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Copolymerization

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COPOLYMERIZATION is undoubtedly the most active phase of present-day drying oil processing technology. It offers an infinite number of formulation possibilities even though a mass of information has already been published by a galaxy of stellar contributors. While polymerization may be traced as far back as Berzelius, the original copolymerization has probably not been duly recorded.

Many polymers are not miscible with each other, but often their monomers may be mixed and copolymerized to a homogeneous product which combines the valuable properties of each single polymer. The drying oil copolymers, and particularly the styrenated alkyds, are excellent examples of such. In some cases a monomer will form a copolymer with another monomer which does not readily polymerize alone. Such copolymers have been called heteropolymers.


A. G. Hovey

Historical

To the oil chemist the simplest copolymers may be regarded as those made by the controlled copolymerization of two or more drying oils. Even these are far from simple when it comes to explaining the mechanism involved and the structures obtained. Little of value seems to have been published on the copolymerization of drying oils until the two papers of the Pittsburgh Club (59) on soya-tung oil combinations. From the practical sense the scope of such oil copolymers is still somewhat limited for, after all, the resulting product is still an unmodified oil. From time immemorial the varnish maker in a practical way has been copolymerizing oils in the presence of hard gums to increase hardness, toughness, and drying speed. Regardless of type, these varnish gums are in general effective principally because they allow the larger copolymer sizes to form but keep them in a soluble and therefore usable condition for forming coatings. The limitations of copolymerizing oils in the presence of a soluble resinous polymer are obvious. The new developments in coating compositions have been achieved through the actual tie-up of small monomeric units to unsaturated centers of oils. Many of the most useful monomeric units form polymers which are either incompatible with bodied drying oils or do not show any particular advantage if they are compatible.

The first attempt of prime importance to improve upon varnishes, the first important type of drying oil copolymer, was the development of the well known oil-modified alkyds. In a sense the drying oil alkyds are copolymeric systems and truly so in accordance with the Carothers' (9) concepts because the oil polymer is actually and effectively tied to the polyhydric alcohol-polybasic acid polymer. The segments of both monomers are present in the chains, but the system is heterogeneous in the sense that part of the copolymer is made up of polymerization units arising from unsaturation and part from units of condensation-polymerization. When the oil acid portion of alkyds is non-drying, it is not more than a polyester complex, but when semi-drying or drying acids are involved, then the alkyd bears a definite relationship to copolymers. Bradley (7) distinguishes between "addition" copolymers and "esterification" copolymers. The alkyds will be discussed on this program in another paper and are being mentioned merely to indicate the relationship. This paper discusses principally "addition" copolymers resulting from unsaturates and poly-unsaturates, in which a substantial proportion of the composition is a drying oil and/or fatty acids. Some glimpses are given of new, competing copolymers which are commercially available today that contain little or no drying oil and constitute a definite threat to compositions hitherto based largely on vegetable oils.

Styrene, on account of its potential low cost and great availability, has received the most attention as a copolymer-forming ingredient. As early as 1931 I. G. Farbenindustrie A. G. (35) disclosed emulsion polymerization of styrene with a drying oil using hydrogen peroxide catalyst. This was the first styrene-oil copolymer unless Kronstein's (45) styrene-tung oil composition of 1909 could have been one. In 1934 Lawson and Sandborn (47) described preparations involving the copolymerization of styrene and a drying oil in the presence of rosin and an inert solvent, using a peroxide catalyst.

Stoesser and Gabel (76) in 1940 copolymerized tung oil and styrene but claimed products only with 5% or less of oil since they were aiming at toughening the plastic rather than improving the oil. In the same year came Flint and Rothrock's (20) disclosure claiming an interpolymer of styrene formed by heating the monomer in the presence of solvent with a preformed frosting oleoresinous varnish base. Ellis (18) also disclosed a composition based on a styrene copolymer of a drying oil varnish base made by solvent method and using a peroxide catalyst. In 1944 Sorenson (74) described a solvent polymerization of styrene with mixed poly-unsaturated esters, one being a drying oil.

In 1945 Dunlap (16) disclosed new and useful linoleum cements having increased water and soap resistance from blown linseed oils copolymerized with styrene by mass method, using in one case catalysts of the boron fluoride type and in the other case various peroxides.

