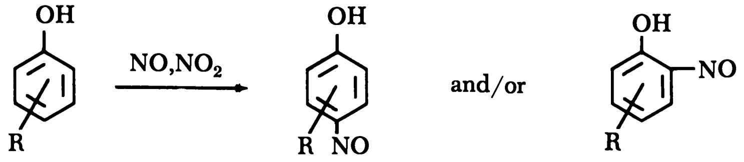
G. R. LAPPIN, C. E. THOLSTRUP, and C. A. KELLY

Research Laboratories, Tennessee Eastman Co., Division of Eastman Kodak Co., Kingsport, Tenn.

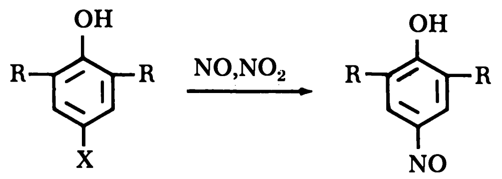
A number of new secondary-alkyl-substituted phenols were prepared by the alkylation of phenol, p*-cresol, 2,4-xylenol, and 2,6-xylenol with long chain alpha olefins. Most of these alkylated phenols had high effectiveness as antioxidants for polypropylene when tested in high temperature accelerated tests. Unlike many high molecular weight phenolic antioxidants, these alkylated phenols do not discolor when exposed to nitrogen oxides. Results of four different oven tests showed that 2,6-dioctadecyl-*p*-cresol had the best over-all potency, followed closely by 2,4,6-trioctadecylphenol. In these tests the major structural factor affecting antioxidant potency was molecular weight. We believe the oven-life of polypropylene samples containing these alkylated phenols is largely determined by the volatility of the antioxidant.*

Polypropylene, when properly stabilized, is one of the most useful and inexpensive engineering plastics. Its good high temperature properties have led to its use in ever more damaging environments. Unfortunately, antioxidants which are good enough for protection under moderate conditions are not good enough for these more demanding applications. The antioxidant potency may be too low, the volatility may be too high, the stabilizer may dissolve in some fluid to which the plastic article is exposed, or some chemical reaction with a reagent present in the use environment may destroy the antioxidant.

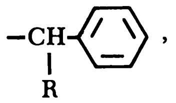
To meet the requirements of higher temperatures and other adverse conditions, phenolic antioxidants having relatively high molecular weights have been developed. These are generally quite effective and retained well in the polymer. However, most of them suffer from a serious defect —the reaction called gas yellowing. On exposure to oxides of nitrogen, always present in urban atmospheres, particularly at temperatures above 60°C., these compounds become yellow with resulting serious discoloration of polymers containing such antioxidants. The chemistry of this reaction is not well understood, but it appears to involve the formation of highly yellow nitrosophenols, as shown in the following reaction:



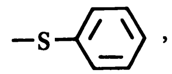
Not only are phenols with unsubstituted ortho or para positions subject to such reactions, but a number of substituents in these positions can be displaced to give yellow products, shown below (*1*).



X can be:

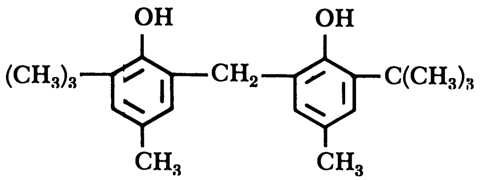


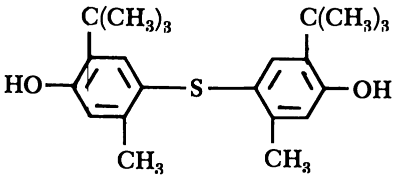
—CH_2OR, —$CH_2OPO(OR)_2$,



—CH_2NR_2, or —Cl

Some of these groups are common units in high molecular weight phenolic antioxidants, such as the methylenebisphenol types and the thiobisphenol types, all of which are gas yellowing.

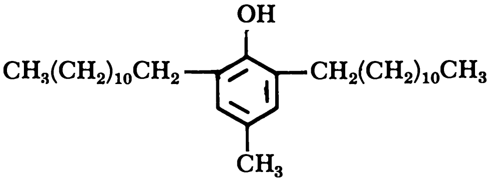




Of all the known types of antioxidants for polypropylene, the 2,4,6-trialkylphenols appear to have the best combination of properties. They have high potency, good compatibility with the polymer, excellent resistance to gas yellowing, and a high degree of chemical resistance to acids, bases, oxidizing agents, and the like. However, most of the commercial 2,4,6-trialkylphenol antioxidants are so low in molecular weight that their consequent volatility makes them of little use in high temperature applications.

The main purpose of the work reported here was to develop a low-cost, effective, and nonvolatile 2,4,6-trialkylphenol antioxidant. We discuss the synthesis of some new types of phenolic antioxidants, particularly those resulting from α-olefin alkylation of phenols. We also report the effectiveness of these stabilizers in polypropylene and speculate on the effect of structure on their effectiveness.

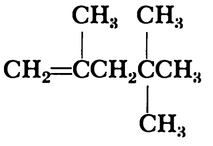
Before this investigation was started we had already produced a rather expensive 2,4,6-trialkylphenol having all but one of the desired properties—2,6-didodecyl-*p*-cresol (DDPC).



DDPC

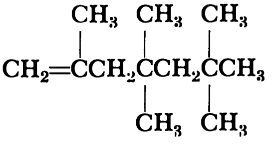
To insert the normal C_{12} alkyl chain requires a multistep process of acylation, reduction, acylation a second time, and finally, reduction to the desired product. Although DDPC is highly effective, nondiscoloring, and nonvolatile, the cost makes its use unattractive. However, it was encouraging to find that swamping the active antioxidant portion, the phenol nucleus, with large alkyl chains did not dilute the effectiveness of the antioxidant. We hoped to find 2,6-dialkyl-*p*-cresol having all the good properties of DDPC but which could be made by the much cheaper process of a one-step alkylation of *p*-cresol with some cheap olefin.

Only a few cheap high molecular weight olefins are available. Di- and triisobutylene



$$CH_2{=}\overset{CH_3}{C}CH_2\underset{CH_3}{\overset{CH_3}{C}}CH_3$$

Diisobutylene

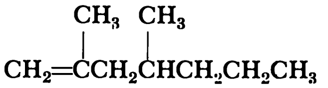


$$CH_2{=}\overset{CH_3}{C}CH_2\underset{CH_3}{\overset{CH_3}{C}}CH_2\underset{CH_3}{\overset{CH_3}{C}}CH_3$$

Triisobutylene

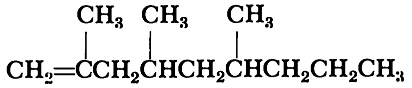
have been used in preparing alkylated phenols. These butylene polymers are easily depolymerized and, in our experience, yield much tertiary butylated product when the alkylation is driven hard enough to give good yields of dialkylated phenol. Hence, we did not investigate their use further.

Similar oligomers from propylene, particularly the trimer and tetramer, are widely used to prepare alkylated aromatics for detergent manufacture, but little use has been made of these olefins in antioxidant synthesis. The structures shown below are idealized.



$CH_2{=}\overset{CH_3}{\overset{|}{C}}CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$

Propylene trimer



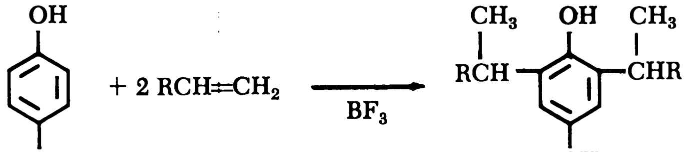
$CH_2{=}\overset{CH_3}{\overset{|}{C}}CH_2\overset{CH_3}{\overset{|}{C}}HCH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$

Propylene tetramer

The actual products are complex mixtures of highly branched olefins containing both terminal and internal unsaturation.

Recently, a number of α-olefins have been offered commercially. These olefins, made by ethylene polymerization or by wax cracking, are available either as relatively pure compounds or as mixtures of several adjacent members in chain lengths of about six to 20 carbon atoms. These products are largely straight-chain terminal olefins.

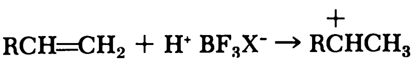
Our initial investigation included a study of the alkylation of *p*-cresol with propylene oligomers and with various α-olefins. Because all alkylations were carried out by a well-known procedure and neither novel reactions nor unexpected results were encountered, no detailed experimental work will be reported As shown by the following reaction, all alkylations were carried out using BF_3 catalyst at 80°–90°C. and excess olefin as the reaction solvent.



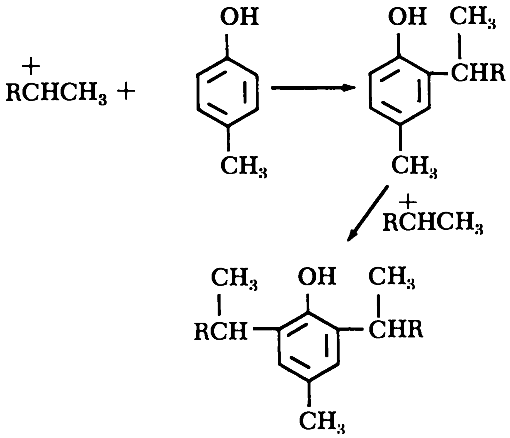
The products, which were obtained as viscous, pale amber oils, were purified by vacuum distillation or molecular distillation, whichever was best suited to the particular product. The yield of dialkylated *p*-cresol was 85–95%. Freedom from appreciable amounts of monoalkylated product was established by vapor phase chromatography (VPC), thin-layer chromatography (TLC), and molecular weight determination. The products obtained from propylene trimer and tetramer had no appreciable antioxidant activity and will not be considered further here.

The α-olefin products were much more promising, and an extensive investigation of this series was carried out. The α-olefins obtained from ethylene polymerization are somewhat different from those obtained from wax cracking. Analysis of a typical ethylene polymerization product, 1-octadecene, is shown in Tables I and II. Because of its source it contains only even-numbered chains and is almost free of olefin containing internal unsaturation. A similar product obtained by wax cracking would have a lower total olefin content, more branched and internal olefins, and would contain some diolefin and cyclic olefin. It would also contain both even- and odd-numbered chains. Despite these differences in composition, very little difference could be found between alkylated phenols derived from the two types of α-olefin. The major difference was that the wax-cracking product gave alkylated phenols having more color. Most of the test results described in this report are for products made from α-olefins derived from ethylene. Alkylations were carried out with both "pure" α-olefins and α-olefin mixtures—*e.g.*, a C_{10}, C_{12}, C_{14} mixture. Alkylated phenols from such mixtures had antioxidant properties close to the average for the products from "pure" α-olefins covering the same molecular weight range. For simplicity, only the products from the "pure" α-olefins will be considered. One might expect that the alkylation of *p*-cresol with an α-olefin (shown below)

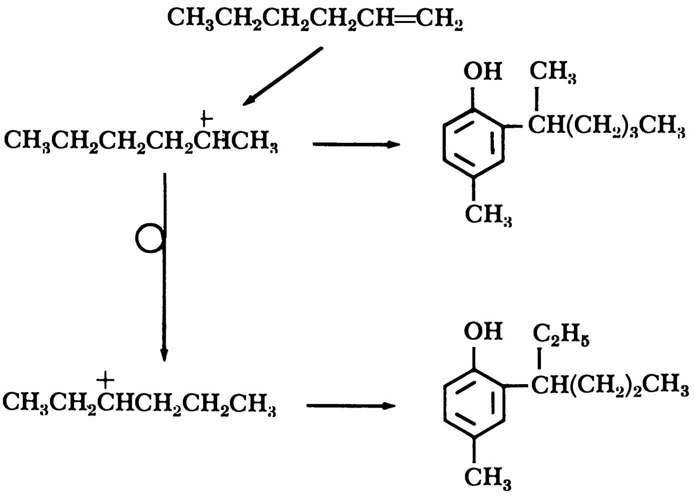
$$BF_3 + HX \rightarrow H^+ BF_3X^-$$



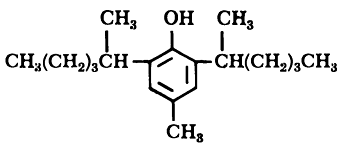
$$RCH{=}CH_2 + H^+ BF_3X^- \rightarrow R\overset{+}{C}HCH_3$$

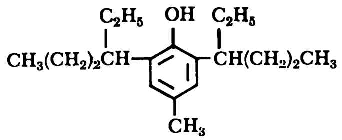


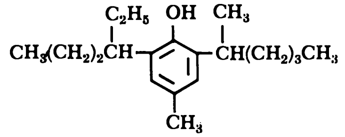
would give a 2,6-di(*sec*-alkyl)-*p*-cresol. However, in this scheme we have ignored the ability of carbonium ions to rearrange by transfer of the electrophilic center down the chain, shown as follows.



If we do not consider possible skeletal rearrangements, 1-hexene can produce either a 1-methylpentyl or a 1-ethylbutyl substituent when alkylating *p*-cresol and thus give three







products: two symmetrical derivatives and one mixed product. When the *p*-cresol alkylation product of 1-hexene is examined by VPC, one major product and two minor products are seen. We believe that the major product is 2,6-bis(1-methylpentyl)-*p*-cresol, but we have not established this experimentally. The important point is that all of the expected products seem to be present. When 1-octadecene is the alkylating agent, the situation is much more complex. This olefin can give eight different alkyl groups and can engender eight symmetrical and 28 mixed 2,6-

Table I. Composition of 1-Octadecene Olefin Types

Olefin Type	*Olefin Concn., Mole %*
RCH=CH$_2$	94
RCH=CHR(trans)	0
RCH=CHR(cis)	1.5
R$_2$C=CH$_2$	2.5
R$_2$C=CHR	1.5
Total Olefin	98%

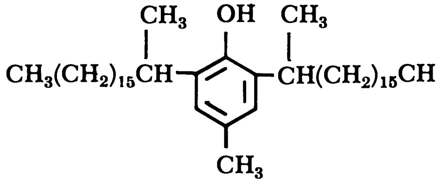
Table II. Composition of 1-Octadecene[a]

Chain Length	*Chain Length Distribution, Mole %*
<C$_{16}$	Not detected
C$_{16}$	3.2
C$_{18}$	93.8
C$_{20}$	3.0

[a] Prepared by ethylene polymerization.

octadecyl-*p*-cresols—36 products in all. We have not been able to effect any satisfactory resolution of this product by VPC or TLC techniques.

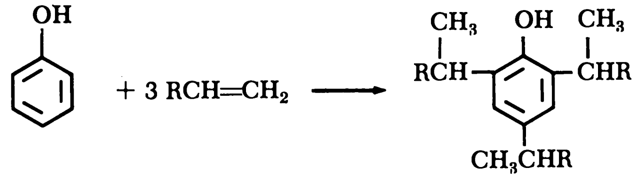
Detailed data concerning the effectiveness of the *p*-cresol α-olefin products will be given later. In general, all were at least moderately effective antioxidants for polypropylene. The 2,6-dioctadecyl-*p*-cresol (DOPC) from 1-octadecene is almost as effective in polypropylene

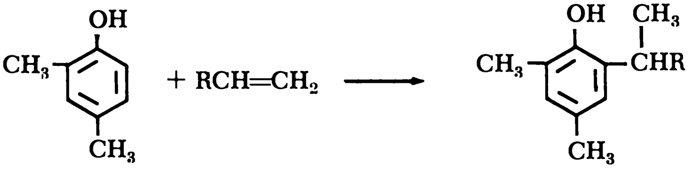


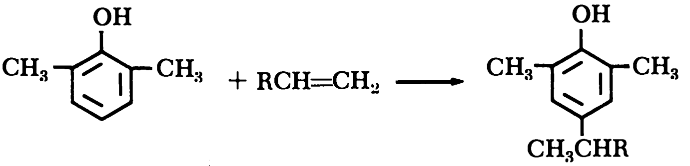
DOPC

as our standard, DDPC, and is equally resistant to discoloration. Furthermore, with about 85% of its weight derived from a 6-cent per pound α-olefin, it is cheap.

Because of the high antioxidant value of the *p*-cresol products, the work was extended to study the alkylation with α-olefins of three other readily available phenols: phenol, 2,4-xylenol, and 2,6-xylenol. The nominal products were 2,4,6-tri(*sec*-alkyl)phenols, 6-(*sec*-alkyl)-2,4-xylenols and 4-(*sec*-alkyl)-2,6-xylenols, as shown in the following reactions. Remember that these structural designations are for convenience; the actual products are complex mixtures. Again, yields of the desired alkylated phenol were very high. The trialykylated phenol products were







highly effective antioxidants, and again the octadecyl derivative was the most effective. This result was quite unexpected since this compound is 90% inert hydrocarbon and only 10% antioxidant. The xylenol products, while moderately effective antioxidants, were not nearly as effective as the *p*-cresol and phenol derivatives.

Let us now examine the antioxidant test results for the various phenols alkylated by α-olefins. They have been evaluated in several tests, but data are presented in Table III for only four different test procedures, chosen to illustrate the effect of increasing severity of test conditions. The least severe of these is the 140°C. stress-crack life test using a 65-mil thick molded bar. The 160°C. oven-life test using the same molded bar is somewhat more severe. Increasing severity is shown by the 140°C. oven-life test and the 160°C. oven-life test using 5-mil film test pieces. The relatively thick bars used in the first two tests provide a reservoir of antioxidant to replace that lost from the surface. These tests probably measure the inherent effectiveness of the antioxidant. In the tests using

Table III. Test Procedures

Test	*Temp., °C.*	*Specimen*	*Criterion of Failure*
Stress crack	140	65-mil bar, bent double	First cracking
Oven life	160	65-mil bar	Surface deterioration
Oven life	140	5-mil film	Embrittlement
Oven life	160	5-mil film	Embrittlement

film, no such reserve supply of antioxidant is available, and antioxidant volatility is probably a major factor in the results.

In all of these tests the samples were prepared from Tenite polypropylene containing 0.1 wt. % of the phenolic antioxidant and 0.3 wt. % of dilauryl 3,3′-thiodipropionate. Under any of the test conditions, the life of the polymer without the phenolic antioxidant is much less than 1 hour.

Most of the data are presented as plots of the time to failure for the polypropylene as a function of the size of the alkyl group derived from the α-olefin. These comparisons are made on an equal antioxidant weight basis, and as the size of the alkyl group is increased, the molar concentration of antioxidant decreases. Presented in this customary way the data are weighted in favor of lower molecular weight compounds because their molar concentration is higher.

Figure 1 shows the results for the 2,6-dialkyl-*p*-cresols. In Figures 1 and 2, the hours-to-failure scale on the right applies to the two most severe tests using the 5-mil film, while the scale on the left is for the less severe tests using 65-mil bars. In general, increasing the size of the alkyl substituent increases the antioxidant potency, although the 140°C. oven-life test shows the effect of decreasing molar concentration as the molecular weight increases, there being a well-defined maximum. The increase in antioxidant potency is not linear with molecular weight, but shows an abrupt increase over a narrow range, about C_{14} to C_{18} for these compounds. Considering all four tests, R = $C_{18}H_{37}$ appears to be about the optimum size. These results will be re-examined later from the viewpoint of the relationship of structure to effectiveness.

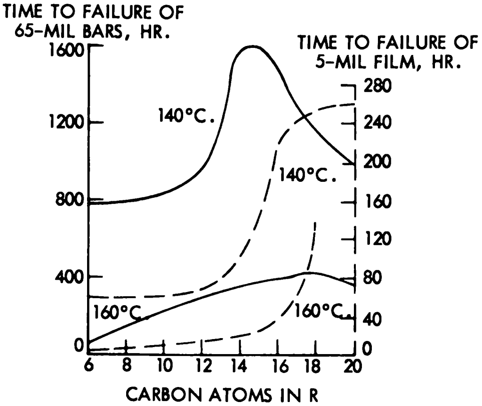


*Figure 1. Antioxidant effect of 2,6-dialkyl-*p-*cresols*

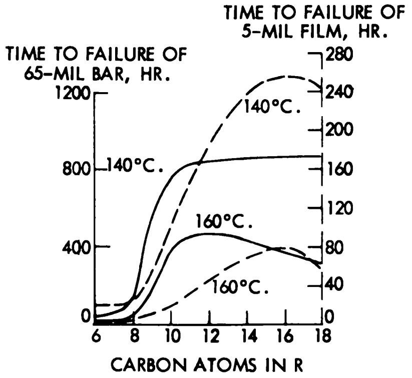
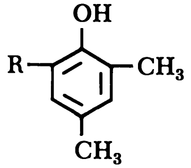
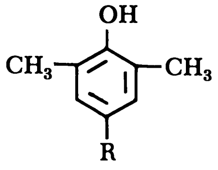


Figure 2. Antioxidant effect of 2,4,6-trialkylphenols

The data in Figure 2 for trialkylated phenol products are similar to those in Figure 1, with two important differences. The abrupt change in effectiveness of the trialkylated phenols occurs when R is $C_{10}H_{21}$ to $C_{12}H_{25}$. Although in the more severe tests these compounds are about as effective as the 2,6-dialkyl-*p*-cresols, in the least severe test they are considerably less effective. It is evident that 2,4,6-trioctadecylphenol is also a very potent antioxidant.

The alkylated xylenols had rather low antioxidant value, and we have not investigated them extensively. The data in Table IV indicate

Table IV. Antioxidant Effect of Alkylated Xylenols

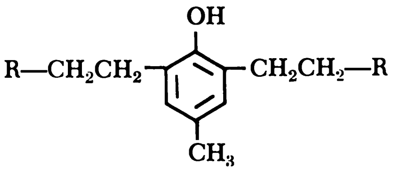
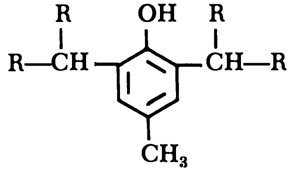
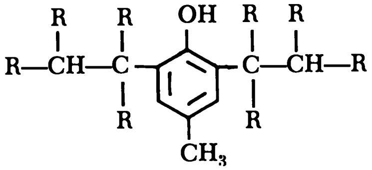
		Time to Failure, hours	
Alkylated Xylenol	*R*	*140°C., 5-mil film*	*160°C., 65-mil bar*
	$C_{12}H_{25}$	5	15
	$C_{18}H_{37}$	40	175
	$C_{12}H_{25}$	35	15
	$C_{18}H_{37}$	50	100
DOPC		260	450

an increase in effectiveness with increasing chain length of R, but the best values fall far short of those of the *p*-cresol or phenol products.

All four types of phenols alkylated by α-olefins are effective antioxidants. However, the alkylated *p*-cresols are the most effective, followed closely by the 2,4,6-trialkylated phenols. The alkylated xylenols have a lower degree of effectiveness in polypropylene. Of the entire series, 2,6-dioctadecyl-*p*-cresol has the best over-all properties. It is one of the most effective non-discoloring antioxidants now known for polypropylene. It is especially useful under adverse conditions, such as high temperatures, or in thin films.

One of the objectives of this investigation was to study the effect of structure on antioxidant activity for high molecular weight-hindered phenols. Unfortunately, tests such as those reported here measure both the inherent ability of an antioxidant to terminate free radical chains and its ability to persist in the polymer for a considerable time at a high temperature. Thus, low volatility may be a greater advantage than high efficiency in terminating radical chains, and meaningful conclusions are

Table V. Effect of Alkyl Group Structure on Antioxidant Value

Alkylated p-*Cresol*		
Type	*Structure*	*Antioxidant Value*
A		Very high
B		Very high, but less than Type A
C		Very low

hard to make. However, certain structural effects do become evident when the data are examined with this in mind.

The three different types of alkylated *p*-cresols we have examined (Table V) show an obvious effect of the structure of the 2- and 6-alkyl groups. The highest effectiveness is shown by DDPC (Type A, Table V). In the *p*-cresols alkylated by α-olefins, such as DOPC (Type B), a somewhat lower degree of antioxidant activity is observed, and the propylene tetramer product (Type C) has no appreciable value. The antioxidant ability of a phenol depends on its having the hydroxy hydrogen sufficiently accessible so that it may be attacked by a radical, yet hindered enough so that it is not reactive in direct oxidation reactions. The normal alkyl groups in DDPC must represent a near-optimum degree of hindrance. The secondary alkyl groups of DOPC provide somewhat more than optimum hindrance and thus reduce the antioxidant potency. In the highly branched propylene tetramer products so much hindrance is present that radical termination does not occur. The low effectiveness obtained from the alkylated xylenols may be partly a result of less than optimum hindrance.

Another important factor is molecular weight. In fact, for the α-olefin alkylation products it appears to be the controlling factor. When the effectiveness of the compounds is plotted as a function of the molecular weight (Figure 3), the curves show a sharp increase in effectiveness over a narrow range of molecular weight increase. The plot of the 140°C. oven-life test data shown here is typical. If the midpoint of the sharp upward break is taken as the point for comparison, it comes at about 525 molecular weight for the *p*-cresols and about 550 molecular weight for the trialkylated phenols. In the more severe 160°C. oven-life test using 5-mil film these points are increased to about 575 and 650 molecular

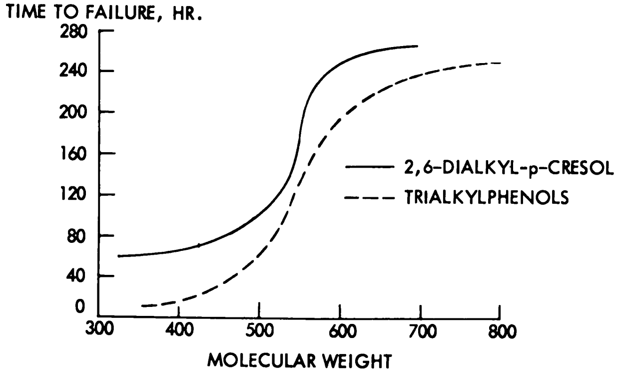


Figure 3. Oven life at 140°C. of 5-mil films as a function of molecular weight of antioxidant

weight for the *p*-cresols and phenols, respectively. The effectiveness in this test increases with increasing molecular weight throughout the whole range studied. A similar result is seen in the 160°C. tests on film.

A somewhat different effect is shown in Figure 4 by the data from the tests using 65-mil bars. The curves shown are for the 160°C. test, but those for the 140°C. test have similar shapes. A definite maximum in effectiveness is observed for both types. Again, a somewhat higher molecular weight is needed for the trialkylated phenols than for the dialkylated *p*-cresols.

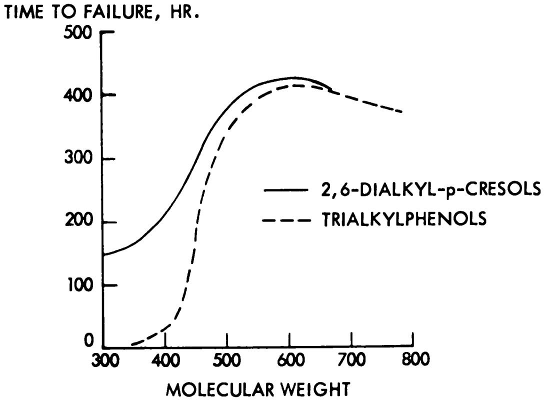


Figure 4. Oven life at 160°C. of 65-mil bars as a function of molecular weight of antioxidant

We believe that the most reasonable explanation for the results in Figure 4 is that volatility is the controlling factor in the tests used. Below some critical molecular weight, about 475–650, depending on the test, the compounds are lost so rapidly that they show little antioxidant effect. In thin films, volatility continues to be in control beyond the maximum molecular weight available in this study. The samples failed because all the antioxidant had been lost. In the thicker 65-mil bars, a maximum effectiveness was observed. Beyond this point the effect of volatility no longer was controlling, and a decrease in apparent antioxidant potency occurred because of the decrease in molar concentration of antioxidant as the molecular weight increased. If this hypothesis is correct, the alkylated xylenols had no chance to show good effectiveness in these tests because even the largest of these has a molecular weight of only 374.

Two differences were observed between the dialkylated *p*-cresols and the trialkylated phenols. First, the sharp increase in activity always occurs at a somewhat higher molecular weight for the trialkylated phenols; secondly, the *p*-cresol products are generally somewhat more effective throughout the entire range of molecular weights. The first may be explained by assuming that for a given molecular weight, the more compact trialkylated phenols have higher volatility and greater mobility in the polymer. The lower general activity of the trialkylated phenols may arise from an adverse effect of a bulky group para to the hydroxy. Such an effect has been observed for low molecular weight phenols.

Summary

We have prepared a number of new phenolic antioxidants by alkylating phenol, *p*-cresol, 2,4-xylenol, and 2,6-xylenol with α-olefins. All show appreciable antioxidant effectiveness in high temperature accelerated tests. In over-all potency, 2,6-dioctadecyl-*p*-cresol is the best, followed closely by 2,4,6-trioctadecylphenol. For the tests used in this study, molecular weight was found to be the controlling factor in the relationship of structure to effectiveness.

Literature Cited

(1) Lappin, G. R., Tholstrup, C. E., Kelly, C. A., unpublished work.

RECEIVED March 7, 1967.

13

Dihydric Phenols as Antioxidants in Isotactic Polypropylene

Derivatives of Pyrocatechol

Published on June 1, 1968 on http://pubs.acs.org | doi: 10.1021/ba-1968-0085.ch013

J. POSPÍŠIL, L. TAIMR, and L. KOTUĽAK

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
Prague, Czechoslovakia

The activity of the 4-alkylpyrocatechols (Ia), 3-alkylpyrocatechols (Ib), 3,5-dialkylpyrocatechols (Ic), 3,6-dialkylpyrocatechols (II), 4,5-dialkylpyrocatechols (III), 3,4,6-trialkylpyrocatechol (IV), and 4,5- and 4,6-dialkyl-2-alkoxyphenols (V and VI) was studied in isotactic polypropylene at 180 ± 0.1°C. The relative activities A_r *were correlated with substituent constants and redox potentials. In the Ia series the activity of 4-*n*-alkyl derivatives exceeded that of 4-*tert*-alkyl derivatives. The length of the main alkyl chain in Ia and Ib and the steric effects in the latter exerted a specific favorable influence. In agreement with these effects, 3-*tert*-alkyl-5-methyl derivatives are the most active compounds in Series Ic; compounds with other combinations of alkyls are weaker antioxidants as are the isomeric substances II and III or compound IV. Etherification of one hydroxyl group exerts an unfavorable effect; influences of substitution in 2-alkoxyphenols (V and VI) are generally the same as in the pyrocatechols I–III.*

To stabilize polypropylene against oxidation by atmospheric oxygen, phenolic mononuclear and polynuclear antioxidants containing one hydroxyl group on the aromatic nucleus are used successfully. Thus far the behavior of antioxidants having the structure of polyhydric phenols has not been studied extensively for stabilizing polyolefins. We have systematically observed the properties of dihydric mononuclear phenols with the structure of pyrocatechol and hydroquinone in isotactic polypropylene. Our results have led to some conclusions concerning the relationship between the structure of these antioxidants and their stabilizing efficiency.

Experimental

Polypropylene. Isotactic polypropylene for all experiments was prepared in the Research Institute for Macromolecular Chemistry in Brno. Technical data: MW = 510,000 (calculated from viscosity measurements in Tetralin), atactic fraction = 0.68%, stereoblocks = 6.75%, ash = 0.29%, Ti = 0.0172% (no compounds with Ti—Cl bonds), Al = 0.11%; free of stabilizers. The polymer was stored in an inert atmosphere in sealed ampoules at low temperature in the dark.

Method of Evaluation. We determined the activity of antioxidants in oxygen at 180°C. and in the presence of 0.05–0.1 mole of antioxidant per kg. of polypropylene (in some cases, concentrations of 0.01 and 0.025 mole/kg. were used).

Powdered polypropylene (*ca.* 2 grams) was mixed with the needed amount of antioxidant; the mixture was homogenized in an inert atmosphere with 10 ml. acetone. The solvent was carefully evaporated from the mixed slurry; the residues of solvent were removed by drying for 24 hours in inert gas and under reduced pressure. Samples of polypropylene (20 mg.) were placed in small quartz dishes and put in the heated section of the absorption apparatus (described in full in Ref. 23). The temperature in the reaction tube was maintained exactly at 180 ± 0.1°C. by a heated aluminum block, designed as a thermostat for a set of six oxidation units. Two complete sets, including all necessary equipment, calibrated burets, and electrolyzers containing a saturated solution of copper(II) sulfate were placed in a large air thermostat with a constant temperature of 35°C. Oxygen consumption was measured at atmospheric pressure either by a U-shaped volumetric tube filled with silicone oil and placed between the electrolyzer and reaction tube, or by calculating it from the automatic recorded data of the consumption of electric current in the electrolyzer. It was possible to check volume changes greater than 0.02 ± 0.01 ml.

To evaluate the activity of antioxidants, we measured the time needed for the absorption of 0.2, 0.5, 1.0, and 1.5 ml. of oxygen in 20 mg. of stabilized polypropylene at constant conditions. The values were denoted $\tau_{0.2}$, $\tau_{0.5}$, $\tau_{1.0}$, and $\tau_{1.5}$, respectively. The scattering of the values of $\tau_{0.2}$ and especially of the values of τ measured at oxygen absorption lower than 0.2 ml. O_2 per 20 mg. polypropylene was considerably greater than that of $\tau_{0.5}$. Figure 1 shows that evaluating antioxidants at $\tau_{0.2}$–$\tau_{1.5}$ values leads to the same conclusions about structural influences. It is advantageous to use more exact data. Therefore, the value of $\tau_{0.5}$ is used in the tables because it illustrates the initial phase of the reaction and it is less influenced by the apparatus error than the value of $\tau_{0.2}$.

The scattering in the measured values was affected considerably by the character of the stabilizer used, and in some cases it reached a maximum of ±10%. Each measurement was carried out at least 12 times.

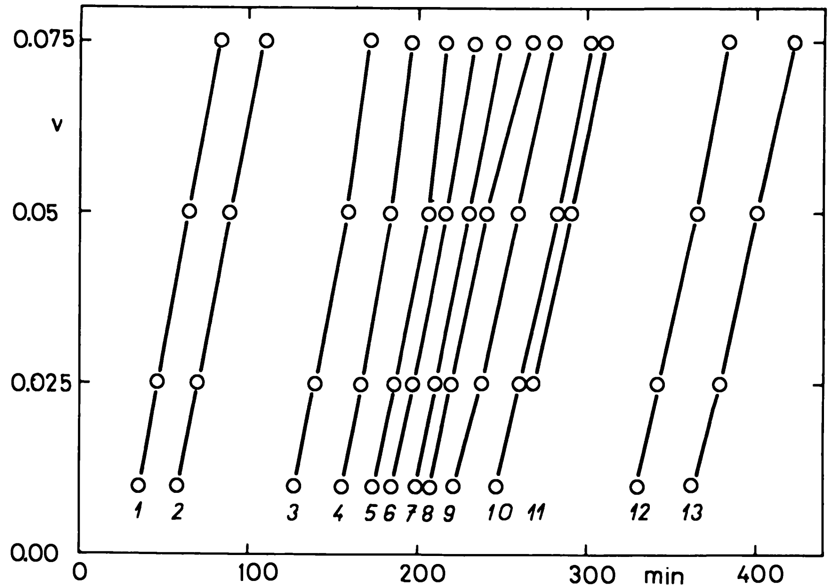


Figure 1. Dependence of the volume of oxygen absorbed in stabilized isotactic polypropylene at 180°C. (ml. O_2/mg. polypropylene) on time (min.). Concentration of antioxidants: 0.05 mole/kg. polypropylene

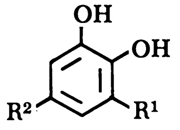
1: *Nonstabilized polypropylene*
2: *2-Ethoxy-4-methylphenol*
3: *2-Methoxy-4-methyl-5-tert-butylphenol*
4: *2-Methoxy-4-methyl-6-tert-octylphenol*
5: *4-tert-Amylpyrocatechol*
6: *3-tert-Octyl-5-tert-butylpyrotechol*
7: *3-Methyl-5-tert-butylpyrocatechol*
8: *3-Methyl-6-tert-butylpyrocatechol*
9: *Pyrocatechol*
10: *3-Methylpyrocatechol*
11: *4-Methylpyrocatechol*
12: *3-tert-Butylpyrocatechol*
13: *4-n-Amylpyrocatechol*

To evaluate the antioxidants, we used the values of relative activities A_r computed from the equation (*36*):

$$A_r = \frac{\tau_x - \tau_o}{\tau_s - \tau_o}$$

where τ is the time in minutes for the amount of fixed oxygen absorption; x is the antioxidant studied; s is the standard; o is without an antioxidant. Pyrocatechol was used as the standard for all derivatives of pyrocatechol.

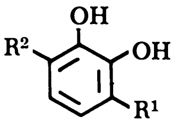
Derivatives of Pyrocatechol. To study the influences of pyrocatechol substitution, we used a series of model substances from the group of 4-alkyl derivatives (Type Ia), 3-alkyl derivatives (Type Ib), 3,5-dialkyl derivatives (Type Ic), 3,6-dialkyl derivatives (Type II), 4,5-dialkyl derivatives (Type III), and 3,4,6-trialkyl derivatives (Type IV); another group was formed by semiethers of pyrocatechol: 2-alkoxy-4,5-dialkylphenols (Type V) and 2-alkoxy-4,6-dialkylphenols (Type VI).



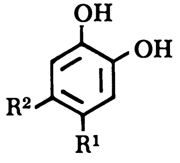
I: a: $R^1 = H, R^2 = \text{alkyl}$

b: $R^1 = \text{alkyl}, R^2 = H$

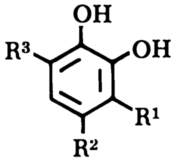
c: $R^1, R^2 = \text{alkyl}$



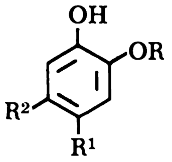
II



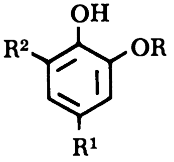
III



IV



V



VI

Model substances were prepared by the alkylation of pyrocatechol and/or its 3- and 4-alkyl derivatives using alcohols or olefins as alkylating agents. Special attention was paid to isobutylene oligomers. Mineral acids, cation exchangers, etherate of boron trifluoride, and fused zinc chloride were used as catalysts. Thus, numerous mono- and disubstituted pyrocatechols were obtained. Alkyl derivatives of 2-alkoxyphenol were synthesized by catalytic hydrogenation of isomeric hydroxyalkoxybenzaldehydes or by alkylation of 2-alkoxyphenols. Details of the reaction conditions and the properties of the compounds prepared are given in details in Refs. *27, 28, 30, 31*. The purity of the model substances was checked by paper chromatography (*33*).

Discussion

The results of our studies on the relationship of activity to the structure of pyrocatechol antioxidants are based on measurements at 180°C.—*i.e.*, close to the real processing temperature of isotactic polypropylene and advantageous in view of the exact measurement of the oxidation rate. At this temperature, the concentrations of peroxidic bodies in polypropylene and their dissociation into active radicals are relatively high; these species are potential chain initiators, and at the same time they react with the phenolic antioxidants that are typical chain-breaking inhibitors. Thus, phenols show their activity better at lower concentrations of alkylperoxy radicals or hydroperoxides—*i.e.*, at lower temperatures. Most phenolic antioxidants are therefore not suitable for stabilizing substrates heated permanently to temperatures higher than 120°–150°C.; on the other hand, they are able to stabilize materials exposed only sporadically and for a short time to high temperatures in air—*e.g.*, polyolefins.

Besides the reactions between phenols and peroxidic bodies, other factors can influence the activity of antioxidants—*e.g.*, compatibility with substrate and volatility. The results show that under the conditions used the influence of the antioxidant structure is dramatic. In this connection we note agreement of the general conclusions dealing with the influences of pyrocatechol antioxidant structure on the activity in polypropylene at 180°C. and those influences found in Tetralin (*28*) at 80°C. Despite great differences in experimental conditions, the sequences of the activities of pyrocatechol antioxidants I-VI were in agreement. Great similarities were also found within each particular group of antioxidants.

The relationship of structure to activity is discussed on the basis of measurements performed in the presence of 0.05 mole of antioxidant per kg. of polypropylene. The results obtained at lower concentrations (0.01 and 0.025 mole/kg.) showed some differences in details. On the other hand, almost identical relationships were found (*45*) in stabilizing polypropylene at higher antioxidant concentrations (0.1 mole/kg.). Analysis of those concentration relationships supports our assumption that the activity of pyrocatechol derivatives is influenced above all by reactions between the peroxidic bodies and antioxidants in the oxidation chain-breaking mechanism.

4-Alkylpyrocatechols. In the group of 4-alkyl derivatives of pyrocatechol (Ia) we studied the antioxidants substituted by methyl, ethyl, or a normal alkyl group with a longer chain and the antioxidants containing tertiary alkyl groups. Some differences in activity are worth mentioning. Figure 2 compares the values of $\tau_{0.5}$ which depend on the length of the main carbon chain of the alkyl group in position 4. The activity of derivatives having normal alkyl groups C_{2-12} as substituents increases with chain length.

4-Isopropylpyrocatechol may be included in this as well; in the system being compared the isopropyl group was considered as alkyl group C_2 substituted on the α-carbon atom. The relative activities of

4-*n*-alkyl derivatives (calculated from $\tau_{0.5}$ and referred to pyrocatechol) are shown in Table I.

Under the conditions used these compounds were the most active derivatives of pyrocatechol. High activity was found also with two derivatives having acyl groups (Table I). The decrease in the rate of oxygen absorption in isotactic polypropylene in the presence of 4-caproyl-, 4-lauroyl-, and 4-stearoylpyrocatechol compared with pyrocatechol is shown by Fic (*10*). The activity of 4-alkyl and 4-acyl derivatives of pyrocatechol found at high temperatures in polypropylene differs from the published data on the activity of 4-dodecyl- and 4-lauroylpyrocatechol in lard (*39*); compared with pyrocatechol, the relative activity decreased in the presence of the first substance by 15%, and it decreased in the presence of the second by as much as 68%. Tamura and co-workers

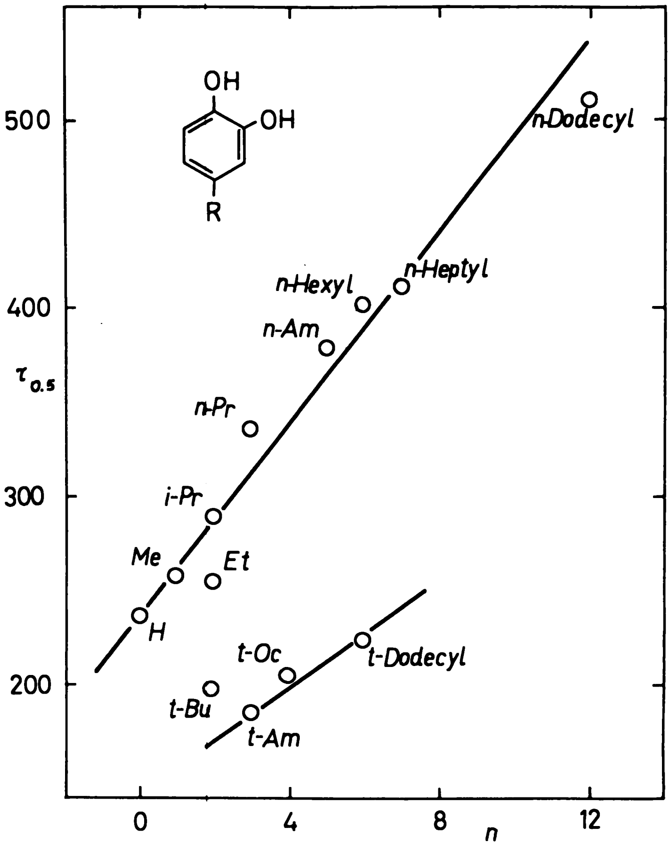
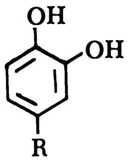


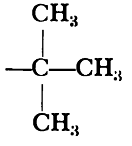
Figure 2. Time of absorption ($\tau_{0.5}$, min.) of 0.5 ml. oxygen in 20 mg. polypropylene at 180°C. vs. *the number of carbon atoms* (n) *in the main chain of 4-alkylpyrocatechols*

Table I. Relative Activities of 4-Alkylpyrocatechols (Antioxidants Ia) Calculated from $\tau_{0.5}$ (Pyrocatechol as Standard)

Antioxidant	*R*	A_r
	Ethyl	1.09
	n-Propyl	1.52
	n-Butyl	1.63
	n-Pentyl	1.74
	n-Hexyl	1.86
	n-Heptyl	1.90
	n-Dodecyl	2.42
Ia	Valeryl	1.59
	Lauroyl	2.83
	Nitro	0.99
	Chloro	0.98

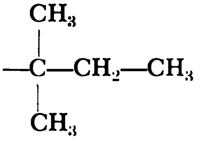
(*46, 47*) found in the same substrate that substitution of the pyrocatechol nucleus with a normal alkyl group influenced the activity favorably; the presence of acyl groups in position 4 caused a rapid decrease in activity. The results of another study (*4*) have shown also that 4-*n*-alkyl derivatives of pyrocatechol were approximately twice as effective as pyrocatechol in stabilizing solutions of carotene in mineral oil.

Activities lower than those of pyrocatechol were found with all the observed substances of Type Ia, where R^2 = *tert*-alkyl group: (a) 1,1-dimethylethyl (denoted further as *tert*-butyl), (b) 1,1-dimethylpropyl (*tert*-amyl), (c) 1,1,3,3-tetramethylbutyl (*tert*-octyl), and (d) 1,1,3,3,5,5-hexamethylhexyl (*tert*-dodecyl); the relative activities (calculated from $\tau_{0.5}$) are given in Table II.



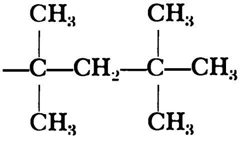
$$-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

a



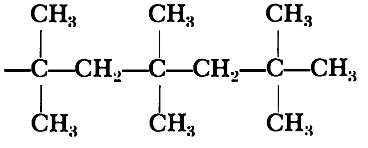
$$-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$$

b



$$-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

c

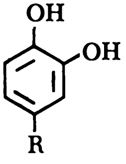
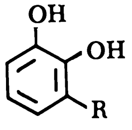


$$-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

d

All tertiary alkyl groups (a–d) are branched in the same way on the α-carbon atom and differ in the length of the carbon chain and the nature of further branching; the activity first decreases until substitution by the alkyl group with three carbon atoms in the main chain (*i.e.*, *tert*-amyl), then it increases to the *tert*-dodecyl group (C_6 chain); nevertheless, the

Table II. Relative Activities of 3- and 4-Alkylpyrocatechols (Antioxidants Ia and Ib) Calculated from $\tau_{0.5}$ (Pyrocatechol as Standard)

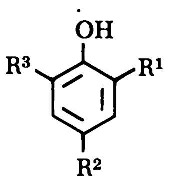
Antioxidant	*R*	A_r
 Ia	Methyl	1.15
	Isopropyl	1.27
	tert-Butyl	0.80
	tert-Amyl	0.72
	tert-Octyl	0.83
	tert-Dodecyl	0.93
 Ib	Methyl	1.12
	Isopropyl	1.40
	tert-Butyl	1.55
	tert-Octyl	1.74

activity of none of these antioxidants exceeded that of pyrocatechol (the values of A_r are in the range 0.72–0.93).

Contrary to our results, other workers (*4, 9, 20, 36*) state that in the stabilization of carotene, paraffin wax, and lard the activity of pyrocatechol is favorably affected by substitution at position 4, not only by normal but by tertiary alkyl groups as well. Disparate influences of substitution are not surprising when comparing the activity in different substrates owing to the possibility of directive influences in the process of inhibited oxidation. The participation of phenolic antioxidants in the inhibition of autoxidation can be demonstrated (*1, 2, 3*) simply as a reaction between the molecule of antioxidant AH and the alkylperoxy radical ROO˙ formed during the autoxidation of the substrate RH. During this process, an aryloxy radical (A˙) is first generated.

$$AH + ROO^{\cdot} \rightarrow A^{\cdot} + ROOH \qquad (1)$$

If this scheme is valid, the activity of an antioxidant will be affected by the relative ratio between the strength of the A—H bond in an antioxidant and the reactivity of ROO˙; further, the properties of the newly generated radical A˙ will become evident as well as its reactivity and the strength of the R—H bond of the substrate. The interaction of the antioxidant with reactive electrophilic intermediates of the autoxidation demonstrated in Reaction 1 is made easier by the substitution of the phenolic nucleus with an alkyl group. Thus, the activity of monohydric phenol is influenced by the number and nature of substituents and by the position of the substituent. In substances containing many alkyl groups the additivity principle need not hold; however, the nature of the substituents in positions ortho and para to the hydroxylic group is important. Interpreting substitution influences in monohydric phenols containing only one active center of primary attack is much easier than in the series of dihydric phenols; the application of quantitative relationships (*5, 13, 14, 15, 16*) is also easier. For comparison we followed the activity of several alkylated phenols (Type VII) under our experimental conditions, and we tried to find similarities in the influences of the character of substituents (the values A_r calculated from $\tau_{0.5}$ referred to pyrocatechol are given in Table III).

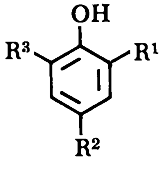


VII

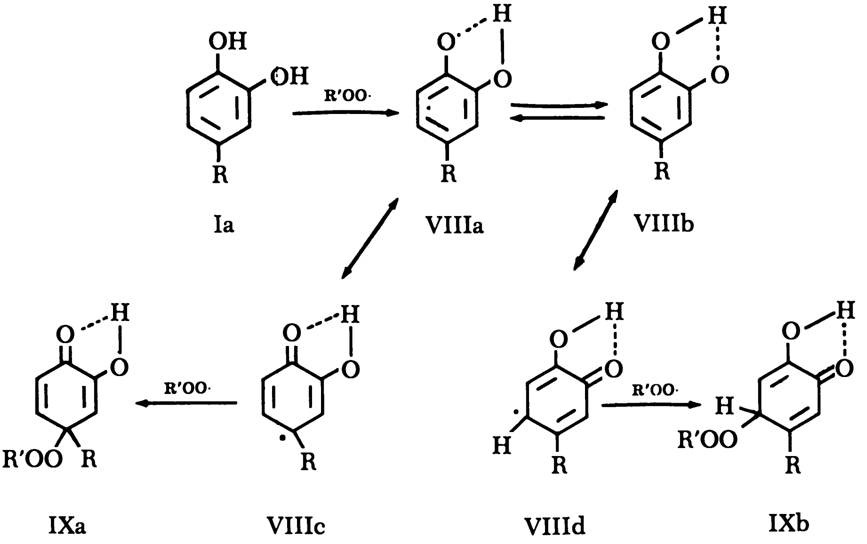
The nature of the substituent in position 4 in 2,4-dialkyl substituted derivatives does not show directly whether the presence of the methyl group is more favorable than that of the *tert*-butyl group. On the other hand, 2,4,6-trialkylphenols clearly displayed lower activity if the derivative were substituted with a tertiary alkyl group para to the hydroxylic group. A similar conclusion was reached by Ingold (*16*), when he studied the activities of phenols in another substrate—the exchange of methyl, ethyl, or butyl groups by an alkyl group with a longer or more branched chain always caused a decrease in activity. We have also found (*30*) a decrease in inhibition activity in isopropyl oleate after exchanging the methyl group in 2,6-di-*tert*-butyl-4-methylphenol for the *tert*-dodecyl group (the strong influence of the substrate is evident by comparing the same two antioxidants in lard (*30*), where, contrary to expectations, higher activity was found with the second substance).

In Type Ia antioxidants substituted by normal or tertiary alkyl groups, the reaction with active radicals formed in the autoxidized sub-

Table III. Relative Activities of Alkylphenols (Antioxidants VII) Calculated from $\tau_{0.5}$ (Pyrocatechol as Standard)

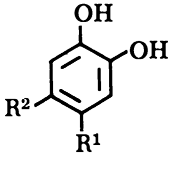
Antioxidant	R^1	R^2	R^3	A_r
	H	H	H	0.008
	tert-Butyl	H	H	0.21
	H	*tert*-Butyl	H	0.09
	tert-Butyl	Methyl	H	0.57
	tert-Butyl	*tert*-Butyl	H	0.67
	tert-Butyl	H	*tert*-Butyl	0.77
	tert-Butyl	Methyl	*tert*-Butyl	1.09
VII	*tert*-Butyl	*tert*-Butyl	*tert*-Butyl	0.60

strate may be affected in a different way. As a result of polar influences of the alkyl group, the reactivity of the hydroxyl group para to the alkyl group is increased, and after interaction with the radical R'OO˙ we may assume generation of the aryloxy radical (VIIIa), which, owing to resonance, is able to react with another radical R'OO˙ to form IVa according to the following scheme.



This second phase of the inhibition mechanism, which is proved by the isolation of a similar peroxide with quinol structure from monohydric phenols (*13*, *15*) is unfavorably affected by steric influence of the present substituent R; however, even physical factors will probably influence the activity—*e.g.*, the change in the solubility of the antioxidant in the substrate caused by substitution. The possible resonance of radical VIIIb is also illustrated in the scheme. In this case the second radical R'OO˙ may be fixed in position 5 (IXb). The reaction may be used to help

Table IV. Relative Activities of 4,5-Dialkyl Pyrocatechols (Antioxidants III) Calculated from $\tau_{0.5}$ (Pyrocatechol as Standard)

Antioxidant	R^1	R^2	A_r
 III	Methyl	H	1.15
	Methyl	*tert*-Butyl	1.12
	Methyl	*tert*-Octyl	1.05

explain the behavior of 4,5-dialkyl derivatives of pyrocatechol (Type III, Table IV). On comparing the antioxidants of Type III (R^1 = methyl, R^2 = tertiary alkyl) with 4-methylpyrocatechol, it is apparent that the occupation of position 5 by a tertiary alkyl group manifests itself by a slight decrease in activity, and this negative influence strengthens with the bulkiness of the alkyl group; thus, the Type III antioxidants are less active when compared with 4-methylpyrocatechol, whose $A_r > 1$. However, a considerable improvement caused by the presence of the methyl group is apparent in comparisons with monoalkyl derivatives, whose $A_r < 1$ (Type Ia, R = *tert*-butyl or *tert*-octyl); the explanation agrees with the influence of both alkyl groups.