Wakeford, Hewitt, and Armitage (81) in 1945 described methods for preparing styrene copolymers which consisted of reacting styrene in the presence of a solvent with a partially polymerized oil or with an alkyd resin solution. In a corresponding patent (82) they described a mass polymerization process for obtaining homogeneous, soluble products by portion-wise addition of the styrene over predetermined intervals of time during the course of the reaction. A little later Wakeford, Hewitt, and Armitage (83) included the use of terpenes, such as alpha pinene or dipentene, in the solvent to improve on the control of compatibility and stability of the copolymers and advanced the opinion that the terpenes promoted the reactivity of the oil with the styrene.

As another means of improving homogeneity of the product with the elimination of milky or opalescent films, the Dow Chemical Company (14) suggested the additional use of minor proportions of alpha-methyl styrene as a second monomer to modify the polymer chain. Schroeder and Terrill (69) used 30% replacement of the styrene by alpha-methyl styrene and in all cases, except with ordinary soybean oil, clear brilliant films resulted.

The first comprehensive review of styrenated drying oils and alkyds was by Hewitt and Armitage (31) in 1946, shortly after their block of patents. Armitage, Hewitt, and Sleightholme later published a review of styrenation of oils and alkyds in which they proposed three mechanisms for non-conjugated, conjugated, and for oxidized oils.

Schroeder and Terrill prepared six copolymers of typical drying oils at 45% styrene level and listed the physical constants and performance data on each. Significant differences in properties were pointed out between the fatty acids obtained from saponification of styrenated raw linseed oil and those from styrenated linseed oil which had been pre-oxidized.

At the 116th meeting of the American Chemical Society four excellent articles on the subject of copolymerization of oils and oil derivatices were presented. Hoogsteen and Young (33) presented data on the styrenation of dehydrated castor oil at different viscosities. Powers (60) showed that oleic acid combines with styrene up to the extent of approximately equal weight. Bhow and Payne (5) showed curves of the rates of reactions of styrene with tung, oiticica, and dehydrated castor fatty acids. They also discussed alkyds made from the dehydrated castor fatty acids and the properties of the finished enamels made from them. The review on "Drying Oil Copolymers" by Hansen, Konen, and Formo (28) was the most comprehensive one thus far available, but it went much farther than a simple review of styrenation. The reactions with oils of cyclopentadiene, butadiene, and more than 30 miscellaneous monomers were compiled. Furthermore, and most important of all, the paper presented extensive and valuable data on the styrenation of several drying oils, using both the boron fluoride and the peroxide type catalysts. Cyclopentadiene-drying oil copolymers were discussed in detail. Trimeric and even higher systems were predicted for the future. Allyl sucrose has been copolymerized with oils and also with styrene (91).

Dyer and Maxwell (17) found copolymers of styrene and oxidized ethyl linoleate prepared by either emulsion or bulk type polymerization yielding a maximum at one mole of ester to 13 of styrene. This seems to be in the same range as reported by Powers (60) for linseed fatty acids.

Cyclopentadiene has been a potentially readily available copolymerizing monomer. It exists in considerable quantities in the streams of several large oil refiners in the form of dicyclopentadiene and is also available from coal tar crudes. The method of purification of cyclopentadiene from a drip oil fraction by Gerhart and Adams (26) was an important step in improving availability. Cyclopentadiene has really been no stranger to the coatings industry since its maleic anhydride adduct has been a commercial dimer acid for alkyds for many years. It is only very recently however that Cosgrove and Earhart (10) have shown that even after the maleic anhydride adduct is formed, there still remains one double bond which will react with linseed oil. Gerhart (23) and Adams disclosed several catalyst processes for making copolymer oils, varnishes, and alkyds with cyclopentadiene. Simple heat polymerization however proved to be very effective (25) especially at high temperatures as shown by Lycan and Gerhart (27). Gerhart (24) described a continuous process and apparatus for producing copolymer oils from dicyclopentadiene and unsaturated glycerides at 200-450°C. at 60-120 pounds' pressure. Outside of the patent literature little was written until the comprehensive review of Hansen, Konen, and Formo (28) which gave considerable data on the mass polymerization of the monomer with linseed oil as well as many useful comparisons with the styrene copolymers. Trimeric systems of cyclopentadiene, styrene, and drying oils have been disclosed (64), and more have been predicted (28).

Most of the commercial copolymer drying oil products now in use are understood to be made of either styrene or cyclopentadiene (see part IX). The excellent review of Hansen, Konen, and Formo (28) included a summary of literature references on more than 30 monomeric substances which with further development or price stimulation might make them potential contenders for copolymer consideration. Styrene copolymerized with some divinyl benzene (75), either with or without drying oil, may result in improved viscosity retention in solvent systems (28).

Butadiene has long been a recognized eligible monomer for copolymer drying oils. Many patents describe copolymers of butadiene and other dienes; most of the processes are by mass method (28) and with wide choice of catalysts. One of the earliest disclosures involving olefins and diolefins with vegetable oils was a very general one by the Dayton Synthetic Chemicals Inc. (11) with application date 1931, naming butadiene, dimethyl butadiene, hexadiene, and isoprene.

Extremely low temperature polymerization and copolymerization of drying oils have been described by the use of the boron fluoride catalysts (49, 73).

The term "vinyl" is scattered through the literature of polymerization and copolymerization not only when it applies to a specific vinyl compound such as vinyl acetate but also as a generic term for any substituted vinyl radical including styrene and acrylonitrile. Actually the term in the broad sense is relatively meaningless since virtually all unsaturated monomeric units capable of copolymerizing with drying oils are "vinyl compounds" in this broadest interpretation.

Theoretical

The study of copolymerization might well begin with Carothers' (9) review of 1931 and extend through Mark's classic volumes. It is beyond the possibilities of a paper of this type to cover more than the salient points and to mention the inspiring work of a few of the many brilliant investigators in this field. Before going into the copolymerization kinetics, a brief orientation regarding some of the concepts, terminology, and kinetics of simple polymerization would be in order.

General Reactions of Polymerization. For vinyl polymerization, the general reactions of the three stages are given by Taylor and Tobolsky (78):

VINYL POLYMERIZATION

Initiation

$CH_2 = CHX + R \rightarrow CH_2RCHX \cdot$

Growth

$CH_2RCHX \cdot + CH_2CHX \rightarrow CH_2RCHXCH_2CHX \cdot$ etc.

Termination

May occur by combination of free radicals or by disproportionation at the functional point.

Even in such relatively simple molecules as xylene, disproportionation to benzene and phenyl methyl has been shown to be possible under specific conditions by Shuikin (70a) and Prokhorova. It is conceivable that a similar effect might be possible near the functional point of a polymer chain, thus terminating the chain, although providing for the possibility of initiation of a new chain through the formation of a new free radical.

For diene polymerization, with the greater functionality of the monomers, the reactions according to Taylor (78) and Tobolsky are naturally more complicated after the initiation:

DIENE POLYMERIZATION

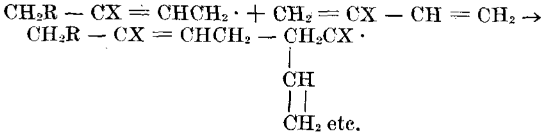
Initiation

$CH_2 = CX - CH = CH_2 + R \rightarrow CH_2R - CX = CHCH_2 \cdot$

Growth (1, 4 addition)

$CH_2R - CX = CHCH_2 \cdot + CH_2 = CX - CH = CH_2 \rightarrow$
$CH_2RCX = CHCH_2CH_2CX = CH - CH_2 \cdot$ etc.

Growth (1, 2 addition)



$CH_2R - CX = CHCH_2 \cdot + CH_2 = CX - CH = CH_2 \rightarrow$
$CH_2R - CX = CHCH_2 - \underset{\underset{CH_2}{\|}}{\underset{CH}{|}}{CH_2CX} \cdot$ etc.

Termination

May occur by combination of free radicals or by disproportionation effecting the functional point.

SUBSIDIARY REACTIONS (To both vinyl and diene types)

Aging

A subsidiary reaction *initiation.* The majority of hydrocarbon free radicals are formed by the action of oxygen or from free radicals persisting from the polymerization, etc.

Depolymerization (Scission)

For both vinyl and diene types, the exact reverse of the growth and initiation steps. It appears to be a chain reaction involving many steps, as compared to pyrolysis.

Branching and Cross-linking

Reaction of hydrocarbon radicals with monomers and neighboring chains.