The attempt to compare the measured values of relative activities of antioxidants of Type Ia with the substituent constants σ_p led to the results shown in Figure 3, which do not correspond to the expected influence of

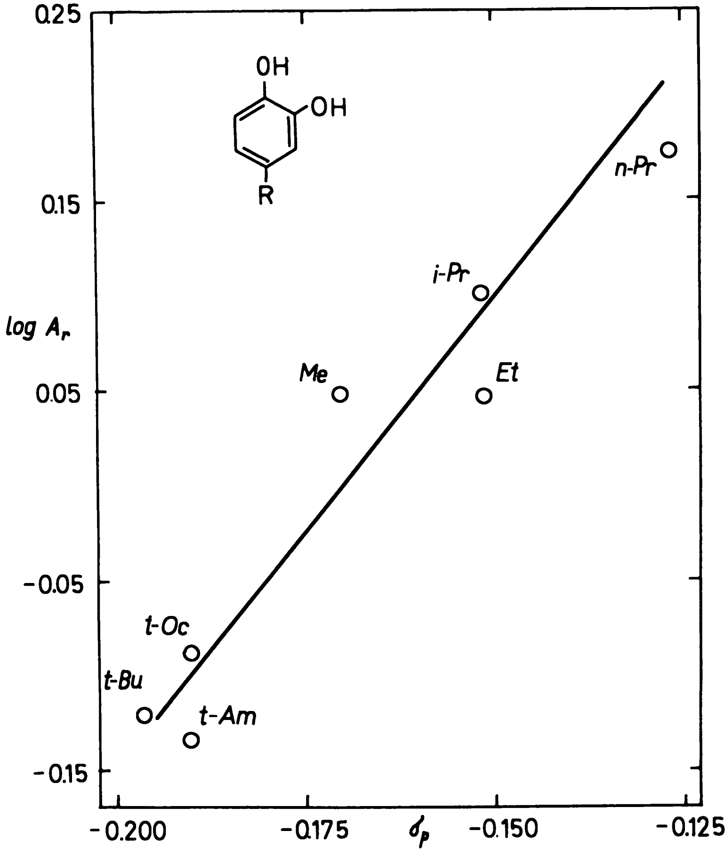


Figure 3. Logarithm of the relative activity A_r vs. *the substituent constants* σ_p *of alkyl groups for 4-alkylpyrocatechols*

the substitution by alkyls (*5, 13, 16*) during Reaction 1. Therefore, we tried to compare the relative activity with the values of half-wave potentials of the same derivatives, which were measured polarographically (*38*). These values may be regarded as characteristic for the change of free energy connected with the cleavage of the A—H bond and with the transition of the antioxidant from the reduced to oxidized form. When the A—H bond is strong, reaction with the alkylperoxy radical is difficult. On the other hand, a weak bond may result in the participation of further competitive reactions in the mechanism of the inhibitive reaction—*e.g.*, direct oxidation by oxygen, causing the deactivation of antioxidant. Great care must be taken in interpreting the results since the half-wave potentials are measured under conditions considerably different from those used to determine antioxidative activity. Other workers (*8, 30, 38*) have found a linear plot of logarithms of relative activities *vs.* redox potentials of antioxidants, which can be expected to occur by the same mechanism. If, however, greater differences can be applied in the action mechanism, the values of redox potentials are then important only for a preliminary judgment of the antioxidant activity: even then it is possible to find within the range of potential values predicted for active substances very weak antioxidants, as we ascertained, for example, when studying the activity of a series of hydroquinone derivatives in lard (*29*).

On analyzing the influence of substitution by alkyl groups in position 4, we found (*38*) that in the shift of half-wave potentials, practically only polar effects become evident. Figure 4 demonstrates the dependence of half-wave potentials and of the logarithm of relative activity of Type Ia antioxidants; this is apparent in that with substances having $A_r > 1$, whose half-wave potentials vary in a narrow range 773.5–787.5 mv., the relative activity increases with E_0. Model substances substituted by tertiary alkyl groups (Ia, R^2 = *tert*-alkyl, $R^1 = H$) have E_0 differing from one another only slightly (778.5–779.5 mv.), and the relationships are not explicit enough in this case. A comparison of these derivatives with methyl or ethyl derivatives reveals an increase in activity with a decrease in E_0. This fact also indicates a disparity of the influence of different alkyl groups on the antioxidative activity of the compounds of Type Ia.

4-Chloro- and 4-Nitropyrocatechol. In comparing the influences of the nature of substitution in position 4 we also studied polypropylene oxidation in the presence of Ia substances, where $R^2 = Cl$ or NO_2. The activity of both compounds at a concentration of 0.05 mole/kg. polypropylene is practically equal to pyrocatechol (A_r being within the range 0.96–1.03). At twice these concentrations where side reactions may be more extensive (*45*), the relative activity of 4-nitropyrocatechol decreased ($A_r = 0.70$); on the other hand the 4-chloro derivative was slightly more active ($A_r = 1.13$). The literature suggests (*20*) a similar favorable influence on introducing the chlorine atom into the para position of the hydroxyl group in 2,2′-methylenebisphenol in stabilizing paraffin wax. (The presence of halogen ortho to the hydroxyl group weakens the antioxidative potency (*21*); the present experimental material does not permit any further conclusions).

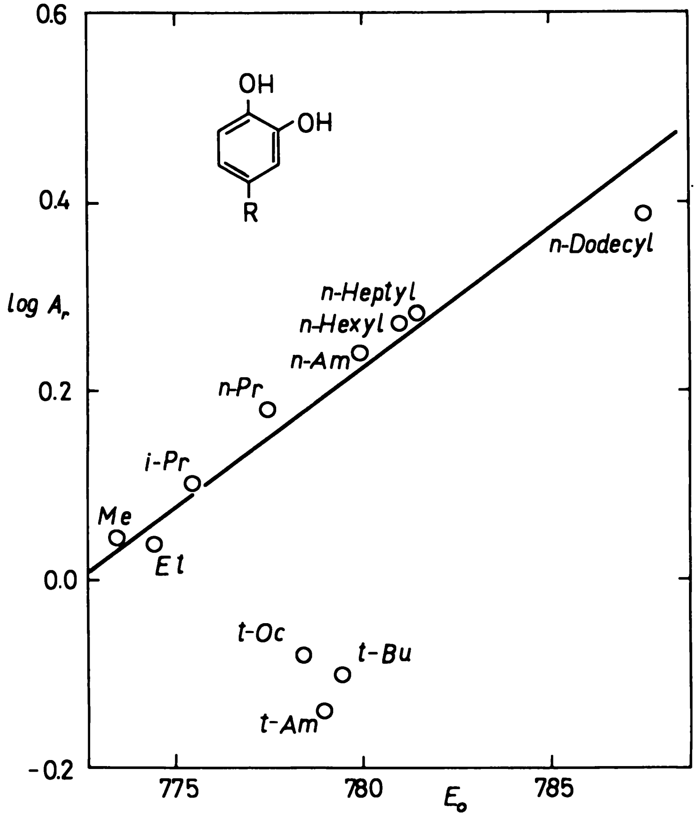


Figure 4. Logarithm of the relative activity A_r vs. *the half-wave potential* (E_0, *mv.) for 4-alkylpyrocatechols*

The behavior of the 4-nitro derivative is surprising since the antioxidative efficiency is known to be adversely affected by the presence of electronegative groups (*21*), limiting the participation of antioxidants in breaking the autoxidation chain reaction, as shown in Reaction 1.

3-Alkylpyrocatechols. In the other group of antioxidants—3-alkyl derivatives of pyrocatechol (Ib)—the course of Reaction 1 can be influenced by both polar and steric effects of an alkyl group; the former increase the reactivity with alkylperoxy radicals; the latter, however, may act unfavorably if the optimum bulkiness of the substituent is exceeded. Therefore, it is necessary to find for the given type of antioxidants an optimum ratio of both influences and to solve it with respect to the stabilized substrate. When the relative activities of monoalkyl derivatives of monohydric phenols (Type VII, Table III) in isotactic polypropylene were compared, substitution at the ortho position was more advantageous than at the para position. Further, in the series of dialkyl derivatives of monohydric phenols higher activity is displayed in glycerides of fatty acids (*19*) by antioxidants substituted in positions 2,6—*i.e.*, in both positions ortho to the hydroxylic group. On the contrary, in gasoline (*37*) 2,4-dialkylphenols were more active; this points out the different importance of substitution in both ortho and para positions in different substrates.

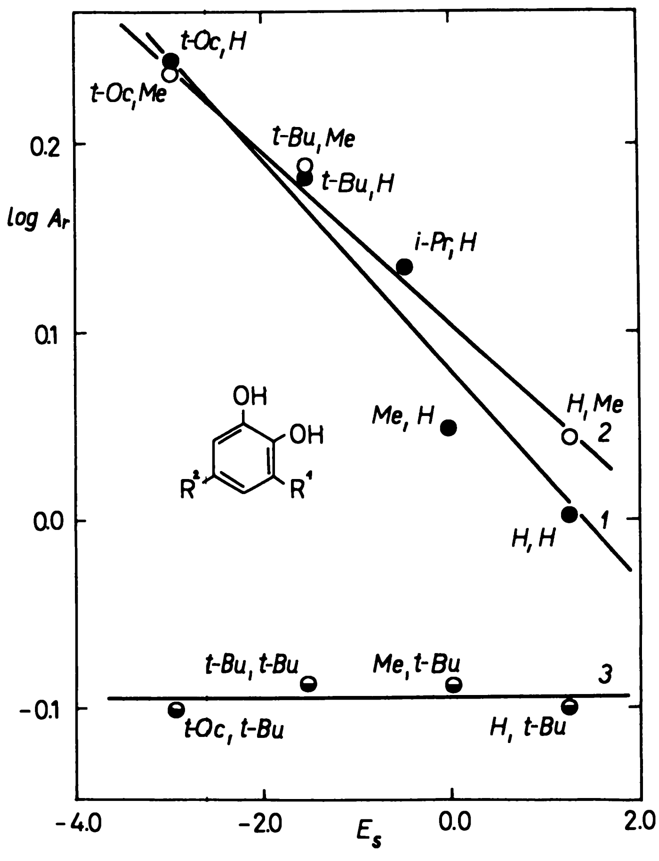


Figure 5. Logarithm of the relative activity of 3-alkylpyrocatechols (line 1) and 3,5-dialkylpyrocatechols (lines 2, 3) vs. *the substituent steric constants* E_s

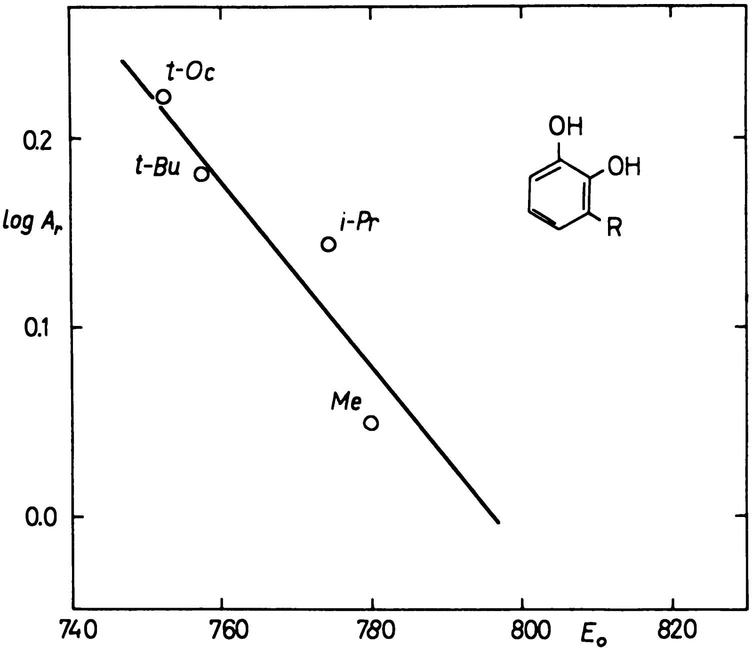


Figure 6. Logarithm of the relative activity A_r vs. *the half-wave potentials* (E_0, *mv.) for the 3-alkylpyrocatechols*

The values of the relative activities of 3-alkyl derivatives of pyrocatechol (Type Ib) are given in Table II; they are compared with analogously substituted 4-alkyl derivatives (Ia) (all A_r values are referred to pyrocatechol). The 3-alkyl derivatives are generally better antioxidants. The relative activity increases with the bulkiness of the substituent in the order: methyl < isopropyl < *tert*-butyl < *tert*-octyl. We tried to compare the relative activity with Taft's (*44*) steric substituent constants E_S. The obtained dependence characterizing the influence of the nature of the substituent is shown in Figure 5 (line 1). For constant δ the value −0.66 was computed. This indicates that differently substituted antioxidants of Group Ib take part in the inhibition of autoxidation by the same mechanism and that reaction with ROO$^\cdot$ radicals is not adversely affected by substitution by the relatively bulky *tert*-octyl group. Despite this fact, the contribution with the steric effect of the ortho substituents to the behavior of 3-alkylpyrocatechols cannot be neglected since it follows (*38*) from the results found on studying the factors influencing the shifts of half-wave potentials (E_0). The relationship of the relative activity to E_0 is demonstrated in Figure 6. The activity decreases in the potential range 753–780 mv., lying in the range usually given for active antioxidants (*6, 11, 12, 14, 18, 21, 24, 29*) with increasing half-wave potential; a similar relationship can be observed by comparing the series of 4-alkyl derivatives of pyrocatechol, substituted by methyl and tertiary alkyl groups (Figure 4) and the series of monohydric, differently substituted phenols (*6, 14*). [A completely reverse dependence was found, however, on comparing the values of relative activities and redox potentials with pyrocatechol substituted by normal alkyl groups in position 4 (Figure 5).] This points to certain analogies in influencing the mechanism of participation of the antioxidant in inhibition caused by the presence of tertiary alkyl groups despite different substitution positions.

3,5-Dialkylpyrocatechols. The influences of the nature of substients were followed further with dialkyl derivatives of pyrocatechol; at the same time some dependences that had been observed with monoalkyl derivatives were verified. Figure 5 shows that the sensitivity of influencing the antioxidative activity of 3,5-dialkyl derivatives (Type Ic; Table V) by steric effects of substituent R^1 decreases when substituent R^2 increases. Plots are shown for R^2 = methyl (line 2) and R^2 = *tert*-butyl (line 3). The mechanism of action is probably influenced by a more complicated complex of influences of both alkyl substituents.

Table V. Relative Activities of 3,5-Dialkylpyrocatechols (Antioxidants Ic) Calculated from $\tau_{0.5}$ (Pyrocatechol as Standard)

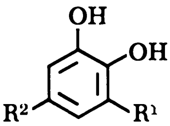
Antioxidant	R^1	R^2	A_r
 Ic	Methyl	H	1.12
		tert-Butyl	0.86
		tert-Octyl	0.68
		tert-Dodecyl	0.60
	tert-Butyl	H	1.55
		Methyl	1.54
		tert-Butyl	0.82
		tert-Octyl	0.92
	tert-Octyl	H	1.74
		Methyl	1.71
		tert-Butyl	0.78
		tert-Octyl	0.81

Table V also shows the negative influence of the increase of substituent R^2 when the substituent R^1 is a methyl group. The difference in activity in substitution by the bulkiest tertiary groups C_8 and C_{12} is no longer outstanding.

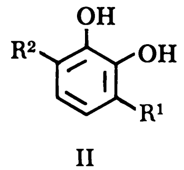
The influence of the change in character of substituent R^2 is of a somewhat different nature; if R^1 is a tertiary alkyl group (as it was with 4-*tert*-alkyl derivatives) first the activity decreases with an increase in alkyl group R^2, then the activity increases; the presence of the *tert*-octyl group was always more advantageous than the presence of the *tert*-butyl group, even though the difference is not as great as in the Ia group of antioxidants.

In general the results indicate that on comparing 3-alkyl and 3,5-dialkyl derivatives, the derivatives of the first group were more active; only the 3,5-dialkyl derivatives (Ic) where R^1 = *tert*-alkyl and R^2 = methyl were similar to the first group in properties. A change in the methyl group for the tertiary alkyl group always resulted in the deterioration of properties. This phenomenon is not commensurate with the behavior of 2,4-dialkylphenols (Type VII, Table III); it is, however, analogous to the effect of the change in substitution in position 4 in 2,4,6-trialkylphenols, and it can be explained similarly as with 4-alkylpyrocatechols by the decrease in the rate of interaction with another radical ROO.

3,6-Dialkylpyrocatechols. Unlike the favorable influence caused by substitution of one ortho position to the hydroxyl by the alkyl group, the substitution of both ortho positions (Type II) was unfavorable. Table VI shows that the relative activities of all the derivatives studied (calculated from $\tau_{0.5}$) are smaller than 1.

At the same time, a relatively weak influence arising from the nature of the substituent is evident. The most active was the derivative containing two *tert*-butyl groups. Here the optimum ratio is probably created between polar and steric effects, which participate in the interaction of antioxidants, with active radicals taking part in the propagation step of the autoxidation. Nevertheless, the activity of 3,6-di-*tert*-butylpyrocatechol again becomes lower than that of 3-*tert*-butylpyrocatechol and is only a little higher than that of 4-*tert*-butylpyrocatechol. In agreement with previous results we found that the trisubstituted derivative, 3-methyl-4,6-di-*tert*-butylpyrocatechol (Type IV; A_r 0.1 from $\tau_{0.5}$) is not suitable for polypropylene as an antioxidant. On the basis of these results it is possible to consider in the series of alkylpyrocatechols the effect of optimum steric hindrance (taking into account the polar effects of the alkyl groups acting simultaneously). This effect can be observed by carefully analyzing the substitution effects on the activities of monohydric phenolic antioxidants in various substrates (*30, 36, 43, 48*) as well as by studying the synergism (*17*).

Table VI. Relative Activities of 3,6-Dialkylpyrocatechols (Antioxidants II) Calculated from $\tau_{0.5}$ (Pyrocatechol as Standard)

Antioxidant	R^1	R^2	A_r
 II	Methyl	Methyl	0.85
		tert-Butyl	0.91
		tert-Octyl	0.75
		tert-Dodecyl	0.82
	tert-Butyl	*tert*-Butyl	0.96

The nature of substitution can influence not only the reaction between antioxidant and ROO˙ according to designation 1; but the mechanism of other reactions as well—*e.g.*, it can determine the extent of the reactivity with molecular oxygen, and it can considerably deactivate the antioxidant in the side reactions. Since the ratio of individual reactions is influenced by antioxidant concentration in the substrate, we followed the concentration effect on the change in activity of pyrocatechol, 4-*tert*-octylpyrocatechol (Ia, R^1 = H, R^2 = *tert*-octyl), and of 5-methyl-3-*tert*-octylpyrocatechol (Ic, R^1 = *tert*-octyl, R^2 = methyl) in the range 0.01–0.3 mole/kg. polypropylene. Figure 7 shows that the dependence on $\tau_{0.5}$ is not linear. Similar dependences were obtained for $\tau_{0.2}$, $\tau_{1.0}$, and $\tau_{1.5}$. Deviation from a linear plot can be explained by the increased participation of antioxidant in side reactions, which can occur at higher concentrations of the antioxidant or the aryloxy radical and lead to a significant consumption of antioxidant. Special consideration must be given to the direct oxidative change of antioxidant according to Reaction 2 or 3, where an arylperoxy radical, AOO˙, is formed; this radical is able to

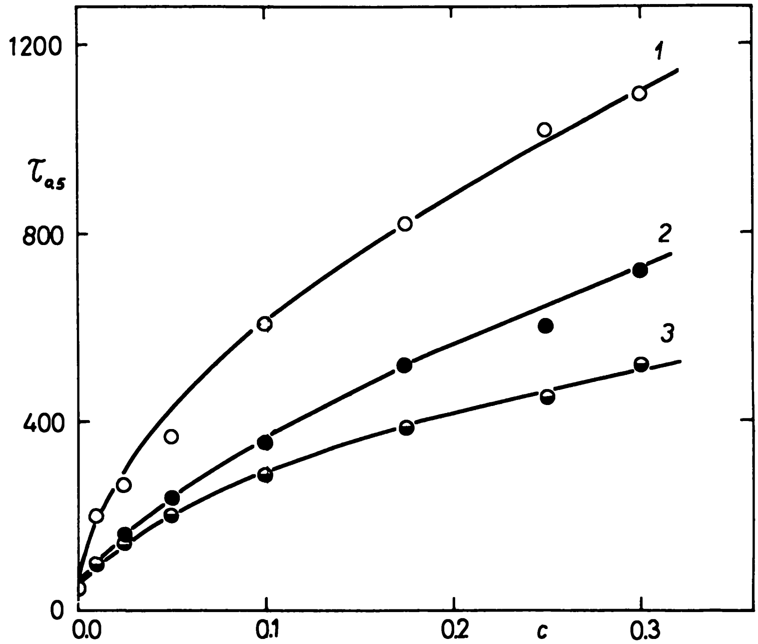


Figure 7. Time of absorption ($\tau_{0.5}$, min.) of 0.5 ml. of oxygen in 20 mg. of polypropylene at 180°C. on antioxidant concentration (c, mole/kg.)

*1: 5-Methyl-3-*tert*-octylpyrocatechol*
2: Pyrocatechol
*3: 4-*tert*-Octylpyrocatechol*

create another active radical, R$^\cdot$, from the substrate RH, as shown in Reaction 4.

$$AH + O_2 \rightarrow A^\cdot + HOO^\cdot \qquad (2)$$

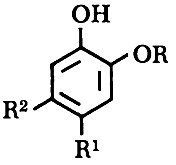
$$A^\cdot + O_2 \rightarrow AOO^\cdot \qquad (3)$$

$$AOO^\cdot + RH \rightarrow AOOH + R^\cdot \qquad (4)$$

The direct oxidation, shown by Reaction 2, is regarded by some authors (*40, 41, 42*) as an important process which initiates new chains in the autoxidation. Within the observed range of concentrations, the reaction ratio causing the deactivation of antioxidant and/or initiation was not large enough with any of the three antioxidants to cause inversion of activity. The results of this study confirm that by a suitable substitution of the pyrocatechol nucleus it is possible to influence the rate of Reaction 1 and to suppress the side reactions of the inhibitor as well.

2-Alkoxyphenols. Interesting dependences, again illustrating the influences of the nature of pyrocatechol substitution, were found on observing the properties of 2-alkoxyphenols (Types V and VI, R = methyl, ethyl, or *tert*-butyl). Ethoxy derivatives were generally more active than methoxy derivatives; however, all substances studied were always less active than the corresponding pyrocatechol derivatives. Etherification of one hydroxyl group causes a deterioration of antioxidative properties. The data are apparent from the values of relative activities calculated from $\tau_{0.5}$, given in Tables VII and VIII.

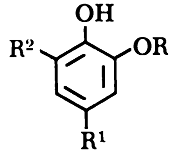
Table VII. Relative Activities of 2-Alkoxyphenols (Antioxidants V) Calculated from $\tau_{.05}$ (Pyrocatechol as Standard)

Antioxidant	*R*	*R^1*	*R^2*	A_r
 V	Methyl	H	H	0.06
	Ethyl	H	H	0.07
	Methyl	Methyl	H	0.07
	Ethyl	Methyl	H	0.14
	Methyl	Propyl	H	0.33
	Ethyl	H	Methyl	0.12
	Methyl	Methyl	*tert*-Butyl	0.48
	Ethyl	Methyl	*tert*-Butyl	0.56
	Methyl	Methyl	*tert*-Octyl	0.44
	Ethyl	Methyl	*tert*-Octyl	0.57
	Ethyl	*tert*-Butyl	Methyl	0.52
	tert-Butyl	*tert*-Octyl	H	0.36

Guaiacol (V, R = methyl, R^1, R^2 = H) as well as guaethol (V, R = ethyl, R^1, R^2 = H) are practically ineffective and resemble unsubstituted phenol. The substitution of the aromatic nucleus by a methyl group increases the activity only slightly; comparison of three isomeric *x*-methyl-2-ethoxyphenols proves that the efficiency of substitution decreases in the order: 4-methyl $>$ 5-methyl $>$ 6-methyl derivative. Guaiacol and its alkyl derivatives show very little activity even in the stabilization of lard (*36, 39*).

The activity of the antioxidants of the group 2-alkoxyphenol is increased considerably when the nucleus is substituted by two alkyl groups. The relative activities of the 4,5-dialkyl derivatives (Type V) are compared in Table VII; the A_r values are quite similar.

Table VIII. Relative Activities of 2-Alkoxyphenols (Antioxidants VI) Calculated from $\tau_{.05}$ (Pyrocatechol as Standard)

Antioxidant	*R*	*R^1*	*R^2*	A_r
 VI	Ethyl	H	Methyl	0.09
	Methyl	Methyl	*tert*-Butyl	0.56
	Ethyl	Methyl	*tert*-Butyl	0.69
	Methyl	Methyl	*tert*-Octyl	0.62
	Ethyl	Methyl	*tert*-Octyl	0.76
	Ethyl	*tert*-Butyl	Methyl	0.34
	Ethyl	*tert*-Octyl	Methyl	0.32
	tert-Butyl	*tert*-Butyl	*tert*-Butyl	0.65
	tert-Butyl	*tert*-Octyl	*tert*-Butyl	0.59

More significant is the influence of the nature of the substituents to that with 3,5-disubstituted pyrocatechols (Ic) and 2,4,6-trialkylphenols with 4,6-dialkyl derivatives (Type VI, Table VIII). The effect is similar (VII)—*i.e.*, substitution at position 4 (R^1) by a methyl group proves advantageous. Considerably lower activity was shown by model compounds of Type VI (R = ethyl), where R^2 = methyl and R^1 = *tert*-alkyl.

Stabilizing Activity of Pyrocatechols in Thermal Oxidation and in γ-Irradiation of Polypropylene. It is interesting to compare the relationships found on stabilizing isotactic polypropylene oxidized over the melting temperature with the results of our previous study (*22, 23*) of the stabilizing properties of some derivatives of pyrocatechol in γ-irradiated polypropylene.

Here the ability to suppress the formation of gel insoluble in boiling *o*-xylene was determined. The 4-alkyl derivatives (Type Ia) studied were less active than 3,5-dialkyl derivatives (Type Ic). To achieve a good stabilizing efficiency, it is necessary for substituent R^1 (in Ic) to be a *tert*-butyl group; the efficiency strongly decreases for a methyl or *tert*-octyl group. Another efficiency condition is the presence of an additional bulky group as substituent R^2; a deviation from this rule, determining the optimum character of the substitution, results in deterioration of the properties.

Observed differences in the influence of the nature of the substituent R^2 on activity during the stabilization of polypropylene against γ-irradiation and oxygen must be ascribed to differences in the mechanism of both processes; in either case, however, the influence of the nature of substituent R^1 was the same. The results obtained by studying the influences of structure in the series of pyrocatechol derivatives made it possible to focus further detailed studies of antioxidative properties on fewer substances.

Literature Cited

(1) Bickel, A. F., Kooyman, E. C., *J. Chem. Soc.* **1953**, 3211.
(2) *Ibid.*, **1956**, 2215.
(3) *Ibid.*, **1957**, 2217.
(4) Bickoff, E. M., *Am. Oil. Chemists' Soc.* **28**, 65 (1951).
(5) Bogdanov, G. N., Bolkin, A. A., *Neftechimiya* **3**, 594 (1963).
(6) Bolland, J. L., ten Have, P., *Discussions Faraday Soc.* **2**, 252 (1947).
(7) Bolland, J. L., ten Have, P., *Trans. Faraday Soc.* **43**, 201 (1947).
(8) Campbell, T. W., Coppinger, G. M., *J. Am. Chem. Soc.* **74**, 1469 (1952).
(9) Everson, C. W., Miller, G. H., Quackenbush, F. W., *J. Am. Oil Chemists' Soc.* **34**, 81 (1957).
(10) Fic, V., *Chem. Prum.* **15**, 25 (1965).
(11) Fueno, T., Ree, T., Eyring, H., *J. Phys. Chem.* **63**, 1940 (1959).
(12) Golumbic, C., *Oil Soap* **23**, 184 (1946).
(13) Hammond, G. S., Boozer, Ch. E., Hamilton, C. E., Sen, J. N., *J. Am. Chem. Soc.* **77**, 3238 (1955).
(14) Hedenburg, J. F., *Ind. Eng. Chem., Fundamentals* **2**, 265 (1963).
(15) Howard, J. A., Ingold, K. U., *Can. J. Chem.* **41**, 1744, 1851, 2800 (1963).
(16) Ingold, K. U., *J. Phys. Chem.* **64**, 1636 (1960).
(17) Knapp, Q. Q., Orloff, H. D., *Ind. Eng. Chem.* **53**, 63 (1961).
(18) Lowry, C. D., Egloff, G., Morrell, J. C., Dryer, C. G., *Ind. Eng. Chem.* **25**, 804 (1933).
(19) Miller, P. J., Quackenbush, F. W., *J. Am. Oil Chemists' Soc.* **34**, 249, 404 (1957).
(20) Morawetz, H., *Ind. Eng. Chem.* **41**, 1442 (1949).
(21) Nash, R. A., Skanen, D. M., Furdy, W. C., *J. Am. Pharm. Assoc.* **47**, 433, 436 (1958).
(22) Nechitaylo, N. A., Pospísil, J., Sanin, P. J., Polak, L. S., *Intern. Symp. Macromol. Chem., Prague, 1965.*
(23) Nechitaylo, N. A., Pospísil, J., Sanin, P. J., Polak, L. S., *Plasticheskie Massy* **1966**, 37.
(24) Penketh, G. E., *J. Appl. Chem.* **7**, 512 (1957).
(25) Pospísil, J., Ettel, V., *Collection Czech. Chem. Commun.* **22**, 1613, 1624 (1957).
(26) *Ibid.*, **24**,341, 729 (1959).
(27) Pospísil, J., Kotulak, L., *Chem. Listy* **60**, 1212 (1966).
(28) Pospísil, J., Kotulak, L., Buben, I., Patera, J., unpublished data.
(29) Pospísil, J., Pokorny, J., *Fette, Seifen, Anstrichmittel* **66**, 1043 (1964).
(30) Pospísil, J., Pokorny, J., *Intern. Fat-Congr., 8th, Budapest, 1966.*
(31) Pospísil, J., Prusíková, M., *Collection Czech. Chem. Commun.* **32**, 2371 (1967).
(32) Pospísil, J., Taimr, L., *Collection Czech. Chem. Commun.* **30**, 1092 (1965).
(33) *Ibid.*, p. 1513.
(34) *Ibid.*, **31**, 1839 (1966).
(35) Pospísil, J., Weisser, O., Landa, S., *Collection Czech. Chem. Commun.* **29**, 1387 (1964).
(36) Rosenwald, R. H., Chenicek, J. A., *J. Am. Oil Chemists' Soc.* **28**, 185 (1951).

(37) Rosenwald, R. H., Hoatson, J. R., Chenicek, J. A., *Ind. Eng. Chem.* **42,** 162 (1950).

(38) Ryba, O., Petránek, J., Pospísil, J., *Collection Czech. Chem. Commun.* **30,** 2157 (1965).

(39) Sethi, S. C., Aggarwal, J. S., Subba, Rao, *Indian J. Chem.* **1,** 435 (1963).

(40) Shelton, J. R., McDonel, E. T., Crano, J. C., *J. Polymer Sci.* **32,** 75 (1958).

(41) *Ibid.*, **42,** 289 (1960).

(42) Shlyapnikov, Yu. A., Miller, V. B., Neiman, M. B., Torsuieva, E. C., *Vysokomol. Soedin.* **4,** 1228 (1962).

(43) Spacht, R. B., Wadelin, C. E., Hollingshead, W. S., Wills, D. C., *Ind. Eng. Chem., Prod. Research Develop.* **1,** 202 (1962).

(44) Taft, R. W., "Steric Effects in Organic Chemistry," Chap. 13, Wiley, New York, 1956.

(45) Taimr, L., Ph.D. Dissertation, Prague, 1967.

(46) Tamura, S., Okuba, H., Kaneta, H., *J. Agr. Chem. Soc. Japan* **28** (1), 4 (1954).

(47) *Ibid.*, p. 24.

(48) Wasson, J. L., Smith, W. M., *Ind. Eng. Chem.* **45,** 197 (1953).

RECEIVED October 13, 1966.

Dihydric Phenols as Antioxidants in Isotactic Polypropylene

Derivatives of Hydroquinone

J. POSPISIL, L. KOTULAK, and L. TAIMR

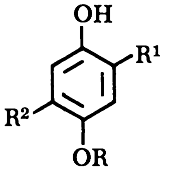
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

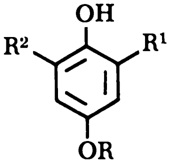
The activity of the 2-alkylhydroquinones (Ia), 2,5-dialkylhydroquinones (Ib), 2,6-dialkylhydroquinones (IIa), and of 2,5- and 2,6-dialkyl-4-alkoxyphenols (Ic and IIb) was studied in isotactic polypropylene at 180 ± 0.1°C. The values obtained were correlated with hydroquinone (A_{r1}) and pyrocatechol (A_{r2}). All compounds studied (Ia) except the tert-*octyl derivative were inferior in activity to hydroquinone. Two alkyls of Types Ib and IIa exerted further but nonadditive unfavorable effects, particularly the Ib type. Despite over-all low values of A_{r1}, a weak favorable steric effect of the* tert-*alkyls is apparent in Type Ia compounds. Etherification even as acetylation of one hydroxyl group (Ic, IIb), has a strong favorable effect. These compounds were the most active antioxidants of the entire hydroquinone series studied; nevertheless their activity did not reach that of pyrocatechol ($A_{r2} < 1$).*

Unsubstituted hydroquinone reportedly possesses antioxidative properties in various substrates. It is a common chemical and by comparison with pyrocatechol does not stain. However, it is less efficient than pyrocatechol and relatively insoluble, especially in nonpolar media—*e.g.*, the difference in efficiency is evident from the data obtained in the study dealing with the stabilization process of carotene solutions in mineral oil; the ratio (*2*) of activity of phenol, hydroquinone, and pyrocatechol is 1:8:84. A lower efficiency of hydroquinone, compared with pyrocatechol, was also found in the stabilization of fats (*5, 7*) and polyethylene (*1*). It is possible to find data which show the reverse order also (*19*). We evaluated hydroquinone derivatives in isotactic polypropylene, and the results are given here.

The preparation of polypropylene and the method of evaluation have been given (*18*). Relative activities (A_r) were determined from values of $\tau_{0.5}$ and are referred either to hydroquinone as a standard (A_{r_1}) or to pyrocatechol (A_{r_2}).

Derivatives of Hydroquinone. To study the influence of substitution on the efficiency of hydroquinone during the autoxidation of polypropylene, we synthesized several series of derivatives, differing in the nature and/or position of the substituent. Hydroquinone, various 2-alkylhydroquinones, and 4-alkoxyphenols were alkylated using alcohols or olefins as alkylation agents. A mineral acid or fused zinc chloride was used as catalyst. The reaction conditions and the properties of the compounds are given in full detail elsewhere (*14, 17*). Admixtures were carefully removed from the model substances, and their purity was checked by paper chromatography (*16*). The following derivatives were used: 2-alkylhydroquinones (Type Ia), 2,5-dialkylhydroquinones (Type Ib), 2,6-dialkylhydroquinones (Type IIa), and derivatives of 4-alkoxyphenol including 4-alkoxy-2,5-dialkylphenol (Type Ic) and 4-alkoxy-2,6-dialkylphenol (Type IIb).





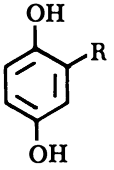
Ia: R=R^2=H; R^1=alkyl
b: R=H; R^1,R^2=alkyl
c: R,R^1,R^2=alkyl

IIa: R=H; R^1,R^2=alkyl
b: R,R^1,R^2=alkyl

Discussion

2-Alkylhydroquinones. In the group of monoalkylderivatives (Type Ia) similar effects of substitution in the 3-alkylpyrocatechols could be expected. The data in Table I show a lower stabilizing efficiency caused by substitution, and only the derivative containing a *tert*-octyl group was more active than hydroquinone. Apparently the antioxidative properties of derivatives Ia in polypropylene were favorably affected by the presence of a bulkier *tert*-alkyl group. Only a very small difference in A_r values was found in comparing the derivatives having alkyl groups C_1–C_5.

Table I. Relative Activities[a] of 2-Alkylhydroquinones (Antioxidants Ia) Calculated from $\tau_{0.5}$

Antioxidant	*R*	A_{r_1}	A_{r_2}
 Ia	H	1.00	0.29
	Methyl	0.78	0.22
	Ethyl	0.69	0.20
	tert-Butyl	0.70	0.20
	tert-Amyl	0.82	0.23
	tert-Octyl	1.13	0.32

[a] Standards: hydroquinone (A_{r_1}) and pyrocatechol (A_{r_2}).

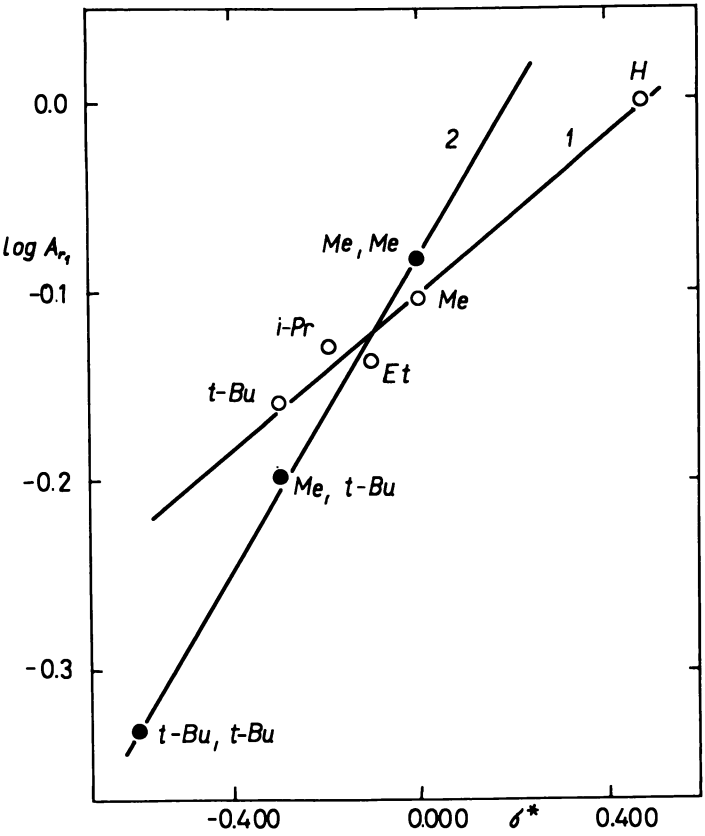


Figure 1. Log A_{r_1} *(referred to hydroquinone)* vs. *the substituent constants* σ^x

○: *2-alkylhydroquinones*
●: *2,6-dialkylhydroquinones*

The relative activities are in good agreement with the values of substituent constants σ^+ (Figure 1, line 1). For δ^+ the value of 0.186 was calculated.

A regular decrease in the half-wave potentials for the hydroquinone series is caused by the substituents in position 2; its shift bears a linear relationship to the substituent steric constants (*20*). It is apparent from the relationship of the logarithm of relative activity to the half-wave potentials E_0 (Figures 2 and 3) that the relationship in the entire series of the derivatives is not linear. The activity declines with the half-wave potentials in comparison with hydroquinone and derivatives substituted by methyl, ethyl, and isopropyl groups; with derivatives substituted by tertiary alkyl groups, however, a reverse relationship was found, as was the case for pyrocatechol (Figure 3). The results suggest that the relationships among the values to be compared are not simple; the obtained dependences are characteristic of the conditions used and of the nature of the substrate studied. Despite the fact that the redox potentials are in the range of values given for efficient antioxidants (*3, 4, 5, 6, 7, 8, 9, 10, 11, 13, 15*), all the substances studied are very poor antioxidants compared with pyrocatechol.

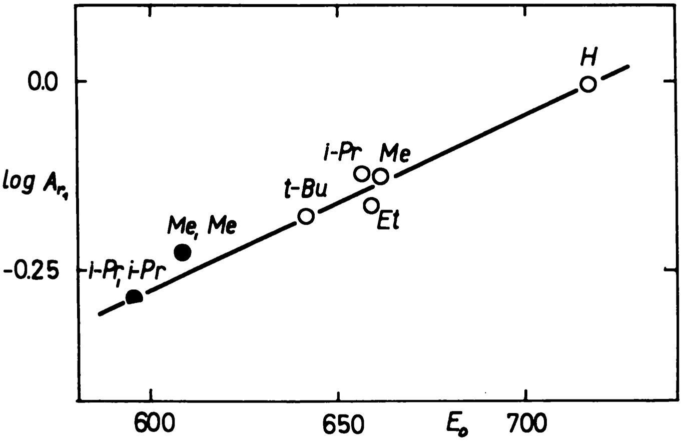


Figure 2. Log A_{r_1} *(referred to hydroquinone)* vs. *half-wave potentials* (E_0, *mv.)*

O: *2-alkylhydroquinones*
●: *2,5-dialkylhydroquinones*

2,5-Dialkylhydroquinones. Some results of this study can be compared with the behavior of dialkyl derivatives of hydroquinone. The relative activities of 2,5-dialkylhydroquinones (Ib, Table II) are very low. The adverse influence of alkylation increased, which was evident

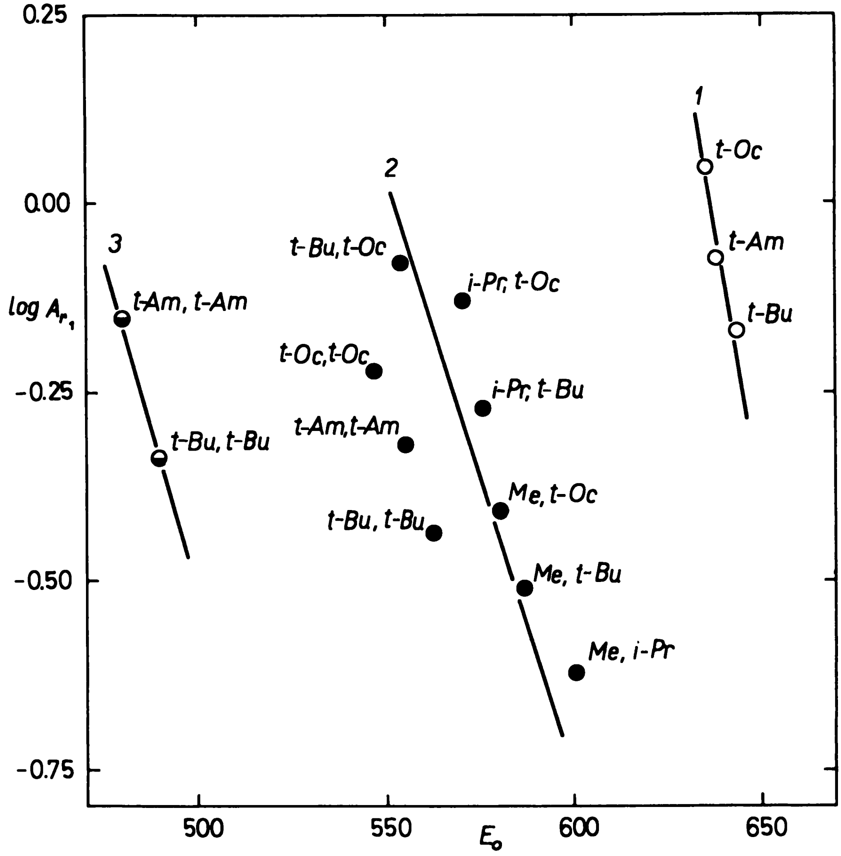
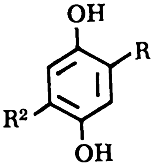


Figure 3. Log A_{r1} *(referred to hydroquinone)* vs. E_0 *(mv.)*

○: *2-alkylhydroquinones*
●: *2,5-dialkylhydroquinones*
○: *2,6-dialkylhydroquinones*

already with 2-alkylhydroquinones, but the contribution of the second alkyl group was not additive; generally the over-all decrease in the efficiency of inhibiting autoxidation is greater than the sum of the contribution of both groups. As shown in Figure 4, the influence of the nature of substituents in 2-alkylhydroquinones (Ia) and symmetrically substituted 2,5-dialkylhydroquinones is the same, and in both cases the minimum efficiency was found in the presence of derivatives substituted with isopropyl or tertiary alkyl groups. In accordance with this fact we also found that the logarithm of relative activity changes with the same dependence on redox potentials as it did with 2-alkyl derivatives; even in this case a different relationship holds for derivatives substituted by methyl or isopropyl groups (Figure 3) and for tertiary alkyl derivatives

Table II. Relative Activities[a] of 2,5-Dialkylhydroquinones (Antioxidants Ib) Calculated from $\tau_{0.5}$

Antioxidant	*R^1*	*R^2*	A_{r1}	A_{r2}
 Ib	Methyl	Methyl	0.60	0.17
	Methyl	*i*-Propyl	0.24	0.07
	Methyl	*tert*-Butyl	0.31	0.09
	Methyl	*tert*-Octyl	0.41	0.12
	i-Propyl	*i*-Propyl	0.52	0.15
	i-Propyl	*tert*-Butyl	0.58	0.17
	i-Propyl	*tert*-Octyl	0.81	0.23
	tert-Butyl	*tert*-Butyl	0.32	0.09
	tert-Butyl	*tert*-Octyl	0.81	0.23
	tert-Amyl	*tert*-Amyl	0.49	0.14
	tert-Octyl	*tert*-Octyl	0.59	0.17

[a] For standards *see* Table I.

(Figure 3). As an estimate of the additive contribution of both substituents, the most active antioxidants of this group should be 2,5-di-*tert*-octylhydroquinone. However, this is not the case, probably for steric reasons. The highest activity ($A_{r1} = 0.81$) was found with 2-isopropyl-5-*tert*-octylhydroquinone and 2-*tert*-butyl-5-*tert*-octylhydroquinone.

All the derivatives, having one substituent as a methyl group, showed very low efficiency. The poor stabilizing properties of 2,5-dialkylhydroquinones, which are easily prepared, were also observed in the study of the inhibition process in other substrates; thus it must be a question of a general phenomenon. The relative activity of the entire series of 2,5-dialkyl derivatives used as antioxidants in lard (*15*) did not exceed 0.85 (referred to hydroquinone) at a concentration of 0.05 wt. %. At the same time similar influences of substitution were observed as those during the stabilization of polypropylene. Under the same conditions the A_r values of all 2-alkylhydroquinones substituted by tertiary alkyl groups were higher than 1; the 2-methyl and 2-ethyl derivatives were slightly weaker antioxidants than hydroquinone. A lower efficiency of individual 2,5-dialkyl derivatives compared with hydroquinone is also reported by other workers (*2, 5, 19*). Isolated data on high activity of 2,5-di-*tert*-alkylhydroquinone are reported by Thompson (*21*) in the stabilization of alfalfa meal.

2,6-Dialkylhydroquinones. The second group of disubstituted derivatives—2,6-dialkylhydroquinones (IIa)—contains two hydroxyl groups which are influenced quite differently by substitution. The total activity of these antioxidants (Table III) was always slightly higher than the sum of the contributions of both substituents; this accounts for the fact that Type IIa substances were stronger antioxidants in polypropylene than the 2,5-dialkyl derivatives (a reverse relationship in activities was shown when tested as antioxidants in lard at 75°C. (*15*)). A common feature shared with 2,5-dialkyl derivatives is the similar relationship of the logarithm of relative activity and half-wave potential for derivatives substituted by two tertiary alkyl groups (Figure 3). If one of the substituents R¹ and R² is a methyl group, the relative activity decreases

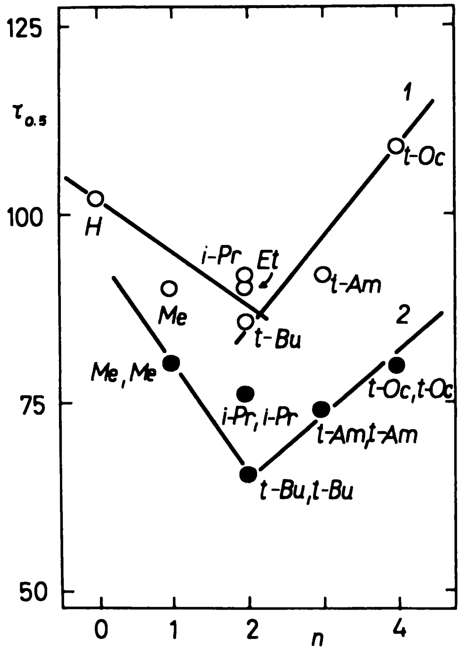
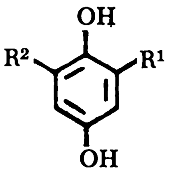


Figure 4. Time of absorption ($\tau_{0.5}$, min.) of 0.5 ml. oxygen in 20 mg. polypropylene at 180°C. on the number of carbon atoms (n) in the main chain

○: *2-alkylhydroquinones*
●: *2,5-dialkylhydroquinones*

Table III. Relative Activities[a] of 2,6-Dialkylhydroquinones (Antioxidants IIa) Calculated from $\tau_{0.5}$

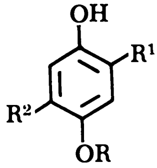
Antioxidant	*R¹*	*R²*	A_{r1}	A_{r2}
 IIa	Methyl	Methyl	0.82	0.23
	Methyl	*tert*-Butyl	0.65	0.18
	tert-Butyl	*tert*-Butyl	0.44	0.13
	tert-Amyl	*tert*-Amyl	0.77	0.22

[a] For standards *see* Table I.

with a decreasing redox potential. In contrast to 2,5-dialkylhydroquinones, a linear relationship of log (A_r) and the sum of substituent constants σ^x holds true; for this case the calculated value of δ^x was 0.42 (Figure 1, line 2).

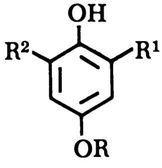
4-Alkoxyphenols. A molecule of hydroquinone contains two active centers—hydroxyl groups—capable of reacting with alkylperoxy radicals to break the radical autoxidation chain reaction. Complete etherification of both hydroxylic groups destroys the antioxidative activity (*10, 19*). For example, 1,4-dimethoxybenzene was practically inactive in polypropylene (A_{r_1} for $\tau_{0.5}$ = 0.006). Isolated reverse data are reported by Baum and Perun (*1*), who found that the efficiency of 1,4-dimethoxybenzene in the stabilization of polyethylene at 110° and 170°C. is similar to that of hydroquinone. (They measured the formation of carbonyl groups by a spectral method.) The final influence of the partial etherification depends on the structure of dihydric phenol; 2-alkoxyphenol derivatives were generally less active than the corresponding pyrocatechol derivatives. On the other hand, the efficiency of all the 4-alkoxyphenols (Ic and IIb) tested (Tables IV and V) exceeded that of hydroquinones, compared with model substance having the same substituent. Etherification exerts a good influence with 4-methoxyphenol and 4-*tert*-butoxy-

Table IV. Relative Activities[a] of 4-Alkoxy- and 4-Acetoxyphenols (Antioxidants Ic) Calculated from $\tau_{0.5}$

Antioxidant	*R*	*R^1*	*R^2*	A_{r_1}	A_{r_2}
	Methyl	H	H	1.24	0.35
	Methyl	*tert*-Butyl	H	3.38	0.97
	tert-Butyl	H	H	1.72	0.49
	tert-Butyl	*tert*-Butyl	H	2.30	0.66
	tert-Butyl	Methyl	Methyl	1.30	0.37
	Acetyl	*tert*-Octyl	H	2.80	0.80
Ic	Acetyl	*tert*-Octyl	*tert*-Octyl	1.24	0.36

[a] For standards *see* Table I.

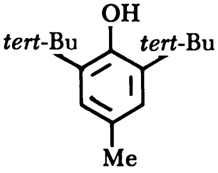
Table V. Relative Activities[a] of 4-Alkoxyphenols (Antioxidants IIb) Calculated from $\tau_{0.5}$

Antioxidant	*R*	*R^1*	*R^2*	A_{r_1}	A_{r_2}
	Methyl	*tert*-Butyl	*tert*-Butyl	2.60	0.74
	tert-Butyl	Methyl	Methyl	1.27	0.36
	tert-Butyl	*tert*-Butyl	*tert*-Butyl	0.56	0.16
IIb					

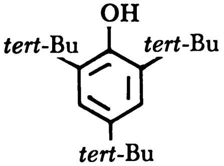
[a] For standards *see* Table I.

phenol. An increase in efficiency is also caused by the presence of one alkyl group on the aromatic nucleus (Table IV); the derivative containing the *tert*-butoxy group (Ic, R=R^1=*tert*-butyl, R^2=H) was a weaker antioxidant than the analogous methoxy derivative (Ic, R=methyl, R^1=*tert*-butyl, R^2=H); of all the hydroquinone derivatives, this substance was the closest in activity to pyrocatechol. 2-Alkyl derivatives of 4-alkoxyphenol are also excellent fat stabilizers (*15*, *19*), especially butylated hydroxyanisole.

Contrary to monoalkyl derivatives, the presence of two alkyl groups in positions 2 and 5 (Type Ic) and 2 and 6 (Type IIb) lowered the efficiency of 4-alkoxyphenols. Similar influences of substitution can be shown when comparing the activities of 4-acetoxy-2-*tert*-octylphenol and 4-acetoxy-2,5-di-*tert*-octylphenol (Table IV). The change in the nature of alkyl groups influences the activity of Type IIb antioxidants in a manner similar to that of 2,4,6-trialkylphenols; the antioxidative efficiency decreased in the latter group, introducing a bulkier alkyl group into position 4, when the substituents in the positions 2 and 6 remained the same (the values of relative activities are referred to hydroquinone).

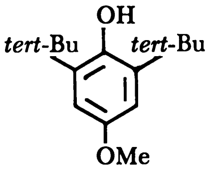


3.80

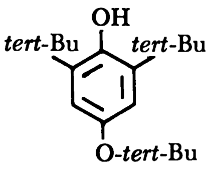


2.09

The bulkier alkyl group in the alkoxy group exhibits a similar decrease.