Gee and Melville (22) drew several additional conclusions regarding termination. It may arise from:

1. Monomer deactivation, i.e., destruction of the activity of the polymer by collision with monomer.
2. Spontaneous termination in which polymer reverts to a stable form.
3. Mutual termination in which two polymers collide, and the activity is destroyed either by combination or by disproportionation.

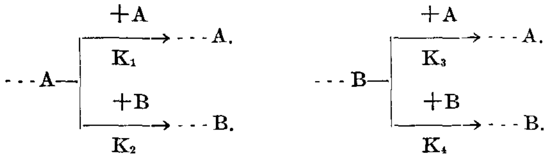
These subsidiary reactions of aging, depolymerization (scission), branching, and cross-linking, all seem to involve the presence of an odd electron active center along the hydrocarbon chain. Probably the majority of these hydrocarbon free radicals are formed by the action of oxygen or are free radicals persisting from polymerization. Thus oxygen or other free radicals can alter the hydrocarbon chain by abstracting an H atom. OOH is relatively very stable. The susceptibility of the alpha-methylene group in rubber to oxidative attack with the formation of the hydroperoxide group has been particularly emphasized by Farmer (19).

The Role of Molecular Oxygen. One of the most confusing and contradictory factors in polymerization and copolymerization for many years has been the influence of molecular oxygen (37). Oxygen has been known to initiate many polymerizations but also to work against the growth. Barnes (3, 4), in studying the mechanisms of vinyl polymerizations, investigated the role of oxygen thoroughly and concluded that the inhibiting action of oxygen is in reality preferential peroxide formation in the presence of oxygen. Menary, Ubbelohde, and Wright (52) in their studies of the propagation of reaction chains in the polymerization of styrene also observed that oxygen sometimes appears to be a promoter and sometimes an inhibitor in addition polymerization. The effect of oxygen is tentatively interpreted by them by a mechanism in which oxygen acts as a chain breaker as well as a chain initiator through formation of peroxides. Kern (37) also was impressed by the double role of oxygen as both the catalyst and inhibitor for polymerization. He wrote an extensive review with 52 references showing the action of the peroxides as accelerators and the subsequent effect of more oxygen adding to the radical-like polymer nucleus or growing chain and thereby inhibiting growth.

General Reactions of Copolymerization. When a mixture of monomers undergoes polymerization, the composition of the polymer formed at any instant may not necessarily be the same as the starting monomer mixture. Assuming a free radical mechanism of chain growth, Norrish and Brockman (57) recognized four different growth reactions during copolymerization of monomers X and Y with R_X and R_Y, the two kinds of free radicals which can be characterized by the least added monomer units:

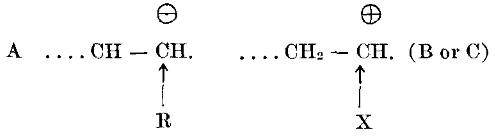
$$R_X + X \xrightarrow{K_1} R_X$$
$$R_Y + X \xrightarrow{K_2} R_X$$
$$R_X + Y \xrightarrow{K_3} R_Y$$
$$R_Y + Y \xrightarrow{K_4} R_Y$$

Thus there are four competing reactions to be considered for the chain propagation step, the reactions of an active growing chain ending with either monomer unit reacting with either monomer molecule.



Using these concepts of Norrish and Brockman (57), a general theory of copolymerization was developed by Alfrey, Mayo, and Wall (1, 84), and several other contributors (61) involving mathematical treatment based on the rate of disappearance of both monomers. Price (61) observed that copolymers form readily when the two ratios of the rate constants K_1/K_2 and K_3/K_4 are less than unity.

Tautomerism. Electron tautomerism is a factor in determining ease of polymerization of monomers and stability of polymers (63). Polarity must have a more important role in copolymerization than previously suspected. Price (61) observed that those pairs of monomers which copolymerize most readily are those in which an electron-rich (negative, type A) double bond is present in one monomer and an electron-poor (positive, type B or C) double bond in the other. The attraction of the negative (or positive) radical for the positive (or negative) double bond would thus be an important factor in facilitating copolymerization, presumably principally by decreasing the activation energy necessary for chain propagation:



$$A \quad \ldots\ CH - \underset{\uparrow \atop R}{\overset{\ominus}{CH}}. \qquad \ldots\ CH_2 - \underset{\uparrow \atop X}{\overset{\oplus}{CH}}.\ (B \text{ or } C)$$

Besides the importance of the attraction of the electron-releasing and electron-attracting groups, Price also called attention to the importance of free radical stability and steric effects. The steric hindrance of alkyl maleates not present in maleic anhydride or in the alkyl fumarates is an important illustration.

Methods

In making copolymers there is need for decision not only in the method of reaction but also in the choice of catalysts. Some of the styrene-oil copolymers have been made by practically all the known methods and with a great variety of catalysts. Even before choice of method, comes the choice between batch or continuous processing, but with homogeneous systems there do not appear to be any serious technical restrictions as to which process may be used.

Mass or Thermal Copolymerization. 1. *Oils.* Copolymerization of two drying oils such as soya and tung are usually accomplished without need for catalysts or solvents (59). One early disadvantage in the use of vinyl compounds to modify drying oils is their great tendency to polymerize under conditions which are much milder than those necessary to activate the double bonds of triglycerides. Consequently they tend to form high polymers with themselves which are generally incompatible with bodied drying oils rather than to react to form copolymers (79). Many initial attempts to copolymerize styrene and drying oils without solvent resulted in heterogeneous mixtures (58). The simple heating of a non-conjugated oil such as linseed with any substantial quantity of styrene monomer gives a non-uniform product which forms a cloudy or opalescent film because styrene forms a self-polymer at lower temperatures than required for activation of the ordinary double bonds in non-conjugated drying oils.

However styrenated drying oils have been prepared by mass polymerization from styrene and linseed oil with no catalyst and no solvent by Young (92) and by Schroeder and Terrill (69). Young accomplished it by the use of alpha-methyl styrene as a partial replacement of the styrene, and so did Schroeder and Terrill, but they used 3% benzoyl peroxide. Young also resorted to "blowing" the unconjugated oil before styrenation.

Conjugated oils such as dehydrated castor, tung, and oiticica copolymerize readily with styrene monomer by simple reflux with no catalyst or solvent. Hewitt and Armitage (31) preferred solvent but showed that homogeneity could be attained in solventless runs by adding the styrene at intervals. Among others supplying information on styrene copolymers of conjugated oils by peroxide catalyzed mass method are Schroeder and Terrill (69), Hoogsteen (33), Young (92), and The Detroit Club (12). The Detroit Club kept the product homogeneous by withholding the bulk of the styrene and adding it over a period of time to prevent the formation of the long styrene polymers at the lower temperatures.

The mass method presents no serious difficulties during the formation of homogeneous copolymers of cyclopentadiene (28) for combination occurs readily even at normal oil-bodying temperatures with non-conjugated oils.

2. *Fatty Acids.* Powers (60) styrenated oleic, linseed, and dehydrated castor oil fatty acids by the mass method at 160-225°C., using no catalyst. His recovery was usually about 99%. There is no report thus far published on alkyds made from them. Bhow and Payne (5) presented data on the benzoyl peroxide catalyzed mass copolymerization of styrene with the following conjugated acids: tung, oiticica, dehydrated castor, and isomerized linseed. An alkyd was prepared from the styrenated dehydrated castor fatty acids.

3. *Alkyds.* Styrenated alkyds can be prepared in several ways: from styrenated oils and/or styrenated fatty acids; from styrenated monoglycerides (54); by styrenation of fusion method alkyd bases (54), and even by simultaneously styrenating as the alkyd is made. However the solvent method offers many advantages for production control.

In almost all of these possible mass processes the presence of peroxide catalysts or certain metal halides greatly assist in smoothing out the reactions by increasing oil reactivity at moderate temperatures. In addition to copolymerization using added catalysts, peroxidation of drying oils through "blowing" can give an *in situ* catalytic activity. The peroxides induced by blowing serve the double role of initiating the copolymer formation and isomerizing the linoleic and linolenic acids to a conjugated structure. Thus, after blowing, two important vegetable oils, soya and linseed, may be styrenated directly.

Solution Methods of Copolymerization. For those who have the proper explosion-proof closed equipment with reflux, the use of solvent offers some added features to the mass method. As shown by Hewitt and Armitage (31), the increase in solvent proportions slows down the rate of styrene polymerization with itself. The refluxing solvent helps in the control of temperature. The lower viscosities of solutions make physical handling much easier, especially filtering. Sometimes catalysts may be more efficiently dispersed. If the reaction is well completed, there is no need of stripping off uncombined styrene, at least for baking finishes. When the end products will be used in aromatic solvent such as xylol, it may be economical to keep the whole process in xylol from beginning to end. It is not economical to cut down the effective production capacity of kettles by operating in solvent systems, but where alkyds are being regularly prepared by the solvent or azeotropic method, there is not any serious reduction of output.