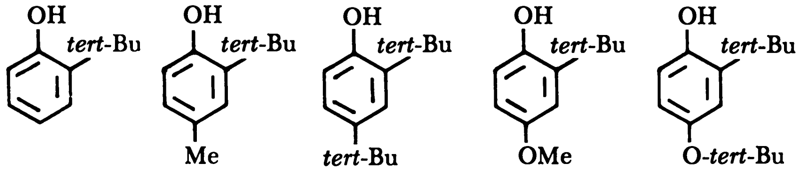


2.60



0.56

At the same time, there is little advantage in having the alkoxy group in position 4 of 2,6-di-*tert*-butylphenol, as shown on comparison with the compound substituted in the same position by the methyl group and with 2,6-di-*tert*-butylphenol itself, a compound with a free position 4 (A_{r1} = 2.69). Different influences of the nature of the substituent in position 4 can be shown in 2-*tert*-butylphenols; it seems that in the mechanism one free ortho position also plays a part.



0.72 1.98 2.34 3.38 2.30

In this case, not only was 2,4-di-*tert*-butylphenol more active than 2-*tert*-butyl-4-methylphenol, but contrary to the 2,4,6-trisubstituted model compounds, a greater efficiency was achieved after exchanging the methyl

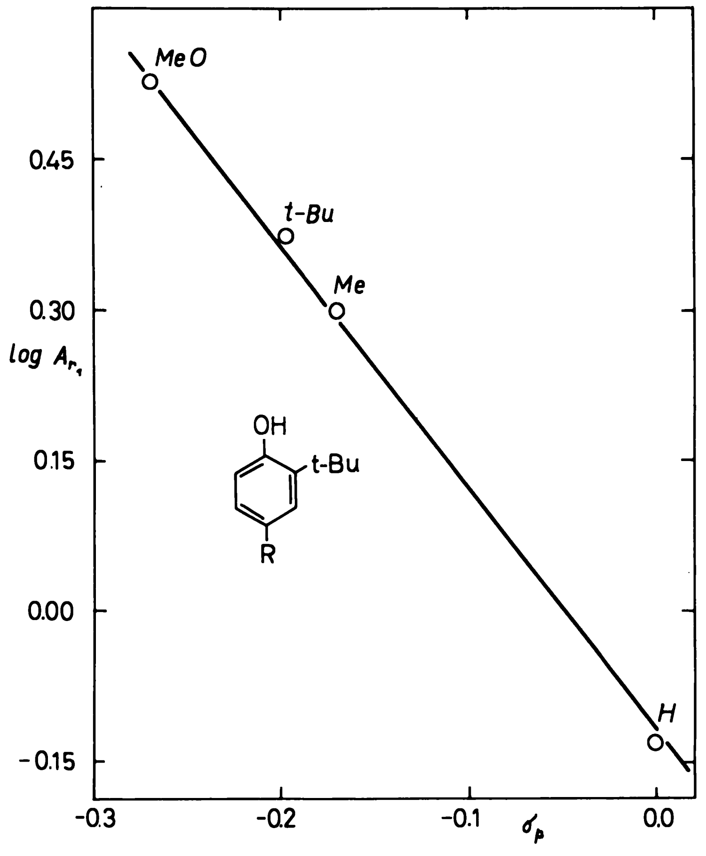


Figure 5. Logarithm A_{r1} *(referred to hydroquinone)* vs. *the substituent constants* σ_p *of 2-*tert*-butyl-4-alkyl(or alkoxy)phenol*

group for the methoxy group. In the series of antioxidants under discussion, a linear plot was found between the logarithm of the relative activity and the substituent constants σ_p (Figure 5).

The activities of all compounds from the hydroquinone series studied as antioxidants in isotactic polypropylene were lower than that of pyrocatechol. A similar conclusion was reached even when comparing both groups of substances as stabilizers in γ-irradiated isotactic polypropylene (*12*); the introduction of one alkyl group improved the efficiency of hydroquinone, the presence of bulkier groups was more favorable, and the activity of the 2,5-dialkyl derivatives was low.

Literature Cited

(1) Baum, B., Perun, A. L., *SPE (Soc. Plastics Engrs.) Trans.* **2,** 250 (1962).
(2) Bickoff, E. M., *J. Am. Oil Chemists' Soc.* **28,** 65 (1951).
(3) Bolland, J. L., ten Have, P., *Discussions Faraday Soc.* **1947,** 252.
(4) Bolland, J. L., ten Have, P., *Trans. Faraday Soc.* **43,** 201 (1947).
(5) Everson, C. W., Miller, G. H., Quackenbush, F. W., *J. Am. Oil Chemists' Soc.* **34,** 81 (1957).
(6) Fueno, T., Ree, T., Eyring, H., *J. Phys. Chem.* **63,** 1940 (1959).
(7) Golumbic, C., *Oil Soap* **23,** 184 (1946).
(8) Hedenburg, J. F., *Ind. Eng. Chem., Fundamentals* **2,** 265 (1963).
(9) Lowry, C. D., Egloff, G., Morrell, J. C., Dryer, C. G., *Ind. Eng. Chem.* **25,** 804 (1933).
(10) Miller, P. J., Quackenbush, F. W., *J. Am. Oil Chemists' Soc.* **34,** 249, 404 (1957).
(11) Nash, R. A., Skanen, D. M., Furdy, W. C., *J. Am. Pharm. Assoc.* **47,** 433, 436 (1958).
(12) Nechitaylo, N. A., Pospísil, J., Sanin, P. J., Polar, L. J., *Plasticheskie Massy* **1966,** 37.
(13) Penketh, G. E., *J. Appl. Chem.* **7,** 512 (1957).
(14) Pospísil, J., Petránek, J., Taimr, L., *Collection Czech. Chem. Commun.* **31,** 98 (1966).
(15) Pospísil, J., Pokorny, J., *Fette, Seifen, Anstrichmittel* **66,** 1043 (1964).
(16) Pospísil, J., Taimr, L., *Collection Czech. Chem. Commun.* **29,** 374 (1964).
(17) *Ibid.*, p. 381.
(18) Pospísil, J., Taimr, L., Kotulak, L., ADVAN. CHEM. SER. **85,** 169 (1968).
(19) Rosenwald, R. H., Chenicek, J. A., *J. Am. Oil Chemists' Soc.* **28,** 185 (1951).
(20) Ryba, O., Petránek, J., Pospísil, J., *Collection Czech. Chem. Commun.* **30,** 843 (1965).
(21) Thompson, C. R., *Ind. Eng. Chem.* **42,** 922 (1950).

RECEIVED October 12, 1966.

15

New Phenolic Phosphite Stabilizers for Polypropylene

P. A. DE PAOLO and H. P. SMITH

Uniroyal Chemical, Naugatuck, Conn. 06770

New phenolic phosphites prepared from dihydric phenols and phosphorus halides prevent degradation of polypropylene by heat, oxidation, processing, and ultraviolet radiation. These products are active and synergistic with dithiopropionate esters. They seem to function as both free radical scavengers and peroxide decomposers.

Polypropylene is a versatile and widely used thermoplastic. By 1970, sales volume in the United States should be over one billion pounds, compared with sales of approximately 500 million pounds for 1967, and polypropylene should be well on its way to joining polyethylene, polystyrene, and poly(vinyl chloride) as a commodity resin.

Of prime importance to the continued growth of polypropylene are the stabilizer systems which must be used to protect the resin during processing, and during exposure of finished products to various environmental and use conditions. The weak tertiary carbon—hydrogen bonds in polypropylene make it particularly susceptible to degradation caused by heat, oxidation, process shearing, and ultraviolet radiation (*24*).

The oxidative degradation of polypropylene presents more of a problem than that of polyethylene (*22*). Many antioxidants which give excellent protection to polyethylene at concentrations of 0.1% or less are either ineffective when used in polypropylene or must be present in concentrations greater than 0.5% to provide any significant degree of protection. Therefore, potent chemical antioxidants and stabilizers must be used to allow full benefit of the outstanding properties of polypropylene, which include high tensile strength, ease in processing, unlimited flexibility in hinge designs, greater rigidity than high density polyethylene, excellent dielectric properties, low creep, low density, and smooth surfaces of molded parts which resist attack of most chemicals.

In many polypropylene formulations three or more additives must be used to produce a resin with the desired stability. A wide variety of antioxidants and other stabilizers are available for this purpose. The choice of antioxidant for a given application is determined by compatibility, stabilizing efficiency, color, odor, toxicity, and cost (*15*).

The necessity of multicomponent stabilizer systems in polypropylene introduces problems for resin manufacturers. Since there is no single antioxidant that will sufficiently stabilize the resin against all environmental conditions, producers must determine optimum concentrations to use for each additive in multicomponent systems, suitable methods for incorporating the additives—a special problem if both liquid and solid stabilizers are required—testing procedures to use in evaluating each additive and combinations of additives, mutual effects, if any, of the additives on each other, and finally, but still important, the costs of formulating different grades of resin with different combinations of additives.

A simplification of stabilizer systems for polypropylene would be desirable. The ideal situation, of course, would be to have one inexpensive additive which could protect polypropylene to such a degree that a single resin could be used across the board, regardless of processing conditions or final application. This does not seem likely, however, because of the complexity of polypropylene degradation mechanisms which take place under various exposure conditions.

Four main types of antioxidants are commonly used in polypropylene stabilizer systems although many other types of chemical compounds have been suggested. These types include hindered phenolics, thiodipropionate esters, aryl phosphites, and ultraviolet absorbers such as the hydroxybenzophenones and benzotriazoles. Other chemicals which have been reported include aromatic amines such as *p*-phenylenediamine, hydrocarbon borates, aminophenols, Zn and other metal dithiocarbamates, thiophosphates, and thiophosphites, mercaptals, chromium salt complexes, tin-sulfur compounds, triazoles, silicone polymers, carbon black, nickel phenolates, thiurams, oxamides, metal stearates, Cu, Zn, Cd, and Pb salts of benzimidazoles, succinic acid anhydride, and others. The polymeric phenolic phosphites described here are another type.

The hindered phenolics are primary antioxidants and are normally used in conjunction with the thiodipropionate esters. These combinations are synergistic. They are of only limited value as heat stabilizers when used alone; the thiodipropionate esters are secondary antioxidants, also of only limited value when used alone.

The aryl phosphites also are secondary antioxidants and protect against process shearing. These chemicals have little value against high temperature oxidation and are normally used with other antioxidants. They may also prevent discoloration arising from actinic radiation.

Ultraviolet absorbers are added to polypropylene resins which are used where exposure to sunlight is high. These chemicals are essentially ineffective as heat or processing stabilizers.

Here we discuss a new class of polypropylene stabilizers—the polymeric phenolic phosphites. These compounds exhibit unique, broad-spectrum activity which may allow simplification of polypropylene stabilizer systems. The most active species are synergistic with thiodipropionate esters, are effective processing stabilizers when used alone or with other compounds, and contribute to photostability. Compounds of this type appear to function as both free radical scavengers and peroxide decomposers, and through a mechanism not yet completely understood, allow significant reductions in the concentration of ultraviolet absorbers required to achieve high levels of photostability.

Degradation of Polypropylene

Polypropylene contains many tertiary carbon atoms (one out of three), each of which constitutes a weak spot open to chemical attack. This configuration leads to a high sensitivity to oxidation and molecular breakdown, two main causes of which are elevated temperatures and ultraviolet light. Molecular breakdown can also occur during processing of the polymer in the molten state. Melt viscosity drops sharply during extrusion and injection molding operations, and the molded product has low impact strength (*20*).

The significance of such degradation is realized when one considers that any reaction which randomly breaks one carbon—carbon bond per thousand bonds in the polymer would reduce the average molecular weight by one-half (*23*). This effect would be observable in properties such as melt viscosity, tensile strength, and bulk modulus.

Degradation Mechanisms. The general scheme for polypropylene degradation involves a free radical chain mechanism which can result in both chain scission and degenerate branching (*16*). Initiation of the chain mechanism occurs most probably when heat, ultraviolet light, or other energy sources produce free radicals in the polypropylene structure by breaking a weak tertiary carbon—hydrogen bond. The resulting radical can then combine with oxygen in propagation reactions, and the autoxidation chain sequence will follow. The generally accepted scheme (*5*, *8*, *17*) for the chain sequence of degradation is presented below.

Autoxidation Sequence

$$\text{Initiation} \qquad RH \xrightarrow[\text{light}]{\text{heat}} R^{\cdot} \tag{1}$$

Propagation $R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$ (2)

$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$ (3)

$ROOH \rightarrow RO^{\cdot} + {}^{\cdot}OH$ (4)

$2\ ROOH \rightarrow RO^{\cdot} + ROO^{\cdot} + H_2O$ (5)

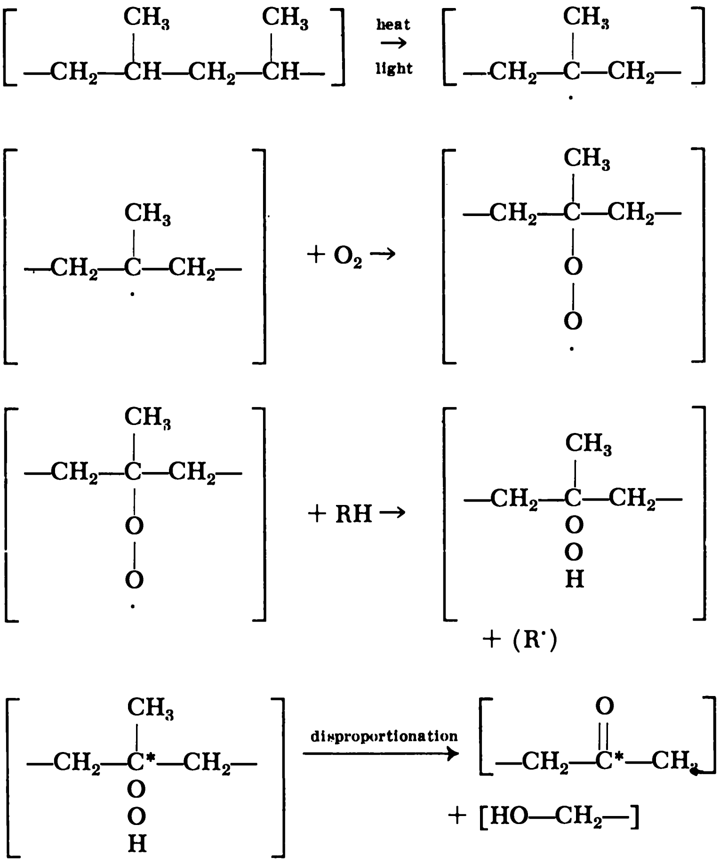
Termination $RO^{\cdot} + ROO^{\cdot} + ROOH \rightarrow$ radicals and molecules (6)

$RO^{\cdot} + ROO^{\cdot} + RH \rightarrow$ radicals, ethers, alcohols (7)

$R^{\cdot} + R^{\cdot} \rightarrow$ crosslinked molecules (8)

Chain Scission

Actual cleavage of the polymer molecules, or chain scission, results from disproportionation reactions involving hydroperoxides in the polymer structure. The mechanisms are presented below.



$$\left[-CH_2-\overset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-\right] \xrightarrow[\text{light}]{\text{heat}} \left[-CH_2-\underset{\bullet}{\overset{CH_3}{C}}-CH_2-\right] \quad (1)$$

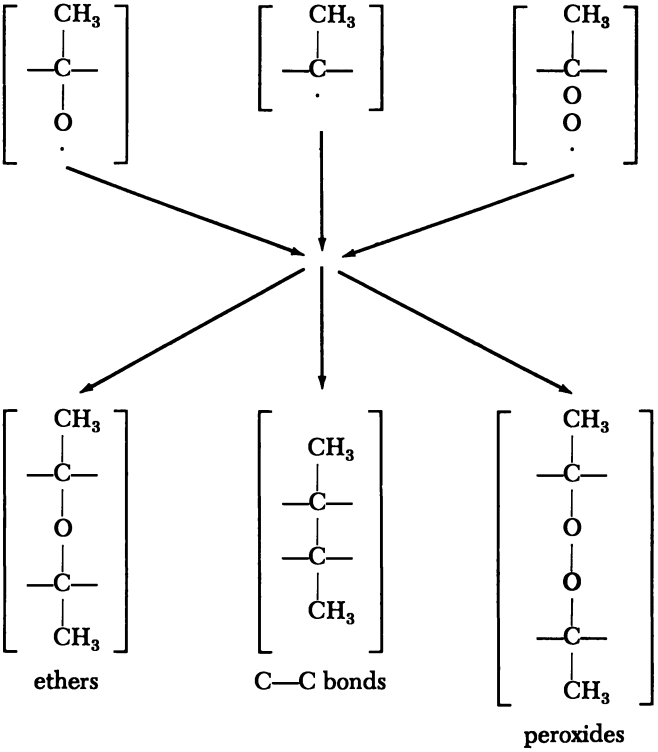
$$\left[-CH_2-\underset{\bullet}{\overset{CH_3}{C}}-CH_2-\right] + O_2 \rightarrow \left[-CH_2-\underset{\substack{| \\ O \\ | \\ O \\ \bullet}}{\overset{CH_3}{C}}-CH_2-\right] \quad (2)$$

$$\left[-CH_2-\underset{\substack{| \\ O \\ | \\ O \\ \bullet}}{\overset{CH_3}{C}}-CH_2-\right] + RH \rightarrow \left[-CH_2-\underset{\substack{O \\ O \\ H}}{\overset{CH_3}{C}}-CH_2-\right] + (R^{\cdot}) \quad (3)$$

$$\left[-CH_2-\underset{\substack{O \\ O \\ H}}{\overset{CH_3}{C^*}}-CH_2-\right] \xrightarrow{\text{disproportionation}} \left[-CH_2-\overset{O}{\overset{\|}{C^*}}-CH_3\right] + [HO-CH_2-] \quad (4)$$

Chain Branching

Degenerate chain branching may occur between various radicals produced in the autoxidation sequence, and involves bi-radical termination reactions.



The free radicals produced initially by heat, light, or mechanical working react rapidly with oxygen to produce the very reactive peroxy radicals ROO˙. Through the mechanisms shown, the peroxy radicals in turn propagate the chain by reacting with another hydrocarbon molecule, extracting hydrogen and producing a new free radical and a hydroperoxide ROOH (8). The peroxide molecules are capable of decomposing unimolecularly (Reaction 4 in the autoxidation sequence), or bimolecularly (Reaction 5) to produce more free radicals.

Stabilization of Polypropylene

A point of direct concern when using a polymer is: what are its aging characteristics? Generally, these embrace any changes in properties that occur with time and are influenced by environmental conditions. The relative importance of these properties may differ according to the application for which the polymer is intended (25). Therefore, mechanical properties, appearance, electrical properties, and barrier properties all may be important, either individually or in combination with other properties.

Mechanisms of Degradation Inhibitors. The degradation mechanisms described above have no little effect on end-use stability and processing stability of polypropylene. Indeed, without stabilizers and antioxidants to inhibit such degradation reactions, polypropylene would have limited usefulness as a structural plastic, if any usefulness at all.

There are four modes of action important in stabilizing polypropylene: (1) free radical scavenging; (2) decomposition of peroxides; (3) regeneration of inhibitors in synergistic antioxidant systems; (4) absorption of ultraviolet light and re-emission of absorbed energy in nondegrading forms.

Free radical scavenging, peroxide decomposition, and regeneration of inhibitors interfere with propagation reactions by (1) stopping active free radicals, and by (2) decomposing unstable peroxides into nonactive species. In the fourth mode of action, ultraviolet absorbers preferentially absorb incident light energy before it can initiate further chain reactions and produce active radicals.

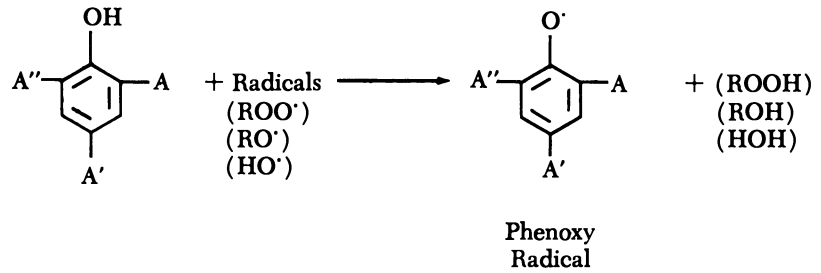
Free Radical Scavengers. Hindered phenolics are the most important free radical scavengers used in polypropylene. These compounds function by hydrogen transfer reactions involving labile hydroxy-hydrogen atoms in the molecule. The results of hydrogen transfer reactions are elimination of active radicals, and formation of resonance-stabilized phenoxy radicals which do not react with weak bonds in the polymer chain.

Aromatic amines and some other compounds are also effective hydrogen transfer agents and will give excellent molecular stability in most cases when used in place of the hindered phenolics. However, these compounds are rapidly oxidized to form color bodies in the polymer and may be toxic compared with the phenolics. Hence, aromatic amines are not widely used in polypropylene stabilizer systems.

One mole of a hindered phenolic is theoretically capable of eliminating two active radicals in the autoxidation sequence. Of course, the position and type of group or groups substituted on the phenol will control to a great extent the activity of the particular phenolic used. However, a discussion of these effects is beyond the scope of this paper and will not be treated here.

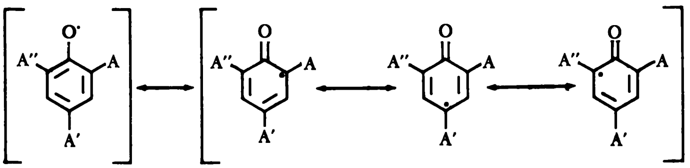
HYDROGEN TRANSFER REACTIONS WITH HINDERED PHENOLICS. The general scheme for hydrogen transfer reactions with hindered phenolics of comparable activity is shown below.

HYDROGEN TRANSFER

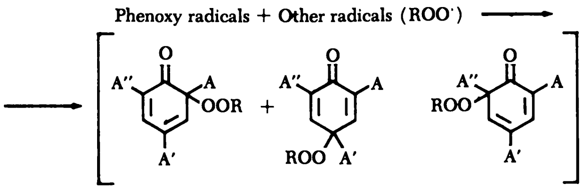


The phenolic initially gives up its labile hydrogen, which in turn reacts with the various radicals produced in chain reactions; then the phenoxy radical becomes stabilized owing to its ability to form resonance structures. The resonance-stabilized forms of the phenoxy radical will not attack tertiary carbon—hydrogen bonds in the polypropylene chain but will react with other radicals such as a peroxide, resulting in the elimination of a second free radical.

Resonance Stabilization of Phenoxy Radicals



Elimination of Second Free Radical



Peroxide Decomposers. Aryl phosphites and certain sulfur compounds such as sulfides, disulfides, and thiodipropionate esters decompose peroxides into inactive compounds which do not promote polypropylene oxidation. These chemicals function by extracting an oxygen atom from the peroxide group and reducing it to an ether or hydroxy group (9).

Representative compounds of importance in polypropylene stabilization are tris(mixed nonyl phenyl)phosphite and dilauryl thiodipropionate (DLTDP). The aryl phosphite is used in film grade resins and in other grades to protect against discoloration and changes in melt flow rate during processing. The thiodipropionate ester is widely used, particularly in synergistic combinations with hindered phenolics. These synergistic combinations are added to almost all formulations, with the possible exception of some film grades, for which the phosphite is more appropriate owing to reduced odor during processing (compared to DLTDP which may give off a strong odor at high temperatures).

Both mono- and disulfides owe a large part of their antioxidant activity toward olefins to their immediate oxidation products—*i.e.*, sulfoxides and thiosulfinates—since these products show an immediate effect, whereas, with the parent compounds a small amount of oxygen must be absorbed before there is appreciable activity (*9*).

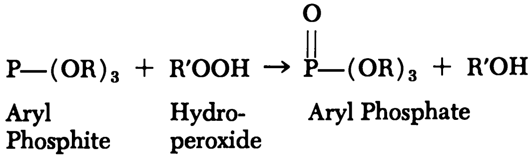
Sulfoxides form complexes with hydroperoxides and can inhibit a partially oxidized substrate, but their inhibiting activity is destroyed by the simultaneous addition of an acidic substance such as stearic acid. The activity of sulfur compounds cannot be wholly accounted for by their peroxide-decomposing action, and although they suppress peroxide-initiated autoxidation, they do not suppress oxidations initiated by free radical sources such as azobisisobutyronitrile (*10*).

It would appear, therefore, that the sulfoxide–hydroperoxide complex retards decomposition of the hydroperoxide to free radicals. However, active sulfoxides decompose readily according to the scheme:

$$2\,BS(O)B \rightarrow 2\,(CH_3)_2{-}C=CH_2 + BS(O)SB + H_2O$$

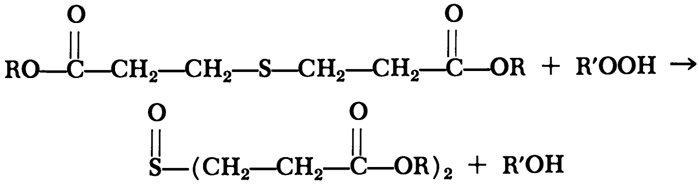
and it is therefore more practical to use the parent sulfides since they provide a "reservoir" for the supply of the active ingredient (*11*).

Aryl Phosphites



$$P{-}(OR)_3 + R'OOH \rightarrow \overset{O}{\overset{\|}{P}}{-}(OR)_3 + R'OH$$

Thiodipropionate Esters (DLTDP)



$$RO{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}S{-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}OR + R'OOH \rightarrow$$

$$\overset{O}{\overset{\|}{S}}{-}(CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}OR)_2 + R'OH$$

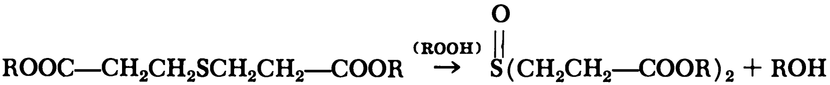
R equals lauryl(DLTDP), or stearyl(DSTDP)

Synergism between Hindered Phenolics and DLTDP in Polypropylene Formulations. When polypropylene is inhibited separately either with a hindered phenolic or with a sulfide such as dilauryl thiodipropionate(DLTDP), the polymer completely degrades within a short time —usually between a few hours and a few days on exposure to air at 130°–150°C. A mixture of the same two inhibitors in the same concentrations, however, successfully inhibits polymer degradation for up to 70–80 days. Several plausible suggestions has been advanced to explain synergism between phenols and sulfur compounds (*6, 19*).

Synergism implies that two-component antioxidants act differently during inhibition. Moreover, in a given mixture of antioxidants, synergism may arise from more than one cause—*e.g.*, a combination of an inhibitor of free radicals with a synergist that can decompose peroxides and can also donate hydrogen (*12*). The mechanisms most supported in the literature are presented below.

Mechanisms of Interaction. The synergistic phenomenon between hindered phenolics and thiodipropionate esters involves free radical scavenging by the phenolic, peroxide decomposition by the sulfide ester and by the products of disproportionation of oxidized forms of the sulfur compound, and finally, regeneration of the phenolic by the disproportionation products.

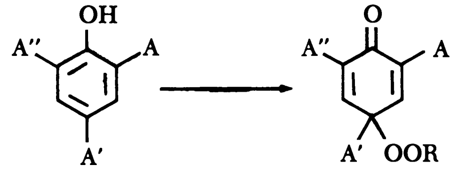
The separate and over-all reactions are presented below.



$$ROOC{-}CH_2CH_2SCH_2CH_2{-}COOR \xrightarrow{(ROOH)} \overset{O}{\overset{\|}{S}}(CH_2CH_2{-}COOR)_2 + ROH$$

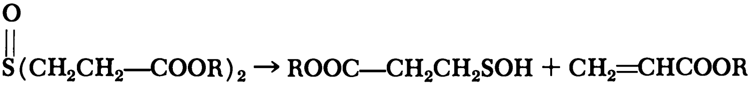
(Decomposition of Peroxide) (1)

2 ROO· +



+ ROOH (2)

(Free Radical Stopper)



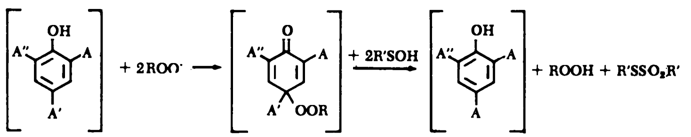
$$\overset{O}{\overset{\|}{S}}(CH_2CH_2{-}COOR)_2 \rightarrow ROOC{-}CH_2CH_2SOH + CH_2{=}CHCOOR$$

(Disproportionation) (R'SOH) (3)

$ROOH + R'SOH^{\cdot} \rightarrow ROH + R'SO_2H$ (4)

(Decomposition of
Second Peroxide)

Over-all Reaction With Regeneration of Phenolic



Photostabilization with Ultraviolet Absorbers. Absorption of ultraviolet light in the region 2900–3900 A. (290–390 mμ) results in the yellowing and loss in physical-mechanical properties of most polymers containing aliphatic C—H bonds. This degradation is usually a combination of ultraviolet absorption and oxidative attack (*21*).

ABSORPTION CHARACTERISTICS OF POLYPROPYLENE. In discussions of the degradative effects of ultraviolet radiation, and photostabilization of polypropylene, absorption characteristics of the polymer as well as the energies involved should be considered.

Only when ultraviolet energy is partly or wholly absorbed can it cause photochemical reactions that result in product degradation. Although saturated hydrocarbons such as polypropylene in general do not absorb significantly in the spectrum of 290–400 mμ, polypropylene resins do absorb light in the presence of oxygen. Chien reports (*3*) that charge-transfer bonds between oxygen and polypropylene, and also the presence of small amounts of carbonyl which form most likely during the polymerization process, are responsible for absorption of ultraviolet light.

Hirt *et al.* (*7*) found that the greatest change in ultraviolet absorbance of polypropylene exposed to a filtered xenon source, and presumably most polymer degradation, at wavelengths of 297 mμ and 370 mμ. Melchore (*14*) conducted a study utilizing a series of glass ultraviolet absorbing filters, and his work indicated that the ultraviolet radiation most damaging to polypropylene, as measured by loss in physical properties, occurs at about 300 mμ.

ENERGY REQUIRED TO BREAK BONDS IN POLYPROPYLENE. The energy required to break bonds between atoms in a molecule generally ranges from 50 to 100 kcal./mole (*4*). Thermal initiation involving the reaction between oxygen and C—H bonds requires less energy (*ca.* 30–45 kcal./mole) than direct thermal cracking (*ca.* 70–100 kcal./mole) (*13*).

Energy from ultraviolet radiation is sufficiently strong to break many molecular bonds in organic substances. A wavelength of 300 mμ, for instance corresponds to an energy of 94 kcal./mole; at 400 mμ the energy is still as high as 70 kcal./mole (*26*).

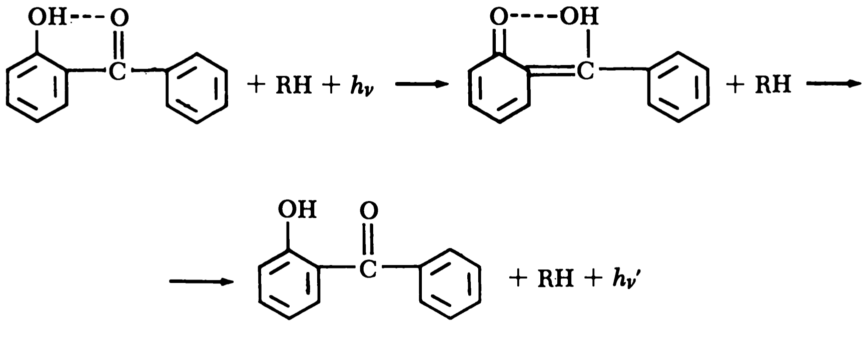
As polypropylene undergoes photoaging, it cracks, becomes brittle, and acquires color. The general picture of the photooxidation is much the same as with thermal oxidation and differs mainly in the stage of initiation. Increases in the concentrations of carbonyl and unsaturated bonds, both of which absorb in the ultraviolet spectrum, occur as the resin is exposed to the radiation source. Consequently, as the resin degrades, more light energy is absorbed causing more degradation. In practice, the deteriorating effect of light is usually enhanced by the presence of oxygen, moisture, and heat (*27*).

COMMONLY USED ULTRAVIOLET ABSORBERS. The practical problem of photostabilization reduces mainly to the addition of compounds that preferentially absorb ultraviolet light. These compounds may become electronically excited, for example, and then emit the light energy at nondestructive wavelengths such as the infrared. The excited molecules may also release absorbed ultraviolet energy as fluorescence of phosphorescence, both also degradative to some small degree, or in collisions with other molecules.

Commonly used ultraviolet absorbers such as hydroxybenzophenones, hydroxybenzotriazoles, and salicylic acid derivatives transfer absorbed light energy rapidly from their excited states, giving off thermal energy and longer wavelength light quanta (*18*).

The transfer of light energy in hydroxybenzophenone, for example, is accomplished by rearrangement of the activated compound into a quinoid structure (*1*, *2*). The absorbed energy is emitted at lower frequencies than that of the incident light.

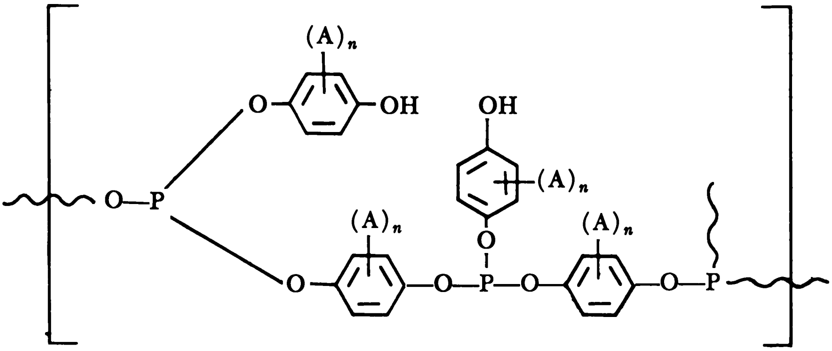
The rearrangement of hydroxybenzophenone ultraviolet absorbers is as follows:



A labile equilibrium between phenyl and quinoidal structures allows conversion of large amounts of energy. The strong ultraviolet absorption of the hydroxybenzophenone structure is attributed to the hydrogen bond of the chelate structure shown and to its highly conjugated structure.

Stabilizing Compounds

The polymeric phenolic phosphites (PPP) are reaction products of substituted hydroquinones and phosphorus trihalides such as phosphorus trichloride. They may be represented by the structure shown at the top of p. 213, where (A) represents subsituent groups on the paraphenylene portion of the hydroquinone.



where *n* may be as high as 4

The most active products prepared are those with highly hindered phenolic groups, and a polyphosphite structure where the ratio of phosphite groups to phenolic-hydroxyl groups is rerely less than 1:2 or greater than 2:1.

Effectiveness in Polypropylene. The effectiveness of polymeric phenolic phosphites is well demonstrated in aging studies. Heat aging tests, for example, indicated an exceptionally high degree of synergism between polymeric phenolic phosphites and thiodipropionate esters such as dilauryl- and distearyl thiodipropionate, suggesting a hindered phenolic functionality. On the other hand, processing stability studies suggest that the compounds also function much like aryl phosphites under conditions of high shearing and low oxygen concentration—*e.g.*, those encountered during extrusion operations. Other studies involving exposure of thin polypropylene films to ultraviolet sources (Fade-ometer and a sunlamp) indicate that polypropylene containing PPP has greater resistance to embrittlement than formulations containing simple hindered phenolics or aryl phosphites. The photostabilizing value of the PPP compounds is most evident when combinations with other additives are used.

Heat Stability. Polymeric phenolic phosphites seem to be efficient hydrogen transfer agents which provide excellent heat stability when used in conjunction with thiodipropionates. Presumably, they scavenge free radicals and form resonance-stabilized phenoxy radicals in much the manner as simple hindered phenolics (*see* reaction scheme on p. 214).

To determine the relative effectiveness of polymeric phenolic phosphites as heat stabilizers, comparisons were made with several commonly used hindered phenolics. Formulations containing 0.4% DLTDP and 0.1% phenolic were prepared and tested for heat stability in a 300°F. forced-draft oven. Three 75-mil, 1-inch diameter discs were placed in the oven, and days to failure were noted as the time for two out of three discs to craze crumble.

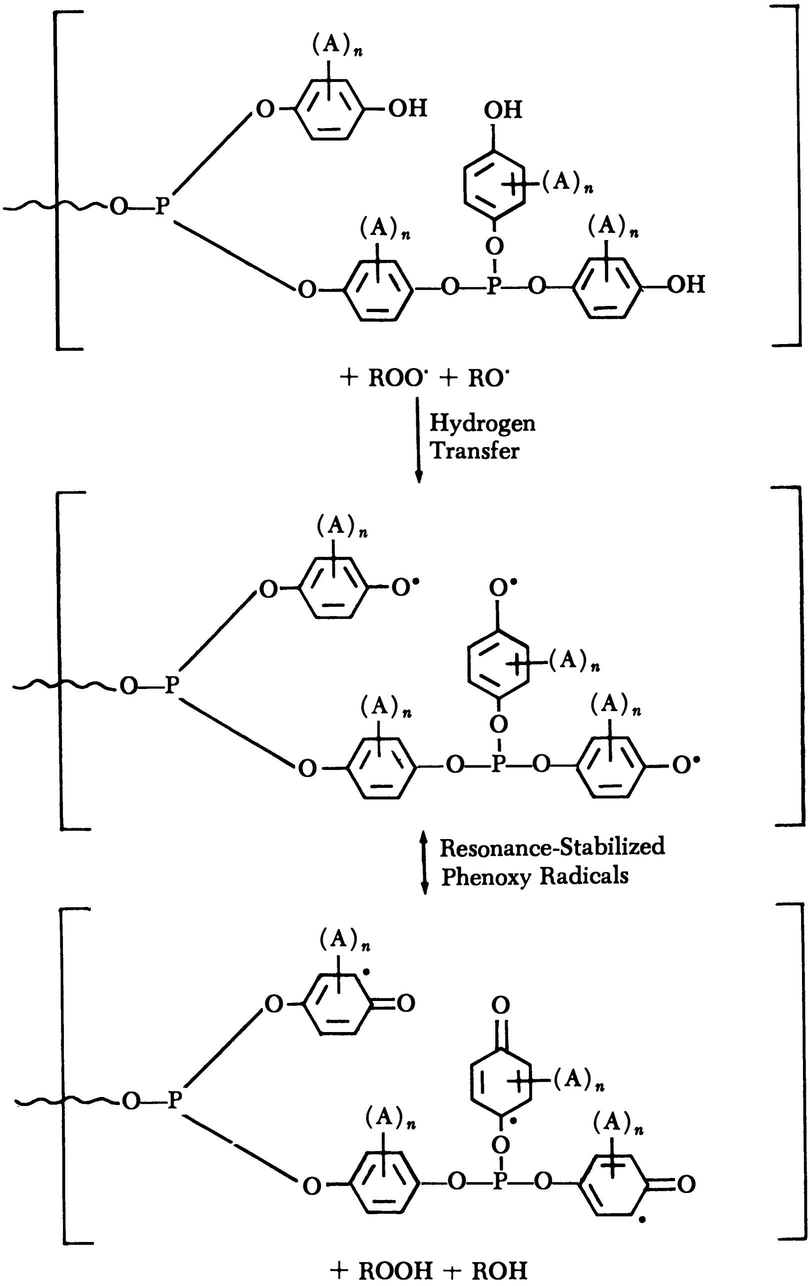

(A)$_n$
O
OH
OH
(A)$_n$
O—P
(A)$_n$
(A)$_n$
O
O—P—O
OH
+ ROO· + RO·
Hydrogen Transfer
(A)$_n$
O·
O·
(A)$_n$
O—P
O·
Resonance-Stabilized Phenoxy Radicals
(A)$_n$
=O
O
(A)$_n$
O—P
=O
+ ROOH + ROH

Table I shows that the PPP tested was more effective than any of the phenolics. It prevented catastrophic degradation for 79 days compared with 20–58 days for the phenolics. A general purpose commercial resin will generally last between 40 and 55 days in this test, while the unstabilized base resin was completely degraded in less than one day.

Table I. Relative Effectiveness of Hindered Phenolics and PPP on Heat Aging of Polypropylene

Formulation	*Days to Failure*[a] *at 300°F.*
Unstabilized Polypropylene (UP)	<1
UP + 0.4% DLTDP	10
UP + 0.4% DLTDP + 0.1% 4,4′-butylidenebis(6-*tert*-butyl-*m*-cresol)	43
UP + 0.4% DLTDP + 0.1% tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane	58
UP + 0.4% DLTDP + 0.1% 2,2′-methylenebis(4-methyl-6-nonyl)phenol	23
UP + 0.4% DLTDP + 0.1% 2,6-di-*tert*-butyl-*p*-cresol	20
UP + 0.4% DLTDP + 0.1% polymeric phenolic phosphite	79

[a] Time for two out of three 75-mil × ¾-inch discs to craze crumble in a forced-draft oven at 300°F.

Table II. Effect of DLTDP–Phenolic Combination with Aryl Phosphite on Heat Aging of Polypropylene

Formulation[a]	*Days to Failure at 300°F.*
0.4% DLTDP + 0.1% tris(nonyl-phenyl) phosphite(tris)	18
0.4% DLTDP + 0.1% tris + 0.1% 4,4′-butylidenebis(6-*tert*-butyl-*m*-cresol)	44
0.4% DLTDP + 0.1% tris + 0.1% tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane	55
0.4% DLTDP + 0.1% tris + 0.1% 2,2′-methylenebis(4-methyl-6-nonyl)phenol	28
0.4% DLTDP + 0.1% tris + 0.1% 2,6-di-*tert*-butyl *p*-cresol	20

[a] Unstabilized base resin.

In general, phenolic phosphites having substituent groups similar in type and location to those on phenolics were more active heat stabilizers. At first this was thought to be caused by an additive effect of phenolic groups trapping free radicals and the phosphite groups decomposing peroxides. While both modes of action are known to occur, further studies revealed that phosphites do not contribute much to heat stability, and the effectiveness of the polymeric phenolic phosphites is not a simple additive effect of two molecular moieties functioning independently in the compound (Table II).

Therefore, additional heat aging tests were conducted to investigate the possibility that hydroquinone-derived phenolic groups might function differently from the monohydric phenols and somehow contribute to the high activity of the phenolic–phosphite systems. Two substituted hydroquinones, two polymeric phenolic phosphites based on those hydroquinones, and combinations of the hydroquinones with triphenyl phosphite and tris(nonylphenyl) phosphite were evaluated in the oven-aging test; again 0.4% DLTDP was included in the formulations.

Table III shows that the two hydroquinones had low activity. In addition, the aryl phosphites did not improve the results significantly when they were added to the formulations. The two polymeric phenolic phosphites based on the hydroquinones, however, had considerably better activity, going 62 and 81 days, respectively, compared with only 20–28 days for the other formulations. Therefore, the polymeric phenolic phosphites are more effective probably because of their low volatility.

Table III. Effectiveness of Aryl Phosphite–DLTDP-Substituted Hydroquinone Combinations on Heat Aging of Polypropylene

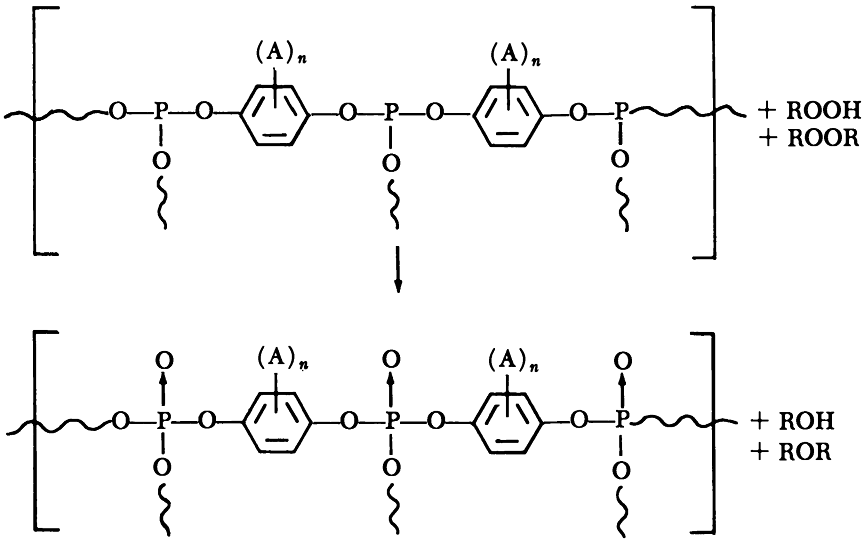
Formulation[a]	*Days to Failure at 300°F.*
0.4% DLTDP + 0.1% substituted hydroquinone (A)	20
0.4% DLTDP + 0.1% A + 0.1% triphenyl phosphite	20
0.4% DLTDP + 0.1% A + 0.1% tris(nonyl phenyl)phosphite	22
0.4% DLTDP + 0.1% substituted hydroquinone (B)	24
0.4% DLTDP + 0.1% B + 0.1% triphenyl phosphite	20
0.4% DLTDP + 0.1% B + 0.1% tris(nonyl phenyl)phosphite	28
0.4% DLTDP + 0.1% PPP of substituted hydroquinone A	81
0.4% DLTDP + 0.1% PPP of substituted hydroquinone B	62

[a] Unstabilized base resin.

Processing Stability. The ability of tris(nonylphenyl) phosphite to prevent degradation of polypropylene during processing is believed related to its efficiency to decompose peroxides into non-active species. In a similar way, the phosphite groups on the polymeric phosphites may also be capable of decomposing peroxides (*see* top of p. 217).

Three separate processing stability tests were run, and comparisons were made between: (1) tris(nonylphenyl) phosphite and a PPP, (2) two commercial resins, and unstabilized resin containing the synergistic DLTDP–PPP combination, and (3) DLTDP alone, a PPP alone, a combination of the two, and unstabilized resin.

The apparatus used for the first tests included a 3/4-inch diameter, 20:1 L/D laboratory extruder. The second series of evaluations was run on a Brabender torque rheometer equipped with mixing head. The third tests utilized large scale processing equipment including a two-roll,



42-inch mill, and a 1–1/2-inch Modern Plastic Machinery Corp. (MPM) extruder with mixing screw.

Repeated Extrusions. 0.25% Tris(nonylphenyl) phosphite and 0.25% polymeric phenolic phosphite were added to unstabilized polypropylene, and the resins were run through the laboratory extruder four times. The barrel temperature was 450°F., and the stock temperature of the extrudate was approximately 500°F. Melt flow rate of samples taken after each pass was measured according to ASTM 1238-62T.

The results are shown in Figure 1. PPP was comparable with the tris(nonylphenyl) phosphite in preventing process degradation, although it wasn't quite as effective. The unstabilized base resin, however, became soupy, discolored, and had a melt flow rate of more than 10 after four passes. Aryl phosphite and the PPP gave considerably less discoloration, and melt flow readings of 3.9 and 4.7, respectively, after four passes through the extruder.

Brabender Processing. In another series of tests, two commercial (stabilized) resins, unstabilized polypropylene, and the latter with 0.4% DLTDP + 0.1% PPP were masticated for five minutes at 50 r.p.m. and 180°C. in the Brabender apparatus, then mixed for 25 minutes at 150 r.p.m. and 200°–215°C. Meter-gram torque readings were plotted over the mixing cycle along with temperature, and intrinsic viscosity was measured for each formulation before and after processing.

The results showed that the DLTDP–PPP formulation has the best over-all stability as measured by both intrinsic viscosity change and meter-gram torque (melt viscosity) readings. All formulations suffered torque decreases as well as intrinsic viscosity decreases (Figure 2).

Intrinsic viscosity of the unstabilized polypropylene decreased 51% after processing (1.35 to 0.65) compared with a decrease in torque of

77% (650 to 150 meter-gram). This same resin containing the DLTDP–PPP combination experienced only a 20% intrinsic voscosity decrease (1.35 to 1.06) after processing. Torque, however, decreased 65% (1000 to 350 meter-gram). Commercial resin A had the greatest intrinsic viscosity decrease (64%) and torque decrease (76%) after processing,

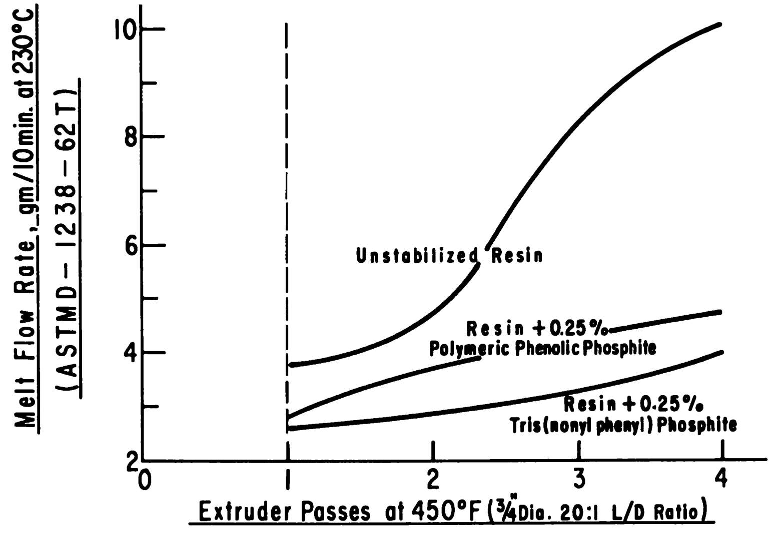


Figure 1. Processing stability of polypropylene, PPP vs. *aryl phosphite*

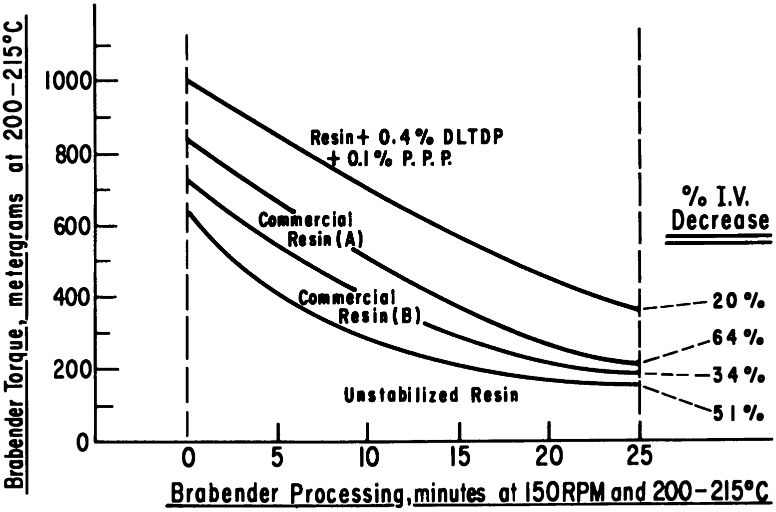


Figure 2. Processing stability of polypropylene in a Brabender torque rheometer

while commercial resin B experienced a 34% intrinsic viscosity decrease along with a torque decrease of about 75%.

Obviously decreases in torque (melt viscosity) are not related linearly to decreases in intrinsic viscosity. Differences may arise from thixotropic and temperature influences as well as differences in degree of degradation.

LARGE SCALE PROCESSING. In large scale processing studies four formulations were evaluated for processing stability on a large mill and extruder. These formulations included: (1) 0.1% PPP, (2) 0.4% DLTDP, and (4) unstabilized polypropylene. The resins were first masticated on the 42-inch mill for 10 minutes at 350°F., then passed through the MPM extruder at barrel temperatures of 500° and 550°F. The extrudate was then chopped and re-extruded. Melt flow readings were made on samples taken after each processing step. The results are shown in Figure 3.

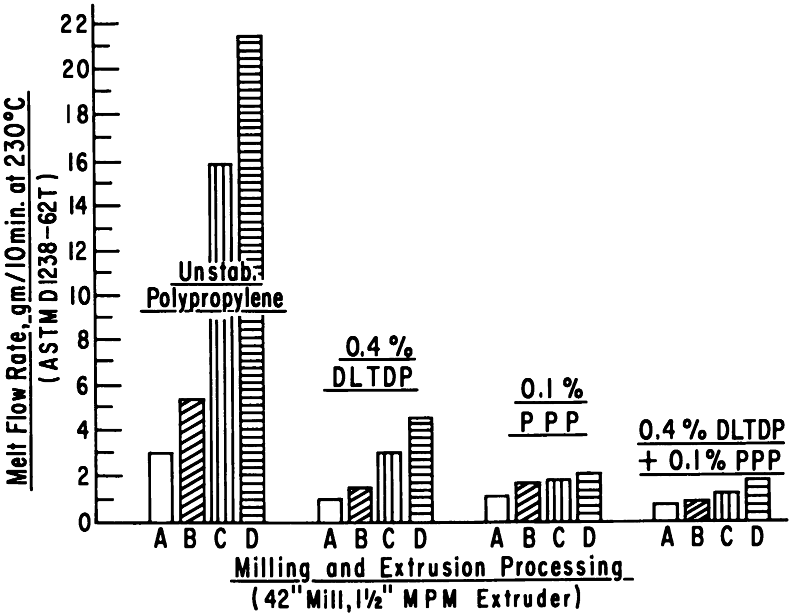


Figure 3. Processing stability of polypropylene on large-scale equipment

Legend:
A—10 minutes mastication at 350°F. on 42-inch, two-roll mill
B—one pass at 500°F.
C—two passes at 500°F.
D—two passes at 550°F.

The additives gave considerable stability to the resin as shown by the graphs. However, unstabilized resin discolored badly, in addition to experiencing a tremendous increase in melt flow (or decrease in melt viscosity). DLTDP alone effectively retarded degradation and discoloration of the resin. PPP alone was even more effective than DLTDP, but the most effective formulation was the DLTDP–PPP combination, with only small decreases in melt viscosity occurring after repeated processing.

The relatively small difference in stability between PPP alone and the DLTDP–PPP combination, however, suggests that the combination is additive rather than synergistic under limited-oxygen, high shearing conditions.

Photostability. A surprising discovery in our work with the new polymeric phenolic phosphites was that compounds inhibit the embrittlement of thin polypropylene films exposed to ultraviolet light.

The phenomenon is evident when the PPP is used alone as well as with other additives, although in the latter case the effects are more pronounced, suggesting a synergism or other interaction between the additives. The mode of photostabilizing action is not yet completely understood, but may again be related to the low volatility of the polymeric form of the compounds.