There is much debate pro and con as to the desirability of the solvent method over the fusion method. At present it appears they will exist side by side, depending upon the specific types of equipment already installed in individual plants.

Emulsion Copolymerization. This third natural method of copolymerization has been repeatedly given the cold shoulder by oil and paint leaders. It is noteworthy that the earliest disclosure of styrene-drying oil copolymers was produced by emulsion technique (35). Also noteworthy is the fact that the world's largest copolymerization production capacity, e.g., the styrene-butadiene synthetic rubbers are practically all made on the emulsion basis because it fits low-cost continuous process requirements. During the past two years the drying oil copolymer chemists have even more reason to note emulsion polymerization. Several copolymers containing little or no drying oil at all have been supplied in stable latex form for water paint for interior walls, concrete floors, chemically resistant finishes, stucco paint, plaster sealers, traffic, and striping. The merits of such new water paint formulations have been advanced by Workman (90), Menaker (51), The New York Club (55), Ryden, Britt, and Viager (68), and by Burr and Malvery (8). Some of these paints are characterized by ease of brushing, fast drying, toughness of film, alkali-resistance, non-bleeding over asphalt, good stand-out over porous surfaces, and usability over fresh plaster and wet concrete. They are a definite threat to the expansion of the alkyds and certainly to many processed oils.

Since the introduction of emulsion polymerization about 1931, when it replaced the cumbersome sodium polymerization method, many improvements have contributed to its further advancement. Butadiene and copolymerizing monomers are first emulsified by soaps or surface active agents. The emulsion is stabilized by a protective colloid, then a polymerization catalyst is added. Modifying agents or regulators (43) such as alkyl mercaptans favoring the formation of linear polymers and determining the degree and velocity of polymerization are also added (72). Kolthoff and Bovey (40) published in 1948 a valuable contribution to emulsion polymerization on the effect of retarders and inhibitors. Papers by Kolthoff (41), Dale, Hohenstein, and Mark (32), Price (61), and Adams (62), while discussing kinetics of emulsion polymerization, have done much to clarify similarities between emulsion and bulk polymerization, particularly where styrene is concerned. Harkins' mechanism (29, 30) of emulsion polymerization locates the initiation of polymer growth in the soap micelles.

More efficient copolymerizations are taking place at lower temperatures through the recent application of catalytic principles in reduction-oxidation systems. High soap and persulfate concentrations favor production of a large number of particles (42, 71). The rate of polymerization of unsaturated compounds is increased by addition of reducing agents in the presence of benzoyl peroxide, provided that the reducing agents are not in themselves inhibitors of polymerization. Specific (38) effective reduction-oxidation systems for emulsion, mass, and solution polymerization are treated and interpreted by Kern (39) according to the concept of free radical activation of the growing chain. Kern (38) also gives an "effectivity" system for reducing sugars, aldehydes, organic acids, etc., on the emulsion polymerization of butadiene-styrene. Wall and Swoboda (85) proposed a mechanism for the reduction-oxidation activation of polymerizations in emulsion systems. Ferrous ion, soluble in oil, promotes the decomposition of benzoyl peroxide into free radicals which initiate polymerization. In this the ferrous ion is oxidized to ferric ion which is subsequently transferred to the aqueous phase, where it exists for example as a pyrophosphate complex. Ferric ion is then reduced by an appropriate water-soluble reducing agent such as sorbose. The reduced ferrous ion is ultimately transferred back to the oil phase to renew the cycle. A typical industrial "redox" copolymerization on a continuous process is described by Laundrie (46) and McCann. Still further improvements in emulsion polymerization technology, such as Mitchell's (53) new alternative accelerators, are frequent occurrences. It would not be surprising to see more of the adventurous vegetable oil chemists moving into this arena of fast action. Up to now most have been discouraged by the need for sensitive control of catalysts, emulsifiers, stabilizers, and regulators. Even after the polymers are made, they still have to be coagulated, washed, and dried, and possibly cut in solvents, except where they would be used in water paint.

Choice of Catalyst

Although many copolymerizations can be made to take place without catalysts, nevertheless for many successful operations the catalyst is the spark plug which must function continually and not merely as a trigger. Its choice and properties are worthy of the most careful consideration. Some of the practical considerations involved are:

Safety in storage and handling. This is obviously most important of all considerations and involves the questions of susceptibility to impact and severe shock, deterioration, violent decomposition, fire hazard, etc.

Cost consideration. This should not be based on initial price per pound, but on cost per unit weight of copolymer produced.

Non-corrosiveness. Catalyst must not attack construction materials of the apparatus nor lose efficiency on contact.

Solubility and dispersion characteristics. The catalyst must be compatible with the materials in the system. (Halides such as $AlCl_3$ or BF_3 are inapplicable in an aqueous system whereas some peroxides are excellent.) The catalyst must not react with the solvent.

Activation temperature. If too low, the catalyst cannot be mixed with monomer or partial pre-polymers without danger of untimely polymerization taking place in storage tanks or drums.

Long life period at temperature necessary for polymerization.

Long life in storage.

Ability to be deactivated when desired polymerization point is reached.

Successful promotion of the reaction at higher speed or higher yield.

How should the catalyst be added to gain maximum effect, all at once, by installments, or in increments?

The role of peroxides in polymerization has recently been summarized by Williamson (89). A few references will be given in this section for the aid of those who wish to go further on these catalysts. In styrene, inhibitors such as quinones can completely suppress thermal polymerization but only retard peroxide catalyzed polymerization (50).

The primary act of peroxides seems to be the formation of free radicals which gives rise to a reaction between the peroxides and the unsaturated compound or with some other H donor. This is the view of Kern (39) and many others (86, 93) who view polymerization in terms of reduction—oxidation systems.

Benzoyl peroxide is probably the oldest of the organic peroxides used for the promotion of polymerization, is in the lower cost bracket, and, if frequency of appearance in the literature indicates anything, it certainly must be widely used. In other words, it has really been the "work-horse" of the polymer catalysts up to now. It has definite hazards but, if properly handled and judiciously used, works out quite satisfactorily for most copolymerizations. The Detroit Club (12) used lead peroxide in conjuction with benzoyl peroxide.

Cumene hydroperoxide is a relatively newcomer to the polymerization industry but, besides having many attractive properties, it is about the lowest cost organic peroxide and "remarkably efficient" (80) in redox emulsion polymerization.

Di-tertiary butyl peroxide and 2.2 Bis (tertiary-butyl peroxy) butane are two additional newcomers to the polymerization field, which it is claimed can be used advantageously to sensitize free radical reactions at temperatures above 100°C. (13, 70, 88).

There seems to be a definite trend towards the use of promoters to increase the polymerization rate by the addition of some reducing agents in the presence of the peroxide, thus increasing the formation of free radicals providing that the added substance does not act as an inhibitor.

Besides the peroxides the other large class of copolymerization catalysts are the metal halides, including BF_3, $AlCl_3$, and $SnCl_4$. BF_3 can be used in the gaseous phase but is more generally used in the form of an ether complex or an acetic anhydride complex. An extensive review of the reactions catalyzed by BF_3 is given by Kastner (36) and for the properties of many addition compound catalysts by Swinehart and Schenk (77). Valuable data on BF_3 catalyzed styrenation of linseed oil was given by Hansen, Konen, and Formo (28), and the same catalyst was the basis of many copolymers of Rummelsburg (67). BF_3 has been effective on iso-olefins (49, 73) at —20°C. $SnCl_4$ and has been used for copolymers of dehydrated castor oil and styrene by Rubens and Boyer (66). It is a powerful catalyst for styrene alone. $AlCl_3$ in solution form is said by Francis (21) to be very effective. The chief trouble with the metal halides is their extreme corrosiveness.

Apparatus

Copolymers from drying oils and liquid monomers may generally be made without difficulty in the same laboratory or production equipment as ordinarily used for the azeotropic preparation of alkyds. The similarity of handling styrene monomer to using xylol while preparing an industrial alkyd is very striking from the standpoint of equipment.

For those copolymers made from drying oils and monomers volatile at the copolymerizing temperatures such as cyclopentadiene, the process must be carried on in special equipment such as the continuous one described by Gerhart (24) or in a high pressure stainless steel autoclave with agitator (28).