Table IV. Ultraviolet Stability of Polypropylene Films Embrittlement *vs.* Fade-Ometer Exposure

Formulation	*Hours to Embrittlement*	*Fim Thickness, mils*
Unstabilized Polypropylene (UP)	120	10
UP + monomeric phenolic phosphite	192	10
UP + polymeric phenolic phosphite	290	10
UP + 0.4% DLTDP + 0.2% monomeric phenolic phosphite	288	12
UP + 0.4% DLTDP + 0.2% polymeric phenolic phosphite	644	12
UP + 0.4% DLTDP + 0.2% tris(2-methyl-4-hydroxy-5-*tert*-butyl-phenyl) butane	216	12
UP + 0.4% DLTDP	225	12

[a] Exposure time at which 1-inch × ½-inch × (10–12 mil) samples crack when flexed 90° at the center.

The importance of the polymeric form was pointed up in Fade-ometer and sunlamp tests where polyphosphites were found to be much more effective than mono(tris)phosphites derived from the same starting hydroquinones, especially when the compounds were used in conjunction with thiodipropionate esters. The data in Table IV show a comparison between a polyphosphite and a mono(tris) phosphite derived from the same substituted hydroquinone. A commonly used hindered phenolic was also tested in place of the phenolic phosphite for comparison. The protection against embrittlement obtained with the polymeric phenolic

Table V. Ultraviolet Stability of Polypropylene Films with Various Ultraviolet-Absorber Formulations

Formulation[a]	*Hours to Embrittlement, 8-mil Films*
0.25% 2-hydroxy-4-*n*-octoxybenzophenone (HOBP)	648
0.05% HOBP	288
0.05% HOBP + 0.2% PPP	432
0.05% HOBP + 0.27% PPP + 0.4% DLTDP	576
0.25% Hydroxybenzotriazole (A)	405
0.25% Hydroxybenzotriazole (B)	554

[a] Unstabilized base resin.

phosphite was more than double that obtained with either the mono(tris) phosphite or the normal hindered phenol.

Results from another series of Fade-Ometer tests indicated that concentrations of expensive ultraviolet absorbers could be reduced by as much as 80%, yet the resin still has nearly as good ultraviolet protection against embrittlement when a DLTDP–PPP combination is used in place of the DLTDP–phenolic system. Table V shows the effect of decreasing the concentration of a common ultraviolet absorber and then adding PPP and a DLTDP–PPP combination. Obviously, PPP contributes significantly to photostability. The combination of 0.2% PPP and only 0.05% ultraviolet absorber is actually more effective than one commercial benzotriazole ultraviolet absorber run for comparison, although not as effective as the 0.25% level of the benzophenone absorber combined with the polymeric phenolic phosphite. By adding DLTDP to the PPP–low ultraviolet concentration mixtures, two significant changes result. The formulation is now well protected against heat oxidation and process degradation, and the film becomes almost as resistant to embrittlement as the high 0.25% concentration of ultraviolet absorber.

The significance of the interaction between PPP and ultraviolet absorbers, such as the hydroxybenzophenones, becomes evident when the high cost of absorbers is considered. The potential cost for polymeric phenolic phosphites is low by comparison. By using a polymeric phenolic phosphite in place of a normal hindered phenolic in the heat-stabilizer system, enhanced photostability is obtained, and less ultraviolet absorber is required for a given degree of stability.

Sunlamp tests were also run to determine the effectiveness of the compounds under another light source. Eight-mil polypropylene films were exposed in the atmosphere 10 inches below a new 275 watt sunlamp; this particular lamp produces visible light and a considerable amount of heat along with the ultraviolet radiation. Results are shown in Table VI.

Table VI. Sunlamp Exposure of Polypropylene Films

Formulation	*Hours to Embrittlement,*[a] *10-mil Films*
Unstabilized Polypropylene (UP)	48
UP + 0.25% PPP	152
UP + 0.50% 2-hydroxy-4-*n*-octoxybenzophenone (HOBP)	580
UP + 0.25% HOBP	298
UP + 0.1% HOBP + 0.25% PPP	525
UP + 0.4% DLTDP + 0.2% PPP	274
UP + 0.25% Hydroxybenzotriazole (A)	290
UP + 0.25% Hydroxybenzotriazole (B)	425

[a] Time for 2-inch × ½-inch × 10 mil films to crack when flexed 180° at the center.

In less than 50 hours, the unstabilized film cracked when flexed 90°. The film containing 0.25% PPP was protected for 152 hours, while the combination of 0.4% DLTDP + 0.2% PPP failed after 274 hours. The commercial hydroxybenzophenone at 0.5% prevented embrittlement for 580 hours, while at 0.25% this compound protected the film for approximately 300 hours. By adding 0.25% PPP and reducing the amount of hydroxybenzophenone to 0.1%, the film lasted for 525 hours before embrittlement. The two commercial benzotriazole ultraviolet absorbers at 0.25% protected the polypropylene films for 290 hours and 425 hours, respectively.

Summary

The new polymeric phenolic phosphites have shown wide activity as polypropylene stabilizers. They apparently function as hindered phenolics in synergism with thiodipropionate esters and give excellent heat stability to polypropylene. They also seem to function much the same as aryl phosphites in preventing degradation during processing, suggesting an active phosphite functionality. In addition, the compounds contribute to photostabilization, although the mechanism involved is not yet well understood.

The photostabilizing characteristic is most evident when the polymeric phenolic phosphite compounds are used in conjunction with thiodipropionate esters and reduced amounts of hydroxybenzophenone ultraviolet absorbers.

Where aryl phosphites are good processing stabilizers, they do not contribute much to light stability or heat stability at elevated temperatures. Where hindered phenolics are good heat stabilizers, they do not contribute much to photostability. Some phenolics are effective processing stabilizers, but the phenolics are not as effective as aryl phosphites or the polymeric phenolic phosphite compounds.

The polymeric phenolic phosphites are excellent heat and processing stabilizers and can contribute significantly to photostability. These broad-spectrum stabilizers offer possibilities for simplifying polypropylene stabilizer systems. They may allow one to use lesser amounts of other additives, and they open up a new area for potential cost savings in formulating polypropylene resins.

Literature Cited

(1) Burgess, A. R., *Chem. Ind.* **4,** 78 (1952).
(2) Burgess, A. R., *Natl. Bur. Std. (U.S.), Circ.* **525,** 149 (1953).
(3) Chien, J. C. W., *J. Phys. Chem.* **69,** 4317 (1965).
(4) Glasstone, S., "Textbook of Physical Chemistry," 2nd ed., pp. 1159-1160, Van Nostrand, New York, 1946.
(5) Hawkins, W. L., Sautter, H., Winslow, F. H., *Am. Chem. Soc. Div. Polymer Chem. Preprints* **4**(I), 4331-4335 (1963).
(6) *Ibid.,* pp. 4332-4333.
(7) Hirt, R. C., Searle, N. Z., Schmitt, R. G., *SPE Trans.* **1,** 21 (1961).
(8) Hunter, B. A., *Proc. Wayne State Univ. Polymer Conf.,* 1966.
(9) Ingold, K. U., *Chem. Rev.* **61,** 568 (1961).
(10) *Ibid.,* p. 569.
(11) *Ibid.,* p. 570.
(12) *Ibid.,* p. 584.
(13) *Ibid.,* p. 564.
(14) Melchore, J. A., *Ind. Eng. Chem. Prod. Res. Develop.* **1,** 232 (1962).
(15) Morawetz, Herbert, *Ind. Eng. Chem.* **41,** 1442 (1949).
(16) Neiman, M. B., "Aging and Stabilization of Polymers," p. 10, Consultants Bureau, New York, 1965.
(17) *Ibid.,* p. 8.
(18) *Ibid.,* p.'129.
(19) Neureiter, N. P., Bown, D. E., *Ind. Eng. Chem., Prod. Res. Develop.* **1,** 236 (1962).
(20) Richard, W. R., *Hydrocarbon Proc. Petrol. Refiner* **41** (3), 123 (1962).
(21) *Ibid.,* p. 124.
(22) Russell, C. A., Pascale, J. V., *J. Appl. Polymer Sci.* **7,** 959 (1963).
(23) Tryon, M., Wall, L. A., "Autoxidation and Antioxidants," Vol. II, p. 920, W. O. Lundberg, Ed., Interscience, New York, 1962.
(24) Verschoore, K. T. M., *Proc. Conf. Advan. Polymer Sci. Technol., 1966,* p. 170.
(25) *Ibid.,* p. 172.
(26) Weicksel, J. A., *Tappi* **46** (11), 1963.
(27) Zussman, H. W., "Modern Plastics Encyclopedia," McGraw-Hill, New York, 1960.

RECEIVED April 5, 1967.

16

Correlation of Test Methods for Evaluating Antioxidants in Polypropylene

DAVID A. GORDON

Geigy Industrial Chemicals, Division of Geigy Chemical Corp.,
Ardsley, N. Y. 10502

The various methods which have been proposed and are being used to evaluate the oxidative stabilities (processing and end-use environmental) of stabilized polypropylenes were compared. Nine commercial polypropylenes were evaluated by the following tests: oven aging of plaques, water extraction resistance, U-tube, oxygen uptake, differential thermal analysis, carbonyl formation, melt flow drifts, re-extrusions, injection spiral molds, and the torque rheometer. The results show that there is no ideal simulated test method for measuring oxidative and/or processing stabilities. At best, there is only a fair correlation between the test methods. The more the tests differ from actual environmental (use) and processing conditions, the less likely are the performances of the polymers expected to correlate with commercial usage and processing.

A variety of methods for evaluating antioxidants in polypropylene has been developed during the past several years. Polymer producers, end-use manufacturers, additive suppliers, academicians, and others have developed widely disparate test methods, all of which presumably yield the same results—*i.e.*, the test methods rate the antioxidants and antioxidant systems in the same relative order of effectiveness. Many of these test methods are useful tools in distinguishing unstabilized polymer, moderately stabilized polymer, and highly stabilized polymer systems. Today, all of the polypropylene producers offer highly stabilized polymers. Effective antioxidants are available from several additive suppliers. How does one select the best antioxidant or polymer formulation for a particular end use? This paper compares the results obtained by various test methods used to evaluate the two basic types of oxidative stability, processing stability and end-use or environmental stability. The correlation or lack of correlation among test methods is discussed. Eight commercial high heat or long term heat aging (LTHA) polymers and one general purpose resin have been evaluated. The most commonly used test method for evaluating end-use stability is oven aging of molded plaques (*6, 8, 9, 10, 14, 16, 17, 18, 20, 21, 22, 25, 28, 33, 34*).

Oven Aging

At 140°C. Table I illustrates the relative stabilities of 25-mil plaques of nine commercial polypropylene resins designated A through I, which have been exposed at 140°C. in a forced-draft oven equipped with revolving shelves. The polymers are arranged in increasing order of stability. The failure point was taken as the first observation of powdery disintegration or brittleness and is the average of three replicates. Polymer A, the general purpose resin, is least stable, and Polymer I is the most stable resin under these test conditions. The long-term heat stable resins H and I have more than twice the stability of B and C.

Table I. Days to Failure in Oven-Aging Test at 140°C.

25 mil		*60 mil*		*120 mil*	
A	22	A	43	B	53
B	34	B	43	A	71
C	35	C	61	C	92
D	53	D	84	D	141
E	57	F	92	F	142
F	64	E	104	I	151
G	66	I	105	E	156
H	72	G	109	G	189
I	74	H	118	H	202

Table I also compares the heat stabilities of 60- and 120-mil plaques at 140°C. The relative order of stabilities has changed slightly. The stability of Resin A in the thicker sections has equalled or surpassed the stability of the long term heat aging Resin B. Resins E, G, and H have improved their position, displacing I, the most stable resin in the 25-mil sheets, which is now third best in the 60-mil plaques and only fourth best in the 120-mil plaques.

At 125°C. The stabilities of 2.5, 25, 60, and 120-mil thick plaques were also obtained at 125°C. (Table II). The resins are arranged in the relative order of increasing stabilities. The relative order of stability depends on sample thickness. The relative stability of A increases significantly with increasing thickness of sample, while that of I increases with decreasing sample thickness. At 2.5-mil thickness, Resin A, as one might expect, is less stable than the LTHA resins. In thicker sections, however, A is more stable than several of the LTHA resins. At 120-mil thickness, A is a better buy than B, C, or E. Resin H is only fourth best at 2.5 mil but is the most stable resin at 25 mils and thicker. Table III compares 60- and 120-mil thicknesses at 125° and 140°C. exposures. The data show a fair degree of correlation. Resin B at thicker sections is consistently the least stable, while H is the most stable polymer.

At 100° and 150°C. Samples of 25-mil thickness were also exposed at 100°C. in a forced-draft oven with revolving shelves and at 150°C. in a forced-draft tubular oven (TO). The data are shown in Table IV.

Table II. Days to Failure in Oven-Aging Test at 125°C.

2.5 mil	*25 mil*	*60 mil*	*120 mil*
A 22	B 117	B 151	B 166
B 29	A 130	C 185	C 219
C 34	C 140	A 240	E 368
E 34	E 187	E 287	A 390
H 34	F 226	F 375	F 453
D 50	D 256	I 418	I 501
F 50	G 259	G 460	G > 600
G 75	I 288	D 479	D > 600
I 95	H 297	H 552	H > 600

Table III. Days to Failure in Oven-Aging Test for 60- and 120-mil Samples

60 mil		*120 mil*	
125°C.	*140°C.*	*125°C.*	*140°C.*
B 151	B 43	B 166	B 53
C 185	A 43	C 219	A 71
A 240	C 61	E 368	C 92
E 287	D 84	A 390	D 141
F 375	F 92	F 453	F 142
I 418	E 104	I 501	I 151
G 460	I 105	D > 600	E 156
D 479	G 109	G > 600	G 189
H 552	H 118	H > 600	H 202

Table IV. Days to Failure of 25-mil Oven Exposures

100°	*125°*	*140°*	*150° (TO)*
B 167	B 117	A 22	A 9
C 183	A 130	B 34	B 15
A 286	C 140	C 35	D 15
E 300	E 187	D 53	C 17
G 387	F 226	E 57	H 19
H 466	D 256	F 64	F 27
I 507	G 259	G 66	G 30
F > 600	I 288	H 72	E 31
D > 600	H 297	I 74	I 33

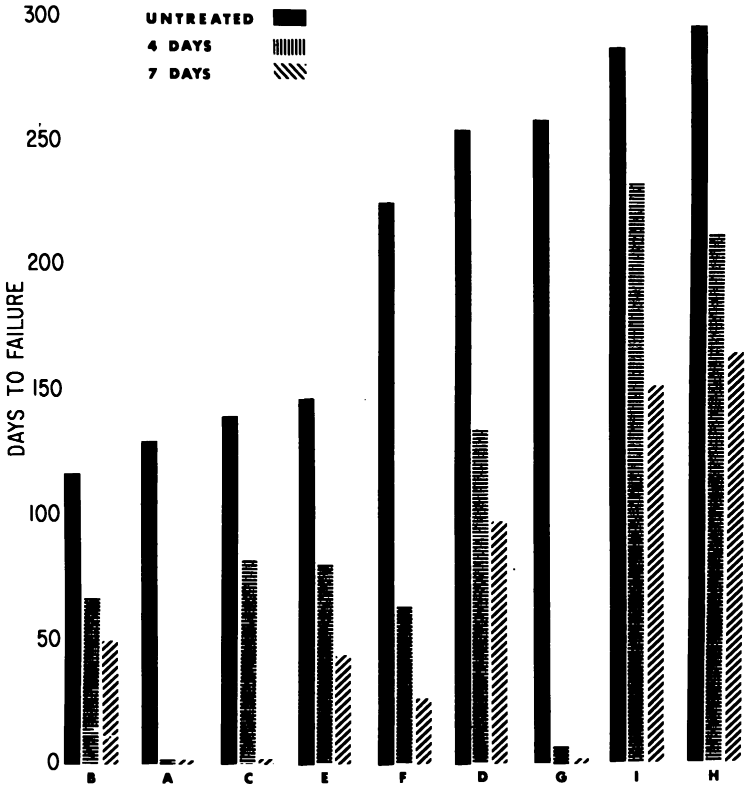


Figure 1. Water-extraction resistance test with treated boiling water using 25-mil samples at 125°C.

As seen with increasing thickness (Table II), the relative stability of Resins A and D increases with decreasing temperatures. Resins B and E increased in relative stability with increasing temperatures. This may indicate that A and D are stabilized with relatively volatile phenolic antioxidants and/or synergists and that B and E contain relatively nonvolatile antioxidants which are only moderately effective.

Water Extraction Resistance

Some applications require materials which are continuously or intermittently in contact with aqueous systems. Therefore, it is desirable to evaluate resins in a simulated test to determine water-extraction resistance (3). A commonly used test is the so-called seven-day boiling water test. Samples of 25-mil thickness were treated with boiling water for four and seven days (water changed daily) and then exposed in a circulating air oven at 125°C. The relative stabilities are shown in Figure 1. The data indicate that Resin G, which has excellent stability untreated, and Resins A and C would be poor choices for hot aqueous environments. B, E, and F also would be unacceptable. Resins H and I are best, followed by D.

U-Tube Test Method

The U-tube test method [ASTM D2445-65T (*7, 8, 20, 34*)] was recently approved as a tentative method for testing the thermal oxidative stability of propylene plastics. ASTM recommends an oxygen atmosphere at 150°C. but states that air may be used as an alternative and that other temperatures may also be used. The nine commercial resins were tested at the recommended 150°C. in both oxygen and air. The data are shown in Table V. The polymers, arranged in increasing order of stability in oxygen, show fair correlation between the air and oxygen atmospheres with some notable exceptions. Resin D is best in oxygen but is only sixth best in air. E is best in air but only fourth best in oxygen. Resin B is also out of place. Figure 2 compares the U-tube data with the relative stability of the 25-mil plaques exposed at 140°C. in a forced-draft oven. The resins are arranged in order of stability of the 25-mil plaques. There is little correlation between the U-tube test method in oxygen and the 25-mil plaques exposed at 140°C. Resin D, which is best in the U-tube oxygen test, is only sixth best in 25-mil plaques at 140°C. Except for Resins E, B, and I, there is a fair correlation between the 25-mil oven exposures at 140°C. and the U-tube/air test.

Table V. Oven Aging, Oxygen Uptake, and U-Tube Data for 25-mil Samples at 150°C.

		U-Tube	
TO	*O_2 Uptake*	*O_2*	*Air*
A 9	C 1	C 3	B 27
B 15	E 6	B 5	A 46
D 15	A 8	A 8	C 47
C 17	B 8	I 16	D 55
H 19	I 8	F 19	I 58
F 27	F 14	E 21	F 64
G 30	H 21	H 26	H 73
E 31	G 23	G 28	G 77
I 33	D 28	D 28	E 89

Table V also compares the U-tube methods with 25-mil plaques exposed at 150°C. in a tubular oven. The resins are arranged in order of stability of the 25-mil tubular oven exposures. Again, there is considerable lack of correlation between the tubular-oven exposure of plaques and the U-tube test methods. Resin D, which is best in the U-tube/

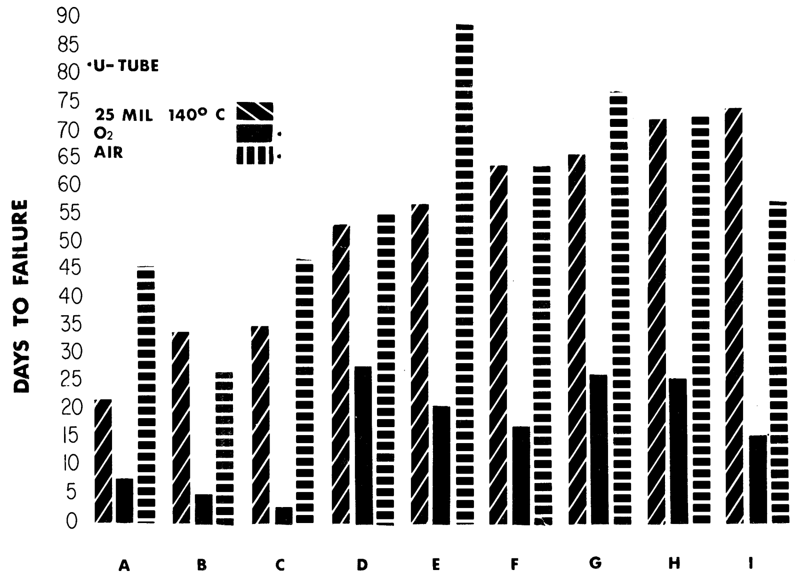


Figure 2. U-tube vs. *oven test in oxygen and air with 25-mil samples at 140° and 150°C.*

oxygen test, is only seventh best in the tubular oven test. Resin I, which is best in 25-mil plaques exposed at 140°C. in a forced-draft oven and at 150°C. in a tubular oven, is only fifth best in the U-tube/air and sixth best in the U-tube/oxygen test.

Oxygen Uptake

Oxygen uptake (*1, 4, 11, 12, 13, 14, 16, 19, 20, 23, 25, 28, 30, 31, 34*) has also been proposed as a test method and is being used by some laboratories to determine polymer stability and performance. In this study, the oxygen uptake test was run at 150°C. Failure, or the end point, was recorded when 10 cc. of oxygen per gram of polymer were absorbed. Figure 3 compares the oxygen uptake results with the oven test using 25-mil sheets at 140° and 150°C. The data show that this test also does not correlate with oven exposures of 25-mil plaques. Resin I is best in both oven exposure tests but only sixth best in the oxygen uptake test. D is best in oxygen uptake but only sixth best at 140°C. exposure of 25-mil plaques, while F, which is second best in the tubular oven at 150°C., is only eighth best, or next to the poorest resin in the oxygen uptake test at 150°C.

Table V also compares oxygen uptake with the U-tube test methods at 150°C. Except for E and I, there appears to be a fair degree of corre-

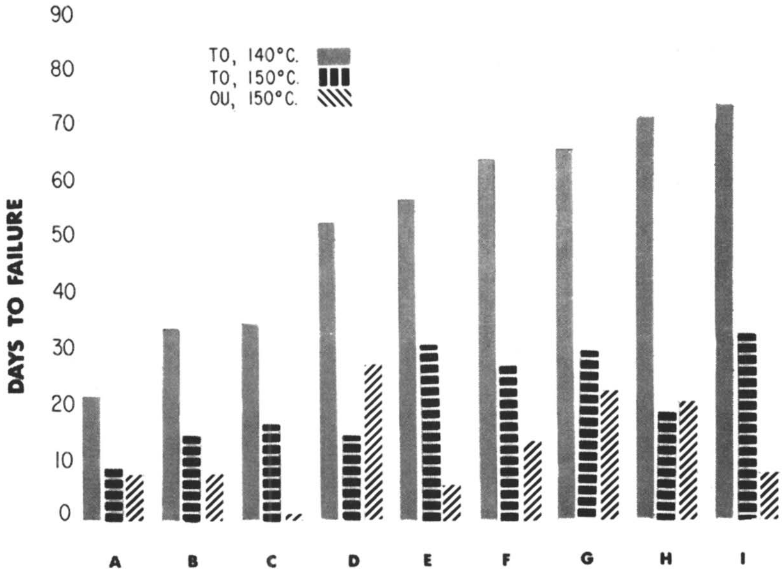


Figure 3. Oxygen uptake test vs. *oven exposure test*

lation between the oxygen uptake and the U-tube/oxygen test. There is considerably less correlation with the U-tube/air test method.

Differential Thermal Analysis (DTA)

Differential thermal analysis (*15*, *29*) has also been proposed as a method for measuring polymer performance. The commercial resins were evaluated by two methods.

Oxidation Exotherm. Samples were heated at a rate of 20°C. per minute from room temperature to decomposition temperature (193°C. for unstabilized resin) as noted by a significant exotherm.

Induction Period. The resins were heated in a nitrogen atmosphere to 190°C. and maintained isothermally at 190°C. for five minutes. Nitrogen was then replaced with oxygen, and the time was noted (zero minutes for unstabilized resin) to a significant exotherm. The data are shown and compared with oxygen uptake and U-tube data in Table VI. Resin A, which was least stable in 25-mil plaques at 140° and 150°C., is best by the DTA oxidation exotherm method, while I, which was best in 25-mil plaques at 140° and 150°C., is next to the poorest material in DTA oxidation exotherm and induction period test methods. Resin C is relatively consistently poor, and H consistently tests high.

Relative Carbonyl Content

An increase in carbonyl content (*2, 14, 20, 25, 30, 32*) has been used by some investigators to determine the stability of polyolefins. Instability was related to the relative increase in carbonyl content. In this study, the relative carbonyl content of the nine commercial polymers was measured in 25-mil plaques after 0, 100, 200, 300, and 400 hours exposures at 140°C. in a forced-draft oven. The following formula was used to obtain the percent carbonyl:

Table VI. DTA, Oxygen Uptake, and U-Tube Data for 25-mil Samples

Differential Thermal Analysis			*U-Tube, Days*	
Oxidation Exotherm, °C.	*Induction Period, min.*	*Oxygen Uptake, days*	*Oxygen*	*Air*
C 233	C 0	C 1	C 3	B 27
I 235	I 3	E 6	B 5	A 46
D 245	E 31	A 8	A 8	C 47
E 249	D 46	I 8	I 16	D 55
B 252	A 74	B 8	F 19	I 58
F 254	G 75	F 14	E 21	F 64
G 255	B 124	H 21	H 26	H 73
H 256	F 242	G 23	G 28	G 77
A 257	H 326	D 28	D 28	E 89

Table VII. Relative Carbonyl Content of 25-mil Sheets Exposed at 140°C.

		Hours			
Resin	*Unexposed*	*100*	*200*	*300*	*400*
A	144	74	34	17	5
B	29	12	11	10	7
C	34	22	21	18	13
D	303	174	97	62	45
E	52	38	33	30	27
F	129	104	70	57	50
G	92	73	63	54	49
H	104	103	102	88	87
I	112	70	46	33	24

$$\%\ \text{carbonyl} = \frac{\text{absorbance of sample at 5.8}\ \mu}{\text{absorbance of reference material at 5.8}\ \mu} \times 100$$

The reference material was 1% benzophenone in carbon tetrachloride in a 0.535-mm. cell (absorbance = 0.392). The relative percent carbonyl content is shown in Table VII. The carbonyl content decreased rather than increased for all the polymers, as might be expected. Highly stabilized commercial resins usually contain the classical hindered phenol antioxidants and synergists such as dilauryl or distearyl 3,3′-thiodipropionate, which contain carbonyl groups. As plastic additives, these synergists are relatively volatile. It was suggested that the relatively volatile carbonyl containing stabilizers are lost during oven aging, which accounts for the decrease in carbonyl content. To test this suggestion, unstabilized polymer was formulated with a known antioxidant which does not contain a carbonyl functional group and also with the same antioxidant in combination with a carbonyl containing synergist. The carbonyl content was measured as described above before and after oven aging. The carbonyl content of the material formulated with a non-carbonyl containing stabilizer did indeed increase with oven exposures. The carbonyl content of the formulated polymer prepared with a carbonyl containing synergist decreased with oven exposures. It appears that the carbonyl method,

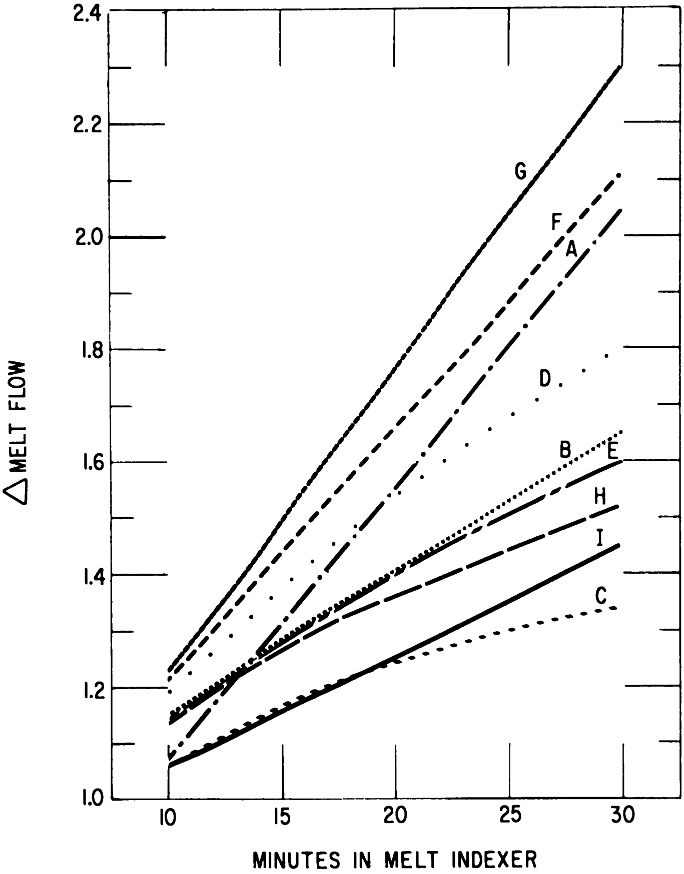


Figure 4. Change in melt flow with time at 275°C.

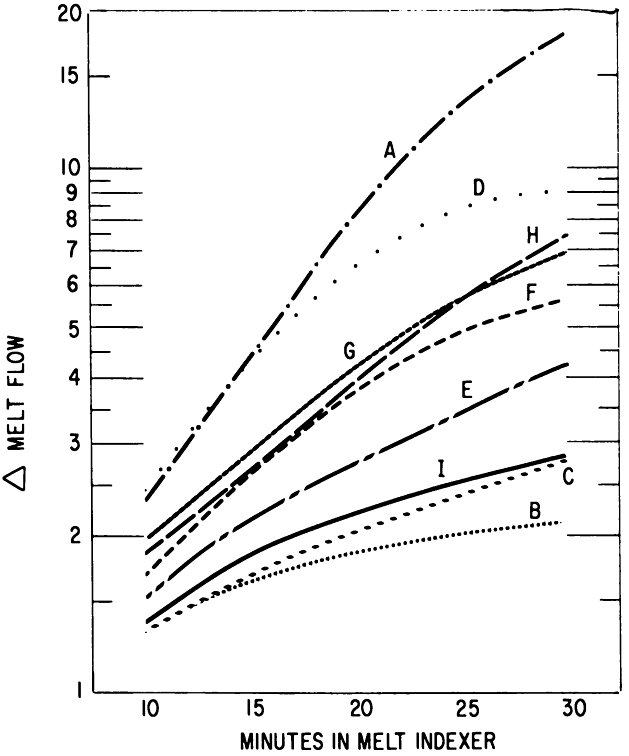


Figure 5. Change in melt flow with time at 300°C.

since it depends on the type of stabilizers used, is of little value in assessing and comparing stabilized polyolefin resins.

Processing Stability

Some of the test methods being used to measure the processing stability of polypropylene include melt flow drift measurements at elevated temperatures using an extrusion plastometer (melt indexer), melt viscosity retention measurements using a torque rheometer, retention of melt flow after repeated extrusions, and injection molded spiral test measured by the flow in inches at various temperatures and the retention of melt flow of the injected spirals. The nine commercial resins were evaluated by these methods.

Melt Flow Drift—Extrusion Plastometer (*16, 17, 18, 20, 26, 27, 28, 32, 33, 34*). Melt flow drift determinations were made at 275° and 300°C. using a 6-gram charge and a 2160-gram piston weight. Melt flows were obtained after 5, 10, 15, and 30 minute intervals. The changes in melt flows with time at 275° and 300°C. are shown in Figures 4 and 5.

Figure 6 shows the melt flow drift data (melt flow at 275°C. at the indicated time periods divided by the standard melt flow, ASTM, D 1238-65T, Condition L). Resins C, I, and H are the most stable, while F, G, and A are the least stable. At 300°C., it appears that Resins B, I, and C are most stable, and A, D, and F are least stable.

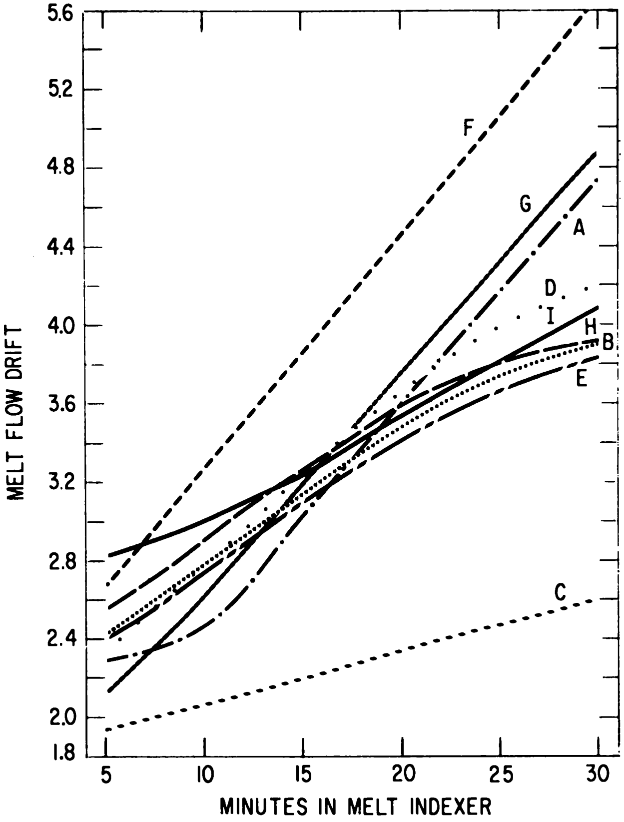


Figure 6. Melt flow drift data at 275°C. (see text)

Extrusion Stability (*20*). Processing stabilities were also determined by six succesive extrusions of the resins through a 1-inch extruder and measuring the change in melt flow (ASTM D 1238-65T, Condition L) after each extrusion. The data shown in Figure 7 indicate that Resins C, E, and I are least stable and G, A, and D are the most stable.

Spiral Mold Test. Processing stabilities were also determined by the spiral mold test (*5*). The resins were injection molded in a 3-ounce reciprocating screw injection molder at 25°F. (14°C.) intervals from 425° (219°C.) to 600°F. (316°C.) using a 55-inch spiral mold under the following conditions: mold temperature, 80°F.; injection pressure, 16,000 p.s.i.g.; holding pressure, 8000 p.s.i.g.; open cycle, 4 seconds; cooling, 20 seconds; injection stroke, 1 inch. The spiral lengths in inches at the designated molding temperatures are shown in Figure 8. The melt flows (Condition L) of the injection-molded spirals are shown in Figure 9. The polymers are fairly stable up to 550°F. (288°C.), with the possible exception of Polymer D. Above 288°C., Resins G, A, F, E, and H are less stable. Polymer C appears to be the most process-stable resin tested under these conditions.

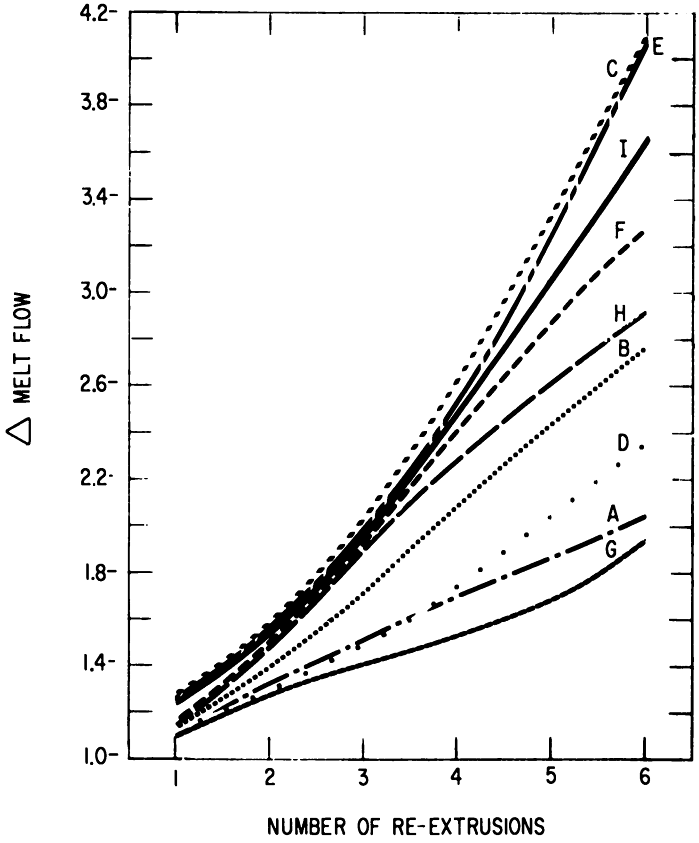


Figure 7. Change in melt flow after six successive extrusions at 258°C. Melt flow, 230°C., 216 kg.

Torque Rheometer. The Brabender plastograph was also used to study the relative processing stabilities of the polymers. The conditions were those recommended by P. G. O'Leary (*24*). The melt viscosity–time curves are shown in Figure 10. Resins D, I, and E are the least stable, and A, H, G, and B are the most stable.

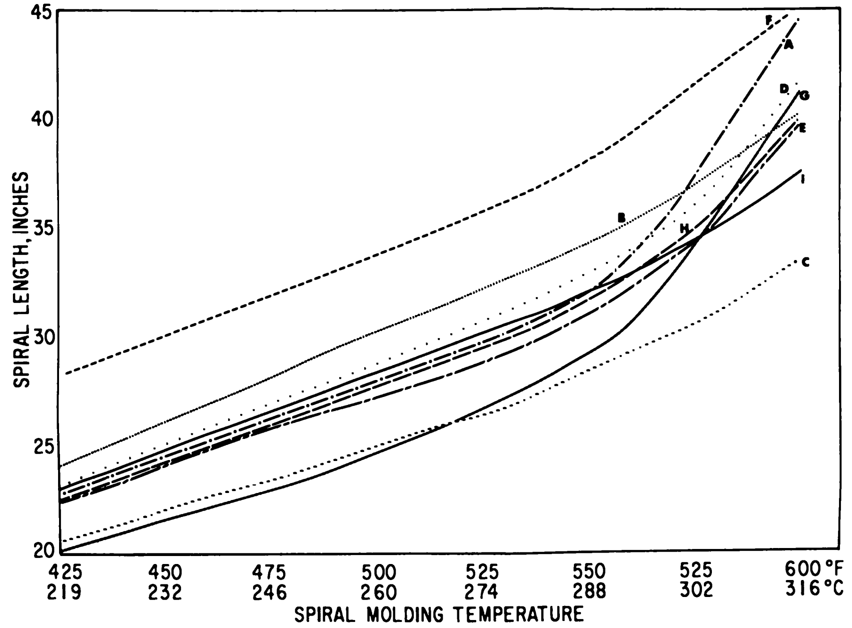


Figure 8. Spiral mold test. Spiral lengths at designated molding temperatures

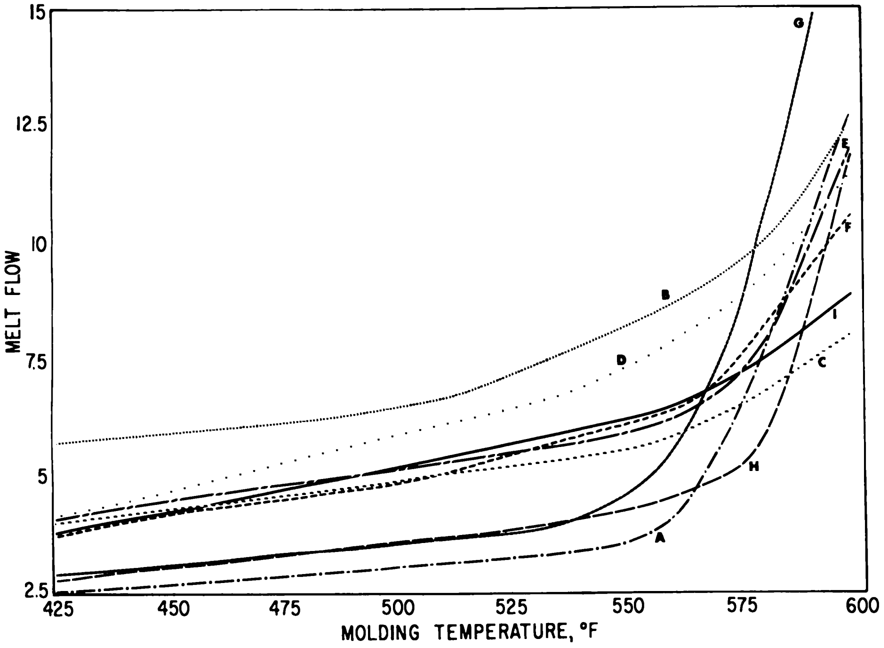


Figure 9. Spiral mold test. Melt flows of the injection molded spirals at 230°C.

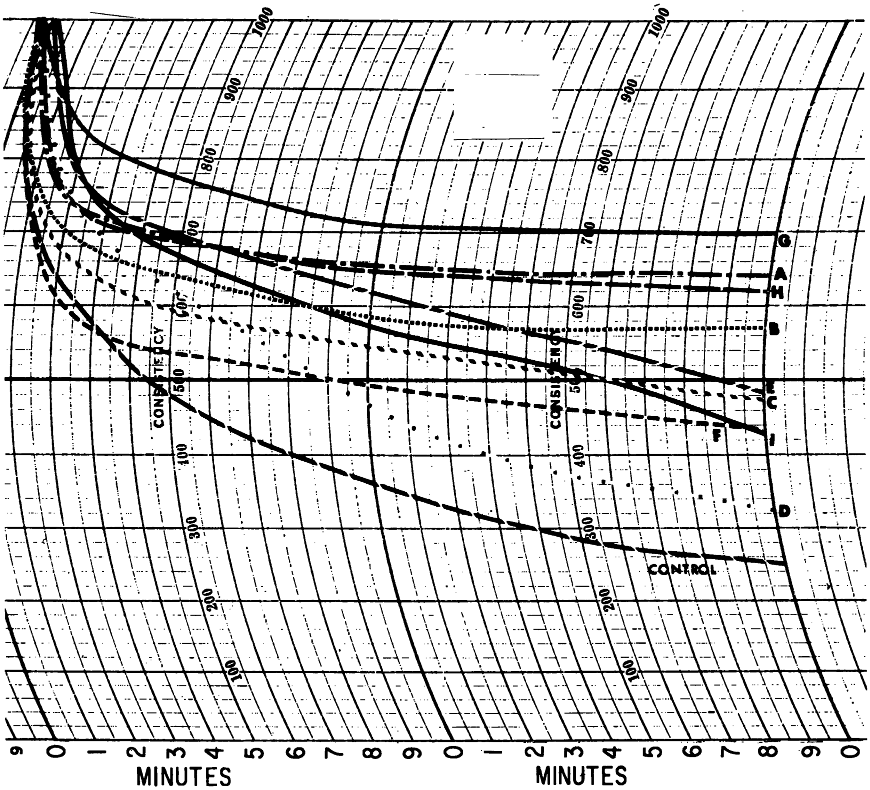


Figure 10. Melt viscosity vs. *time at 215°C., 35-gram charge, 30 r.p.m.*

Conclusions

There is no ideal simulated test method for measuring oxidative and/or processing stabilities. The further one gets from actual environmental (use) and processing conditions, the less likely will the performances of the polymers correlate with commercial usage and processing.

The size and shape of the specimens, the test temperatures, the air flow, and the test environment all effect the relative stabilities of the polymers. Processing stability also depends on temperature, time, pressures, the environment, etc. At best, there is only a fair correlation between the simulated processing test methods and actual processing conditions. The various simulated test methods are useful tools for differentiating polymers whose stabilities vary considerably. The accelerated test conditions and simulated test methods are valuable tools if used prudently.

Literature Cited

(1) Bell, G. W. Jr., Heyd, C. E., *S.P.E. (Soc. Plastics Engrs.) Tech. Papers* **9**, XVII-2 (1963).
(2) Bishop, W. A., Samuels, M. E., "Abstracts of Papers," 152nd Meeting, ACS, Sept. 1966, H12.
(3) Blumberg, M., McTigue, G. H., private communication.
(4) Davis, L. L., Lincoln, B. H., Byrkit, G. D., Joves, W. A., *Ind. Eng. Chem.* **3**, 339 (1941).
(5) Deeley, C. W., Terenzi, J. F., *Mod. Plastics* **42** (12), 111 (1965).
(6) Forsman, J. P., *S.P.E. (Soc. Plastics Engrs.) Tech. Papers* **10**, VIII-2 (1964).
(7) *Ibid.*, **12**, XXXII-3 (1966).
(8) Forsman, J. P., *S.P.E. J.* **20**, 729 (1964).
(9) Forsman, J. P., *Mod. Plastics* **44** (5), 155, 244 (1967).
(10) Geigy Chemical Corp., *Bull.* **M686, M707A, M720.**
(11) *Ibid.*, **M683.**
(12) Hawkins, W. L., *S.P.E. Trans.* **4**, 187 (1964).
(13) Hawkins, W. L., Hansen, R. H., Haterye, W., Winslow, F. H., *J. Appl. Polymer Sci.* **1**, 37 (1959).
(14) Hiltz, A. A., Beck, D. L., *Textile Res. J.* **35**, 716 (1965).
(15) Howard, John, private communication.
(16) I.C.I., Organics Inc., *Tech. Bull.* **193, 194.**
(17) *Ibid.*, **193A.**
(18) *Ibid.*, **H-D 47E-63-3C.**
(19) Kelleher, P. G., *J. Appl. Polymer Sci.* **10**, 843 (1966).
(20) Marshall, B. A., "Modern Plastics Encyclopedia," pp. 418-419, McGraw-Hill, New York, 1968.
(21) Neureiterm, N. P., Brown, E., *Ind. Eng. Chem., Prod. Res. Develop.* **1**, 236 (1962).
(22) Newland, G. C., Tamblyn, J. W., *J. Appl. Polymer Sci.* **9**, 1947 (1965).
(23) Notley, N. T., *Trans. Faraday Soc.* **60**, 88 (1964).
(24) O'Leary, P. G., Plastics Institute of America, Third Annual Conference, Nov. 1965.
(25) *Plastics (London)* **33**, 1127 (1966).
(26) Rudin, A., Schreiber, H. P., Waldman, M. H., *Ind. Eng. Chem.* **53**, 137 (1961).
(27) Rudin, A., Schreiber, H. P., *S.P.E. J.* **20**, 533 (1964).
(28) *Shell Tech. Bull.* **IC 64-18.**
(29) Stafford, B. B., *J. Appl. Polymer Sci.* **9**, 729 (1965).
(30) Tamblyn, J. W., Newland, G. C., *J. Appl. Polymer Sci.* **9**, 2251 (1965).
(31) Uri, N., *Chem. Ind. (London)* **1967**, 2060.
(32) Waghorn, P. E., *Paper Film Foil Converter* **38**, 39 (1964).
(33) Western Electric Co., Manufacturing Standard 17,000, Section 1154, Issue 2 (June 21, 1962).
(34) Williamson, C. W., S. A. E. Regional Technical Conference, Philadelphia Section, April 17, 1962.

RECEIVED December 11, 1967.

17

A Modified Oven-Aging Technique for Studying Polymer Antioxidant Systems

H. GYSLING

J. R. Geigy S. A., P. O. Box 4000 Basel 21, Switzerland

Published on June 1, 1968 on http://pubs.acs.org | doi: 10.1021/ba-1968-0085.ch017

By using very thin samples, the oven aging of polypropylene can be appreciably accelerated. Specimens of definite and reproducible shape and thickness were made by using a microtome. The first phase of the work evaluated the influence of sample thickness from 0.2 to 12 mils on oven life at different temperatures. In the second phase, this modified technique was used to study the effectiveness of three antioxidant/DLTDP systems as thermal stabilizers for polypropylene. The results obtained over a wide spectrum of antioxidant/DLTDP combinations are shown in three-dimensional graphs.

Speeding up the tests that help predict the effectiveness of antioxidants for polymers is a crucial problem for those involved in developing new stabilizers or evaluating new polymer formulations. Numerous methods have already been proposed to accelerate aging. Among these are pre-exposure of the samples to high energy radiation or addition of copper as a catalyst to promote oxidation (5). Such methods often work only for a specific formulation and depend strongly on the chemical nature of the stabilizer; hence, they cannot be used in a more general evaluation of polymers.

Among the numerous well-known aging methods, such as the oxygen-uptake test, the U-tube test, the use of differential thermal analyses to indicate the oxidation exotherm, oven aging proved to be one of the most versatile methods. Not only can many specimens of any size and shape be tested simultaneously, but samples can also be withdrawn at convenient intervals for inspection.

Experimental

The reproducibility and precision of the oven-aging test have already been thoroughly analyzed and discussed by Forsman (*4*), whose analysis has been corroborated by our early work. With respect to sample thickness (*2*) we have carried this study further in an attempt to provide an improved method. To achieve good reproducibility, we relied on his analysis of most of the other critical parameters.

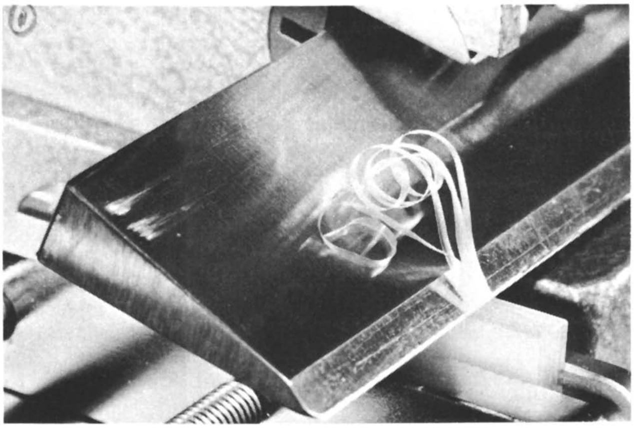


Figure 1. Use of a microtome to cut thin samples

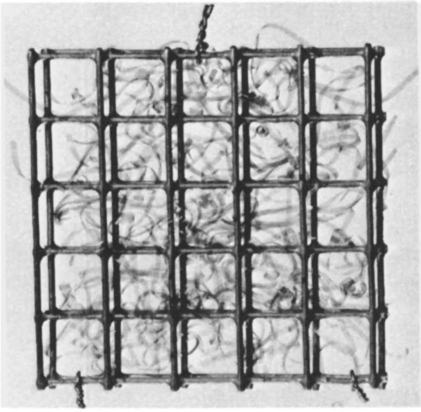


Figure 2. Specimens sandwiched between steel screens

The temperature within our oven was controlled by a multielement air heater and proportional energy input control. Fluctuations were within ±0.5°C.; and the samples were mounted on a rotating rack. To accelerate the aging, very thin specimens were used. In fact, the first goal

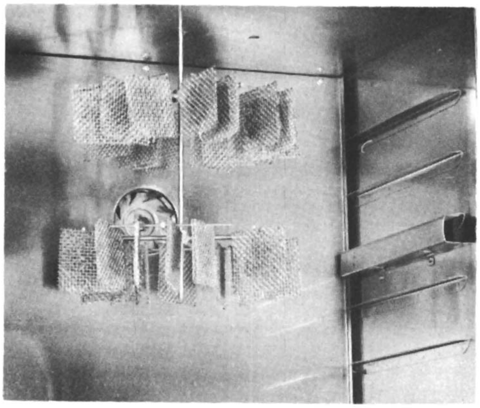


Figure 3. Mounted specimens in a forced-draft oven

of our work was to study the influence of thickness on the oven life of polypropylene samples. Thin specimens prepared in the usual way by pressing or calendering in laboratory equipment vary in thickness. This difficulty has been overcome by using a microtome. Samples of uniform shape and thickness were prepared as follows.

The polymer formulations were processed under a nitrogen blanket in a Brabender plastograph at 200°C. and pressed into 40-mil sheets. Bundles of rectangular small plates cut from such sheets, four or five at a time, were cut into sections of definite thickness from 0.2 to 4 mils, using a heavy microtome equipped with a d-type knife. For the aging test, approximately 80 to 100 cuttings were sandwiched between two steel screens, which were then mounted on a rotating rack in a forced-draft oven (Figures 1, 2, 3).

Since microscopic inspection (60×) of the sections during aging revealed no catalytic effect from the stainless steel wire, and samples sandwiched between aluminum wire-screens (which cannot be cleaned as easily as stainless steel) gave identical results, stainless steel was used in all our tests. The onset of embrittlement is easily recognized and is usually preceded by a reddish fluorescence revealed under a black light. A relatively short time (compared with the total oven life) elapsed between the first signs of degradation and mechanical disintegration.

Since the various methods of estimating failure showed that weight loss, carbonyl-formation (*1*), or solution viscosity did not change markedly until visual signs of degradation occurred (*6*), mechanical degradation upon tapping the sample (screen) was taken as the point of failure. The single data obtained, showed poor precision only at the very short oven lives produced by poor stabilization but better precision with samples of longer oven life. However, the over-all picture of stabilizer performance as obtained from all these tests is not significantly influenced by deviations of individual results. This is especially evident in Figures 8–13.

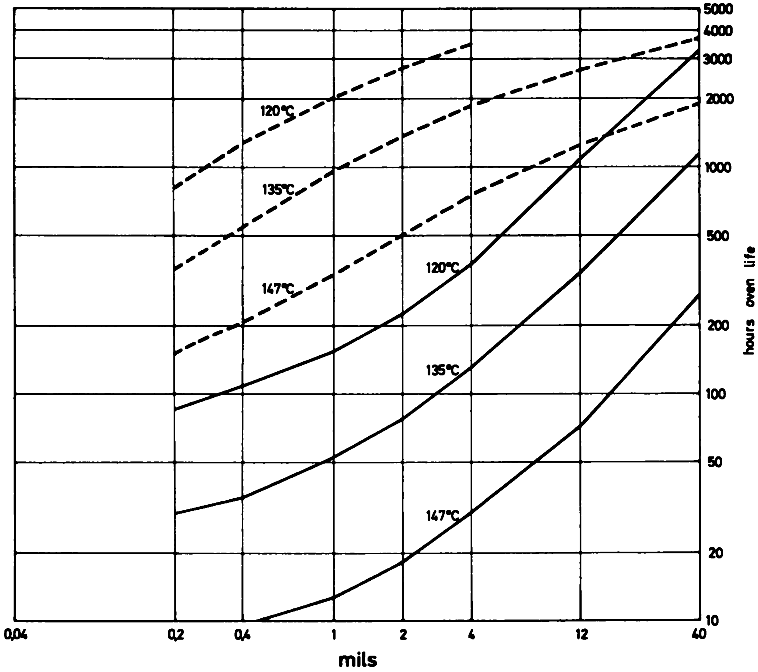


Figure 4. Oven aging of polypropylene samples stabilized with 0.1% Antioxidant A (—) and B (- -). Logarithmic scale

To demonstrate the influence of sample thickness on oven life, two formulations, based on the same batch of resin were tested as described above. One was stabilized with 0.1% of Antioxidant A and the other with 0.1% of Antioxidant B. The samples had a uniform thickness of 0.2, 0.4, 1, 2, 4, 12, and 40 mils. Specimens of 12 and 40 mils were made by compression molding. Oven aging was run at 120°, 135°, and 147°C. The results are given in Figure 4.

Results and Discussion

Oven life and sample thickness are both given on a logarithmic scale to cover the whole range of test conditions. Both formulations yield results which can be interpreted by almost parallel curves, when the temperature is changed from 147° to 135° to 120°C. However, the two formulations do not respond to changes in the specimen thickness to the same degree.

The significant difference is somewhat obscured by the logarithmic presentation of Figure 4, but is easily recognized in the linear presentation of Figure 5. The oven life of Antioxidant A increases almost in proportion to the thickness of the sample over the entire range, 0.2–40 mils; that of

B, however, rises steeply at low thickness but flattens off strongly above *ca.* 4 mils.

To demonstrate the influence of both parameters—specimen thickness and temperature—on oven life, the data from Figure 5 have been replotted three dimensionally. The resulting chart, Figure 6, is characteristic of Antioxidant A and shows how the oven life increases almost linearly with thickness and the reciprocal of the temperature.

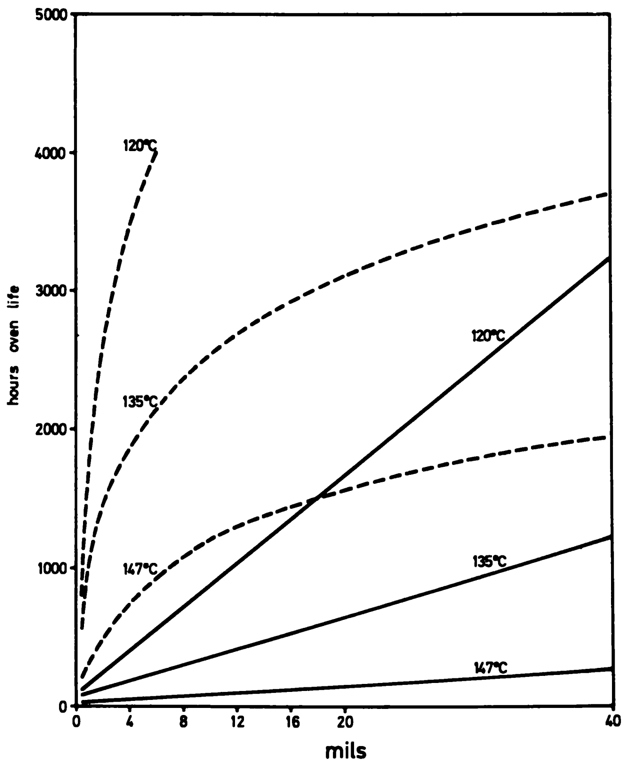


Figure 5. Linear plot of data from Figure 4

A representation such as Figure 6 allows the test results to be extrapolated over a limited temperature range. However, it is often desirable to extrapolate to much lower temperatures to obtain an indication of the service life of a new formulation. Arrhenius plots may be used as a first approximation. It must be emphasized that the straight lines from oven aging tests at only two temperature levels are a simplification of the results obtained in a more thorough evaluation.

In our study, slightly but significantly curved lines were always obtained, whenever the oven-aging tests were carried out at more than two temperature levels. Figure 7 illustrates the results with the Antioxidants A and B at 90°, 120°, 135°, and 147°C. The extrapolation (dotted lines) of the two results at 120° and 147°C. to lower temperatures (90°C.) leads to highly exaggerated values compared with the experimentally determined oven life of the material. As Figure 7 also shows, an increase in the thickness of the test specimen displaces the lines in a parallel direction, whereas a change of the stabilizer system—*e.g.*, from A to B, causes a definite change in the slope, especially at higher temperatures.

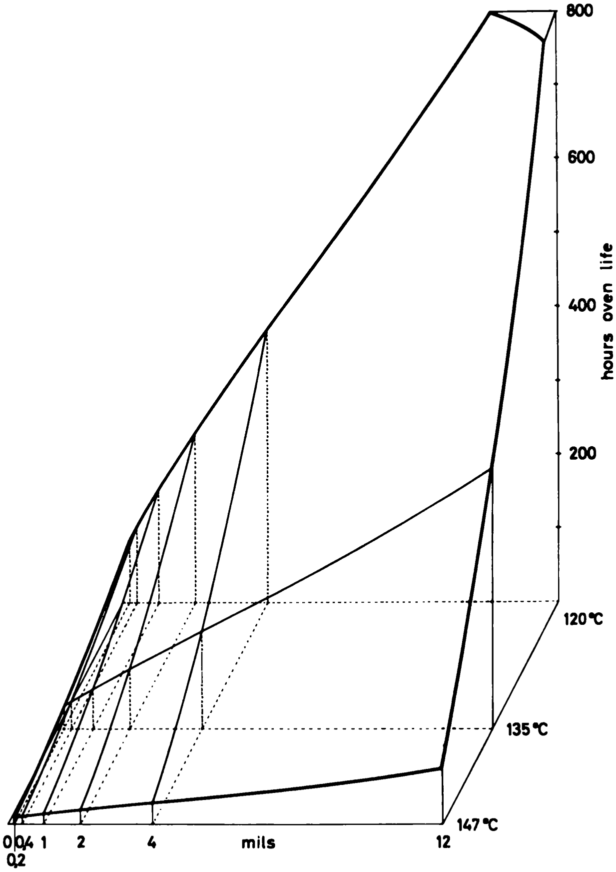


Figure 6. Three-dimensional plot of the influence of specimen thickness and temperature on oven life (data from Figure 5)

That the composition of the resin has a significant influence upon the temperature gradient of the aging rate was also shown in a study of pigmented polypropylene by Fitton and Taylor (*3*). Their data show

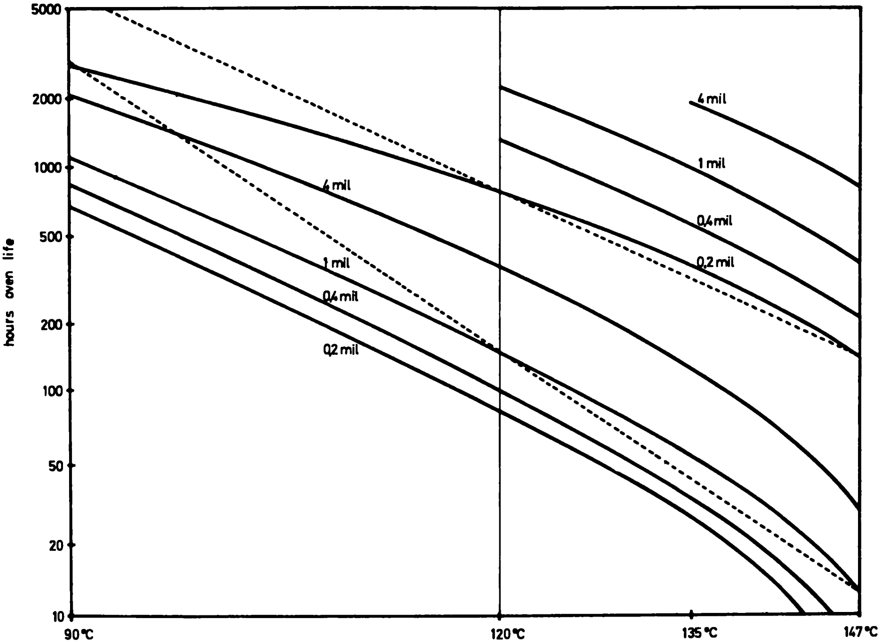


Figure 7. Oven aging of stabilized samples at 90°, 120°, 135°, and 147°C.

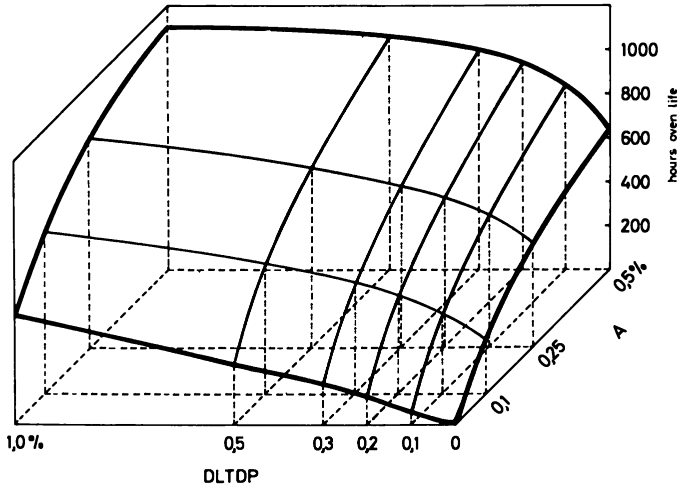


Figure 8. Oven life vs. (DLTDP + Antioxidant A) concentration for 40-mil samples at 147°C.

clearly that the temperature gradient of aging depends strongly on the stabilizer system and pigments used, especially at relatively high test temperatures. An interpretation of their result as an Arrhenius diagram would lead to extremely bent lines.

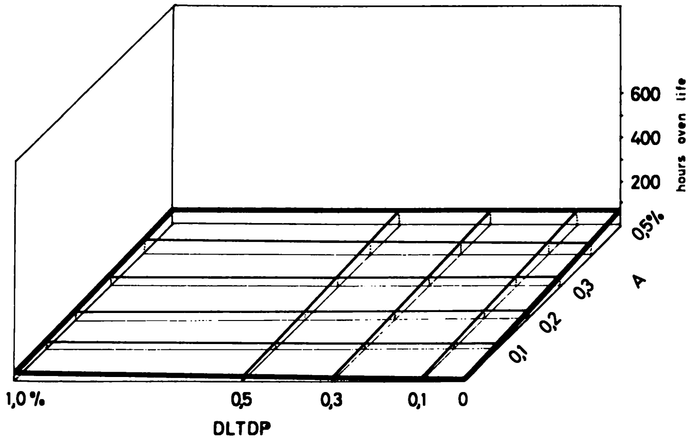


Figure 9. Oven life vs. *(DLTDP + Antioxidant A) concentration for 1-mil samples at 147°C.*

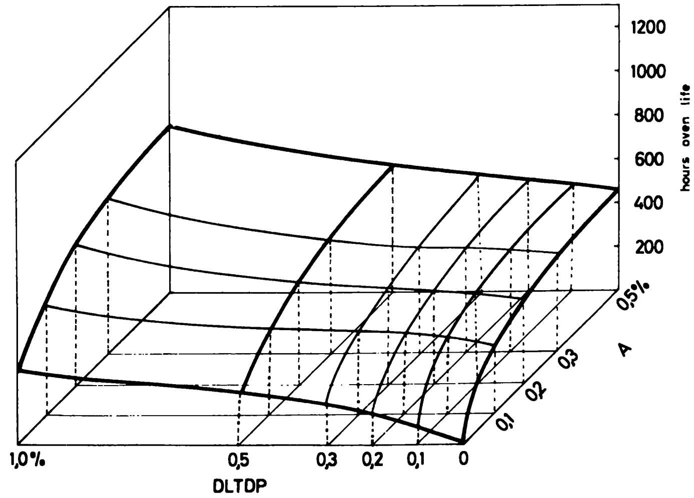


Figure 10. Oven life vs. *(DLTDP + Antioxidant A) concentration for 1-mil samples at 120°C.*

Such findings do not agree with earlier results on oxygen-uptake tests, where almost ideal straight Arrhenius plots were obtained (*1, 2, 5*) and where the slope of the line—*e.g.*, the apparent activation energy (*ca.* 25

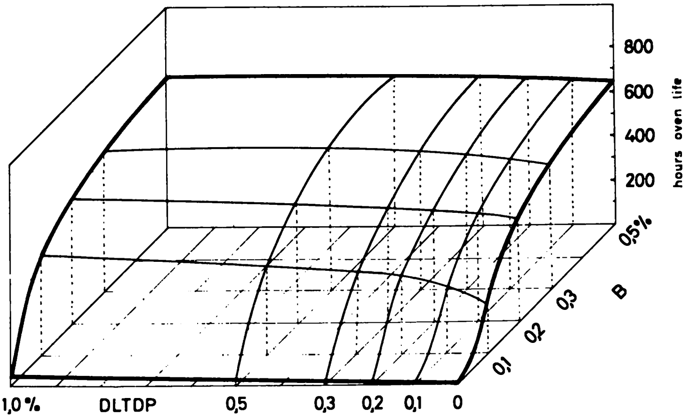


Figure 11. Oven life vs. *(DLTDP + Antioxidant B) concentration for 1-mil samples at 147°C.*

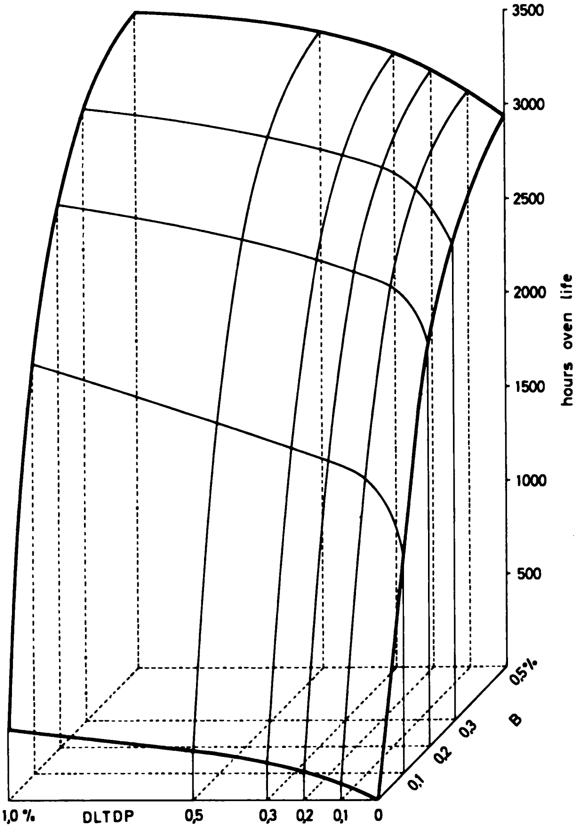


Figure 12. Oven life vs. *(DLTDP + Antioxidant B) concentration for 1-mil samples at 120°C.*

kcal.)—was found to be independent of the type of polyolefin and the type of stabilizer used. One reason for the deviation of the results based on oven aging from such ideal performance certainly arises from the fact that mechanical degradation rather than thermodynamically meaningful reaction rates was the criterion.

Such contradictory results obtained by different aging methods suggest that one should use Arrhenius extrapolations to predict service life only with great reservation. Obviously aging tests should be run over a wide spectrum of temperatures and as near as possible to the anticipated end-use temperature of the resin. One way to shorten the duration of the test at lower temperatures is to use thin specimens, such as microtome cuttings. Figures 5 and 6 show that acceleration by an order of magnitude may be obtained.

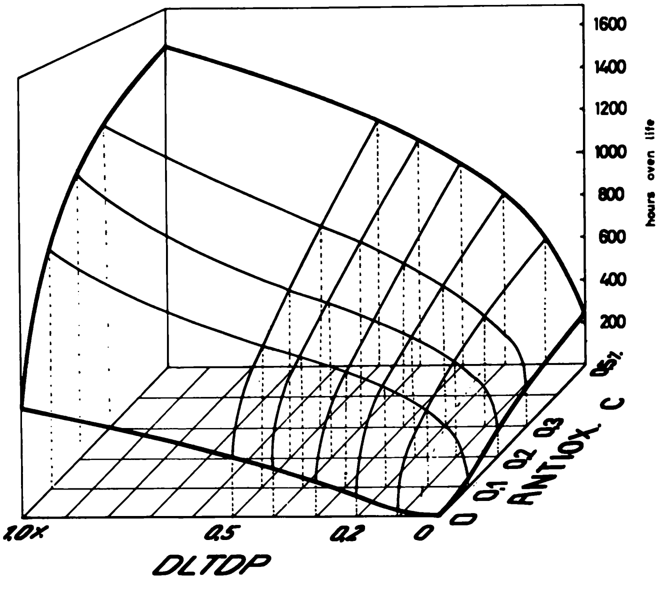


Figure 13. Oven life vs. *(DLTDP + Antioxidant C) concentration for 1.5-mil samples at 120°C.*

In another series of tests the effectiveness of the phenolic Antioxidants A and B in combination with DLTDP (dilauryl thiodipropionate) was evaluated over a wide range of concentrations at 147° and 120°C. The results are shown in Figures 8–13, where the oven life is plotted as a function of stabilizer composition. Figure 8 is an evaluation of normal 40-mil specimens tested at 147°C. It is obvious that no synergism between the antioxidants A or B and the DLTDP exists. Both the phenol and the

DLTDP make an individual contribution, depending on their concentration, to the total stability of the sample.

Figure 9 shows the drastic but proportional reduction of oven life when 1-mil samples were used. Figure 10 shows the results obtained with 1-mil specimens at 120°C. The oven life increases steeply with increasing phenolic antioxidant concentration from 0–0.2%, flattening off above 0.3%. The effect of DLTDP is less noticeable than in Figure 8.

An analogous evaluation was carried out with Antioxidant B, but for the sake of time, the tests were restricted to 1-mil specimens. Figures 11 and 12 are characteristic of the excellent performance of this high molecular weight antioxidant. Again no synergism was found.

Finally, Figure 13 refers to a series of antioxidant/DLTDP combinations (tested as 1.5-mil cuttings at 120°C.), which showed significant synergism. The shape of the figure differs appreciably from that of foregoing combinations.

Literature Cited

(1) Beachell, H. C., Beck, D. L., *J. Polymer Sci.* **A3**, 457 (1965).
(2) Boss, C. R., Chien, J. C. W., *Proc. PIA Conf.* (Nov. 1965).
(3) Fitton, S. L., Taylor, W., *Plastics* **1966**, 1139.
(4) Forsman, J. P., *S.P.E. (Soc. Plastics Eng.) Tech. Papers* **10**, 1 (1964).
(5) Hansen, R. H. *et al., J. Polymer Sci.* **A2**, 587 (1964).
(6) Oswald, H. J., Turi, E., *Polymer Eng. Sci.* **1965**, 152.

RECEIVED June 19, 1967.

18

Microbial Degradation of Plasticized Vinyl Films

RALPH EISENSCHIML

Scientific Chemicals, Inc., 1637 S. Kilbourn Ave., Chicago, Ill.

WILLIAM H. BAUER

Union Carbide Corp., Tarrytown Technical Center, P. O. Box 65,
Tarrytown, N. Y.

Poly(vinyl chloride) films are subject to microbial attack, which can manifest itself in many ways, such as surface contamination, pink staining, or a change in the physical properties of the film. To study the variables affecting microbial degradation, a number of vinyl films were produced and evaluated under outdoor weathering conditions as well as in accelerated laboratory procedures. All films tested, even those made with so-called "funginert" plasticizers, supported surface fungal growth, and their physical properties after exposure were affected in varying degrees. A number of biocides were evaluated for their ability to retard microbial degradation and an arsine-epoxidized soya adduct was developed which proved to be effective over a wide range of formulating parameters.

The subject of microbial degradation is a world where unanswered questions greatly outnumber available answers and where experts contradict each other with alarming frequency. Several years ago Scientific Chemicals, Inc. and Union Carbide Corp. began a cooperative project designed to answer at least a few questions. Today, after over 5000 individual physical tests and countless Petri dishes, the number of unanswered questions has probably been diminished only slightly.

The study was designed to evaluate a number of vinyl formulation parameters, varying the plasticizers, resins, antimicrobials, and other additives to find clues as to which films would be most resistant to degradation, before and after weathering. The first part of this paper deals primarily with general microbial degradation of films; the concluding section summarizes the formulation and performance of some of the films which were produced and evaluated and how that performance may benefit the vinyl formulator.

It was necessary to change our direction several times during this study, and we did not anticipate that there would be a point at which a new product would have to be developed to provide a fresh approach to the problem.

Microbial Degradation

The literature is replete with studies relating to the microbial susceptibility of plasticizers to both fungi and bacteria, and a recent article, describing work by Soviet scientists, suggests that this particular problem does not stop at national boundaries (*4*). Indeed, microbial degradation has been reported from the equator to the Arctic Circle, on items ranging from those beneath the sea to those orbiting the earth.

The term "microbe" or "microbial" includes bacterial and fungal organisms, and the expression "microorganism" denotes a long form of "microbe." "Mildew" and "mold" refer to that surface fungal growth which is generally visible to the naked eye.

Chemicals used to control microbes have various names. They are known as antimicrobials or microbiocides when they control a broad spectrum of microorganisms. Bactericides and fungicides, as their names imply, control bacteria and fungal organisms, and individual industries use their own specific terms. Thus, the wood industry uses "preservatives" to control "rot"; military specifications often call for "mildewproofing agents," and the pharmaceutical industry attacks microorganisms with "antibiotics."

The literature dealing with microbial attack on plasticizers can also be confusing. A typical table, for example, lists 20 general types of plasticizers, and classifies 10 of these as being susceptible to microbial growth, six resistant, and four ambivalent (*3*). For those wondering how ambivalence is possible, consider for a moment another study concerned with a film containing dioctyl phthalate as the only plasticizer. When this film was laminated onto ordinary untreated duck cloth, no degradation was noted after soil burial. The same film, however, tested as an unsupported film, showed significant deterioration (*1*). No attempt is made to explain this ambiguity. Nevertheless, studies in microbial attack frequently turn up these types of data, much to the frustration of those who must produce microbial-resistant products.

The matter of so-called funginert materials is equally in doubt. This coined term is a contraction of "fungus inert," and its definition is more difficult than it sounds. For example, glass is funginert, under many conditions. However, during World War II, lenses in optical systems were seriously damaged by fungus attack, and the secreted acids of these organisms destroyed many optical systems, ranging from binoculars to bombsights (*5*).

Similarly, C. Bruce Lee reports finding microbial growth on all sorts of items one might consider to be funginert. Entire rockets were subjected to accelerated tests, and the following components are cited as being particularly susceptible to microbial attack: elastomer buttons, cable leads containing chromatic materials in their insulations, asbestos tubing (apparently adulterated with cotton threads), cable harnesses, transformers, solenoids, assembled control panels and various types of instrumentation (*8*). Obviously, funginerts are not simple to define.

The definition of a funginert plasticizer is no easier. Studies by Klausmeier and Jones indicate that many of these supposed funginerts will support microbial growth under certain conditions (*7*)—something which many in the industry have suspected.

The other ingredients in vinyl film are not totally free from guilt either. One might expect resins themselves to be impervious to fungus growth, yet films containing various resins differ widely in their susceptibility to attack. At least one factor involved is the residual soap or surfactant on the surface of emulsion poly(vinyl chloride) (PVC) resins. Undoubtedly there are many other causative factors as well.

Types of Microbial Attack

Microbial attack manifests itself in so many ways that recently ASTM (American Society for Testing and Materials) established a new committee whose sole purpose is to advise other ASTM committees on biological degradation.

One way to examine microbial attack on vinyls is to study some commonly used testing procedures since these are basically accelerated methods of producing microbial attack, provided the item is susceptible. Most familiar to everyone is the surface fungal or mildew test which can be conducted in several ways. Two of the most common are the Petri dish inoculation test and the tropical humidity chamber. In the former, the specimen is laid on a bed of moisture-containing colloid (usually agar-agar), into which several minerals have been added to accelerate the growth of the test organisms. A standard group of fungal organisms, which are used to inoculate vinyl samples, are defined in many of the military specifications calling for these tests.

The tropical humidity test simulates hot humid conditions—*e.g.*, 90°F., at 90% relative humidity. The samples are wetted down and sprayed with a mixed fungal population to accelerate mildew growth.

Both tests are designed to produce surface mildew growth on the sample if it is susceptible. These tests are commonly used for such items as shower curtains, bathmats, coated fabrics, marine and automotive fabrics, and wall coverings. Special variations of these tests are also used where indicated—*e.g.*, the use of *Trichophyton interdigitale* (an organism associated with "athlete's foot" conditions) as the test organism for bathmats or shoe fabrics. However, surface growth is not necessarily synonymous with polymer degradation. It is not unusual to see highly susceptible additives promoting the growth of mildew with no measurable degradation of the film itself.

In some types of tests an inhibition zone can be observed on treated samples, and few things are more controversial among industrial microbiologists than the interpretation of this zone. It is a clear area surrounding a sample in which no fungal organisms can be observed. The zone is in turn usually surrounded by fungus growth, and appears visually as a clear buffer area between sample and mold growth. In this type of test the colloid contains sugars or other carbon-containing materials, and the seeded fungal organism tends to grow except where inhibited by the sample or its inhibition zone.

A zone generally indicates fungicidal activity in the tested sample, but it can mean other things, including the leaching out of the antimicrobial into the colloid base (or partial water solubility), or it can mean volatility of the antimicrobial agent. A zone, therefore, must be interpreted carefully and considered only as one part of the entire picture.

A zone of inhibition can be functional in many items. For example, a shower curtain can be relatively non-susceptible to surface fungal growth yet become highly susceptible after a soap film has been deposited through normal use. A properly chosen fungicide can impart a sufficient zone of inhibition to the curtain to inhibit growth on the soap film as well. Here is a case of protection at a distance and an excellent argument for the use of a fungicide in an item which conventional testing might label as non-susceptible.

Another manifestation of microbial attack is known, for lack of a better name, as pink staining. This is an unpredictable and unwelcome splotch which is indelible once it appears and can utterly ruin a wall covering or other decorative vinyl item. The organism responsible is a type of bacterium, although it resembles a fungal organism in many ways. The organism does not necessarily grow on the vinyl itself. It may grow on a supporting structure, such as the backing of a coated fabric, and often grows on the adhesive used to laminate the film to a backing. Once established, it secretes a pink dye which is highly soluble in many plasticizers. The dye is then diffused through the film, even though the film itself is sterile. Many cases of pink-stained vinyl coated fabrics have occurred, and in most the organism could not be made to grow on the vinyl itself.

Our laboratory recently examined a badly stained piece of marine upholstery which illustrates this point. The upholstery, which exhibited a pink blotch on its vinyl surface, was constructed by sandwiching a layer of urethane foam between a cotton backing and the vinyl surface. The stain originated in the cotton backing, appearing originally as a black discoloration. The organism spread through the foam, developing the pink dye about halfway through the foam layer, and the developed dye then migrated into the vinyl film, where it discolored the outer surface.

Although the causative organism obviously did not originate on the vinyl film, the film was still discolored once the organism got a foothold on the backing. Salesmen in the industry know only too well that when a pink splotch appears on a customer's wall or favorite boat cushion, it makes little difference where the trouble started. The vinyl gets the blame. A laboratory procedure has been developed to determine susceptibility to pink staining, using *Streptomyces rubrireticuli* as the test organism (9). Blue staining has also been reported on vinyl films, but, to the best of our knowledge, no positive identification has been made of causative microorganisms.

A zone of inhibition can be extremely functional in preventing microbial growth in adjacent materials. Earlier we mentioned that fungal attack on optical glass can be a problem. It is quite probable that the microorganisms themselves are growing on fingerprints, dirt particles, or other organic materials which have come into contact with the lens. In glass it is not always possible to establish a zone of inhibition to prevent this; in vinyl the solution is much simpler. The adhesive and fabric backing on coated vinyl fabric should be treated to inhibit microbes, but if this cannot be done, there is a strong argument for incorporating an antimicrobial agent into the vinyl no matter how funginert itself the film may be.

This brings us to another class of microorganisms—the bacteria. These are really single-celled fungal organisms in many ways, and reports going back to World War II show bacteria to be among the prime culprits when it comes to plasticizer attack (2, 6). That their action is largely invisible does not lessen their ability to degrade flexible vinyls. For an antimicrobial agent to be completely effective, it should have broad-spectrum activity—*i.e.*, it should control not only the fungal organisms, but the two main classes of bacteria, the gram positives and the gram negatives, as well. Not all antimicrobial agents qualify, but experience has shown the advisability of broad-spectrum protection.

Vinyl films, in addition to being protected against bacterial attack themselves, serve another and a growing function today. More and more films contain bactericides as a means of killing surface contamination in addition to protecting the vinyl itself. There is increasing interest in specifications (*e.g.*, New York State Specification 625) for institutional vinyl coverings, where the film is tested for its ability to kill bacteria.

The organism used in this test is *Staphylococcus aureus* #*209*, a strain known to be resistant to antibiotics and one responsible for some serious infectious epidemics in nurseries, institutions, and hospitals. The New York Specification requires a 98% reduction of organisms in 24 hours. The U. S. Department of Agriculture, which approves commercial claims concerning bactericidal action, in addition requires data showing a progressive kill rate (kill rate *vs.* time). The antimicrobial here has two distinct functions—the prevention of film degradation and control of surface growth.

Recent work sponsored by the Department of Agriculture also pinpoints another group of microorganisms, the viruses, as being carried and spread by fabrics and capable of being controlled chemically. While this work is presently limited to textiles, it is quite likely that it will apply equally to vinyl surfaces, and no doubt work will be done in this area in the near future. If vinyls containing an antimicrobial can be shown to be virucidal as well as bactericidal, some interesting new applications may present themselves.

The following test procedures are most commonly used to determine microbial susceptibility of vinyls.

(1) Fungal inoculation. This can be a Petri dish test, a tropical humidity test, or sometimes a soil burial test, which can be considered a type of superinoculation.

(2) Pink staining test (usually a Petri dish procedure).

(3) Bacterial inoculation tests. While bacterial organisms are not included as part of a normal inoculation test for surface-growing organisms, they are becoming widely used to determine bactericidal properties of the film itself.

In addition to these three accelerated procedures, plasticizer degradation can be measured in terms of physical properties of the film itself—flexibility, elongation, and tensile strength. This is discussed more fully later in the text.

The original purpose of this study was to prepare a group of vinyl films which would incorporate representative groups of plasticizers, resins, and antimicrobial agents and then attempt to correlate the various factors which affected their microbial susceptibility and physical properties, both before and after outdoor exposure. In the early formulation work some interesting results developed. For example, all plasticizer systems tested —*i.e.*, those containing no antimicrobial agent, could be made to support surface fungal growth under standard laboratory test conditions. These conditions involved inoculating the film with a mixed population of eight fungal organisms and then incubating the samples for 14 days. Typical of such films were those containing dioctyl phthalate as the sole plasticizer component. Therefore, if dioctyl phthalate were truly funginert, other components of the vinyl film were playing a direct role in the susceptibility of the film. An investigation of the individual components then became the topic of a comprehensive study (summarized in a later section).

Development of an Arsine–Epoxy Adduct

The initial part of this study conclusively pointed out the desirability, if not the necessity, of including a biocide as an essential ingredient of a

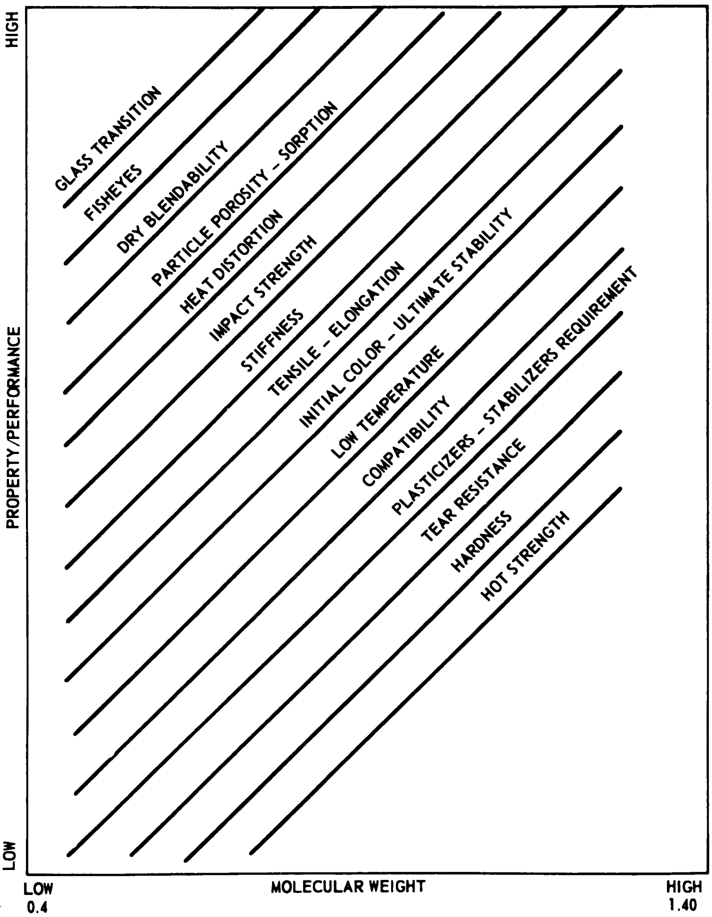


Figure 1. Poly(vinyl chloride) resin general performance/property characteristics vs. molecular weight. Molecular weight was evaluated by intrinsic viscosity (ASTM D-1243-A).

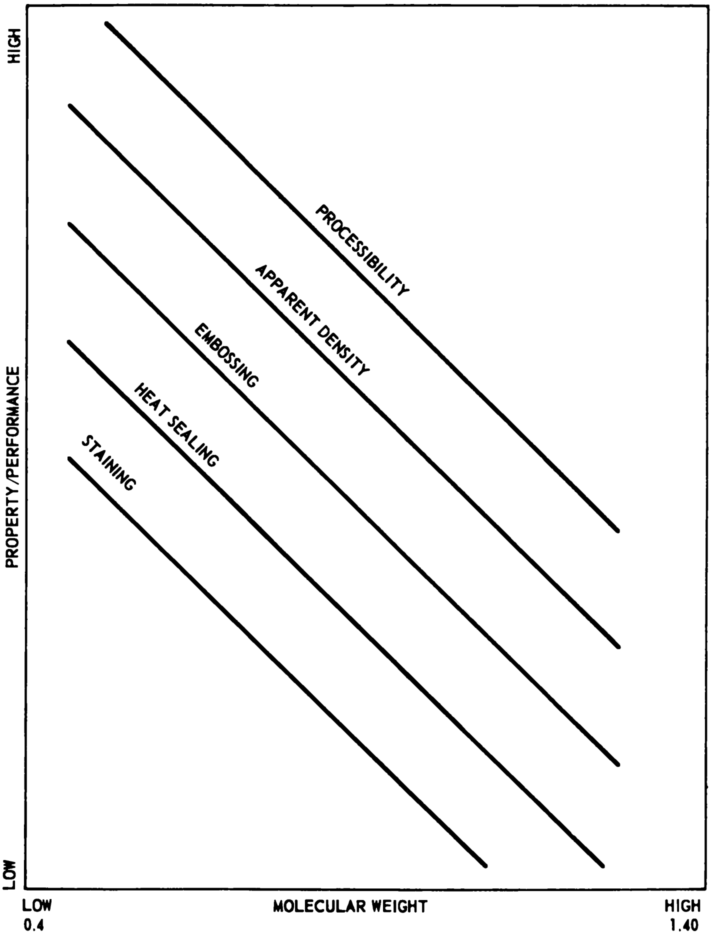


Figure 2. Poly(vinyl chloride) resin general performance/property characteristics vs. *molecular weight. Molecular weight was evaluated by intrinsic viscosity (ASTM D-1243-A).*

vinyl formulation to avoid the adverse effects of microbial and fungal attack. Past experience indicated that deleterious side effects were noted in vinyl films which utilized the commonly available antimicrobials. In some cases, heat and light stability of the film were downgraded; some induced exudation or spewing of the liquid components. The majority were insoluble in plasticizer and, hence, immobile in the vinyl matrix, reducing surface activity as a function of concentration and minimizing surface replenishment during exposure.

It appeared desirable, therefore, to develop a new system which would eliminate these shortcomings. The biocide eventually developed was essentially a condensation of 10,10′-oxybisphenoxarsine with an intermediate phenolic component, and subsequent adduction with epoxidized soybean oil (*10*). Extensive laboratory screening confirmed that the arsine-epoxy adduct produced no adverse effect on compatibility and heat stability, and biocidal activity remained unaltered by compounding and processing. Comprehensive toxicology tests on film containing the adduct indicated that no problems would occur under use conditions. While the history of the development program is a chapter in itself, the choice of epoxidized soybean oil as the biocide carrier was not unfounded. The epoxidized soyas are a universally accepted component of a vinyl compound; the presence of this plasticizer-stabilizer would not detract from

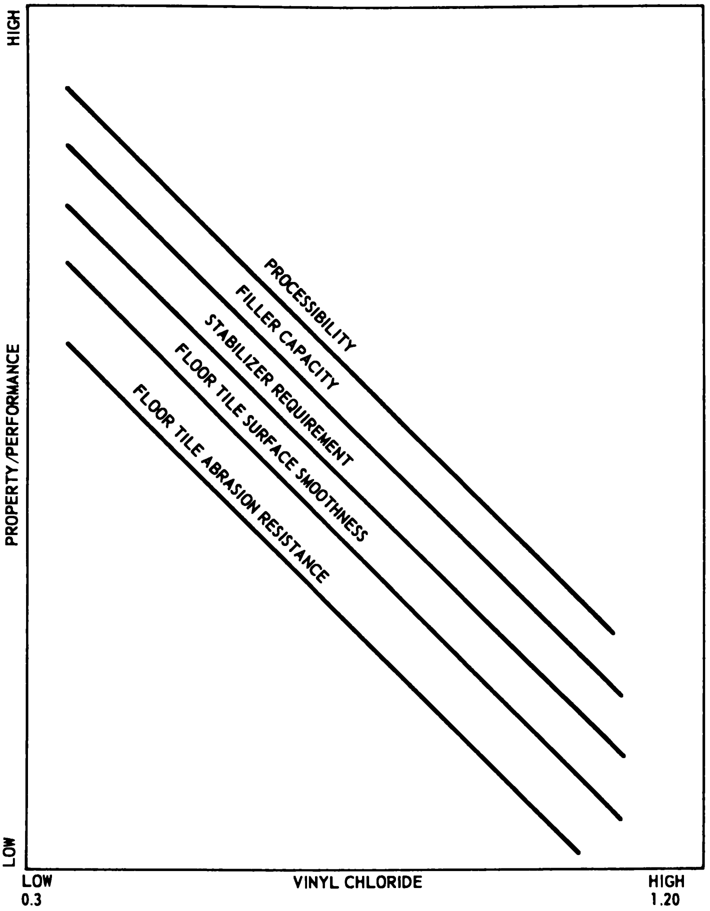


Figure 3. Vinyl chloride–vinyl acetate copolymer resin general performance/property characteristics vs. vinyl chloride content. Molecular weight was evaluated by intrinsic viscosity (ASTM D-1243-A).

the physical performance of the compound in any foreseeable end-use application. Only field testing remained before the system could be finally judged.

Formulating Parameters in Vinyl Compounds

The ability of a flexible vinyl film to withstand the rigors of environmental exposure has been the subject of many studies, both reported and unreported. The extreme complexity of a vinyl system stems not only from the number of individual components necessary from a processing and performance point of view, but it is factorially compounded by the number of choices between components and their relative resistance to the environment. In many cases, the ability to formulate is not totally compatible with the performance requirement, and a compromise must be struck that will provide the optimum conformity to the most critical specifications. The development of unique products or additives to existing commercial materials to broaden formulating latitude has been and is a major stimulus to the growth of the vinyl industry.

The true complexity of the problem is fully appreciated when one examines in detail the performance requirements placed on vinyl compounds and the choice of components to meet these specifications. A plasticized vinyl compound may be required to meet to some degree any combination of the following physical properties:

Volatility

Low temperature flexibility

Low temperature impact

Extraction by aqueous media (Water, soapy water, dilute chemical reagents)

Extraction by hydrocarbon media (Gasoline, kerosene, hexane, oil)

Migration into various substrates including marring

Thermal stability

Resistance to ultraviolet radiation

FDA sanction

Resistance to fungus and mildew

Tensile and elongation

Hardness

Electrical resistance

Flame retardance

Gloss and clarity

Rheology (in plastisols and and organosols)

The selection of components must allow efficient preprocessing by high or low shear dryblending, preblending by Banbury or by plastisol technique, and capability of final fabrication by calendering, extrusion, injection molding, blow molding, dip, rotational or slush molding, spread coating, spraying, or solution casting. Each manufacturing technique has its own unique combination of formulating variables which can be utilized only within the limits of performance of the finished product.

However, the more specific concern of this study is to assess the value of a specific additive in broadening the utility of vinyl compounds to meet certain end-use requirements. A brief look at the possible ingredients in a plasticized vinyl, their good properties, and their limitations will indicate the range of performance which may be achieved.

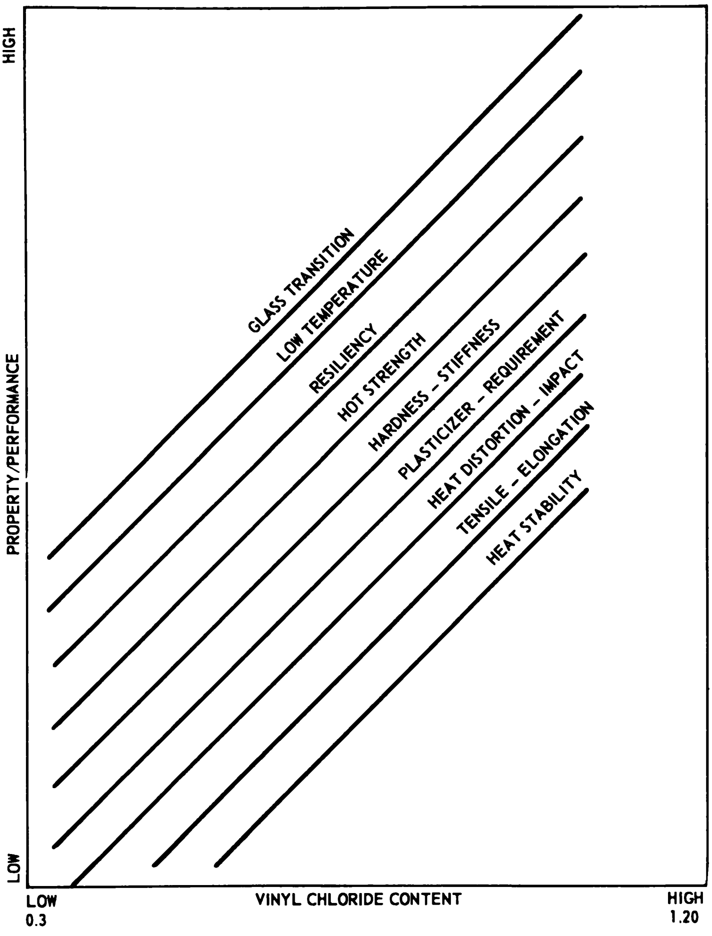


Figure 4. Vinyl chloride–vinyl acetate copolymer resin general performance/property characteristics vs. *vinyl chloride content. Molecular weight was evaluated by intrinsic viscosity (ASTM D-1243-A).*

Resin. This component may be poly(vinyl chloride) or vinyl chloride copolymerized with vinyl acetate, maleate esters, olefin, or any other desirable reactive species. These may be manufactured by suspension, solvent, non-solvent, or emulsion technique and can be varied over a wide range of molecular weights. Figures 1 through 4 indicate qualitatively the influence of molecular weight and comonomer content on physical properties and processibility. Ultimate choice is obviously a compromise, keeping in mind the following general points:

(1) Homopolymers are more stable to degradation by heat and light than are copolymers.

(2) Residual materials (*e.g.*, surfactants, emulsifiers) from polymerization which remain on the surface of the resin particle can exhibit unique secondary manifestations of degradation, such as poor heat and light stability and susceptibility to fungal attack not associated with the polymer itself. This is particularly true of emulsion-prepared polymers (dispersion or paste resins) where the surfactant level may be as high as 3% to provide appropriate rheological properties to the resin.

Plasticizers. With over 300 chemical moieties to choose from, plasticizer selection is complex. Some reason for specific choice may become apparent if these materials are divided into general classes, and their contribution, good and bad, to ultimate performance is noted.

GENERAL PURPOSE. These are, in general, the phthalate diesters offering an over-all balance of physical property performance in vinyls, giving them a 60% share of the total plasticizer market. For vinyl applications, the carbon chain length of each ester group can vary from four to 13. Dibutyl phthalate is mostly limited to vinyl solution coatings because of volatility; above ditridecyl phthalate incompatibility occurs. As the average carbon chain length of the ester group increases, volatility, water extraction, solvency, and efficiency decrease; oil extraction increases. Dioctyl phthalate must be considered the industry standard. Additional specific points must be kept in mind:

(a) The use of normal, primary alcohols for esterification significantly improves low temperature properties and outdoor weatherability at the expense of oil extraction and fungus resistance compared with their branched chain analogs.

(b) Methyl branching on the alcohol chain, particularly in the 1-position, increases degradative susceptibility to ultraviolet radiation when compared with higher carbon branching.

(c) The use of secondary alcohols results in a plasticizer of higher volatility, poorer heat and light stability, increased oil extraction and poorer efficiency than the primary branched chain alcohol.

(d) Increased branching, excluding the 1-methyl group, decreases fungus susceptibility.

LOW TEMPERATURE. Plasticizers imparting improved low temperature flexibility and impact resistance are linear and include the esters of adipic, azelaic, and sebacic acids. Epoxidized monoesters of tall oil and oleic acids, along with certain fatty acid esters are also included. They are characterized by limited compatibility, poor resistance to hydrocarbon extraction, high migratory aptitude, and are susceptible to fungus and mildew. The choice of alcohol exerts the same relative restrictions as in the phthalate series.

EPOXY PLASTICIZERS. These plasticizers, which includes the epoxy esters, epoxidized soybean, linseed oils, and certain specialty types perform a dual role in a vinyl compound. They act synergistically with the metallic component of the stabilizer system and impart their own contribution to the plasticization of the vinyl polymer. The epoxidized soybean oils are more permanent; the epoxy esters, being linear, impart low temperature flexibility in proportion to their concentration. The epoxidized oils exhibit the deficiencies of polymeric plasticizers; the epoxy esters, as noted, have the shortcomings of low temperature plasticizers. Both strongly enhance heat and light stability; outdoor exposure should not be contemplated without their use. They are extremely prone to fungal attack. Epoxy resins may be used for heat and light stabilizing action; they are not subject to fungal attack but do not contribute to plasticization.

POLYMERIC TYPES. When extreme resistance to volatility, marring, migration, and hydrocarbon extraction is required, polymeric plasticizers —the reaction product of aliphatic dicarboxylic acids and low molecular weight diols—are used. Performance varies directly as molecular weight.

Table I. Outdoor Exposure Data

	1	*2*	*3*	*4*
PVC (emulsion, high soap)	100	100	100	100
Di-2-ethylhexyl phthalate	50	42.3	—	—
Di(*n*-octyl, *n*-decyl)phthalate	—	—	50	42.3
Diisodecyl phthalate	—	—	—	—
Polymeric A (medium molecular weight)	—	—	—	—
Diisodecyl adipate	—	—	—	—
Octyl epoxytallate	—	—	—	—
Arsine–epoxy adduct	—	7.7	—	7.7
Ba–Cd–Zn	3.5	3.5	3.5	3.5
Original				
Tensile, p.s.i.g.	3200	2900	2500	2500
Elongation, %	180	200	265	260
180 Days, Arizona				
Elongation, %	145	230	120	240
Δ% Elongation	−19	+13	−55	−8
180 Days, Florida				
Elongation, %	160	190	130	250
Δ% Elongation	−11	−5	−51	−4

These materials, unfortunately, have certain severe limitations. Polymeric plasticizers are viscous, difficult to process, and inefficient. Their heat and light stability are poor, low temperature performance is very poor and they are readily attacked by fungi. Albeit, they are permanent and find significant use in vinyl compounding.

SPECIALTIES. This group is too heterogeneous to allow general comment. It includes the phosphate plasticizers used in flame retardant systems—*e.g.*, tricresyl phosphate, cresyldiphenyl phosphate, octyldiphenyl phosphate, and to a lesser extent, trioctyl phosphate. The latter is utilized when extreme low temperature performance is required. Citrates and glycollates are used in FDA applications. Selected high solvating types (butylbenzyl phthalate, dipropylene glycol dibenzoate, etc.) are used in flooring compositions, adhesives, and as extrusion aids.

Stabilizers. Ideally, the metallic stabilizer should perform four major functions in a vinyl system: (1) HCl acceptor; (2) ultraviolet absorber; (3) antioxidant; (4) reactive dieneophile.

The selected organic salts of Ba, Cd, Zn, Sn, Pb, and Ca perform with varying degrees of acceptability. Barium–cadmium and barium–cadmium–zinc are the most widely used; tin mercaptides and organotin complexes are utilized where ultimate clarity is required; lead salts dominate in electrical applications, and calcium–zinc combinations have been traditionally used when FDA approval is necessary. Organic phosphites are also utilized as so-called "chelators," complexing the half-chloride salt

as a Function of Plasticizer Choice

5	*6*	*7*	*8*	*9*	*10*	*11*	*12*
100	100	100	100	100	100	100	100
—	—	—	—	25	21.2	25	21.2
—	—	—	—	—	—	—	—
50	42.3	—	—	—	—	—	—
—	—	50	42.3	—	—	—	—
—	—	—	—	25	21.1	—	—
—	—	—	—	—	—	25	21.1
—	7.7	—	7.7	—	7.7	—	7.7
3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
2700	2250	2200	2350	1900	1650	2600	3050
215	180	180	170	180	190	220	240
40	140	60	180	80	150	240	250
−81	−22	−64	+5	−56	−21	+8	+4
85	150	60	180	100	180	190	290
−61	−17	−64	+5	−44	−5	−14	+17

and rendering it more soluble in the vinyl matrix, thus decreasing haze. This is a highly proprietary field, and most data are empirical.

Lubricants. This component may be added to vinyl formulations which are to be fabricated by calendaring, molding, or extrusion techniques. Lubricants render processibility and machine operation easier. The classical materials used are mineral oil, stearic acid, low molecular weight polyethylene, and microcrystalline waxes. Stearic acid finds the greatest use but has very limited compatibility and is fungus susceptible; polyethylene is funginert but imparts haze to clear films; mineral oil is inefficient at low levels and incompatible at high levels; the waxes are not sufficiently heat and light stable where critical performance is required. Silicone oils are contraindicated because of exceedingly poor compatibility.

Fillers. Inert inorganic substances such as calcium carbonate, clay, silicates, and asbestos are often utilized in vinyl compositions where clarity is not a requirement. While the carbonates and clay are used ostensibly to reduce cost, beneficial results are forthcoming. The carbonates produce a dry, matte surface and are claimed, because of their alkaline nature, to benefit heat and light stability. Clay improves electrical insulation. Silicates enhance surface dryness. Asbestos fibers provide the reinforcement necessary for dimensional stability in floor tile. Antimony oxide, *per se* or as a surface coating on an inert carrier, provides flame retardance. Their only major adverse effects are to reduce tensile strength and elongation and require an increase in plasticizer level to compensate

Table II. Outdoor Exposure Data as a Function of Resin Choice

	13	*14*	*15*	*16*	*17*	*18*
PVC (suspension)	100	100	—	—	—	—
PVC (emulsion, high)	—	—	100	100	—	—
PVC (emulsion, low)	—	—	—	—	100	100
Di-2-ethylhexyl phthalate	33	—	25	—	25	—
Di(*n*-octyl, *n*-decyl) phthalate	—	50	—	50	—	50
Octyl epoxytallate	17	—	25	—	25	—
Ba–Cd–Zn	3.5	3.5	3.5	3.5	3.5	3.5
Original						
Tensile p.s.i.g.	2800	2750	2600	2500	3000	3200
Elongation, %	230	205	220	265	220	225
180 Days, Arizona						
Elongation, %	220	210	240	120	160	210
Δ% Elongation	−4	+2	+8	−55	−27	−7
180 Days, Florida						
Elongation, %	230	210	190	130	190	180
Δ% Elongation	NC	+2	−14	−51	−14	−20

for their presence if the same hardness, flexibility, and low temperature performance are to be achieved.

Ultraviolet Absorbers. These additives are included whenever prolonged outdoor exposure is a prerequisite to performance. They absorb light in the ultraviolet region and prevent polymer chain scission at points of unsaturation created by dehydrochlorination. They are not known to produce adverse effects on the vinyl compound at use concentrations.

Table III. Outdoor Exposure Data as a Function of Alcohol Branching

	19	*20*	*21*
PVC (suspension)	100	100	100
Di-2-ethylhexyl phthalate	50	—	—
Di-(*n*-octyl, *n*-decyl) phthalate	—	50	—
Diisodecyl phthalate	—	—	50
Arsine–epoxy adduct	8	8	8
Salicylate ester	0.8	0.8	0.8
Polyethylene (low molecular weight)	0.2	0.2	0.2
Ba–Cd–Zn	3.5	3.5	3.5
Original			
Tensile, p.s.i.g.	3000	3100	3500
Elongation, %	210	260	280
180 Days, Arizona			
Elongation, %	170	250	200
Δ% Elongation	−19	−4	−29
180 Days, Florida			
Elongation, %	155	265	200
Δ% Elongation	−26	+2	−29

Biocides. The attack of fungi on the several components of a vinyl formulation may manifest itself as an unsightly growth looking much like dirt or may result in the formation of discolored areas (yellow, pink, blue, clear) on the finished goods. Outdoor exposure, indoor exposure in humid atmosphere, soil burial or contact, and electrical insulation compounds are typical areas where biocide addition is indicated. Since most commercial biocides are heavy metal derivatives, care must be taken to assess their effect on heat and light stability and compatibility with the vinyl system in which they are used.

Scope of Present Study

With the foregoing for reference, the significance of the choice of components to provide the broadest assessment of the performance of

Table IV. Outdoor Exposure Data at a Phosphate Plasticizer Level

	22	*23*	*24*	*25*	*26*	*27*
PVC (suspension)	—	—	100	100	—	—
PVC (emulsion, high)	100	100	—	—	—	—
PVC (emulsion, low)	—	—	—	—	100	100
Di-2-ethylhexyl phthalate	25	21.2	25	21	25	21.2
Tri-2-ethylhexyl phosphate	25	21.1	25	21	25	21.1
Arsine–epoxy adduct	—	7.7	—	8.0	—	7.7
Ba–Cd–Zn	3.5	3.5	3.5	3.5	3.5	3.5
Polyethylene (low molecular weight)	—	—	0.2	0.2	—	—
Original						
Tensile, p.s.i.g.	1800	2000	2700	2550	3300	3400
Elongation, %	200	150	220	210	205	250
180 Days, Arizona						
Elongation, %	10	130	55	140	30[a]	210[a]
Δ% Elongation	−95	−13	−75	−33	−85	−16
180 Days, Florida						
Elongation, %	NS[b]	180	90	170	65[a]	210[a]
Δ% Elongation	NS	+17	−58	−19	−68	−16

[a] 90-Day data.
[b] NS = no sample returned.

Table V. Outdoor Exposure Data

	28	*29*	*30*
PVC (emulsion, high)	100	100	100
Di-2-ethylhexyl phthalate	50	42.3	47
Octyl epoxytallate	—	—	—
Arsine–epoxy adduct	—	7.7	—
Organic sulfur	—	—	3.0
Organic tin	—	—	—
Ba–Cd–Zn	3.5	3.5	3.5
Original			
Tensile, p.s.i.g.	3200	2900	3600
Elongation, %	180	200	210
180 Days, Arizona			
Elongation, %	145	230	70
Δ% Elongation	−19	+13	−67
180 Days, Florida			
Elongation, %	160	190	30
Δ% Elongation	−11	−5	−86

the arsine–epoxy adduct is evident. Data were derived for the following components.

- Resin
  - PVC (emulsion), high soap
  - PVC (emulsion), low soap
  - PVC (suspension), medium molecular weight
- Plasticizers
  - Di-2-ethylhexylphthalate
  - Di(*n*-octyl, *n*-decyl) phthalate
  - Polyester, medium molecular weight
  - Di-2-ethylhexyl phthalate/diisodecyl adipate
  - Di-2-ethylhexyl phthalate/tri-2-ethylhexyl phosphate
  - Di-2-ethylhexyl phthalate/octyl epoxytallate
  - Diisodecyl phthalate
- Stabilizers
  - Barium–cadmium–zinc
  - Tin mercaptide
  - Phosphite chelator
- Lubricants
  - Stearic acid
  - Polyethylene
- Ultraviolet Absorbers
  - Salicylic acid ester
  - Substituted benzophenone
  - Substituted benzotriazole

as a Function of Biocide Choice

31	*32*	*33*	*34*	*35*
100	100	100	100	100
49.7	25	21.2	23.5	24.9
—	25	21.1	23.5	24.8
—	—	7.7	—	—
—	—	—	3.0	—
0.3	—	—	—	0.3
3.5	3.5	3.5	3.5	3.5
2850	3000	2850	3300	2500
240	220	225	210	210
140	160	210	155	90
−42	−27	−7	−26	−57
180	190	240	190	155
−25	−14	+6	−10	−26

- Biocides
  - Arsine–epoxy adduct
  - Organic sulfur
  - Organic tin
- Antioxidants
  - 2,2-Diphenylolpropane
  - Proprietary hindered phenol

Experimental

The 121 sample films were formulated into a replicate series. Those utilizing emulsion polymerized PVC were cast from plastisol onto glass plates and fused in a circulating hot air oven. Those incorporating suspension polymerized PVC were fluxed *via* a Banbury and two-roll compounding mill and finished on an inverted "L" 8-inch × 16-inch four-roll calender. Plastisol films were of nominal 8-mil thickness; calendered film was 4 mils.

The films thus obtained were exposed in South Florida and in Arizona for 180 days; interim samples were withdrawn at 90 days. Tensile and elongation data were determined on the original and four aged samples by use of an Instron after equilibration at ASTM conditions (73.4°F., 50% relative humidity).

Table VI. Outdoor Exposure Data as a Cofunction

	36	*37*	*38*	*39*
PVC (emulsion low)	100	100	100	100
Di(*n*-octyl, *n*-decyl) phthalate	49.25	49.25	49.25	41.55
Arsine–epoxy adduct	—	—	—	7.7
Organic sulfur	—	—	—	—
Organic tin	—	—	—	—
Salicylate ester	0.75	—	—	0.75
Benzophenone	—	0.75	—	—
Benzotriazole	—	—	0.75	—
Ba–Cd–Zn	3.5	3.5	3.5	3.5
Original				
Tensile, p.s.i.g.	2550	2400	2300	2250
Elongation, %	280	230	230	270
180 Days, Arizona				
Elongation, %	200	270	230	310
Δ% Elongation	−29	+15	NC	+13
180 Days, Florida				
Elongation, %	230	250	260	265
Δ% Elongation	−18	+8	+12	−2

Table VII. Outdoor Exposure Data as a Function of Stabilizer Choice

	48	*49*
PVC (suspension)	100	100
Di(*n*-octyl, *n*-decyl) phthalate	50	50
Arsine–epoxy adduct	8	8
Salicylate ester	0.8	0.8
Polyethylene (low molecular weight)	0.2	0.2
Ba–Cd–Zn	3.5	—
Tin mercaptide	—	1.5
Original		
Tensile, p.s.i.g.	3100	2900
Elongation, %	260	190
180 Days, Arizona		
Elongation, %	250	Too Brittle
Δ% Elongation	−4	
180 Days, Florida		
Elongation, %	265	90
Δ% Elongation	+2	−53

of Biocide and Ultraviolet Absorber Choice

40	*41*	*42*	*43*	*44*	*45*	*46*	*47*
100	100	100	100	100	100	100	100
41.55	41.55	46.25	46.25	46.25	48.95	48.95	48.95
7.7	7.7	—	—	—	—	—	—
—	—	3.0	3.0	3.0	—	—	—
—	—	—	—	—	0.3	0.3	0.3
—	—	0.75	—	—	0.75	—	—
0.75	—	—	0.75	—	—	0.75	—
—	0.75	—	—	0.75	—	—	0.75
3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
2250	2050	2250	2400	2650	2300	2700	2500
200	235	260	240	275	240	225	270
240	240	30	90	50	160	270	260
+17	+2	−89	−63	−82	−33	+17	−4
200	250	80	90	20	200	270	260
NC	+6	−69	−63	−93	−17	+17	−4

Analysis of Test Results

Critical examination of the data indicated the following general performance characteristics:

(1) The arsine–epoxy adduct provided exceptional protection for all plasticizers. Further, an epoxy-containing component must be included in a vinyl composition if optimum resistance to outdoor weathering is to be achieved (Table I).

(2) When using emulsion-prepared PVC, the chemical nature of the residual emulsifier is as much a determining factor as the amount of emulsifier remaining on the polymer surface (Table II).

(3) In terms of outdoor weathering, the nature of alcohol moiety in the phthalate series is significant. The order of ultraviolet stability is *n*-alkanol > 2-ethylhexanol > oxo-derived alcohol (methyl branching) (Table III).

(4) The effect of the epoxy constituent is particularly pronounced where the trialkyl phosphate is a major component of the primary plasticizer system (Table IV).

(5) Organic sulfur and, to a lesser extent, organic tin biocides exert a deleterious effect on outdoor exposure of vinyl films, even in the presence of epoxy plasticizer (Table V).

(6) In general, the substituted benzophenone and substituted benzotriazole ultraviolet absorbers were equally effective in protecting vinyl films during outdoor exposure in the absence of biocide. In the presence of the organic sulfur biocide failure was evident; the arsine-epoxy adduct produced no adverse effect. The organic tin biocide was only slightly less effective (Table VI).

(7) The system containing barium–cadmium–zinc stabilizer significantly outperformed the corresponding system based on tin mercaptide. The addition of the phosphite did not alter relative performance in Ba–Cd–Zn systems (Table VII).

Conclusions

(1) The universal activity of the arsine–epoxy adduct suggests its use in all vinyl formulations requiring weathering and/or fungal resistance. Such activity greatly increases the formulating latitude available to the vinyl compounder, allowing materials to be used that will provide optimums in processibility and performance.

(2) The data support specifically the use of epoxy-containing plasticizers in all systems for exterior exposure. Performance is enhanced by using *n*-alkyl phthalates and 2-ethylhexyl analogs as opposed to plasticizers derived from oxo-alcohols.

(3) The response of films containing polyester plasticizers or the trialkyl phosphate to the arsine–epoxy adduct was noteworthy and, to the degree obtained, unexpected.

Literature Cited

(1) Baskin, A. David, Kaplan, Arthur M., *Appl. Microbiol.* **4,** 288 (1956).

(2) Boor, L., Shurtleff, S. J., Research Service Test Report C & P—58-CF, Research and Development Branch, Office of Quartermaster General (1950).

(3) Encyclopedia of Polymer Science and Technology," Vol. 2, p. 391, Interscience Publishers, New York, 1963.

(4) Gamova-Kayukova, Sharashkina, V. N., *Nauch-Issl. Tr., Vses, Nauch-Issl., Inst. Plenok Iskusstv, Koshi* **16,** 12 (1965).

(5) Greathouse and Wessell, "Deterioration of Materials," p. 60, Reinhold, New York, 1954.

(6) Harvey, J. V., Meloro, F. E., Research Report Microbiology Series Report No. 15, Research and Development Branch, Office of the Quartermaster General (1949).

(7) Klausmeier, Dr. R. E., Jones, W. A., "Developments of Industrial Microbiology," Vol. 2, p. 47, Plenum, New York, 1961.

(8) Lee, Dr. C. Bruce, "Developments of Industrial Microbiology," Vol. 2, p. 55, Plenum, New York, 1961.

(9) Yeager, Dr. C. C., *Plastics World* **20,** 14 (Dec. 1962).

(10) Yeager, C. C., U. S. Patent **3,288,674** (March 15, 1965).

RECEIVED April 14, 1967.

19

Fundamental Processes in the Photodegradation of Polymers

J. E. GUILLET, J. DHANRAJ, F. J. GOLEMBA, and G. H. HARTLEY

University of Toronto, Toronto 5, Canada

A study has been made of the mechanism of some of the more fundamental photochemical processes which lead ultimately to polymer degradation. By locating ketone chromophore groups in different positions within the polymeric molecule, the relationship between molecular structure and the quantum efficiency for various modes of energy dissipation have been established. This study, along with studies on the effects of molecular weight, temperature, and internal viscosity, indicates that the major cause of degradation in polymers containing ketone groups is the Norrish Type II photoelimination. The quantum efficiency of the reaction appears to be nearly independent of temperature and of the physical state of the polymer. At normal temperatures the quantum efficiency for radical processes is quite low. The mode of action of two types of stabilizers is briefly described.

The deterioration of polymers in outdoor applications is usually caused by a complex series of reactions, initiated by the absorption of ultraviolet light. This paper discusses the nature of certain primary photochemical reactions which lead ultimately to degradation and establishes how they are affected by experimental conditions. Since photochemical reactions of relatively small organic molecules have been studied extensivly, it would also be of interest to be able to predict the photochemistry of polymer molecules from the known chemistry of simpler compounds.

The effect of various types of radiation on polymers has been studied extensively; however, if we are interested mainly in effects which occur in a terrestrial atmosphere (*i.e.*, conventional "weathering") we must restrict our attention to a rather narrow band of electromagnetic spectrum. In fact, we must concern ourselves primarily with the energy emitted by the sun and transmitted by the earth's atmosphere.

Photochemical Considerations

The energy distribution of solar radiation as a function of wavelength (λ) is shown in Figure 1, Curve A (*11*). This is the energy which would reach an object on the surface of the earth if there were no atmosphere to absorb part of the radiation. Curves B and C represent the energy distribution reaching the earth after passing through the atmosphere at high noon and when the angle of the sun is 30° to the horizontal, respectively. It is readily apparent that no radiation with a wavelength shorter than 3000 A. is transmitted by the atmosphere. This fact has important practical implications in that the number and type of photochemical reactions which may occur are thereby severely restricted. Since the energy of light is inversely proportional to the wavelength (*i.e.*, $E_\lambda = hc/\lambda$), the removal of the short wavelength radiation means that only the relatively low energy light reaches the earth's surface. If, for example, we are concerned with processes involving the breaking of chemical bonds, radiation will be available to break only the weakest of such bonds. This is shown in Figure 2 where the proportion of the sun's total energy greater than hc/λ is plotted as a function of E_λ. Values of the strengths of several chemical bonds are included for reference. Although over half of the sun's radiation has sufficient energy to break weak bonds such as O—O or N—N, only about 5% of the total is sufficiently energetic to break a carbon-carbon bond, and none is expected to break strong bonds such as C—H, O—H, C═C, and C═O.

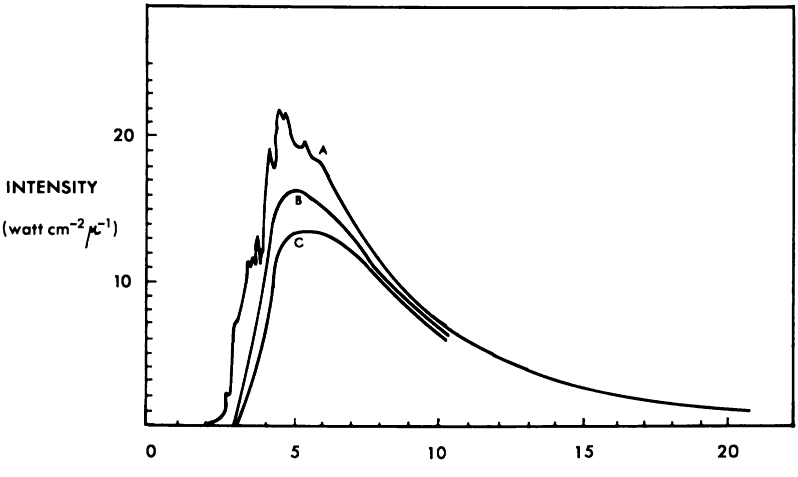


Figure 1. Energy distribution of solar radiation

A further restriction on the possible reactions is imposed by the elementary photochemical principle that light must be absorbed by the polymer if a reaction is to occur. However, most pure synthetic polymers do not absorb at wavelengths longer than 3000 A. and hence should not be affected by terrestrial ultraviolet light. This is demonstrated in Figure 3 which shows the absorption spectra of two typical vinyl polymers.

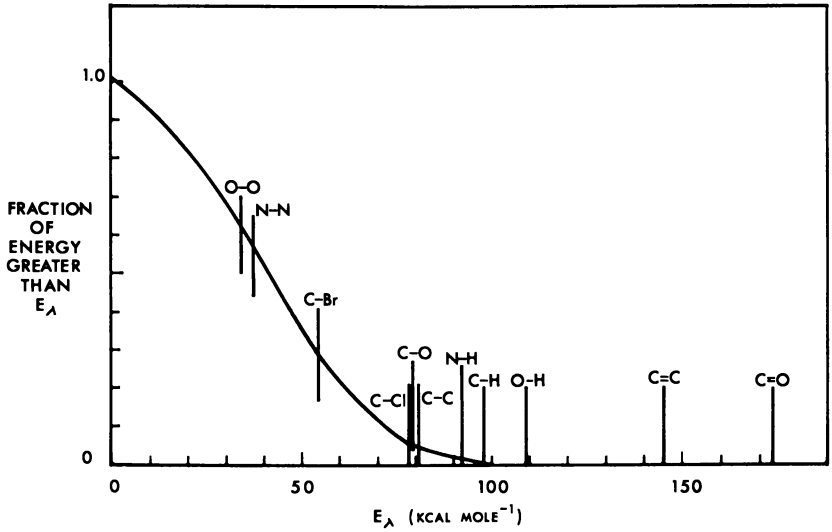


Figure 2. Distribution of solar energy with bond strengths of simple chemical bonds

However, these polymers do degrade when subjected to terrestrial ultraviolet radiation, and this has been attributed to the presence of small amounts of impurities which absorb light and initiate oxidative chain reactions within the polymer. In the oxidation process, compounds containing peroxy and keto groups are formed, and these absorb in the long wavelength region and accelerate the breakdown of the polymer chains. Obviously a detailed study of such reactions in polymers will be difficult because of the frequently unknown nature of the trace impurities which initiate the reactions and of the multiplicity of products formed in the photooxidation.

In the present studies this difficulty has been eliminated by synthesizing polymers with well-defined chromophoric groups situated at known locations with respect to the polymer chains. By studying the photoreactions of these polymers in comparison with those of suitable model compounds, it was possible to infer much about the photochemistry of macromolecules.

Experimental

Two light sources were used; one was a 1-kw. high pressure (110 atm.) water-cooled mercury arc, type AH-6 (General Electric); the other was a 250-watt, medium pressure (30 atm.) compact source mercury arc, type ME/D (Associated Electrical Industries Ltd.). The 3130-A. line was isolated by a sheet of borosilicate glass plate and 2 cm. of filter solution containing nickel and cobalt sulfate. Analysis of the light from the ME/D lamp filtered by this system showed a main peak at 3130 A., with smaller peaks at 2900 and 3360 A. The light intensity from the lamp was monitored by a 1P28 photomultiplier tube, powered by a Lambda

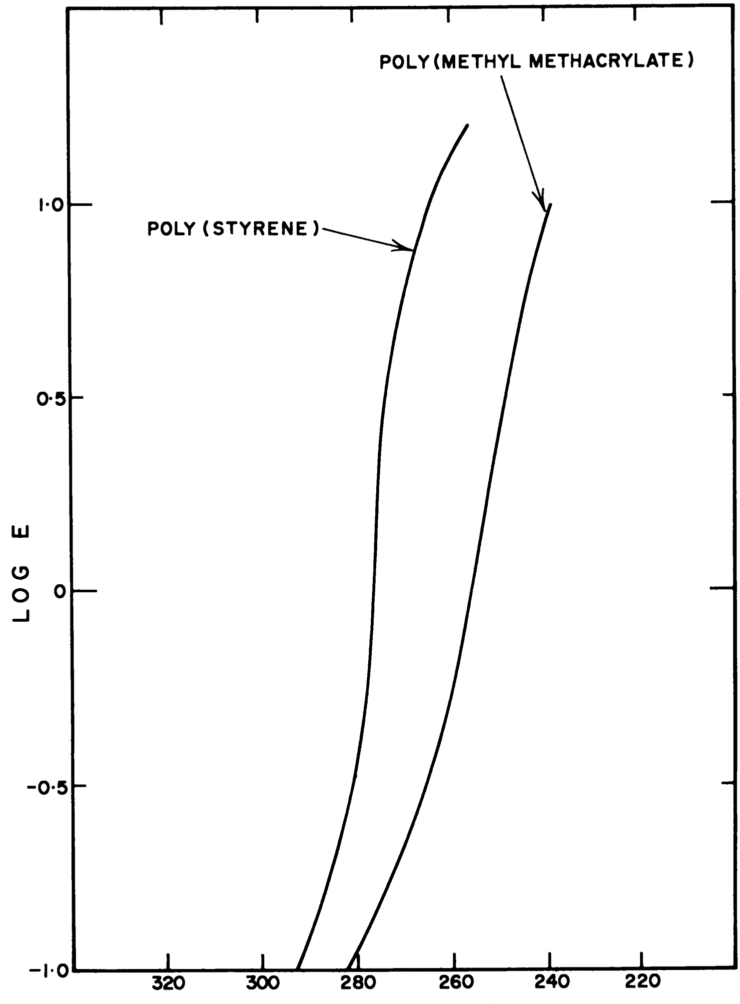


Figure 3. Absorption spectra of polystyrene and poly(methyl methacrylate)

model 24 regulated power supply; the signal from the phototube was measured on a L & N model G recorder. The intensity of the light was measured, and the photomultiplier tube was calibrated using uranyl oxalate actinometry. The response of the photomultiplier tube was linear over the range of intensities measured (0–8.5×10^{-4} Einst./hr.).

The light from the lamp was focused by a quartz lens into a parallel beam, which passed successively through a filter cell, a bath containing the reaction cell, and into the photomultiplier tube.

The filter cell, the reaction cell, and the windows of the bath were all of fused quartz. The lens, bath, and photomultiplier tube housing were rigidly mounted on an optical bench. Temperature control inside the bath was achieved by using either a circulating water pump (± 0.25°C.) or a hot air blower (± 1°C.).

For photolysis of the ethylene–carbon monoxide copolymer in solution, the AH-6 lamp and a 20-mm. path-length quartz cell were used. The cell was filled with the solvent, pure *n*-heptane, and the intensity of the lamp was measured at the experimental temperature. Freeze-dried polymer was then added to make a 2% solution, which absorbed about 25% of the light. The polymer was dissolved, and the solution was mixed by a dry nitrogen stream, which also flushed out any air dissolved in the solvent. The light beam was then allowed to enter the cell, and the photolysis commenced; the intensity of the emergent beam was monitored by the photomultiplier tube and the recorder. At the end of the photolysis the cell was filled with pure solvent, and the intensity of the lamp was measured again. The polymer was recovered from solution by evaporating the heptane; it was then dissolved in benzene and freeze-dried.

The number average molecular weight of the degraded polymers was measured on an ebulliometer, using toluene as a solvent and a tristearin standard. Intrinsic viscosities of the polymers were determined using a Desreux dilution viscometer.

Infrared spectra of the polymer, before and after photolysis, were run on a Perkin Elmer 521 double-beam grating spectrophotometer, using compression-molded films. Film thicknesses were determined by a micrometer.

The solvents used in the photolyses were purified by distillation and filtered through silica gel columns until they were completely transparent over the range of wavelengths passed by the filter system. A Perkin Elmer model 800 gas chromatograph with flame ionization detectors and 1/8-inch × 5-foot columns, 5% w/w silicone SE30 on chromosorb G, was used to analyze the photolysis products. Ultraviolet spectra were run on a Bausch and Lomb Spectronic 505 double-beam spectrophotometer.

Carbon monoxide, a product of the polymer and ketone photolyses, was collected and measured on a gas chromatograph, in a separate series of experiments. The polymer solution was flushed with hydrogen, before, during, and after photolysis, sweeping any evolved gases through activated charcoal cooled in liquid nitrogen. The tube containing the charcoal was then closed, most of the hydrogen was pumped off at liquid nitrogen temperature, and the tube was connected to the gas chromatograph. After the tube warmed to room temperature, any desorbed gases were swept into the gas chromatograph by a hydrogen stream (carrier gas), where they were separated by a 5-A. molecular sieve column using a thermal conductivity detector. The peak areas were compared with the peak areas of known volumes injected before and after the collected sample.

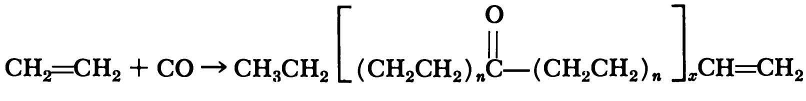
The 1% ethylene–carbon monoxide copolymer was also irradiated in the solid phase (thin film). Compression-molded films were fixed on plates which fitted into the Perkin Elmer 521 infrared spectrophotometer. An infrared spectrum of the polymer could thus be obtained after each period of photolysis without disturbing the film. For photolyses at room temperature and above the plates were mounted in a solid brass cell through which a stream of inert gas could be passed while the cell was being heated.

The ketones used were in most cases obtained from commercial sources and purified by distillation. Analysis by gas chromatography showed a purity greater than 98% in all cases. Dialkyl ketones not available commercially were synthesized from the appropriate acids using an iron catalyst and the method of Davis and Schultz (3).

Results and Discussion

Photochemistry of Ketones. From the point of view of weathering damage the most important of the chromophores absorbing in the near ultraviolet will be those containing oxygen since they are most likely to be formed in polymers degraded in an oxygen atmosphere. The group which has been studied most extensively is the ketone group, C=O. This shows a relatively weak absorption maximum in the range of 270-290 mμ. This is caused by the transition when an electron is raised from a nonbonding *n* orbital localized on the oxygen atom into a delocalized antibonding π^* orbital which extends over the entire carbonyl group. Using Kasha's notation this is an n-π^* transition, and is always the electronic transition of lowest energy in carbonyl and nitroso compounds. It is characteristic of groups containing "lone pair" electrons such as C=O, C=S, —N=O, —NO_2, and —O—N=O. Some vibrational structure can be seen in the vapor state, but in solution the absorption is essentially continuous.

One of the simplest polymers containing the ketone group can be synthesized by the high pressure copolymerization of ethylene and carbon monoxide:



$$CH_2{=}CH_2 + CO \rightarrow CH_3CH_2\left[(CH_2CH_2)_n\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2CH_2)_n\right]_x CH{=}CH_2$$

where *n* can be any integer, and *x* is a large number. The structure approximates that of a linear hydrocarbon chain containing ketone groups at random intervals, determined by the mole ratio of carbon monoxide used in the polymerization. If the polymer is formed at high temperatures, it will also contain short branches (*ca.* four carbon atoms), and if the concentration of CO is small, the physical properties of the polymer are almost indistinguishable from those of "high pressure" polyethylene. The ultraviolet absorption spectrum of such a polymer (containing 1 mole % CO) is compared in Figure 4 with that of a typical model ketone (12-tricosanone).

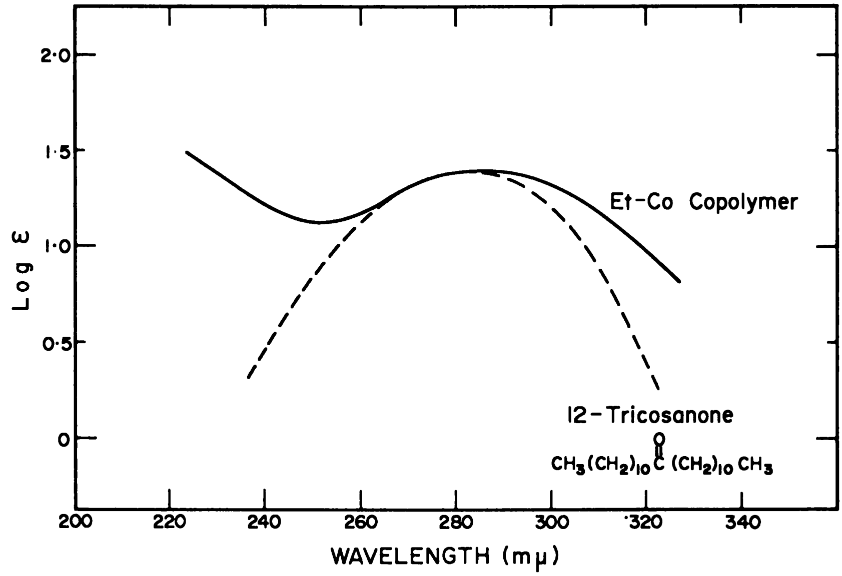


Figure 4. Absorption spectrum of ethylene-carbon monoxide (1%) copolymer in heptane at 80°C.

The molar extinction coefficient (ϵ) and λ_{max} for the polymer and the model compound are almost identical, and the spectra are sufficiently similar to suggest that the nature of the absorption process is the same in both cases.

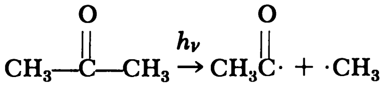
When a molecule absorbs a quantum of radiation, it is raised to an excited state. At first the energy will be localized, usually in the electronic energy of a particular electron associated with a chromophoric group. The quantum of energy so absorbed may be dissipated by either photophysical or photochemical processes such as those listed below:

Photophysical	Photochemical
Fluorescence	Photoionization
Phosphorescence	Free Radical Formation
Thermal	Cyclization
Energy Transfer	Intramolecular Rearrangement

Since most chemical reactions if carried to completion will result in deterioration of polymer properties, it is desirable to be able to ensure that all of the energy is dissipated in photophysical processes and to eliminate the photochemical reactions. However, in some cases, such as in the manufacture of photographic resists, it is desirable to maximize the photochemical effects. The polymer chemist is particularly concerned with the problem of how the relative efficiency of these various processes may be affected by the polymeric nature of the molecules he uses.

It is convenient for photochemical studies in the near ultraviolet to use the mercury resonance line at 3130 A. from a medium pressure mercury arc as a light source. This particular wavelength can be separated in high intensity from the remainder of the spectrum by suitable filters.

Light quanta of this wavelength have an energy equivalent to 91.4 kcal./mole. This is less than the strength of the carbon-oxygen bond in the carbonyl group but more than enough to break a carbon-carbon single bond. For example, for acetone the following reaction:

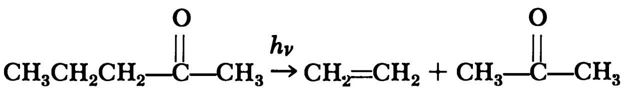


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{h\nu} CH_3\overset{\overset{O}{\|}}{C}\cdot + \cdot CH_3 \qquad (1)$$

requires about 71 kcal./mole. If this is the reaction path, the two fragments would retain an additional 20.4 kcal. as thermal energy.

Norrish and co-workers in a series of early papers (2) showed that the chemical products of decomposition of aliphatic ketones could be explained on the basis of two primary reactions, the first designated Type I (Reaction 1)—a homolytic split of the molecule to give two free radicals—

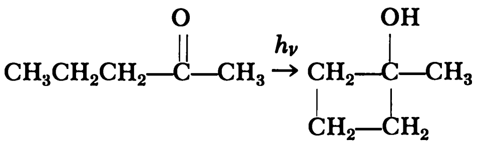
and Type II, which gives an olefin and a methyl ketone (Reaction2)



$$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{h\nu} CH_2{=}CH_2 + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \qquad (2)$$

This step does not appear to proceed by a free radical mechanism and often has about the same quantum efficiency at all temperatures.

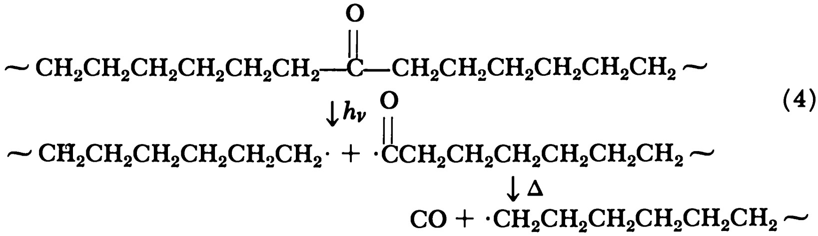
In addition to these, a third reaction has been identified recently (*15*) which results in the formation of a cyclobutanol derivative:



$$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{h\nu} \begin{array}{l} CH_2-\overset{\overset{OH}{|}}{C}-CH_3 \\ \,|\qquad\;\; | \\ CH_2-CH_2 \end{array} \qquad (3)$$

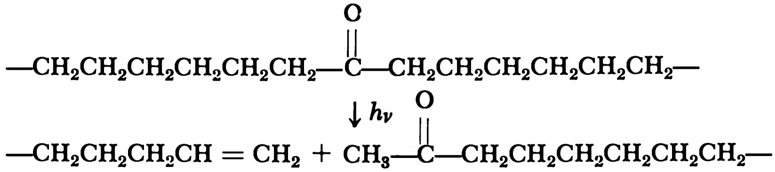
This process usually has lower quantum efficiency than the Type II reaction and is less likely to occur in the higher ketones.

Polymer Photochemistry. The occurrence of these reactions in polymeric ketones was first demonstrated by Guillet and Norrish (*6, 7*), who studied poly(methyl vinyl ketone) in solution and showed that the main features of the photodegradation could be accounted for quantitatively on the basis of Type I and Type II reactions. The conclusion was later confirmed by Wissbrun (*13*). Recent studies of the ethylene–carbon monoxide polymer (*9*) confirm that both Type I and Type II reactions occur. The Type I reaction results in the formation of two polymer radicals, one of which is an acyl radical which may subsequently decarbonylate (Reaction 4).



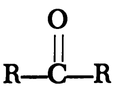
$$\sim CH_2CH_2CH_2CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_2CH_2CH_2\sim$$
$$\downarrow h\nu \qquad (4)$$
$$\sim CH_2CH_2CH_2CH_2CH_2CH_2\cdot + \cdot\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2CH_2CH_2\sim$$
$$\downarrow \Delta$$
$$CO + \cdot CH_2CH_2CH_2CH_2CH_2CH_2\sim$$

The Type II reaction also leads to a break in the "backbone" of the polymer chain with the formation of a methyl ketone and a terminal vinyl group (Reaction 5).



$$-CH_2CH_2CH_2CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_2CH_2CH_2-$$
$$\downarrow h\nu \qquad (5)$$
$$-CH_2CH_2CH_2CH=CH_2 + CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_2CH_2CH_2-$$

At 25°C. the predominant reaction is Type II, and it is the primary cause of the decrease in molecular weight which occurs on irradiation. At higher temperatures Type I becomes more favorable, and the decrease in molecular weight is slowed down by a "repolymerization" caused by addition of the polymer radicals to the double bonds formed by the Type II reaction (*7*). The Type II reaction has been shown to cause polymer degradation not only in poly(methyl vinyl ketone) and poly(ethylene—CO) but in polyesters such as polyethylene terephthalate (*12*). It has been suggested that it may be the major cause of degradation in a wide variety of synthetic polymers containing ester or keto carbonyl groups (*12*).

Effect of Molecular Weight. Studies of the variation in the quantum efficiencies of various primary photochemical processes in polymers showed very little dependence on molecular weight. Accordingly, model compounds of the general structure  $R-\overset{O}{\overset{\|}{C}}-R$ were studied (*9*). The results are shown in Figure 5 in which the quantum efficiency for the Type I reaction (estimated from the yield of CO) at 120°C. (ϕ_I) is plotted as a function of total chain length. There is an abrupt decrease in ϕ_I for ketones with chain length greater than seven (*i.e.*, $R = C_3$), after which ϕ_I decreases gradually with chain length to a limiting value of .012. The value for poly(ethylene—CO) is about twice this limiting value, which suggests strongly that some of the CO groups are in side branches rather than in the main chains. Approximately the same value of ϕ_I (0.018) was obtained when the polymer was irradiated in film form at 120°C. in a hydrogen atmosphere.

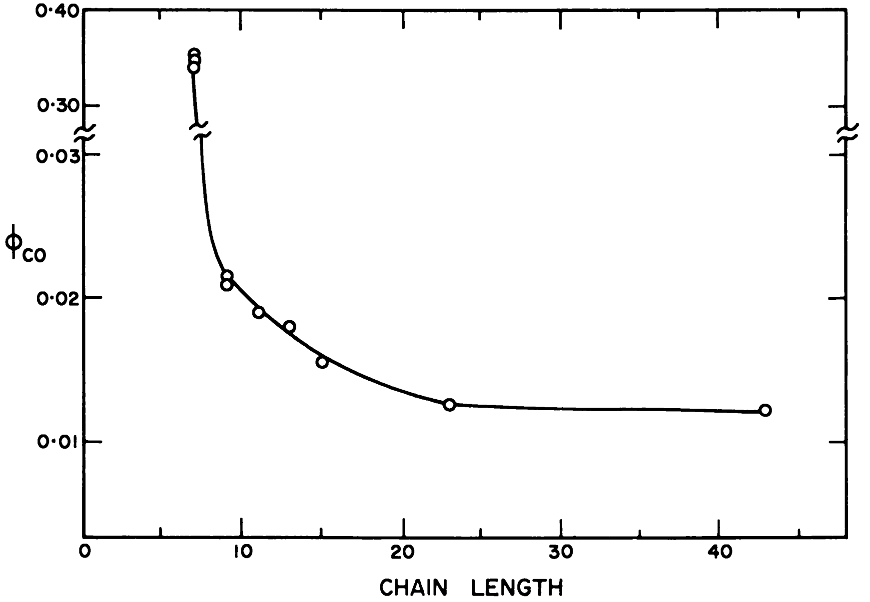
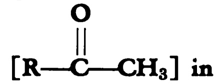


Figure 5. Quantum yields for carbon monoxide formation in ketones of type $R\text{—}\overset{O}{\overset{\|}{C}}\text{—}R$*, determined in hydrocarbon solvent at 120°C.*

Similar data on methyl ketones (*11*) $\left[R\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_3\right]$ at 25°C. are shown in Table I. Again there is a sharp decrease in ϕ_I after $R = C_3$. However, the value of ϕ_I for poly(methyl vinyl ketone) is considerably higher than that of any of the model ketones probably because of the lower energy required to form a secondary rather than a primary radical. The value of ϕ_{II} varies from 0.11 to 0.22 in both types of model ketones and is almost independent of chain length over the range studied. On the other hand, both poly(methyl vinyl ketone) and poly(ethylene—CO) have values of $\phi_{II} = 0.025$, and this value appears to be independent of temperature, and more surprising, it is the same whether the polymer is in solution or in film form. If one accepts the cyclo-elimination mechanism (Figure 6) for the Type II reaction, the excited state involved must have a sufficiently long lifetime so that large changes in the mobility of the polymer chain do not affect the probability of reaction.

Table I. Quantum Efficiencies at 25°C. for Methyl Ketones



$[R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3]$ in Hydrocarbon Solution

R	ϕ_I	ϕ_{II}	*Ref.*
C_3	0.023	0.21	[a]
C_5	0.003	0.21	5
C_7	0.0022	0.21	5
C_9	0.0003	0.22	5
Poly(methyl vinyl ketone)	0.04	0.025	7

[a] Estimated from data of Ausloos and Rebbert (*1*).

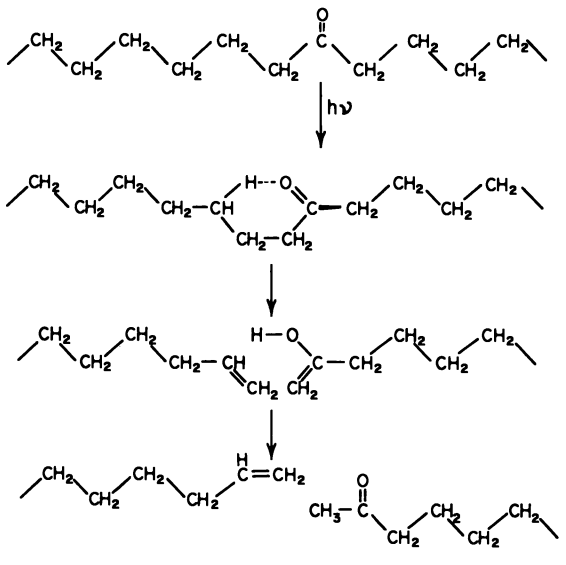


Figure 6. Mechanism of Type II photoelimination

Polymers which for structural reasons cannot undergo the Type II photoelimination show much lower quantum efficiencies for bond breaking in the backbone. For example, polymers containing γ-keto pimellic acid (which does not contain a γ-hydrogen atom),

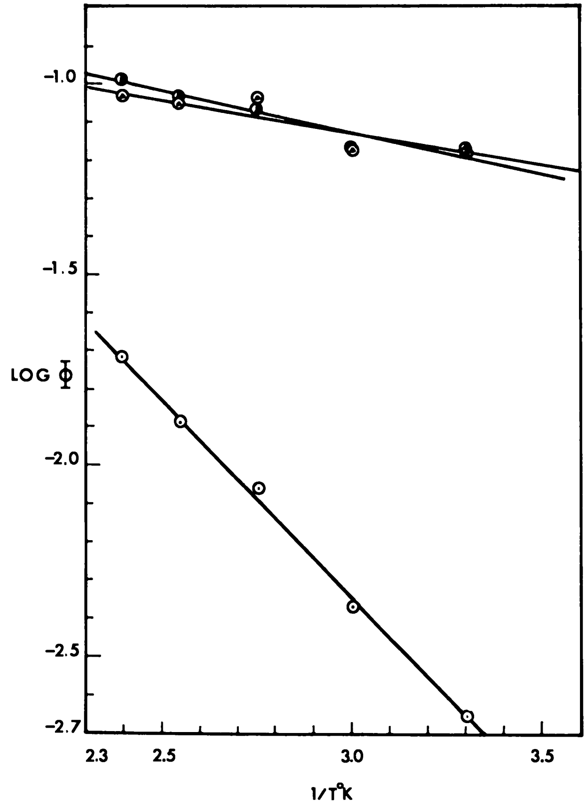
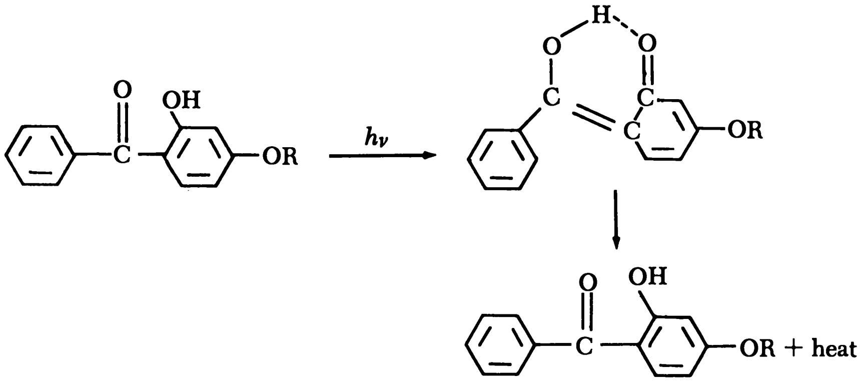


Figure 7. Arrhenius plots for Type I and Type II reactions in 8-pentadecanone


$\mathrm{HOOC{-}CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2COOH}$, have a quantum efficiency for bond breaking of 0.004, about one-sixth that of the other two polymers which can undergo cycloelimination (*4*).

Effect of Temperature. The effect of temperature on the primary quantum efficiencies for a model ketone, 8-pentadecanone ($\mathrm{C_7{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C_7}$), is shown in Figure 7. The activation energy for the Type I reaction is 4.8 kcal./mole compared with 0.85 kcal./mole for the Type II. This is expected since the ability of two free radicals to separate will depend strongly on their mobility in solution. At higher temperatures the Frank-Rabinowitch principle would predict a higher quantum efficiency for processes involving the separation of two molecular fragments. A similar increase in ϕ_I with temperature was observed with poly(ethylene—CO), and the activation energy was estimated to be 5.2 kcal./mole. The formation of free radicals by the Type I process has been confirmed by the synthesis of graft and block copolymers by the photolysis of poly(methyl vinyl ketone) (*8*) and poly(tetramethylene sebacate) CO–γ-ketopimellate (*4*) respectively.

Stabilization of Polymers. There are several ways in which a polymer can be protected from the action of ultraviolet light, apart from the obvious expedient of using an opaque screen or coating to prevent light from reaching the polymer. One way is to mix with the polymer a compound which will absorb most of the light and use up the energy in some way which does not harm the polymer. To do this, the stabilizer must usually have a very high absorption coefficient in the near ultraviolet range of the spectrum, but it should not absorb in the visible range or it will add color to the polymer, which is frequently undesirable. However, the requirement of a high absorption coefficient is not sufficient since if the compound re-emits radiation of the same wavelength (fluorescence), it will be ineffective. It must have a route for dissipating the energy of the ultraviolet light which does not lead to the emission of harmful ultraviolet radiation or the formation of active chemical intermediates which might attack the polymer. Compounds which have been found particularly effective with polyethylene, for example, are the substituted 2-hydroxybenzophenones. These compounds undergo a reversible photoenolization which gives a low energy path for the photochemical energy to be degraded to heat (*14*):



The absorption spectrum for a typical stabilizer of this type, 2-hydroxy-4-dodecyloxybenzophenone, is shown in Figure 8 (*10*) along with that of poly(ethylene—CO). Over the near ultraviolet range, the absorption coefficient of the stabilizer is much greater than that of the polymer, and even at low concentrations the stabilizer will absorb most of the light, thereby protecting the polymer.

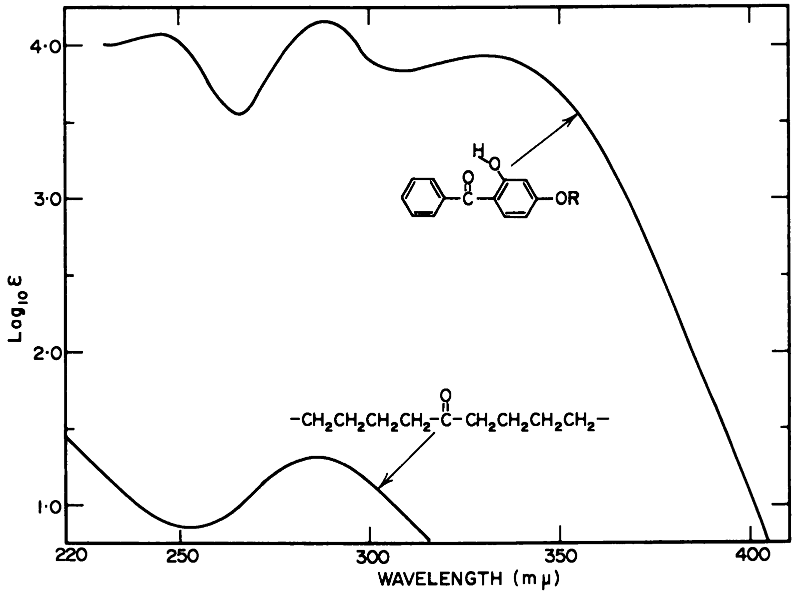


Figure 8. Absorption spectra of polymer and stabilizer in hydrocarbon solution

A second possible mechanism for polymer stabilization depends on energy transfer from the excited states induced in the polymer molecule by the absorption of light. This involves a direct transfer of the excitation energy from the polymer molecule to an acceptor molecule which has excited state energy levels slightly lower than those of the chromophore in the polymer. Since such transfer will usually involve molecular collisions, only excited states having relatively long lifetimes, such as the triplet ($n - \pi^*$) of the carbonyl group, would be effectively quenched by such a mechanism.

The process can be described as follows:

$$\begin{array}{l} \mathrm{P} \xrightarrow{h\nu} \mathrm{P}^* \text{ (singlet)} \rightarrow \mathrm{P}^* \text{ (triplet)} \xrightarrow{\mathrm{A}} \mathrm{P} + \mathrm{A}^* \text{ (triplet)} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \rightsquigarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \mathrm{P} + \mathrm{A} + \text{heat} \end{array}$$

Where P is a polymer molecule containing a chromophore group, and A is an acceptor molecule with a suitable triplet energy level slightly below that of the excited chromophore in the polymer.

Recent studies in this laboratory (*5, 10*) indicate that although energy transfer may indeed occur with the hydroxybenzophenones, at the concentrations used the effect would be negligible compared with their screening effect. One may conclude that these compounds owe their efficacy to their ability to prevent light from reaching the polymer rather than by interfering with the path of the photochemical reaction after light has been absorbed.

Conclusions

From the foregoing discussion, certain general conclusions may be drawn regarding photochemical reactions in polymers:

(1) The quantum efficiency for radical processes will be low at 25°C. (of the order of 0.001) but will increase with temperature with an activation energy of about 5 kcal./mole.

(2) Whenever a carbonyl is in or adjacent to the backbone of a polymer chain, the main cause of molecular weight breakdown will be the Norrish Type II photoelimination reaction. The quantum efficiency of the reaction in polymers appears to be nearly independent of temperature and physical state (*i.e.*, solid or liquid).

(3) Polymers in which the carbonyl group is located in regions where there are no hydrogen atoms on the γ-carbon will be more resistant to photochemical degradation.

(4) 2-Hydroxybenzophenones probably stabilize polymers by a screening mechanism rather than by energy transfer.

Acknowledgment

The authors express their appreciation to the National Research Council of Canada, Dunlop Research Ltd., Tennessee Eastman Co., and the Paint Research Institute for financial assistance. The Tennessee Eastman Co. kindly supplied samples of ethylene–carbon monoxide polymers and 2-hydroxy-4-dodecyloxybenzophenone.

Literature Cited

(1) Ausloos, P., Rebbert, R. E., *J. Am. Chem. Soc.* **83,** 4897 (1961).
(2) Bamford, C. H., Norrish, R. G. W., *J. Chem. Soc.* **1935,** 1504.
(3) Davis, Schultz, *J. Org. Chem.* **27,** 854 (1962).
(4) Dhanraj, J., Guillet, J. E., *J. Polymer Sci.* **C23,** 433 (1968).
(5) Golemba, F. J., Guillet, J. E., unpublished work.
(6) Guillet, J. E., Norrish, R. G. W., *Nature* **173,** 625 (1954).
(7) Guillet, J. E., Norrish, R. G. W., *Proc. Roy. Soc.* **A233,** 153 (1955).
(8) *Ibid.*, p. 172.
(9) Hartley, G. H., Guillet, J. E., *Macromolecules* **1,** 413 (1968).
(10) Heskins, M. H., Guillet, J. E., unpublished data.
(11) Koller, L. R., "Ultraviolet Radiation," p. 114, Wiley, New York, 1965.
(12) Osborn, K. R., *Am. Chem. Soc. Div. Org. Coatings Preprints* **21,** 2, 411 (1961).
(13) Wissbrun, K. F., *J. Am. Chem. Soc.* **81,** 58 (1959).
(14) Yang, N. C., Rivas, C., *J. Am. Chem. Soc.* **83,** 2213 (1961).
(15) Yang, N. C., Yang, D.-D.H., *J. Am. Chem. Soc.* **80,** 2913 (1958).

RECEIVED April 6, 1967.

The Light Stabilization of Polystyrene

CHRIS SAVIDES, JOSEPH A. STRETANSKI, and LEO R. COSTELLO

American Cyanamid Co., Organic Chemicals Division, Bound Brook, N. J.

Published on June 1, 1968 on http://pubs.acs.org | doi: 10.1021/ba-1968-0085.ch020

It is well recognized that polystyrene discolors appreciably on exposure to both outdoor and artificial light sources. Certain phenolic antioxidants, in combination with ultraviolet absorbers, afforded greater light stability to the polymer than the ultraviolet absorbers alone. Correlation studies between accelerated devices and actual fluorescent lamp exposure indicated that high output, cool white, fluorescent lamps are the best sources for predicting performance characteristics of light-stabilized polystyrene. Phenolic antioxidants inhibit both the rate of discoloration and the rate of photooxidation under irradiation with ultraviolet sources rich in energy above 3000 A.

The discoloration of polystyrene on exposure to light has long been recognized as an undesirable property. This deficiency is particularly important to the lighting industry since polystyrene has gained wide acceptance for use in fluorescent lighting fixtures. Because of the many advantages of polystyrene for this application—ease of fabrication, good dimensional stability, clarity, and especially low cost—considerable efforts have been made to improve its light stability. While these efforts have been met with some success and polystyrene light fixtures are now commercially produced in large quantities, there is continued demand for improved stabilization. The most common approach for photostabilizing polymers is by incorporating ultraviolet absorbers. These materials are light-stable organic compounds which absorb strongly in the region 3000–4000 A. Their mode of action is mainly through competitive absorption of the ultraviolet energy responsible for the polymer degradation.

Figure 1 shows the activation spectrum of polystyrene measured by Hirt and co-workers (*8*). It represents the yellowing, as measured by the increase in absorbance at 4000 A., caused by the various wavelengths of ultraviolet radiation between 2800 and 4000 A. The ultraviolet source used for these measurements was a xenon arc equipped with a borosilicate glass filter. Maximum degradation occurs with wavelengths of 3000–3200 A. The activation spectrum is of practical importance because it can be used to select ultraviolet absorbers for stabilization.

Among the types of ultraviolet absorbers that may be used as stabilizers are salicylates, *o*-hydroxybenzophenones, *o*-hydroxyarylbenzotriazoles, and certain acrylonitriles. The stabilization of polystyrene by other additives has also been reported. Matheson and Boyer (*10*) found that certain aliphatic amines and amino alcohols improved the light stability of the polymer.

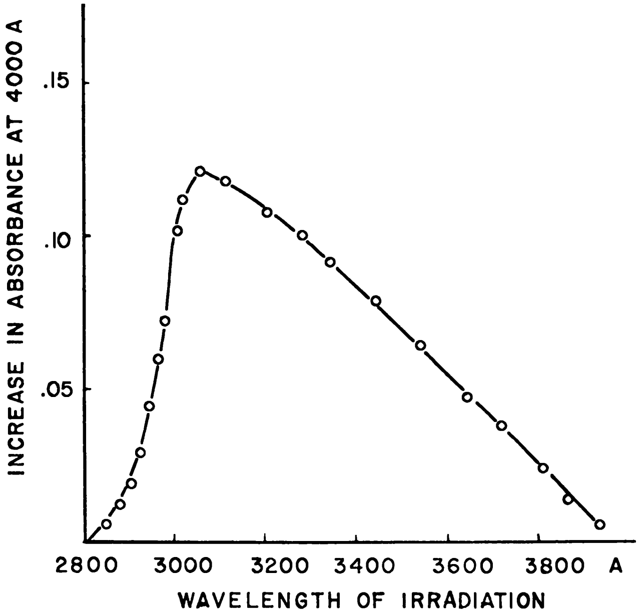


Figure 1. Activation spectrum of polystyrene measured by Hirt et al. (8)

This paper deals with a study of phenolic antioxidants and their usefulness in the light stabilization of polystyrene (*3*), especially as applied to indoor lighting applications, and their mode of action. It is generally agreed that light degradation of polystyrene is a photooxidation reaction caused by ultraviolet radiation. Evidence for such reaction has been derived through spectrophotometric measurements, both infrared (*2*) and ultraviolet (*12*), mass spectrometry (*1*), and oxygen absorption studies (*5*).

Achhammer (*2*) and co-workers, who originally studied the effect of ultraviolet radiation on this polymer, reported that on exposure to a sunlamp the infrared absorption bands increase in the regions of 2.8μ and

5.8μ. This increase was attributed to the formation of hydroxyl and carbonyl groups, respectively. Figure 2 shows the typical increase in the carbonyl absorption band of a commercial polystyrene film irradiated with a carbon arc.

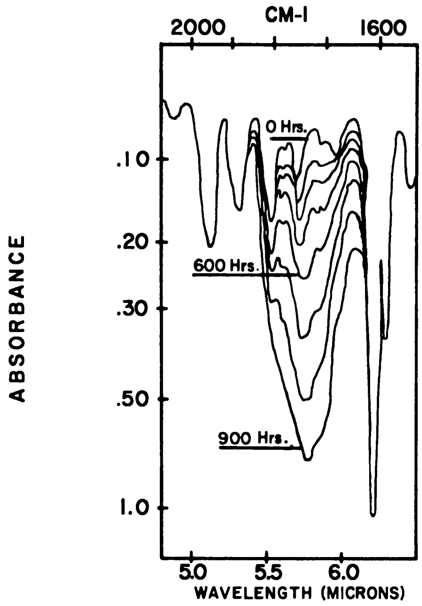


Figure 2. Carbonyl absorption of irradiated polystyrene (Fade-ometer exposure)

Accompanying the change in carbonyl absorption, there is also a general progressive increase in the ultraviolet absorption which extends into the visible region and is responsible for yellowing (Figure 3).

Reiney (*12*) attributed this to conjugated carbonyl products. Matheson and Boyer (*10*), who also observed carbonyl formation, reported that the yellow discoloration occurs only in the presence of air or oxygen and is primarily a surface phenomenon.

Experimental

Sample Preparation. All polymer samples were prepared from commercial general purpose polystyrene (Monsanto HF-77). The additives were incorporated into the polymer by fluxing on a two-roll laboratory mill at about 350°F. Two types of samples were molded from the milled polymer: (a) 50-mil plaques, compression molded at 350°F.; (b) 1.5–2.5-mil films, compression molded at 390°F.

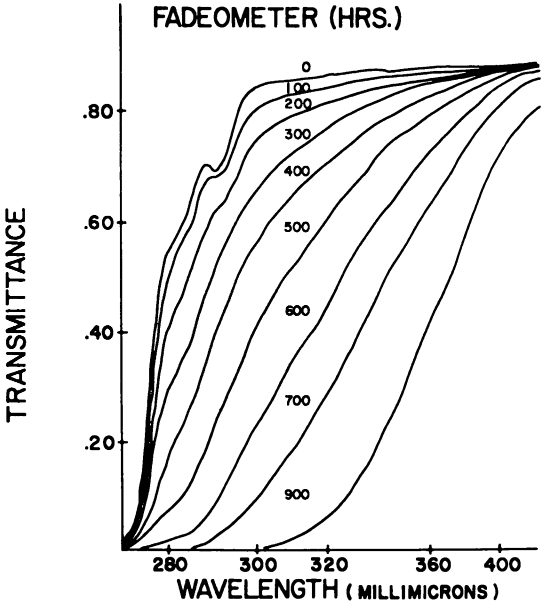


Figure 3. Ultraviolet transmission of irradiated polystyrene

Exposure Conditions. Fade-ometer (Atlas, model FDA-R): all samples were mounted and exposed according to standard procedures.

Xenon-arc Weatherometer (Filtered, 6000 watts) Model 60-WR: samples were exposed according to standard procedure, except no water spray was used. The xenon lamps used were preaged for 100 hours.

Fluorescent blacklamp (GE F40 BL-B): sample to lamp distance was 3/8 inch.

Mercury-arc (Hanovia, 100 watts): sample to lamp distance was 2 inches.

High output fluorescent lamp (Westinghouse F48 T12/CW/SHO): sample to lamp distance was 1 inch.

Fluorescent cool white lamp (GE F40 CW): sample to lamp distance was 1/2 inch.

Yellowness Index. The yellowness of the 50-mil plaques used for stabilization studies was measured directly from a Hunter D-25 color difference meter equipped with a 90° sphere attachment. The samples were placed in the reflectance port of the sphere using a standard white ceramic as backing. The instrument is designed to give direct yellowness index values as described in ASTM D-1925.

Spectrophotometric Measurements. Carbonyl measurements of thin films (1.5–2.5 mils) were made using a Perkin-Elmer, model 237-B, recording spectrophotometer. Ultraviolet absorption measurements were made using a Beckman DK-2 recording spectrophotometer. The instrument was operated with a collection sphere.

Results and Discussion

Hindered Phenols. Because of the relationship between photooxidation and discoloration, we became interested in the effect of hindered phenols which are well-known oxidation inhibitors. A preliminary study was carried out to determine the relative effectiveness of a variety of such compounds, many of which are commercially available. The additives were incorporated into polystyrene at 0.1% concentration, and 50-mil molded plaques were exposed to a carbon-arc Fade-ometer.

Table I. Effect of Bisphenols on Light Stability of Polystyrene

	Fade-ometer Exposure, hrs. Yellowness Index		
0.1% Additive	*0*	*400*	*600*
Control (no additive)	5	23	35
2,2′-Methylenebis(6-*tert*-butyl-*p*-cresol)	6	42	31
2,2′-Methylenebis(6-*tert*-butyl-4-ethylphenol)	4	22	27
4,4′-Methylenebis(2-methyl-6-*tert*-butylphenol)	38	20	36
4,4′-Methylenebis(2,6-di-*tert*-butylphenol)	39	13	15
4,4′-Isopropylidene bisphenol	7	23	35
4,4′-Thiobis(3-methyl-6-*tert*-butylphenol)	6	37	57

Table II. Effect of Phenols on Light Stability of Polystyrene

	Fade-ometer Exposure, hrs. Yellowness Index		
0.1% Additive	*0*	*400*	*600*
Control (no additive)	5	23	35
2,4,6-Tri-*tert*-butylphenol	5	6	8
2,6-Di-*tert*-butyl-p-cresol	5	6	9
2,6-Di-*tert*-butyl-4-phenylphenol	7	10	16
2,6-Di-*tert*-butyl-4-hydroxymethylphenol	7	9	20
2-Methyl-4-*tert*-butylphenol	8	12	20
2,6-Di-*tert*-butyl-4-methoxyphenol	4	15	25
4-*tert*-Butylphenol	10	23	33

Table I shows the results obtained with various bisphenols which are generally considered quite effective as thermal antioxidants. Most of these additives did not retard the discoloration of the polymer. One compound, 4,4′-methylenebis(2,6-di-*tert*-butylphenol), showed some promise, but it discolored the polymer initially and, therefore, cannot be considered of practical importance.

The best results were obtained with hindered monophenols. Table II shows that compounds of this type imparted little or no color to the polymer, and all afforded some protection. Of special interest was the finding that 2,4,6-tri-*tert*-butylphenol and 2,6-di-*tert*-butyl-*p*-cresol inhibited the discoloration of polystyrene quite effectively.

Ultraviolet Absorber–Phenol Combinations. Ultraviolet absorbers are commonly used to stabilize polystyrene against light. Experimentally, it was found that their efficiency in this polymer does not increase linearly with increasing concentration. Figure 4 shows that above 0.2% concentration only a minimal increase in stabilization is obtained with 2-hydroxy-

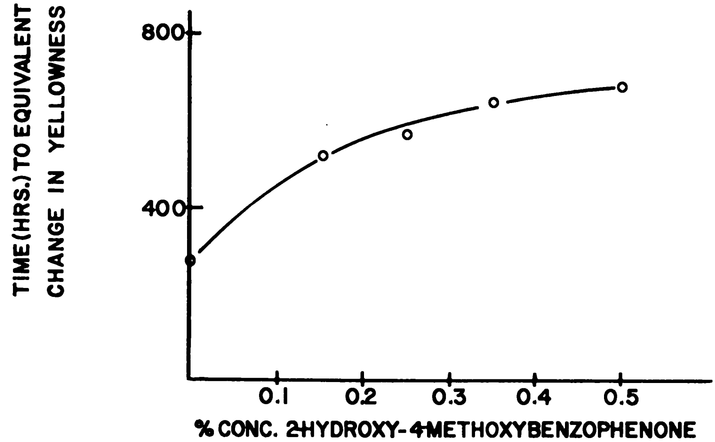


Figure 4. Inhibition of discoloration vs. *ultraviolet-absorber concentration (Fade-ometer exposure)*

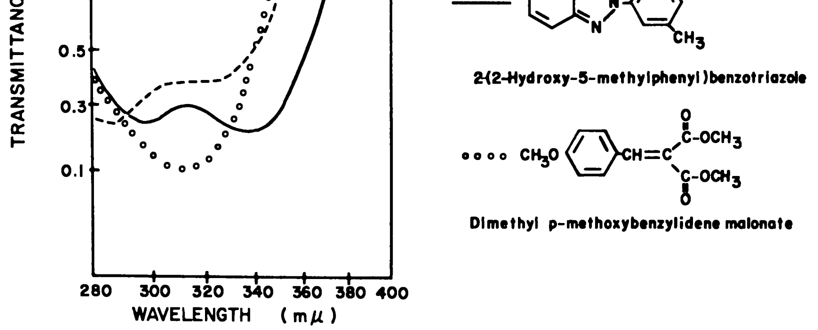


Figure 5. Ultraviolet-absorber transmission spectra

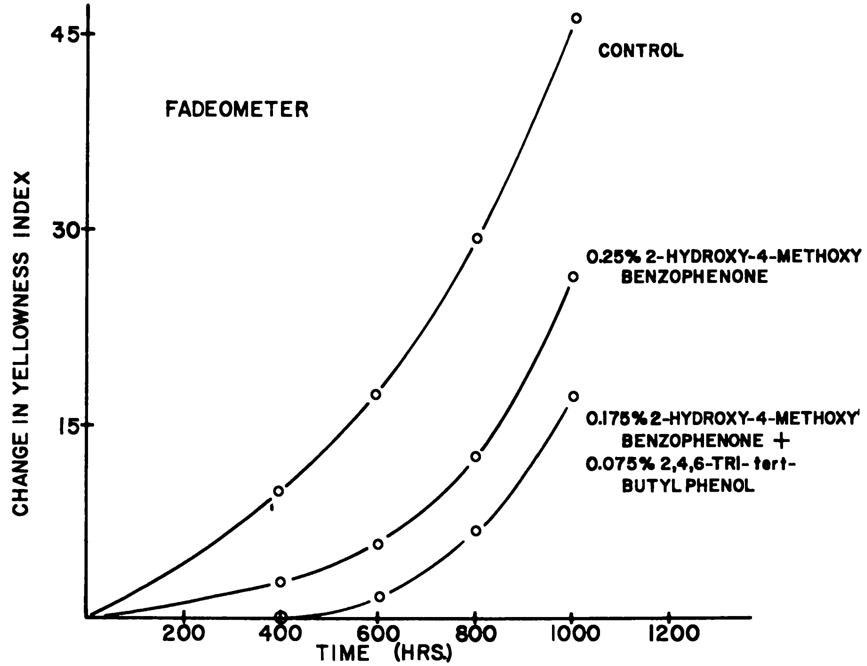


Figure 6. Inhibition of discoloration with benzophenone-antioxidant combination—Fade-ometer exposure

4-methoxybenzophenone. This relationship was also observed with other types of ultraviolet absorbers. In view of this performance characteristic of ultraviolet absorbers in polystyrene and the effectiveness of certain phenolic antioxidants, combinations of these materials were evaluated. Figure 5 shows the ultraviolet transmission spectra of the absorbers selected for these studies. Included is a member of a new class of light-stable ultraviolet absorbers—the benzylidene malonates. All three compounds have ultraviolet absorption bands in the region of maximum wavelength sensitivity of polystyrene.

Figures 6, 7, and 8 show the stabilizing efficiency of the combinations consisting of the above absorbers and the antioxidant 2,4,6-tri-*tert*-butylphenol, on Fade-ometer exposure. The total additive concentration in each polystyrene sample was 0.25%. The data show that the rate of discoloration of the polymer was inhibited to a greater extent with the ultraviolet absorber–antioxidant combinations than with the absorber alone. Only a small amount (0.075%) of the antioxidant was required for increased effectiveness of the combination.

Because of the potential commercial importance of such combinations, their effectiveness was also studied under end-use fluorescent lamp exposure conditions. Figure 9 shows the results obtained with 2-hydroxy-

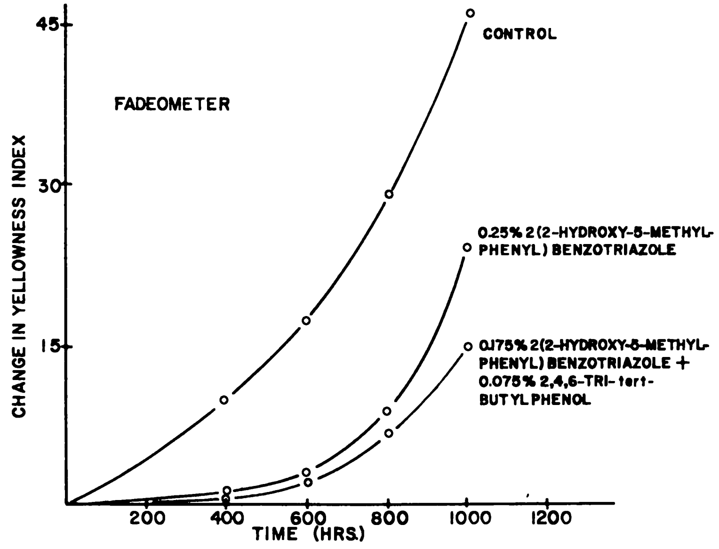


Figure 7. Inhibition of discoloration with benzotriazole-antioxidant combination—Fade-ometer exposure

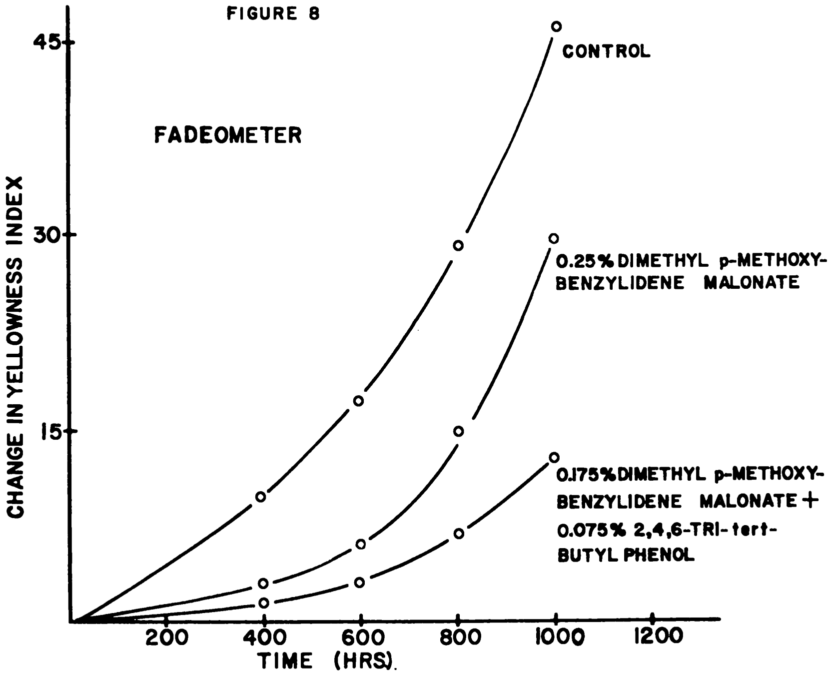


Figure 8. Inhibition of discoloration with benzylidene-antioxidant combination—Fade-ometer exposure

4-methoxybenzophenone. Similar results were also obtained with 2-(2-hydroxy-5-methylphenyl)benzotriazole (Figure 10) and diethyl-*p*-methoxybenzylidene malonate (Figure 11). Figure 11 also illustrates that the effectiveness of 0.35% of the absorber–antioxidant combination is greater

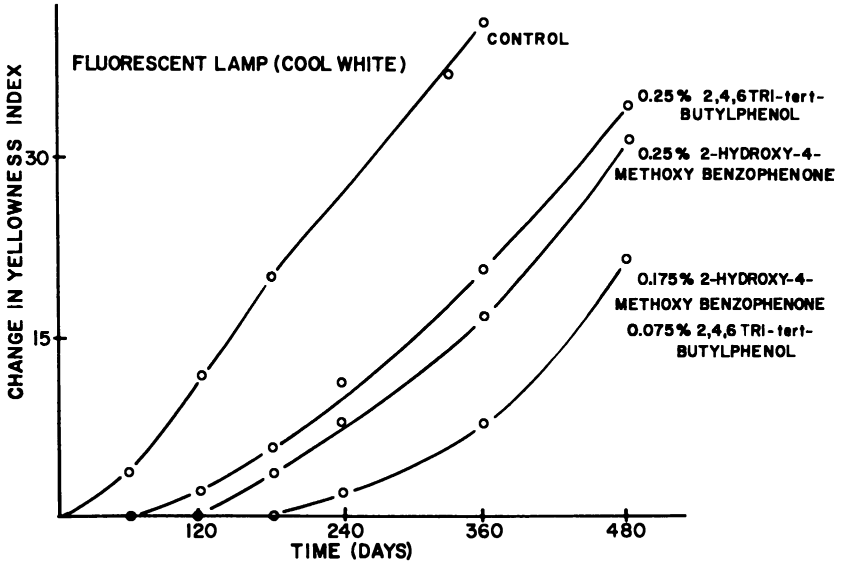


Figure 9. Inhibition of discoloration with benzophenone-antioxidant combination

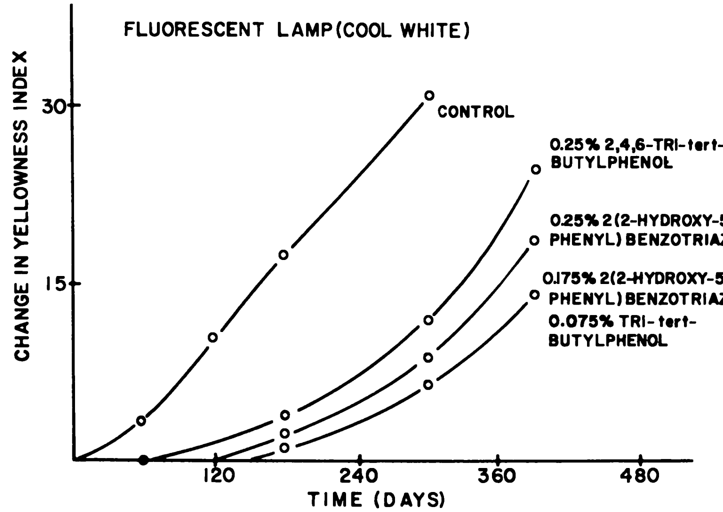


Figure 10. Inhibition of discoloration with benzotriazole-antioxidant combination

than obtained with 0.5% of the absorber alone. The improved efficiency of the stabilizer combinations was observed under both the accelerated exposure of the carbon-arc as well as the normal fluorescent lamp exposure.

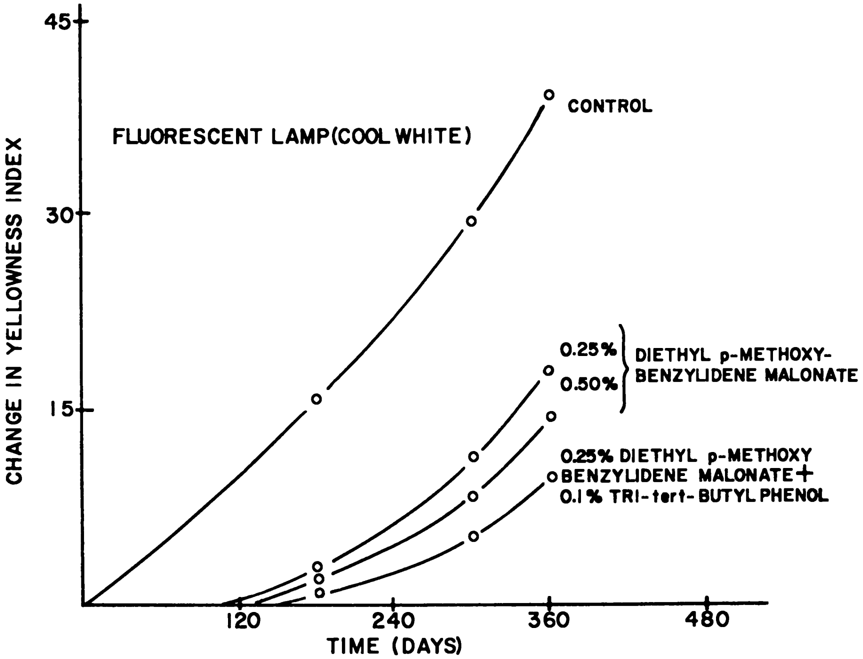


Figure 11. Inhibition of discoloration with benzylidene-antioxidant combination

Exposure Correlations. The prediction of end-use performance based on accelerated exposure data is a major problem in light stabilization studies. Accelerated devices are needed not only to evaluate additives, but also to establish specifications, and for quality control purposes.

Ideally, the best accelerated light source should be one which simulates the emission characteristics of fluorescent lamps in all wavelengths of the ultraviolet region critical to the degradation of polystyrene. However, none of the commercially available devices meet this requirement, and therefore, a compromise is needed. Several test methods have been investigated (*4*, *11*), and in 1958 the carbon-arc Fade-ometer was approved by the Council of Illuminating Engineering Society (*9*) as an accelerating device for polystyrene light diffusers.

In our stabilization studies on polystyrene, we also examined various light sources and found that in addition to the carbon-arc Fade-ometer, the xenon-arc and a recently proposed high output fluorescent lamp also merit consideration. Figure 12 shows the ultraviolet energy distribution of the carbon-arc, xenon-arc and a normal cool white fluorescent lamp as measured by Hirt and co-workers (7). The peak intensities of the fluorescent lamp are at 3140 and 3650 A., with no measurable energy emitted below 3000 A. The carbon arc has considerably more intensity at the higher wavelengths, and the emission extends below 3000 A. The xenon-arc has high intensity at all wavelengths between 3000 and 4000 A. The spectral distribution of the high output fluorescent (cool white) lamp (not shown) is similar to the fluorescent (cool white) lamp, but it has higher intensity in both the ultraviolet and visible regions. Figures 13, 14, and 15 show the relationship between the exposure data obtained with the accelerated devices compared with the cool white fluorescent lamp exposure. Several polystyrene samples were used containing ultraviolet absorbers and antioxidant–absorber combinations. The points represent the time for each sample to reach the same change in yellowness under both exposure conditions.

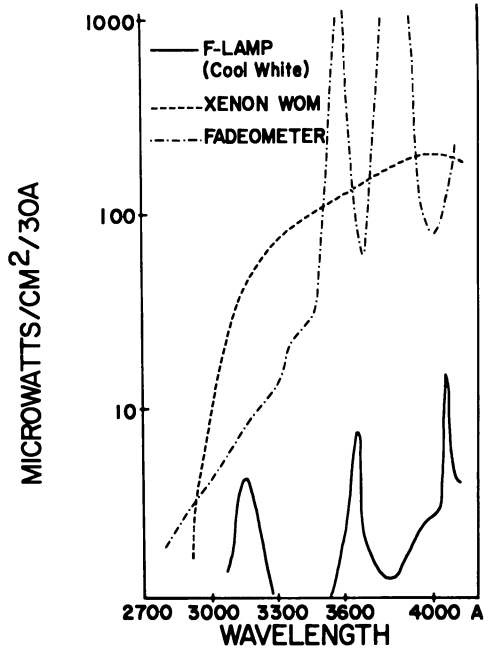


Figure 12. Ultraviolet spectral distribution of carbon arc, xenon arc, and fluorescent lamp

The Fade-ometer (Figure 13) did not show a single line relationship. However, in view of the necessity for short term exposures, the qualitative correlation obtained could be quite useful for laboratory screening and

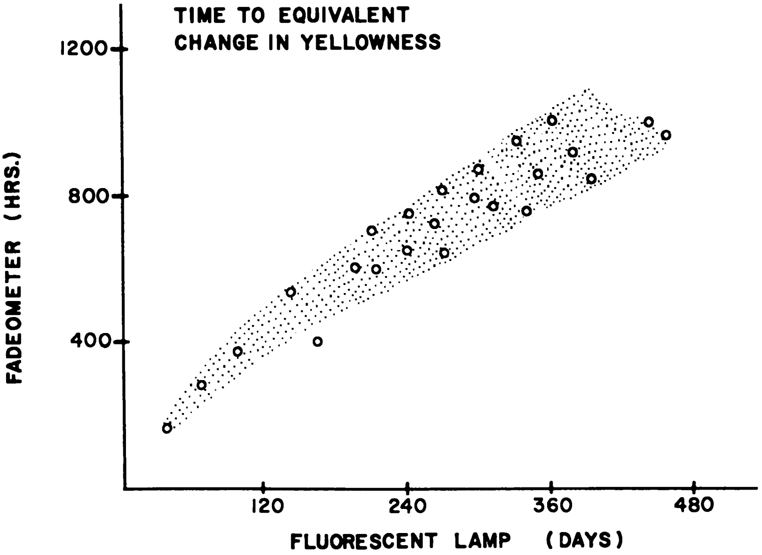


Figure 13. Exposure correlation

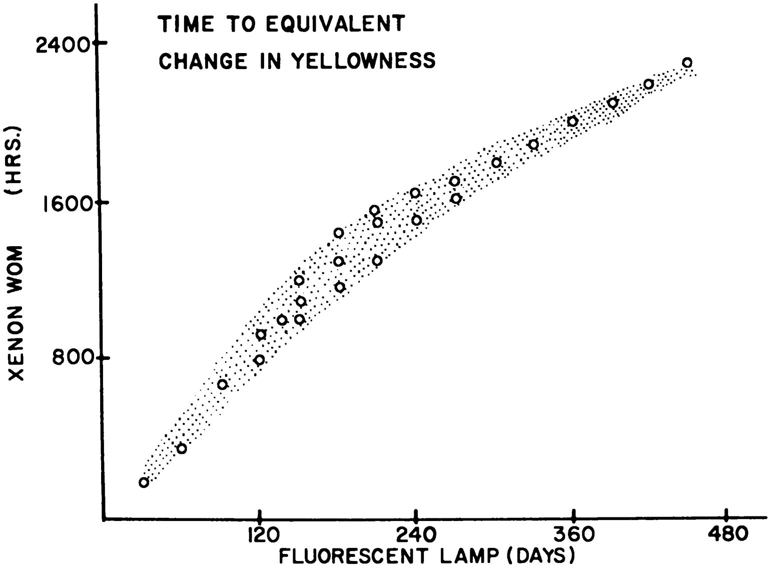


Figure 14. Exposure correlation

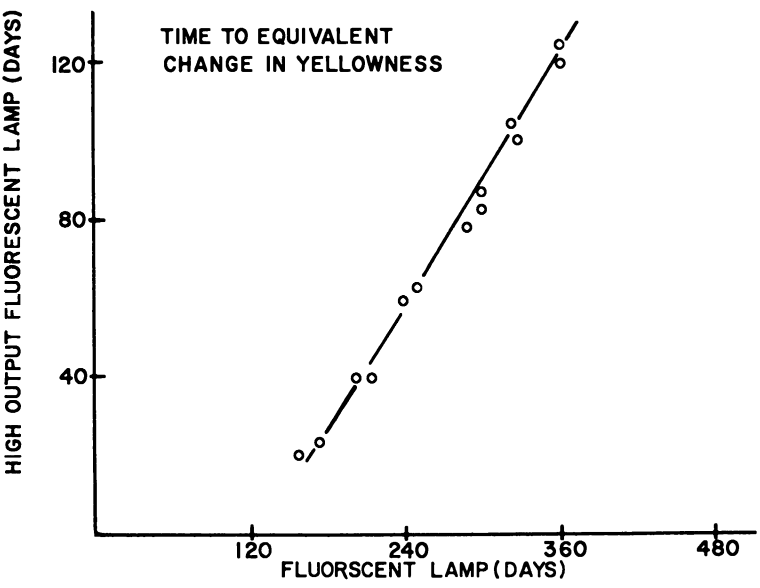


Figure 15. Exposure correlation

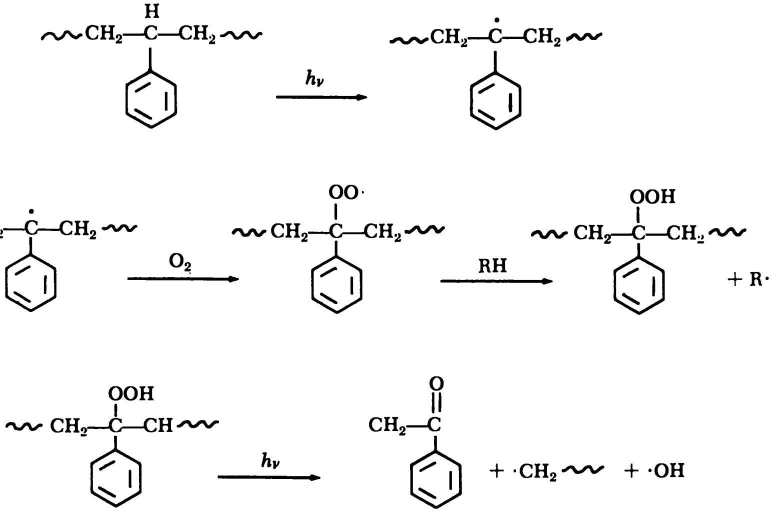
evaluation studies. We have found that this source can adequately describe the relative performance of additives, provided that sufficient control samples are exposed simultaneously.

The xenon arc (Figure 14) showed a better correlation, but somewhat longer time is required to obtain useful data. Figure 15 shows the correlation obtained with high output fluorescent lamp. The use of this source, as an accelerated exposure device, was suggested by Subcommittee V ASTM D-20 Committee on plastics. An ASTM task group study is currently working to establish its utility. The unit was operated on a double current to increase its intensity, and further acceleration was obtained by exposing the samples on both sides. The correlation obtained was quite good, but the exposure times are rather long.

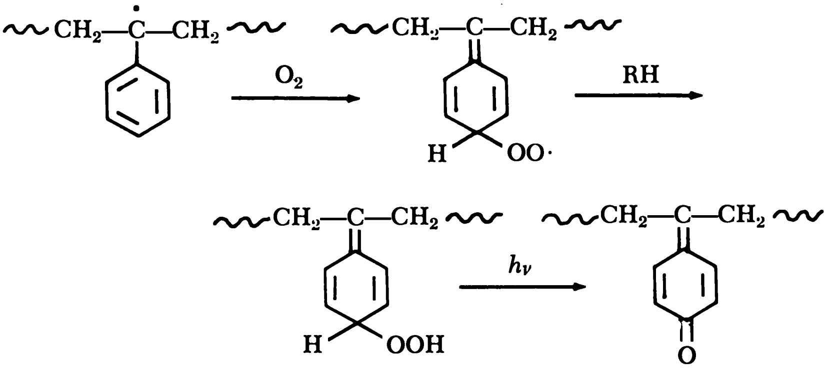
It appears, therefore, that two accelerated devices may be needed: an exposure unit, such as the Fade-ometer, for quick screening and relative performance studies of light-stabilized polystyrene samples, and a second unit, such as the high output fluorescent lamp, for predicting more accurately long term exposures.

Role of Antioxidants. The inhibition of color development by phenolic antioxidants is rather interesting since it points out the relationship between discoloration and oxidation. It is generally assumed that the photooxidation of polystyrene is a free radical reaction involving oxygen attack on a polymer radical, produced by the action of ultraviolet light.

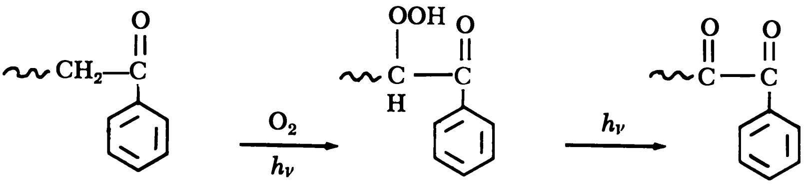
The photodecomposition of the intermediate hydroperoxide results in cleavage of the polymer chain and formation of a ketone.



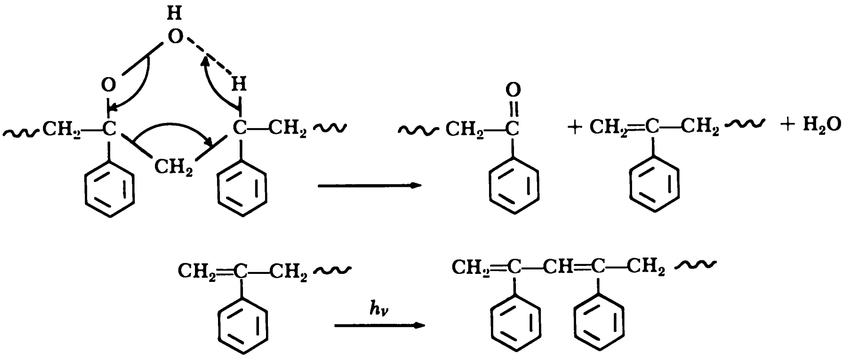
Achhammer (2) proposed that in addition to above, a second hydroperoxide may form on the benzene nucleus to give a quinone-type compound.



In addition to the above two ketones, additional carbonyl compounds have been suggested to explain the discoloration and absorption spectra of irradiated polystyrene. Reiney (*12*) and more recently Zapol'skii (*13*) postulated that further photooxidation results in the formation of α-diketones.



In contrast to the above mechanisms, Grassie and Weir (6) recently proposed that the discoloration is not a manifestation of oxidation. They reported that under 2537-A. irradiation the rate of polymer discoloration was greater in nitrogen than in oxygen. They postulated that the photooxidation and subsequent discoloration involves the decomposition of tertiary hydroperoxide to give a ketone and an unsaturated compound. The latter is then further photolyzed to form conjugated color products.



While there appears to be some discrepancy in the conclusions derived from these studies, the difference can be explained as being caused by the exposure conditions. To illustrate the effect of irradiation wavelength on the photooxidation, unstabilized polystyrene films were exposed to the following three ultraviolet light sources having different emission characteristics (Figure 16):

(1) A Hanovia mercury lamp having strong emission bands in the lower ultraviolet region (below 3000 A.).

(2) A carbon-arc Fade-ometer with emission in the region of 3000–4000 A.

(3) A fluorescent blacklamp which emits predominantly in the region of 3500 A.

Figure 17 shows the relationship between discoloration, as measured by the change in ultraviolet absorbance at 365 mμ, and oxidation, as measured by the change in carbonyl absorbance at 5.85μ. Under carbon-arc and fluorescent blacklamp irradiation, color development is accom-

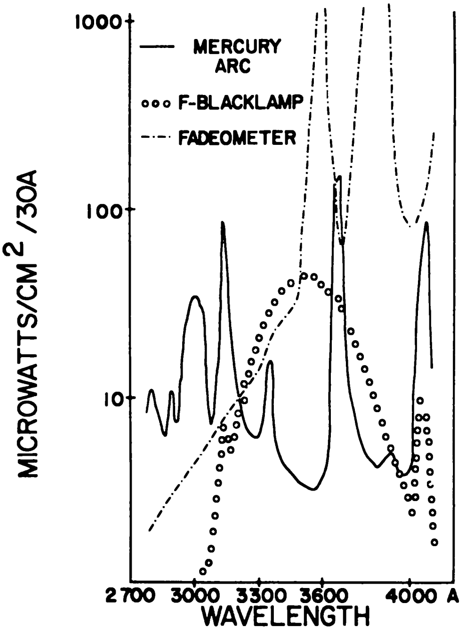


Figure 16. Ultraviolet spectral distribution of carbon arc, mercury arc, and fluorescent black lamp

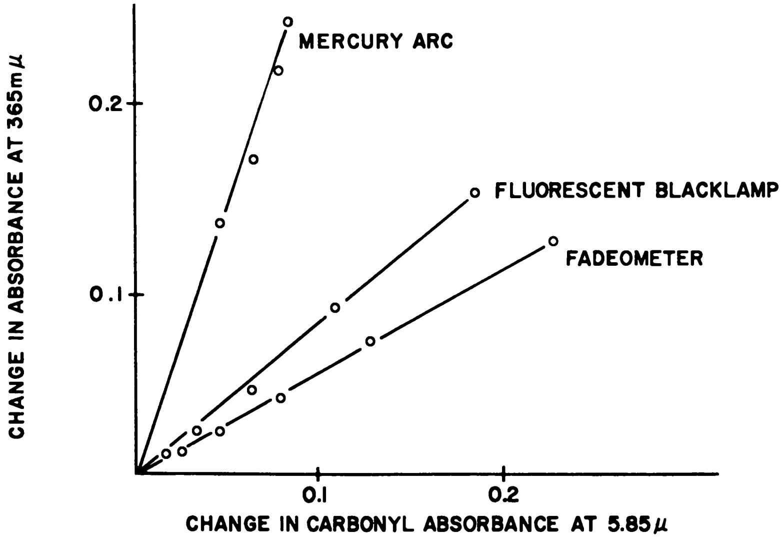


Figure 17. Relationship between discoloration and carbonyl formation

panied by significant carbonyl formation. However, under mercury-arc exposure discoloration occurred at a greater rate relative to carbonyl formation. The latter results suggest that under irradiation with sources rich in short wavelength energy the discoloration may be predominantly caused by noncarbonyl conjugated species. On the other hand, irradiation

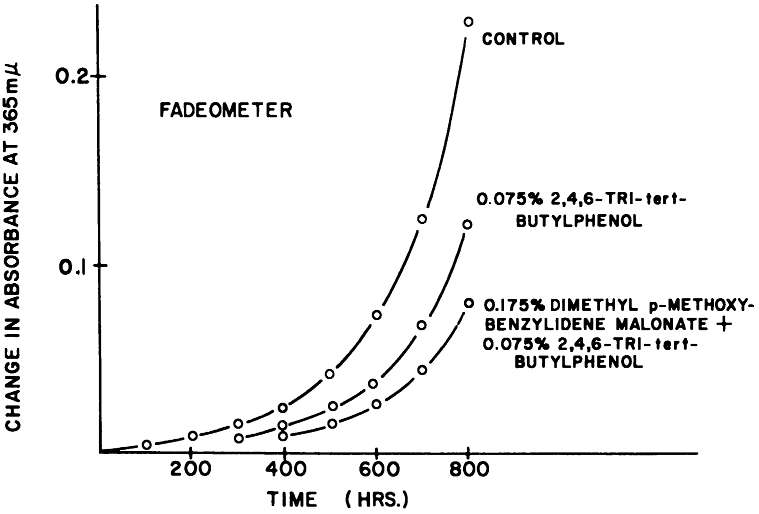


Figure 18. Inhibition of discoloration of polystyrene films

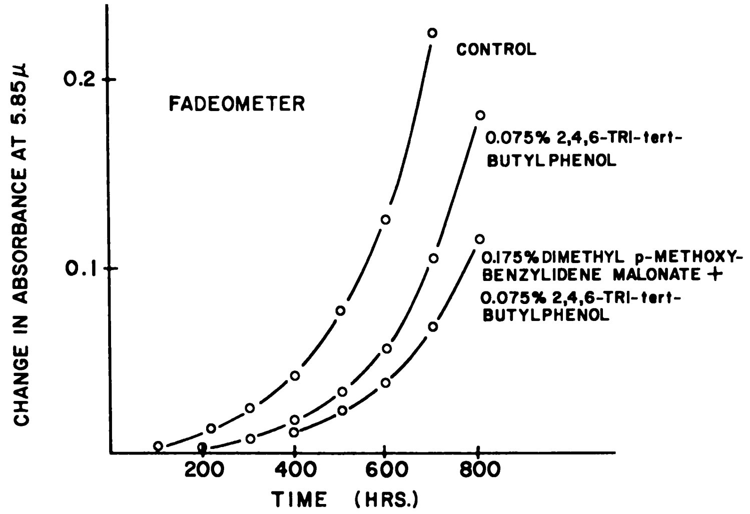


Figure 19. Inhibition of carbonyl formation of polystyrene films

with light sources emitting above 3000 A. results in the formation of colored products, which are mainly carbonyl containing compounds.

In view of this wavelength dependence on photooxidation further studies were carried out to determine the role of antioxidants and ultraviolet absorber–antioxidant combinations in photooxidation reactions.

Figures 18 and 19 show that inhibition of discoloration by these additives under Fade-ometer exposure was also accompanied by inhibition of carbonyl formation.

Figure 20 illustrates that a similar reduction in the rate of carbonyl formation also occurs under fluorescent blacklamp exposure. These results suggest that the antioxidant acts as a free radical inhibitor, reducing the over-all rate of photooxidation. The similarity in the relationship between the change in absorbance at 365 mμ and carbonyl formation observed in the presence of the additives also lends further support to the previous conclusion that under exposures of this type, discoloration is caused by carbonyl products.

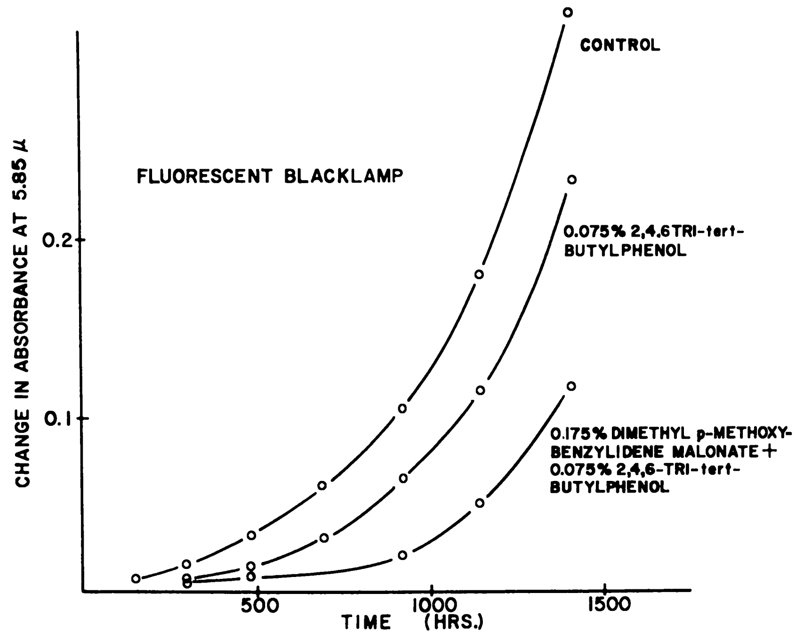


Figure 20. Inhibition of carbonyl formation of polystyrene films

In contrast to the above, Figure 21 shows that the antioxidant did not inhibit the rate of either discoloration or carbonyl formation under mercury-arc exposure. Grassie and Weir (5) also reported that under 2537-A. irradiation the antioxidant, 2,6-di-*tert*-butyl-*p*-cresol, had no effect on the rate of polystyrene photooxidation. It may be concluded,

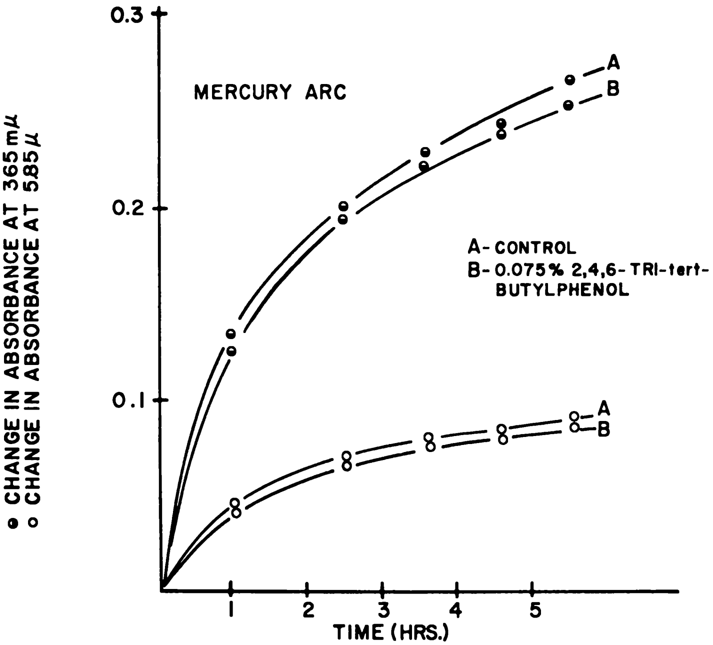


Figure 21. Effect of antioxidant

therefore, that ultraviolet irradiation with short wavelength energy substantially alters the course of photooxidation, and inhibitors of this type are not effective.

Conclusions

Certain phenolic antioxidants in combination with ultraviolet absorbers improve substantially the light stability of polystyrene. Combinations of this type can be used advantageously to prevent polymer discoloration in indoor fluorescent lamp fixture applications. However, studies of this type require further investigation, and an explanation must be sought for the striking differences in behavior of the various antioxidants tested.

In addition, a great need exists for improved test procedures to predict end-use performance. The correlations between accelerated exposure devices and normal fluorescent lamps, described in this report, represent only a preliminary effort to refine and establish meaningful laboratory methods for evaluating light stabilizers. Exposure data from a greater number of samples, containing a greater variety of formulations, are needed for more accurate correlations.

Further work will be necessary to determine the products formed on light exposure and thus elucidate more fully the mechanism of polystyrene photooxidation. Such investigations are quite useful for stabilization purposes, provided, however, that careful consideration is given to the irradiation conditions used.

Acknowledgments

The authors thank N. Z. Searle for the activation spectrum of polystyrene and M. Maiullo for carrying out part of the experimental work.

Literature Cited

(1) Achhammer, B. G., Reiney, M. J., Wall, L. A., Reinhart, F. W., *J. Polymer Sci.* **8,** 555 (1952).
(2) Achhammer, B. G., Reiney, M. J., Reinhart, F. W., *J. Res. Natl. Bur. Std.* **47,** 116 (1951).
(3) Costello, L. R., U. S. Patents **3,134,748, 3,134,749, 3,134,751, 3,134,752.**
(4) Estes, P. H., Smith, E. R., Woodland, P. C., Veazey, E. W., *Mod. Plastics* (Sept. 1958).
(5) Grassie, N., Weir, N. A., *J. Appl. Polymer Sci.* **9,** 987 (1965).
(6) *Ibid.*, p. 999.
(7) Hirt, R. C., Schmitt, R. G., Searle, N. Z., Sullivan, A. P., *J. Opt. Soc. Am.* **50,** 706 (1960).
(8) Hirt, R. C., Searle, N. Z., *Preprint SPE RETEC*, Washington, D. C. (1964).
(9) IES-SPI-NEMA Subcommittee of the Light Control and Equipment Design Committee, *Illum. Eng. Soc., Trans.* **53,** 284 (1958).
(10) Matheson, L. A., Boyer, R. F., *Ind. Eng. Chem.* **44,** 867 (1952).
(11) McCarthy, R. A., *Plastics Technol.* (July 1958).
(12) Reiney, M. J., Tryon, M., Achhammer, B. G., *J. Res. Natl. Bur. Std.* **51,** 155 (1953).
(13) Zapolskii, O. B., *Polymer Sci. U.S.S.R.* **7,** 678 (1965).

RECEIVED April 19, 1967.

Fire Retardants for Thermoplastics

Phosphine Oxides, Phosphonic Acids, and Phosphinic Acids

ALLAN E. SHERR,[1] HELEN C. GILLHAM, and HARVEY G. KLEIN

Central Research Division, American Cyanamid Co., Stamford, Conn.

Phosphine oxides, phosphonic acids, and phosphinic acids have been found to be flame retardants for various thermoplastic polymers. While there are many reasons for their effectiveness, we postulate that the acidity of the compounds is directly related to their activity and that the formation of polyphosphates (or phosphate glasses) is vital to the mechanism by which they function.

We have had a continuing interest in flame retardants, methods of test and mechanisms of action of such materials. Recently, we reported studies involving fire retardant additives, syntheses of monomers, and the preparation of copolymers to achieve flame resistance (*41*). In addition, considerable synthetic work in phosphorus chemistry has been pursued at our Stamford Research Laboratories. Some of this has been reported by Grayson, Rauhut, Buckler, Wystrach, and co-workers. This chapter and the one following result from this background.

In this paper we report the use of some phosphine oxides, phosphonic acids, and phosphinic acids to impart fire retardant properties to polymers. In addition, we postulate a mechanism by which these compounds behave as flame retardant agents.

Fire Retardant Schemes

There are many techniques for imparting self-extinguishing characteristics to polymers (*1, 2, 8, 10, 11, 32, 34, 36, 37, 38, 43*). The following is a partial list.

---

[1] Present address: Organic Chemicals Division, American Cyanamid Co., Bound Brook, N. J.

Inorganic Fillers. Smith (*43*) listed the physical addition of inorganic fillers such as ammonium phosphate, ammonium bromide, ammonium sulfamate, or antimony oxide as one such scheme. Borate salts also are used as inorganic fillers.

Organic Additives. Boyer and Vajda have described the physical addition of organic fire retardants (*5*). Examples are phosphate esters, chlorinated waxes, halogenated phosphate esters, and/or halogen-containing polymeric materials. Gouinlock *et al.* (*18*), among others, have discussed highly halogenated compounds.

Polymer Structure Modification. Chemical modification of the polymer structure includes the use of tetrahalophthalic acids or anhydrides, diallylphenyl phosphonate, brominated allyl phosphates, chlorendic anhydride, and tetrakishydroxymethyl phosphonium chloride.

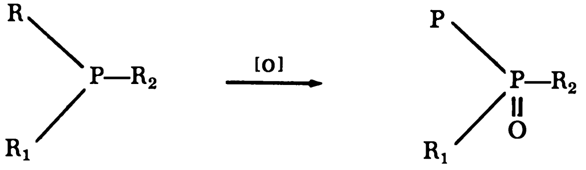
Inherently Stable Structure. Inherent stability of the polymer structure includes resins such as unplasticized poly(vinyl chloride) containing about 56% chlorine which is self-extinguishing and poly(vinylidene) chloride.

Fire Retardant Tests

There is a wide variety of procedures for measuring the self-extinguishing properties of plastic materials. These include ASTM Tests D568, D635, D757, D1692, and D1433; Military Specification LP 406b Test 2023.1; ASTM Test E84 (Underwriters Tunnel Test); etc. Summaries and discussions of these tests have been presented by Sauber (*40*), Feuer (*14*), and Hammerl (*21*). Briber has questioned the significance of fire retardant tests for plastics (*6*). Thus, the value of the individual tests is a subject of considerable debate, particularly regarding the relationship of the test to the actual occurrence and prevention of fires.

Preparation of Phosphine Oxides

Generally, the phosphine oxides were prepared by mild oxidation of the corresponding phosphine (*26*). This was accomplished by refluxing an alcoholic solution of the phosphine in the presence of oxygen and/or hydrogen peroxide. The resultant phosphine oxide was isolated by filtration or solvent evaporation.

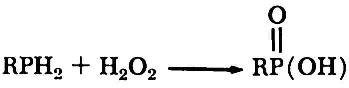


Feshchenko and Kirsanov more recently have reported the reaction of red phosphorus with iodine and an alcohol to prepare tertiary phosphines in 85–90% yield (*13*).

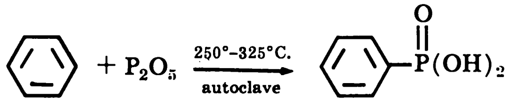
$$ROH + I_2 + P \rightarrow R_3P{=}O + RI$$

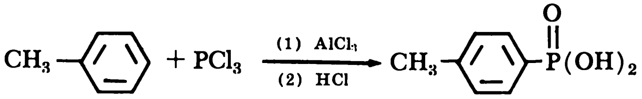
Preparation of Phosphonic Acids

Phosphonic acids can be prepared in yields of 50–100% by the types of reactions shown in the equations below (*22, 27, 28, 29, 30, 31, 41, 44*).

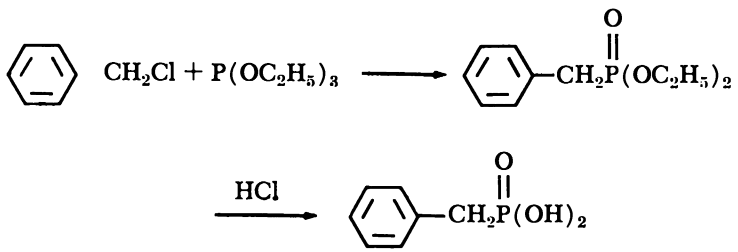


$$RPH_2 + H_2O_2 \longrightarrow \overset{O}{\overset{\|}{RP}}(OH)_2$$





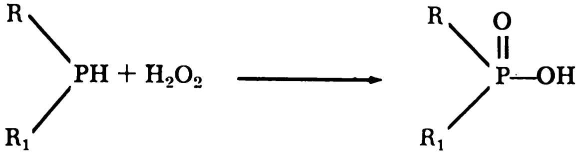
The Arbuzov reaction is frequently used to prepare phosphonic acids as shown below (*22*).



Preparation of Phosphinic Acids

The reaction of secondary phosphines with hydrogen peroxide in a suitable solvent is a convenient method for preparing the phosphinic acids (*27*).

Yields are usually from 50 to 90% of theoretical.



Burning Test

The synthesized phosphorus compounds were evaluated as follows.

The additive was added gradually to the polymer fused on a two-roll mill at 170°–174°C. After addition, polymer sheets were taken off the mill and put back on the mill endwise. Several such passes were made until the sample was thoroughly mixed. The specimen was removed from the mill in thin sheets and, while hot, cut into small pieces. The polymer was compression molded at 700 p.s.i.g. and a temperature of *ca.* 155°C. into a 6 × 6-inch sheet of about 0.045-inch thickness. This sheet was cut into the 5 × 1/2 × 0.045-inch specimens for burning in the modified D635 test. The sample was initially evaluated with 25% additive. If the compound was effective, lower concentrations were used until the additive would not confer fire retardant activity, or until the supply of additive was exhausted. With poly(methyl methacrylate), PMMA, cast samples also were prepared.

A slight modification of ASTM Test D635-56T appeared suitable for use in our studies to obtain preliminary evaluations of new phosphorus compounds. Our deviations were to use a 5-inch specimen, 0.5-inch wide, and 0.045-inch thick instead of the 0.05-inch thickness prescribed. We omitted the use of a wire gauze under the specimen.

Effective Compounds

In our studies we found that phosphonic acids (*16*), phosphinic acids (*25*), and phosphine oxides (*17*) are additives capable of imparting fire retardant properties to thermoplastic polymers. Tables I and II present data for some of these compounds when added to polyethylene or to poly(methyl methacrylate). The concentration reported is not necessarily the lowest effective concentration for the additive in the polymer. These additives also were effective in other thermoplastic polymers such as polystyrene, impact polystyrene, polypropylene and ABS. The compounds were completely compatible with the polymers.

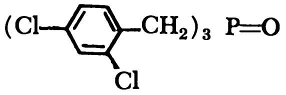
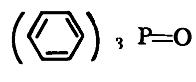
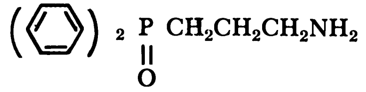
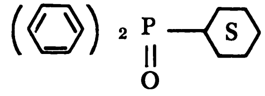
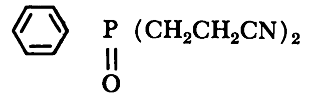
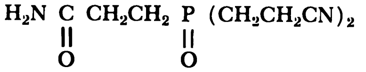
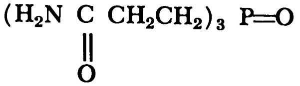
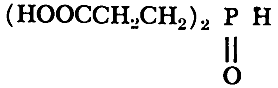
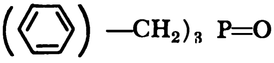
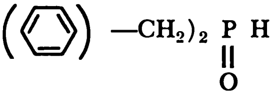
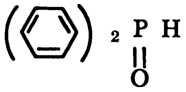
Reported Mechanisms of Action

The mechanism of action of flame retardants in thermoplastic materials (polyethylene, polypropylene, polystyrene, cellulosics, PMMA, etc.) is unknown and is certainly quite complex. Broido (*7*) presented a good example in the difficulties of explaining how fire retardants work. He found that materials which were most effective in preventing flaming combustion of cellulose were also effective in causing sugar cubes to support flame!

Generally, fire retardant activity is attributed to one of the following mechanisms:

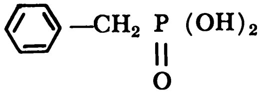
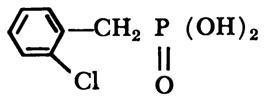
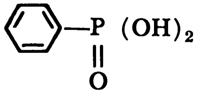
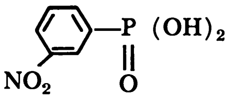
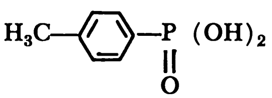
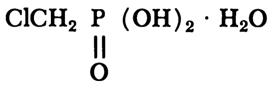
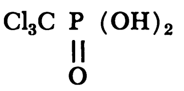
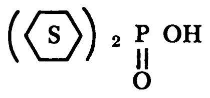
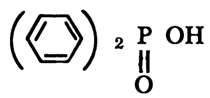
(a) Modification of the mechanism of decomposition or change in the rate of decomposition of the polymer. Broido (*7*) uses this explana-

Table I. Phosphine Oxides as Flame Retardants

Compound	*Melting Point, °C.*	*Empirical Formula*	*Polymer*[a]	*Concentration, %*
	185–188	$C_{21}H_{15}Cl_6PO$	PE	15
	156	$C_{18}H_{15}PO$	PMMA	5
	156	$C_{18}H_{15}PO$	PE	15
	159	$C_{15}H_{18}NPO$	PMMA	15
	166–167	$C_{18}H_{21}PO$	PMMA	15
	103–105	$C_{12}H_9N_2PO$	PMMA	10
 $H_2N\underset{\underset{O}{\Vert}}{C}CH_2CH_2\underset{\underset{O}{\Vert}}{P}(CH_2CH_2CN)_2$	160–164	$C_9H_{14}N_3PO_2$	PMMA	15
 $(H_2N\underset{\underset{O}{\Vert}}{C}CH_2CH_2)_3P{=}O$	203–206	$C_9H_{18}N_3PO_4$	PMMA	15
$(HOOCCH_2CH_2)_3P{=}O$	155–156	$C_9H_{15}PO_7$	PE	15
 $(HOOCCH_2CH_2)_2\underset{\underset{O}{\Vert}}{P}H$	127–130	$C_6H_{11}PO_5$	PE	15
	212–214	$C_{21}H_{21}PO$	PE	15
	105.5–107.5	$C_{14}H_{15}PO$	PE	10
	72–75	$C_{12}H_{23}PO$	PE	15

[a] PE = Polyethylene; PMMA = Poly(methyl methacrylate).

Table II. Phosphonic and Phosphinic Acids as Flame Retardants

Compound	*Melting Point, °C.*	*Empirical Formula*	*Polymer*[a]	*Concentration, %*
	166	$C_7H_9PO_3$	PMMA	2.5
	188–189	$C_7H_8ClPO_3$	PE	15
	162	$C_6H_7PO_3$	PMMA	2.5
	150–154	$C_6H_6NPO_5$	PMMA	15
	189	$C_7H_9PO_3$	PMMA	15
 $\mathrm{ClCH_2}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{(OH)_2 \cdot H_2O}$	90–94	CH_6ClPO_4	PMMA	5
 $\mathrm{Cl_3C}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{(OH)_2}$	80–82	$CH_2Cl_3PO_3$	PMMA	15
	144–145	$C_{12}H_{23}PO_2$	PE	5
	189–192	$C_{12}H_{11}PO_2$	PE	15

[a] PE = Polyethylene; PMMA = Poly(methyl methacrylate).

tion as have Gruntfest and Young (*19*) in discussing flame retardants for PMMA.

(b) Retardation of combustion in the vapor phase, including cooling of the flame by radiation from carbon particles.

(c) Boyer discussed insulation of the substrate from the flame (*4*). Amosov (*1*) and Broido (*7*) mention isolation of the fuel from oxygen or dilution of oxygen with nonflammable gases. Bubbling, foaming, or evolution of nonflammable gases such as ammonia, carbon dioxide, nitrogen or water isolate the fuel from oxygen. Decomposition products may provide nonflammable coatings which fuse to the surface, usually as glassy or foamy coatings and insulate the substrate from the flame. Formation of stable chemical compounds with the fuel prevent access of oxygen. Amosov (*1*) reports that phosphonic acid and/or phosphates form stable esters with cellulose.

(d) Another possible mechanism is to increase the specific heat of the surface layer of the substrate.

(e) Gruntfest (*19*) and Broido (*7*) discuss the reduction of the flame temperature as a route to fire retardance. Opp (*35*) gives as an example a mixture of 10% petroleum ether, 40% carbon disulfide and 50% carbon tetrachloride which will burn when ignited but will not kindle other articles with which it comes in contact. The combustible liquids burn, but the noncombustible carbon tetrachloride evaporates rapidly and keeps the temperature below the fire point of other substances.

(f) Gruse (*20*) and Amosov (*1*) describe the breaking of the chain reactions in the flame; Rosser (*39*) has postulated the following reactions for combustion and inhibition of a hydrocarbon flame where RH is any hydrogen containing species in the flame. The reduction of HO· radicals with HBr slows the exothermic propagation reaction.

$HO\cdot + CO \rightarrow CO_2 + H\cdot$ Exothermic propagation (1)

$H\cdot + O_2 \rightarrow HO\cdot + O$ Chain branching (2)

$HO\cdot + HBr \rightarrow HOH + Br\cdot$ Inhibition (3)

$Br\cdot + HR \rightarrow HBr + R\cdot$ Regeneration (4)

(g) Rosser *et al.* (*39*) attribute action to thermal decomposition of a free radical initiator, accelerating the breakdown of polymer, and promoting reaction between polymer fragments and halogen-containing materials. This leads to a delay in loss of halogen from the polymer mass.

Fenimore and Jones (*12*) report the first of their investigations into the modes of inhibiting polymer flammability. They show that chlorine substituted in polyethylene inhibits by affecting the pyrolysis of the condensed phase, but the pair of reactants, antimony plus a little chlorine, poisons the flame. Bromine is more effective than chlorine because it also poisons the flame. They speculate that halogen seems necessary to vaporize Sb from Sb_2O_3.

Which of the above is responsible for the effectiveness of a particular agent is a matter of conjecture at present It seems likely that a combination of mechanisms is required for fire retardant activity!

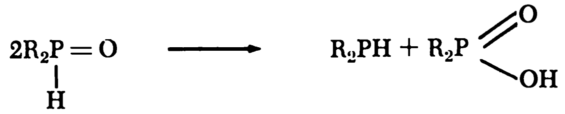
Mode of Action of Phosphine Oxides, Phosphonic Acids, and Phosphinic Acids

We believe that the activity of the phosphine oxides, the phosphonic and the phosphinic acids is related to the acidity of the compounds, as well as the thermal stability of the carbon-phosphorus bond in the compounds and of the phosphorus-oxygen bond of the derived acids.

Collins (*9*) proposed that phosphine oxides are converted to phosphinic acids and phosphonic acids. These, in turn, produce phosphoric acids. We suggest that the phosphoric acids then are decomposed into polyphosphates, $(PO_3)_x^{x-}$ and exist as stable phosphate glasses.

The thermal stability of the phosphate glass [as well as the stability of the oxides and phosphonic or phosphinic acids (*15*)] enables it to shield the polymer from the flame by formation of a continuous glassy coating. Thus, the fuel (polymer) is isolated from oxygen.

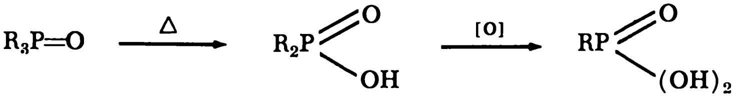
Secondary phosphine oxides thermally disproportionate into secondary phosphines and phosphinic acids (*3*). The phosphine can be reoxidized to the phosphine oxide and continue this cycle.



$$2R_2\underset{\displaystyle H}{\underset{|}{P}}=O \longrightarrow R_2PH + R_2P\genfrac{}{}{0pt}{}{\diagup O}{\diagdown OH}$$

Dicyclohexylphosphine oxide would thermally disproportionate into dicyclohexylphosphinic acid and dicyclohexylphosphine. We found that both the phosphine oxide, m.p. 72°–75°C., at 15%, and the phosphinic acid, m.p. 144°–145°C., at 5%, in polyethylene are flame retardants.

Hudson (*23*) has suggested that tertiary phosphine oxides form phosphinic acids on heating. Such acids

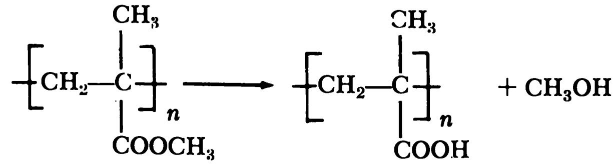


can be further oxidized to the phosphonic acid and then to the phosphoric acid (*9*). We believe the phosphoric acid next forms a polyphosphate

$$x\,H_2PO_4^- \rightarrow (PO_3)_x^{x-} + x\,H_2O$$

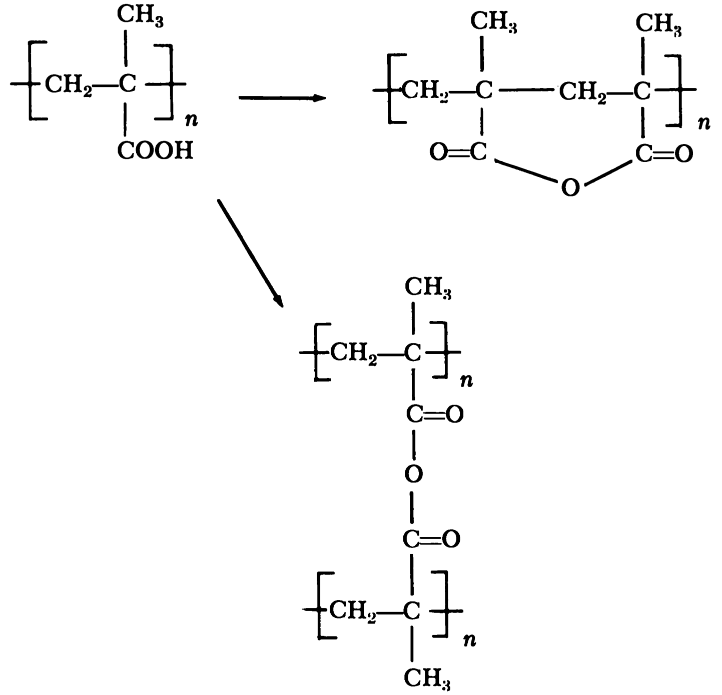
Note also the formation of water, which would aid flame retardance.

The acidic nature of the phosphorus compounds (*24*) alters the course of the pyrolysis of certain polymers. Gruntfest and Young (*19*) previously postulated that with poly(methyl methacrylate) an acid functions as a chain stopper or causes a primary alteration of the PMMA, such as crosslinking. They noted the formation of high yields of dimethyl



$$\left[CH_2-\overset{CH_3}{\underset{COOCH_3}{C}} \right]_n \longrightarrow \left[CH_2-\overset{CH_3}{\underset{COOH}{C}} \right]_n + CH_3OH$$

$$2CH_3OH \xrightarrow{\Delta} CH_3OCH_3 + H_2O$$



ether during pyrolysis. The ether may well arise by acid hydrolysis of the methacrylate, liberating methyl alcohol which dehydrates to the ether. The poly(methacrylic acid) then probably dehydrates to poly(methacrylic anhydride) and water, further helping to promote flame retardance.

Literature Cited

(1) Amosov, G. A., *Fire Res. Abstr. Rev.* **7** (2), 136 (1965).
(2) Bailey, W. J., U. S. Patent **3,334,064** (Aug. 1, 1967).
(3) Bailey, W. J., Muir, W. M., Marktscheffel, F., *J. Org. Chem.* **27**, 4404 (1962).
(4) Boyer, N. E., *Plastics Technol.* **8** (11), 33 (1962).
(5) Boyer, N. E., Vajda, A. E., *SPE (Soc. Plastics Engrs.) Trans.* **4**, 45 (1964).
(6) Briber, A. J., *SPE Soc. Plastics Engrs. Tech. Papers* **13**, 1041 (1967).
(7) Broido, A., *Science* **133**, 1701 (1961).
(8) Carpenter, C. H., Mack, G. P., *British Plastics* **34**, 541 (1961).
(9) Collins, J. D., *Chem. Ind.* **1965**, 1286.
(10) Dahms, R. H., *Petrol. Refiner* **41** (3), 132 (1962).
(11) Drake, Jr., G. L., Beninate, J. V., Guthrie, J. D., *Am. Dyestuff Reptr.* **50** (4), 27 (1961).
(12) Fenimore, C. P., Jones, G. W., *Combustion Flame* **10**, 295 (1966).
(13) Feshchenko, N. G., Kirsanov, A. V., *J. Gen. Chem. USSR* **1966** (3), 36.
(14) Feuer, S. S., Torres, A. F., *Chem. Eng.* **69** (7), 138 (1962).
(15) Freedman, L. D., Doak, G. O., *Chem. Rev.* **57**, 479 (1957).
(16) Gillham, H. C., Klein, H. G., U. S. Patent **3,345,432** (Oct. 3, 1967).
(17) Gillham, H. C., Sherr, A. E., U. S. Patent **3,341,625** (Sept. 12, 1967).
(18) Gouinlock, Jr., E. V., Long, F. W., Creighton, S. M., *Plastics Technol.* **8** (12), 40 (1962).
(19) Gruntfest, I. J., Young, E. M., *Am. Chem. Soc. Div. Organic Coatings Plastics Chem.* **21** (1), 113 (1961).
(20) Gruse, A. B., *Natl. Fire Protection Assoc. Quart.* **53**, 330 (1960).
(21) Hammerl, A. J., *Reinforced Plastics* **2** (5), 22 (1963).
(22) Harvey, R. G., De Sombre, E. R., "Topics in Phosphorus Chemistry," M. Grayson, Ed., pp. 57-112, Vol. 1, Interscience, New York, 1964.
(23) Hudson, R. F., private communication.
(24) Kabachnik, M. I., Mastrukova, T. A., Shipov, A. E., Melentyeva, T. A., *Tetrahedron* **9**, 10 (1960).
(25) Klein, H. G., Gillham, H. C., U. S. Patent **3,322,716** (May 30, 1967).
(26) Kosolapoff, G. M., "Organic Phosphorus Compounds," pp. 99-120, Wiley, New York, 1950.
(27) *Ibid.*, p. 137.
(28) *Ibid.*, pp. 121-170.
(29) Kosolapoff, G. M., *J. Am. Chem. Soc.* **74**, 4119 (1952).
(30) Kosolapoff, G. M., Huber, W. F., *J. Am. Chem. Soc.* **69**, 2020 (1947).
(31) Lecher, H. Z., Chao, T. H., Whitehouse, K. C., U. S. Patent **2,717,906** (1955).
(32) Mack, G. P., "Modern Plastics Encyclopedia," p. 479, McGraw-Hill, New York, 1962.
(33) Milks, J. E., Wystrach, V. P., Siegele, F. H., U. S. Patent **3,032,500** (1962).
(34) "Modern Plastics Encyclopedia," p. 451, McGraw-Hill New York, 1966.
(35) Opp, C. J., *Official Digest* **346**, 840 (1953).
(36) Parkyn, B., *British Plastics* **32**, 29 (1959).
(37) Roberts, C. W., *SPE Trans.* **3**, 111 (1963).
(38) Rockey, K. W., *Plastics (London)* **26** (283), 103 (1961).
(39) Rosser, W. A., Wise, H., Miller, J., "Seventh Symposium (International) on Combustion," Butterworth & Co., London, 1959.

(40) Sauber, W. J., Patten, G. A., *Plastics World* **18** (12) (1960).
(41) Saunders, B. C., Stacey, G. J., Wild, F., Wilding, I. G. E., *J. Chem. Soc.* **1948,** 699.
(42) Sherr, A. E., Klein, H. G., *J. Appl. Polymer Sci.* **11,** 1431 (1967).
(43) Smith, J., *Chem. Ind.* **1965,** 1289.
(44) Van Winkle, J. L., Morris, R. C., U. S. Patent **2,874,184** (1959).

RECEIVED May 9, 1967.

22

Fire Retardants for Thermoplastics

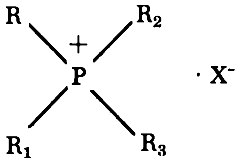
Phosphonium Halides

ALLAN E. SHERR,[1] HELEN C. GILLHAM, and HARVEY G. KLEIN

Central Research Division, American Cyanamid Co., Stamford, Conn.

Mono- and diphosphonium halides have been found to be flame retardants for plastic materials. Their effectiveness can be related to the formation of various active phosphorus compounds, as well as to many of the postulated mechanisms for flame retardant action. The compounds are postulated to be effective because they decompose on ignition to thermally stable phosphine oxides or phosphonic acids which, in turn, are decomposed to continuous films of phosphate glass. In addition, the phosphonium halides form alkyl halides which cool the flame and/or form halogen acids which are flame retardants.

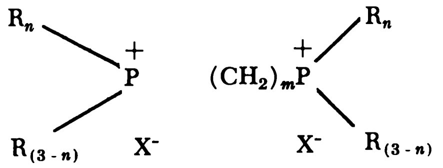
In the preceding chapter (19) we described the use of phosphine oxides, phosphonic acids, and phosphinic acids as flame retardants for thermoplastic materials. We also have found phosphonium halides to be effective flame retardants for plastics (*5*, *6*). These compounds were either the monophosphonium halides,



or diphosphonium halides (top of p. 319).

---

[1] Present address: Organic Chemicals Division, American Cyanamid Co., Bound Brook, N. J.



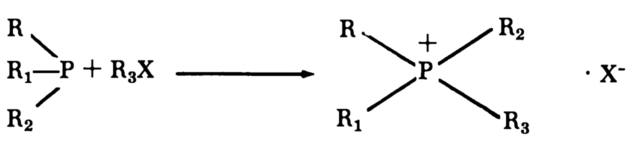
Surprisingly, these halides are compatible with a wide range of plastic materials while inorganic salts are not, and moisture does not appear to be damaging.

The thermoplastic polymers we studied included the polyolefins as polyethylene and polypropylene; the polyacrylates and methacrylates as poly(methyl methacrylate); styrene polymers including both clear and impact types; and acrylonitrile–butadiene–styrene (ABS) plastics. Fire retardance was evaluated by the D-635 procedure as described previously (*19*).

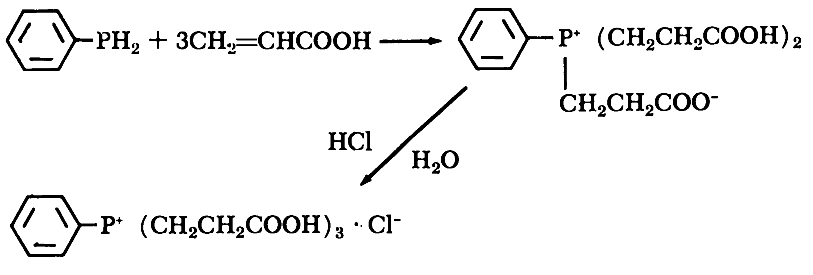
Early in our studies, we found that ethylene-bis[tris(2-cyanoethyl)-phosphonium bromide] (*6*) is an effective fire retardant for polyethylene. When this compound showed flame retardant activity, a wide variety of other related compounds were synthesized and evaluated.

Preparation of Monophosphonium Halides

The monophosphonium halides can be formed readily by the reaction of a phosphine with an alkyl halide. Usually the phosphine and the halide are heated in a solvent such as butyl alcohol or acetonitrile. The phosphonium halide is isolated by filtration (if insoluble), by precipitation with ethyl ether, or by evaporation of the solvent (*10, 11, 12, 13, 14, 16, 18*). Yields are from 50 to 100%.



Carboxyalkyl phosphonium compounds can be prepared by the following reaction.



Preparation of Diphosphonium Halides

The diphosphonium halides are prepared in high yields (*9, 12*) in a manner similar to the monophosphonium halides:

$$R_3P + X(CH_2)_nX \rightarrow R_3\overset{+}{P}(CH_2)_n\overset{+}{P}R_3 \cdot 2X^-$$

Grayson (*12*) gives details of the preparation of the ethylenebis-[tris(2-cyanoethyl)phosphonium bromide].

Experimental

The phosphonium halides were incorporated into the thermoplastic polymers by the milling and molding technique described previously (*19*). The samples were tested for flame retardance using the modified ASTM D-635-56T test (*19*).

Results

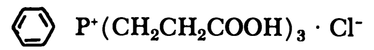
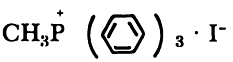
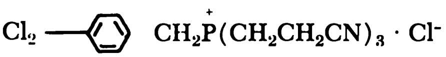
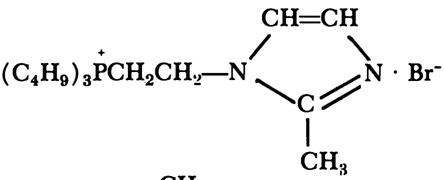
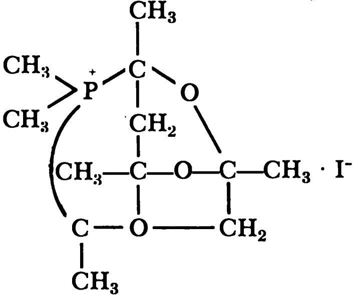
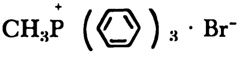
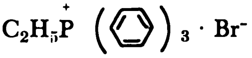
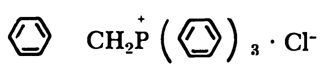
Tables I and II list some of the many phosphonium compounds studied and indicate their effectiveness. Many of our evaluations were halted by limited supplies of the phosphonium halides.

Ethylenebis[tris(2-cyanoethyl)phosphonium bromide] was effective at 1% in natural crystal polystyrene. As soon as the burner in the D635 Flame Test was removed, the sample containing the flame retardant extinguished. Ethylenebis[tris(2-cyanoethyl)phosphoium bromide] at 2% in pigmented crystal polystyrene gave a self-extinguishing polymer, and at 4% in natural impact polystyrene such samples were self-extinguishing.

Effect of Phosphonium Halide on Properties of Polymer

Table III lists some of the physical properties of polymers which contain ethylenebis[tris(2-cyanoethyl)phosphonium bromide]. This additive caused an increase in the dissipation factor and dielectric constant and lowered the dielectric strengths of polyethylene and poly(methyl methacrylate). The effects on mechanical properties were mixed. Obviously, lower concentrations of phosphonium halides would have less effect on mechanical and electrical properties. At levels of 1–3% very little change in properties would be expected. It was surprising that the phosphonium salts were compatible with such a range of polymers. We did not observe any tendency for the phosphonium salts to plate out of or exude from the polymer. In all cases homogeneous blends were obtained.

Table I. Monophosphonium Halides as Flame Retardants

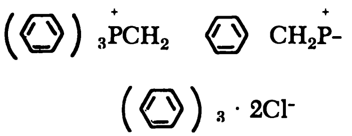
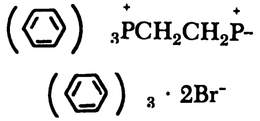
Compound	*Melting Point, °C.*	*Empirical Formula*	*Polymer*[b]	*Concentration,*[a] *%*
	176–178	$C_{15}H_{20}O_6PCl$	PE	20
$CH_3\overset{+}{P}(CH_2CH_2CN)_3 \cdot I^-$	240–243	$C_{10}H_{15}N_3PI$	PMMA	10
	240–243	$C_{10}H_{15}N_3PI$	PE	10
	183–186	$C_{19}H_{18}PI$	PE	10
	158–165	$C_{16}H_{17}N_3PCl_3$	PE	10
$(C_4H_9)_3\overset{+}{P}\ CH_2CH_2N(C_2H_5)_2 \cdot Br^-$		$C_{18}H_{41}NPBr$	PE	10
	163–164	$C_{18}H_{36}N_2PBr$	PE	10
	245–246	$C_{12}H_{23}O_3PI$	PE	10
	230–232	$C_{19}H_{18}PBr$	PE	15
	203–208	$C_{20}H_{20}PBr$	PE	15
	>280	$C_{25}H_{22}PCl$	PE	15
	214–218	$C_{20}H_{20}OPBr$	PE	15

---

[a] The concentrations reported are not necessarily the lowest level at which the specific additive is effective in the polymer shown.

[b] PE = polyethylene. PMMA = poly(methyl methacrylate).

Table II. Diphosphonium Halides as Flame Retardants

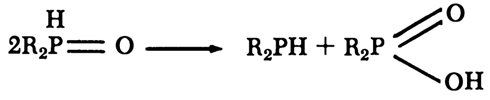
Compound	*Melting Point, °C.*	*Empirical Formula*	*Polymer*[b]	*Concentration,*[a] *%*
$(NCCH_2CH_2)_3\overset{+}{P}CH_2CH_2\overset{+}{P}\text{-}(CH_2CH_2CN)_3 \cdot 2Br^-$	>280	$C_{20}H_{28}N_6P_2Br_2$	PMMA PE PS	10 15 1
	>285	$C_{44}H_{38}P_2Cl_2$	PE	15
$(NCCH_2CH_2)_3\overset{+}{P}(CH_2)_{10}\overset{+}{P}\text{-}(CH_2CH_2CN)_3 \cdot 2Br^-$	104–106	$C_{28}H_{44}N_6P_2Br_2$	PE	15
	297–308	$C_{38}H_{34}P_2Br_2$	PE	20

[a] The concentrations reported are not necessarily the lowest level at which the specific compound is effective in the polymer.

[b] PMMA = poly(methyl methacrylate). PE = polyethylene. PS = crystal polystyrene.

Mechanism of Action

Previously we described the high thermal stability of phosphine oxides and phosphonic acids and indicated that this stability may allow a shielding of the polymer from the flame (*19*). The thermal disproportionation of secondary phosphine oxides into secondary phosphines and phosphinic acids (*1*) was also reviewed.



$$2R_2\overset{H}{P}{=}O \longrightarrow R_2PH + R_2P(=O)OH$$

The thermal decomposition of phosphonium halides is reported to give phosphines and alkyl halides as shown below (*7, 15*):

$$R_4\overset{+}{P}X \rightarrow R_3P + RX$$

If RX is methyl iodide, bromide, or chloride, it may cool the flame and, consequently, reduce combustion. Further, the phosphine can be oxidized readily to the phosphine oxide. The latter reaction may lead to self-extinguishing properties either by absorption of energy to complete the reaction and/or more likely by formation of the polyphosphates and the subsequent shielding of the polymer by this thermally stable glass (*19*).

Table III. Physical Properties of Polymers with and without a Phosphonium Bromide[a]

Polymer →	*Polyethylene*[b]		*Polypropylene*[c]		*Polyester*[d]		*Poly(methylmethacrylate)*[e]	
Conc. of $R_3\overset{+}{P}R'\overset{+}{P}R_3 \cdot 2Br$	0%	15%	0%	15%	0%	25%	0%	12.5%
Dielectric strength, volts/mil	960	930	1030	625	356	340	650	600
Dielectric constant, 60 c.p.s.	2.16	2.92	2.17	2.88	3.24	4.11	3.56	4.19
Dissipation factor, 60 c.p.s.	0.0007	0.0138	0.0009	0.035	0.0034	0.104	0.054	0.093
Flexural modulus, × 10^6 p.s.i.g.	0.035	0.052	0.26	0.35	0.67	0.63	0.38	0.38
Flexural strength, × 10^3 p.s.i.g.	1.4	1.6	—	—	15.1	4.8	13.3	12.5
Tensile modulus, × 10^6 p.s.i.g.	0.028	0.037	—	—	—	—	—	—
% Elongation at yield	62.8	20.2	9.8	4.5	—	0.9	5.9	3.9
Tensile strength at yield, p.s.i.g.	1300	1200	4800	4000	—	2300	8800	7200
Vicat softening point, °C.	86	83	128	152	—	—	—	—
Density	0.927	0.960	0.912	0.965	—	—	—	—

[a] $(NCCH_2CH_2)_3\overset{+}{P}CH_2CH_2\overset{+}{P}(CH_2CH_2CN)_3 \cdot 2Br^-$.
[b] Union Carbide DYNH-1, sample thickness 0.04 inch.
[c] Enjay Escon 125, sample thickness 0.04 inch.
[d] American Cyanamid Co., Laminac 4123, sample thickness 0.125 inch, casting.
[e] Rohm & Haas Plexiglas VM-1000, sample thickness 0.06 inch.

The mechanism of action of the phosphonium halides as flame retardants also may be related to the formation of phosphine oxides and/or phosphinic acids from the halide, according to the following reactions (*8, 14, 17*).

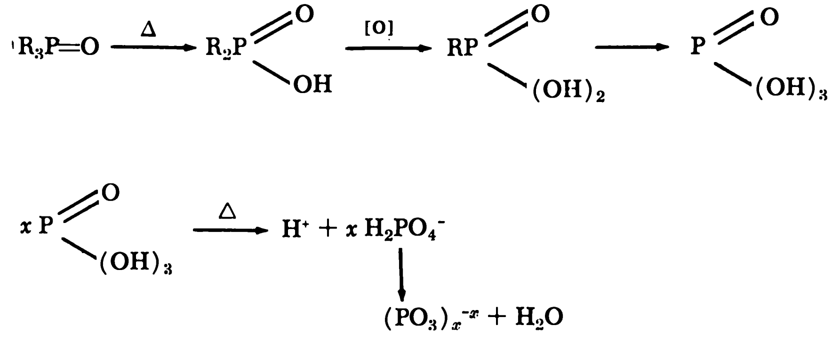
$$R_4P^+X^- + HOH \rightarrow R_4POH + HX$$

$$R_4P^+ + OH^- \rightleftarrows R_4POH \xrightarrow[H_2O]{OH^-} R_4P{-}O^-$$

$$RH + OH^- \rightarrow R^+ + R_3P{=}O$$

In this case, presumably HX also is formed. The HX often is considered an effective flame retardant (*4*).

Tetrakishydroxymethyl phosphonium chloride (THPC) is well established as a flame retardant agent with textiles (*3*). Collins (*2*) has suggested that THPC and urea break down to produce phosphoric acid *via* a phosphine oxide, phosphinic acid, and phosphonic acid. For cellulose, Collins concludes flameproofing is essentially caused by the dehydrating action of the phosphoric acid formed.



We would carry the suggestions of Collins further and postulate that the phosphoric acid gives a polyphosphate. The polyphosphate exists as a continuous glassy covering on the polymer surface protecting it from the flame.

Acknowledgment

We thank G. N. Maher, who did many of the burn tests, and J. Cannelongo, who performed the experiments with the styrene polymers.

Literature Cited

(1) Bailey, W. J., Muir, W. M., Marktscheffel, F., *J. Org. Chem.* **27**, 4404 (1962).
(2) Collins, J. D., *Chem. Ind.* **1965**, 1286.
(3) Drake, Jr., G. L., Beninate, J. V., Guthrie, J. D., *Am. Dyestuff Reptr.* **50** (4), 27 (1961).
(4) Eichorn, J., *J. Appl. Polymer Sci.* **8**, 2497 (1964).
(5) Gillham, H. C., Sherr, A. E., U. S. Patent **3,309,425** (March 14, 1967).
(6) *Ibid.*, **3,322,861** (May 30, 1967).
(7) Fenton, G. W., Hey, L., Ingold, C. K., *J. Chem. Soc.* **1933**, 989.
(8) Fenton, C. W., Ingold, C. K., *J. Chem. Soc.* **1929**, 2342.
(9) Grayson, M., U. S. Patent **3,148,205** (1964).
(10) Grayson, M., Keough, P. T., *J. Am. Chem. Soc.* **82**, 3919 (1960).
(11) Grayson, M., Keough, P. T., U. S. Patent **3,005,013** (1961).
(12) Grayson, M., Keough, P. T., Johnson, G. A., *J. Am. Chem. Soc.* **81**, 4803 (1959).
(13) Griffin, C. E., Gordon, M., *J. Organometal. Chem.* **3**, 414 (1965).
(14) Hoffman, H., Diehr, H. J., *Angew. Chem. Intern. Ed.* **3**, 737 (1964).
(15) Kosolapoff, G. M., "Organophosphorus Compounds," pp. 18, 84, Wiley, New York, 1950.
(16) *Ibid.*, pp. 78-97.
(17) *Ibid.*, p. 104.
(18) Rauhut, M. M., Semsel, A. M., *J. Org. Chem.* **28**, 473 (1963).
(19) Sherr, A. E., Gillham, H. C., Klein, H. G., ADVAN. CHEM. SER. **85**, 307 (1968).
(20) Zanger, M., Vander Werf, C. A., McEwen, W. E., *J. Am. Chem. Soc.* **81**, 3806 (1959).

RECEIVED May 9, 1967.

INDEX

A

- Absorption spectrum of ethylene–carbon monoxide copolymer . 278
- ABS plastics ... 319
- Accelerating aging ... 239
- Acetic acid ... 146
- Acrylonitrile–styrene–butadiene plastics ... 319
- Activation spectrum of polystyrene 288
- Aeration conditions *vs.* oxidative stability ... 100
- Aging
  - of carboxylated SBR latex ... 141
  - oven-accelerated ... 239
  - of *cis*-polybutadiene ... 140
  - of *cis*-polyisoprene ... 132
    - heat ... 140
- Alcohol branching, exposure effects *vs.* ... 265
- 2-Alkoxyphenols ... 187
- 4-Alkoxyphenols ... 198
- Alkylated xylenols, antioxidant potency of ... 164
- Alkylation
  - of *p*-cresol with an α-olefin ... 159
  - with 1-octadecene ... 160
  - phenol ... 158
  - with phenol ... 161
  - of phenols with α-olefins, antioxidants from ... 155
  - with propylene trimer and tetramer ... 158
  - with triisobutylene ... 157
  - with 2,4-xylenol ... 161
  - with 2,6-xylenol ... 161
- Alkyl group structure *vs.* antioxidant value ... 165
- 2-Alkylhydroquinones ... 192
- 4-Alkylpyrocatechol ... 173
- 3-Alkylpyrocatechols ... 181
- 4-(*sec*-Alkyl)-2,6-xylenols ... 161
- 6-(*sec*-Alkyl)-2,4-xylenols ... 161
- Allylic chloride ... 5
- Allyl mechanism ... 58
- Amine
  - derivatives, oxidation half-wave potentials of ... 113
  - *vs.* oxygen absorption of Tetralin 117
  - *vs.* viscosity of SBR ... 115, 117
  - as antioxidants and antiozonants 110
  - as radical acceptors ... 116
  - for rubber, mechanism of antioxidation and antiozonation of 110
- Antioxidant
  - activity *vs.* molecular weight .. 166
  - activity *vs.* structure ... 165
  - effect of alkylated xylenols ... 164
  - in polystyrene, effect of ... 305
  - potency
    - of alkylated xylenols ... 164
    - of dialkyl-*p*-cresols ... 163
    - of trialkylated phenol ... 164
    - *vs.* volatility ... 167
  - systems, polymer ... 239
  - test procedures ... 162
  - value, alkyl group structure *vs.* 165
- Antioxidants ... 20, 288
  - from alkylation of phenols with α-olefins ... 155
  - amines as ... 110
  - in isotactic polypropylene, dihydric phenols as ... 169, 191
  - phenolic ... 291
  - in polypropylene, test methods for evaluating ... 224
  - role of ... 299
  - for silicone fluids, iron, and cerium ... 98
  - for silicones, redox metal ... 97
- Antioxidation of amines for rubber, mechanism of ... 110
- Antiozonants, amines as ... 110
- Antiozonation amines as polypropylene antioxidants ... 203
- Arrhenius plots for reactions in 8-pentadecanone ... 283
- Arsine-epoxy adduct ... 256
- Aryl phosphites as polypropylene antioxidants ... 203
- Automatic device for evaluating thermal stability of PVC ... 50
- Azobisisobutyronitrile ... 116

B

- Bacterial attack on vinyl films ... 251
- Barium–cadmium
  - dilaurate ... 25
  - soaps ... 26
  - synergism ... 5
- Barium soaps ... 26
- Benzotriazole–antioxidant combination ... 294
- Benzotriazoles as polypropylene antioxidants ... 203
- Benzoyl peroxide ... 20

Benzophenone–antioxidant combination 295
Benzylidine–antioxidant combination 294
Benzylidine malonates 293
Biocide *vs.* exposure effect 266-9
Biocides for vinyls 265
Bis(8-hydroxyquinoline) 84
Bis(8-hydroxy-5-quinolyl)methane 84
Bisphenol A 34
Bisphenols *vs.* light stability of polystyrene 291
Bond strengths, solar energy *vs.* .. 274
Butanone 22
tert-Butyl hydroperoxide 141
Butyl rubber 112

C

Carbon monoxide–ethylene copolymer, adsorption spectrum of .. 278
Carbon monoxide formation in ketones 281
Carbonyl absorption of irradiated polystyrene 289
Carbonyl content 231
Carbonyl formation *vs.* discoloration 302
Carbonyl formation of polystyrene, inhibition of 303-4
Carboxylated SBR latex, aging of . 141
Cadmium–
  barium synergism 15
  compounds 40
  containing additives 26
  stearate 25
Cerium antioxidants for silicone fluids 98
Chain branching in oxidation of methyl silicones 102
Chloroform 22
4-Chloro-2-pentene 3
4-Chloropyrocatechol 180
Chromophores 277
Color change in PVC *vs.* stability 50
Coordination compounds 80
Coordination polymers
  crosslinked 90
  synthesis 84
  oxidative stability of 91
  thermal stability of 88
Copolymers of vinyl chloride 68
Cr(III) coordination polymer 90
p-Cresol
  2,6-didodecyl- 157
  2,6-dioctadecyl 165
  with an α-olefin, alkylation of .. 159
  antioxidant potency of dialkyl- . 163
Crosslinked coordination polymer . 90

D

DBPC 26
DDPC 157
Degradation of polypropylene ... 204
Dehydrochlorination 18
  of vinyl chloride copolymers .. 71
Degraded PVC, polyene sequences in 67
Deterioration of polymers, outdoor 272
Dialkyl-*p*-cresols, antioxidant potency of 163
2,5-Dialkylhydroquinones 194
2,6-Dialkylhydroquinones 196
Dialkylhydroxybenzyl-*N*,*N*-dimethyl dithiocarbamates .. 126
3,5-Dialkylpyrocatechols 184
3,6-Dialkylpyrocatechols 185
2,6-Di-*tert*-butyl-*p*-cresol 292
2,6-Di-*tert*-butyl-4-methylphenol 28
Dibutyltin
  bis(monobutylmaleate) 13
  compounds 40
  dilaurate 11, 25
  laurate 61
2,6-Didodecyl-*p*-cresol 157
Diethyl silicone fluid 104
Differential thermal analysis 230
Dihydric phenols as antioxidants in isotactic polypropylene 169, 191
Dilauryl sulfinyldipropionate 146
Dilauryl thiodipropionate ..141, 208, 248
N,*N*-Dimethylformamide 84
Dimethyl silicone fluids 95
2,6-Dioctadecyl-*p*-cresol 161, 165
Diphosphonium halides 318
Discoloration *vs.* carbonyl formation 302
Discoloration
  vs. oxidation 299
  of polystyrene, inhibition of 303
  of PVC 67
Distearyl thiodipropionate 147
Dithiocarbamates 126
DLTDP 208, 245
DMS 95
  fluids, inhibition of oxidation by 102
  gelation time of 100
  vs. MPS fluids inhibited by redox metal, comparative oxidation of 105
DOPC 161

E

Electrical conductance, stability of PVC compounds *vs.* 47
Energy distribution of solar radiation 273
Epon 828 25
Epoxy plasticizers for vinyls 262
Epoxy resin 26
Epoxystearate as plasticizer for vinyls 64
Ethylene–carbon monoxide copolymer, absorption spectrum of .. 278
Ethylene polymerization, α-olefins from 159

Exposure
  data correlations for polystyrene 296
  effect
    vs. alcohol branching 265
    vs. biocide 266-9
    vs. phosphate plasticizer level .. 266
    vs. ultraviolet absorber 268
Extrusion plastometer 233

F

Fade-ometer 290
Fillers for vinyls 264
Fire retardants for thermoplastics 307, 318
Fire retardant tests 308
Flame retardants
  mechanism of action of 310
  phosphine oxides as 311
  phosphonic and phosphinic acids as 312
Formulating parameters for vinyls 259
Free radical chain oxidation of methyl silicones 102
Free radical scavengers 207
Frontier electron theory 112
Fungal attack of vinyl films 251
Funginert materials 251

G

Gas yellowing 155
Gelation time of DMS 100
Gelation of silicone fluids, oxidative 95
Gel-permeation chromatography .. 24
Glass transition temperature of PVC 66

H

Half-wave potentials 180, 194
Haze, redox metal antioxidants *vs.* 97
Heat aging of polyisoprene 140
Heat stability of polypropylene .. 213
Heat-stabilizing additives 18
High temperature, stability of PVC compounds against 45
Hindered phenol 26
Hindered phenolics 207
  as polypropylene antioxidants .. 203
Hindered phenols 291
  sterically 126
Hückel molecular orbitals 111
Hydrocarbontin esters 73
Hydroperoxide decomposition by sulfur compounds 140
Hydroquinone 169, 191
2-Hydroxybenzophenones 284
Hydroxybenzophenones as polypropylene antioxidants 203
2-Hydroxy-4-methoxybenzophenone 292

I

Inhibition of oxidation by DMS fluids 102
Inorganic fillers as self-extinguishing agents 308
Internal stabilization of PVC 65, 71
Instability of PVC, thermal 65
Iron antioxidants for silicone fluids 98
γ-Irradiation of polypropylene ... 188
Isotactic polypropylene, dihydric phenols as antioxidants in ..169, 191

K

Ketones
  carbon monoxide formation in .. 281
  photochemistry of 277
  photoelimination reaction of ... 279

L

Lead undecylenate 74
Light sources ultraviolet spectral distribution of 297, 302
Light stability of polystyrene, bisphenols *vs.* 291
Light stability of polystyrene, phenols *vs.* 291
Light stabilization of polystyrene . 287
Lubricants for vinyls 264

M

Mannich bases 129, 132, 133, 134
Mechanism of antioxidation and antiozonization of amines for rubber 110
Melt rheology for poly(vinyl chloride), stabilizers *vs.* 38
Metallic stabilizers 39
Metallo-organic systems with high thermal stability 82
Metal, stability *vs.* central 88
Methylenebisphenol 156
Methyl ketones, quantum efficiency of 282
Methylphenyl silicone fluids 95
Methyl silicones, oxidation of ... 96
Mildew on vinyl films 251
Microbial degradation of plasticized vinyl films 250
Molecular orbitals, Hückel 111
Molecular weight *vs.* antioxidant potency 166
Molecular weight, PVC performance *vs.* 256-7
Mononuclear antioxidants, phenolic 169
Monocyclic phenols 126
MPS 95
  vs. DMS fluids inhibited by redox metal, comparative oxidation of 105

N

4-Nitropyrocatechol 180
Nomogram, thermal stability test .. 49

O

1-Octadecene
  alkylation with 160
  composition of 164
  olefin types 161

- α-Olefin, alkylation of *p*-cresol with an 159
- α-Olefin mixtures 159
- Olefin types, 1-octadecene 161
- α-Olefins 158
  - antioxidants from alkylation of phenols with 155
  - from ethylene polymerization 159
- Organic systems with high thermal stability, metallo- 82
- Organometallic stabilizers 39
- Organotin mercaptide stabilizers 39
- Organotin soap 26
- Organovinyltin compounds 73
- Outdoor deterioration of polymers 272
- Oven aging 225
  - technique 239
- Oven life, thickness of polypropylene *vs.* 241
- Oxidation
  - *vs.* discoloration 299
  - of DMS *vs.* MPS fluids inhibited by redox metal, comparative 105
  - half-wave potentials of amine derivatives 113
  - of methyl silicones 96
    - free radical chain 102
- Oxidative
  - gelation of silicone fluids 95
  - stability *vs.* aeration conditions 100
  - stability of coordination polymers 91
  - stabilization of silicone fluids 95
- 10,10′-Oxybisphenoxyarsine 258
- Oxygen absorption of Tetralin, amine *vs.* 117
- Oxygen uptake 229
- Ozone with rubber, reaction of 111

P

- Peroxide decomposers 208
- 8-Pentadecanone, Arrhenius plots for reactions in 283
- Phenol
  - alkylation 158
  - alkylation with 161
  - antioxidant potency of trialkylated 164
- Phenolic
  - antioxidants 146, 248
  - phosphite stabilizers for polypropylene 202
  - polymer stabilizers 126
- Phenols
  - as antioxidants in isotactic polypropylene, dihydric 169, 191
  - *vs.* light stability of polystyrene 291
  - with α-olefins, antioxidants from alkylation of 155
  - sterically hindered 126
  - 2,4,6-tri(*sec*-alkyl)- 161
- Phosphate plasticizer level *vs.* exposure effect 266
- Phosphinic acids 307
- Phosphite 26
  - stabilizers for polypropylene, phenolic 202
  - tris(mixed nonyl phenyl)- 208
- Phosphine oxides 307
- Phosphonic acids 307
- Phosphonium halides 318
  - mechanism of action of 322
  - *vs.* polymer properties 320
- Photochemistry of ketones 277
- Photochemistry, polymer 280
- Photodegradation of polymers 272
- Photoelimination reaction of ketones 279
- Photooxidation by ultraviolet radiation 288
- Photostabilization 211
- Photostability of polypropylene films 220
- Phthalate plasticizers for vinyls 261
- Pink staining of vinyl films 253
- Plasticized vinyl films, microbial degradation of 250
- Plasticizer level *vs.* exposure effect, phosphate 266
- Plasticizers to microbial attack, susceptibility of 251
- Plasticizer for vinyls, epoxystearate as 64
- Plastograph 40
- Polyacrylates 319
- *cis*-Polybutadiene, aging of 140
- *cis*-Polybutadiene rubber 112
- Polycyclic phenols 126
- Polyene sequences in degraded PVC 67
- Polyepoxides as stabilizers for PVC 57
- Polyethylene 319
- *cis*-Polyisoprene, aging of 132
- Polymer
  - antioxidant systems 239
  - crosslinked coordination 90
  - properties, phosphonium halide *vs.* 320
  - synthesis, coordination 84
- Polymeric phenolic phosphites as polypropylene stabilizers 204
- Polymeric plasticizers for vinyls 262
- Poly(methyl methacrylate) 319
- Polynuclear antioxidants, phenolic 169
- Polyolefins 319
- Polypropylene 153, 155, 319
  - antioxidants
    - aromatic amines as 203
    - aryl phosphites as 203
    - hindered phenolics as 203
    - hydroxybenzophenones as 203
    - thiodipropionate as 203
  - degradation of 204
  - dihydric phenols as antioxidants in isotactic 169, 191
  - γ-irradiation of 188
  - *vs.* oven life, thickness of 241
  - phenolic phosphite stabilizers for 202

  stabilization of 206
  stabilizers, polymeric phenolic phosphites as 204
  test methods for evaluating antioxidants in 224
Polystyrene
  activation spectrum of 288
  bisphenols *vs.* light stability of .. 291
  carbonyl absorption of irradiated 289
  effect of antioxidant in 305
  exposure data correlations for .. 296
  inhibition of carbonyl formation of 303-4
  inhibition of discoloration of ... 303
  light stabilization of 287
  phenols *vs.* light stability of ... 291
  ultraviolet transmission of irradiated 290
Poly(vinyl chloride)
  stabilization 1
  stabilizers *vs.* melt rheology of .. 38
  thermal degradation pathways in 18
  see also PVC
Processing stability of polypropylene 216
2-Propanol 22
Propylene trimer and tetramer, alkylation with 158
PVC
  automatic device for evaluating thermal stability of 50
  compounds *vs.* electrical conductance, stability of 47
  compounds against high temperature, stability of 45
  discoloration of 67
  glass transition temperature of .. 66
  internal stabilization of 65
  mechanism for radical formation in 58
  performance *vs.* molecular weight 256-7
  polyepoxides as stabilizers for .. 57
  polyene sequences in degraded . 67
  pyrolysis 46
  stability *vs.* color change in ... 50
  thermal instability of 65
  see also Poly(vinyl chloride)
Pyrocatechol 169

Q

Quantum efficiency of methyl ketones 282

R

Radical acceptors, amines as 114
Radical formation in PVC, mechanism for 58
Redox antioxidants, regeneration of 103
Redox metal
  antioxidants *vs.* haze and sludge 97
  antioxidants for silicones 97
  comparative oxidation of DMS *vs.* MPS fluids inhibited by 105
Regeneration of redox antioxidants 103
Rheology of poly(vinyl chloride), stabilizers *vs.* melt 38
Rubber
  mechanism of antioxidation and antiozonization of amines for 110
  reaction of ozone with 111
  recipe for vulcanizing 112, 114

S

SBR, amine *vs.* viscosity of 115, 117
SBR latex, aging of carboxylated .. 141
Scavengers, free radical 207
Self-extinguishing agents for polymers 307
Silicone
  fluids, oxidative stabilization of 95
  fluids, oxidative gelation of 95
  resins and rubber 104
Silicones, oxidation of methyl 96
Silicones, redox metal antioxidants for 97
Sludge, redox metal antioxidants *vs.* 97
Solar energy *vs.* bond strengths .. 274
Solar radiation, energy distribution of 273
Spiral mold test 234
Stability
  vs. central metal 88
  vs. color change in PVC 50
  metallo-organic systems with high thermal 82
  of PVC compounds *vs.* electrical conductance 47
  of PVC compounds against high temperature 45
Stabilization of polypropylene ... 206
Stabilization of PVC, internal 65
Stabilizers,
  phenolic polymer 126
  for polypropylene, phenolic phosphite 202
  vs. melt rheology of poly(vinyl chloride) 38
  for PVC, polyepoxides as 57
  for vinyls 263
Stabilizing additives 18
Stabilizing compounds for polypropylene 212
Staphylococcus aureus 255
Sterically hindered phenols 126
Streptomyces rubrireticuli 254
Structure *vs.* antioxidant activity .. 165
Styrene–butadiene rubber 112
Styrene polymers 319
Substituent constants 179, 194
Substituent steric constants 194
Sulfur compounds, hydroperoxide decomposition by 140
Sulfur compounds as stabilizers .. 141
Surface/volume ratio in oxidation of silicone fluids 101

T

Test methods for evaluating antioxidants in polypropylene 224
Tetrahydrofuran 22, 25
Tetralin, amine *vs.* oxygen absorption of 117
Tetralin hydroperoxide 141
Thermal degradation pathways in poly(vinyl chloride) 18
Thermal instability of PVC 65
Thermal stability
  of coordination polymers 88
  metallo-organic systems with high 82
  of PVC, automatic device for determining 50
  test nomogram 49
Thermogravimetric analysis 85
Thermoplastics, fire retardants for 307, 318
Thickness of polypropylene *vs.* oven life 241
Thiobisphenol 156
Thiodipropionate esters as polypropylene antioxidants 203
Thiodipropionate ester stabilizers . 209
Tin compounds 40
Torque rheometer 235
Transmission spectra of ultraviolet absorbers 292
Trialkylated phenol, antioxidant potency of 164
2,4,6-Tri(*sec*-alkyl)phenols 161
2,4,6-Tri-*tert*-butylphenol 292
12-Tricosanone 278
Triisobutylene, alkylation with ... 157
2,4,6-Trioctadecylphenol 164
Triphenol phosphite 25
Tris(mixed nonyl phenyl) phosphite 208

U

Ultraviolet
  absorbers 203-4, 211, 287
    vs. exposure effect 268
    efficiency of 292
    transmission spectra of 292
    for vinyls 265
  light, protecting a polymer from 272
  radiation, photooxidation by ... 288
  spectral distribution of light sources 297
  transmission of irradiated polystyrene 290
U-tube test method 228

V

Vinyl
  chloride
    copolymers of 68
    copolymers, dehydrochlorination of 71
    vinyl acetate copolymer performance *vs.* vinyl chloride content 260
  films
    bacterial attack on 251
    microbial degradation of plasticized 250
    mildew and fungal attack on 251
    pink staining of 253
  biocides for 265
  epoxy plasticizers for 262
  epoxystearate as plasticizer for .. 64
  fillers for 264
  formulating parameters for 259
  lubricants for 264
  phthalate plasticizers for 261
  polymeric plasticizers for 262
  stabilizers for 263
  ultraviolet absorbers for 265
Volatility *vs.* antioxidant potency .. 167
Viscosity of SBR, amine *vs.* 115, 117
Vulcanizing rubber, recipe for 112

W

Water extraction resistance 227
Wax cracking 159
Weathering of polymers 272

X

2,4-Xylenol, alkylation with 161
2,6-Xylenol, alkylation with 161
Xylenols, antioxidant effect of alkylated 164
2,6-Xylenols, 4-(*sec*-alkyl)- 161
2,4-Xylenols, 6-(*sec*-alkyl)- 161

Y

Yellowing, gas 155

Z

Zinc compounds 40
Zipper mechanism 58