Processing

Styrenation. Drying Oils. The reaction has to be directed so that no polystyrene is formed, and all the monomer molecules are attached to oil or to growing styrene chains already attached to oil (65). The first principle to favor the copolymerization rather than styrene polymerization is to keep at a minimum the ratio of the mass of styrene monomer to that of the oil or intermediate copolymer units during the whole course of the reaction and especially at the start of the reaction. Making the law of mass action work in favor of the type of product desired is a principle which will help in processing regardless of the choice of method. The stepwise addition of styrene to the oil has been found to be effective by Hewitt and Armitage (31) and by other investigators in producing homogeneity when other methods fail.

A second condition favoring the ready addition of styrene is the presence of conjugation in the oil. Dehydrated castor oil is a most satisfactory oil to styrenate, not only because of the conjugation but also because of its light color and the inherently good properties of color retention, flexibility, toughness, and adhesion which it imparts to the films. The lower the hydroxyl number and the higher the diene number, the more suitable the oil is for styrenation. The control of viscosity of the dehydrated castor oil is important for uniformity of the styrenated oil, but almost all viscosities styrenate easily and completely. Tung and oiticica oils are also styrenated readily since they are highly conjugated, but in many proportions they gel rapidly before combining with the intended amount of styrene. Tung and oiticica may be used in smaller proportions with non-conjugated oils such as linseed or soya to give styrenated products producing clear films.

Many "blown" linseed and soya oils will styrenate to give clear homogenous products even though the raw or polymerized oils give heterogenous products. The peroxides in the blown oils catalyze the copolymerization while the conjugation induced during the blowing makes styrenation of these abundant oils practical. The optimum conditions for blowing linseed and soya oils does not seem to be available. Young (92) considered that blown soybean oil should have a minimum of 16% oxygen, a peroxide value of about 360, and the viscosity of about E (Gardner Holdt). Presumably Young's consideration was also based on the intended use of about 30% of the styrene content as alpha methyl styrene.

Alpha methyl styrene or certain terpenes are particularly useful in mass polymerization with styrene. Homogeneity is improved by reducing the rate of self-polymerization of the styrene, permitting higher temperature processing at which oils are activated.

The effect of solvent is very important. Increasing the solvent reduces the rate of styrene polymerization, and conversely the decreasing of the solvent level or the use of none at all allows the styrene to polymerize much faster.

The choice between mass and solvent methods is not a serious one, but in the case of oils and fatty acids in which solvent is to be removed later, the mass method is more satisfactory since the stripping operation is less extensive. The mass method permits a larger load in the processing kettle and higher yield. If the oil or fatty acid is to be used in the "solvent" preparation of an alkyd, the solvent copolymerization might be preferable. Melville and Watson (50) state that quinones completely suppress thermal polymerization of styrene but only retard the peroxide catalyzed polymerization.

The details of styrenation of dehydrated castor are adequately given by Hewitt and Armitage (31) and make excellent starting points for this purpose. The use of various catalysts may cut down the processing time to meet special requirements. Practical starting points using alpha methyl styrene with the styrene are given by Schroeder and Terrill (69) with several oils and also by Young (92).

Non-conjugated oils such as linseed which give heterogenous products and hazy films with peroxide type catalysts give clear films and homogeneous products with the powerful BF_3 catalysts. Hansen, Konen, and Formo (28) show that over a wide range of composition in the styrene-linseed oil system, styrenation of the oil may be carried out very completely and in a short period of time at a catalyst concentrations of 0.2-0.4%, based on the oil.

Drying Oil Fatty Acids. The styrenation of drying oil fatty acids is important from a practical point for the easy preparation of styrenated alkyds, particularly for the varnish manufacturer who does not have the equipment for making alkyds by azeotropic methods.

Powers (60) has given details on the preparation of styrenated oleic acid, linseed acids, and dehydrated castor acids by mass method and by using no catalyst. In each case the processing temperature was either 160°C. or 225°C. Substantially homogeneous products were obtained in all cases, even with the non-conjugated linseed acids. With the linseed acids the runs at 225°C. seemed to be more uniform, probably because the styrene was added dropwise, a condition which would greatly favor copolymerization. No data have been available as yet on the performance of Power's styrenated fatty acids in alkyd preparation or in reconstituted oils.

Bhow and Payne (5) however have styrenated tung, oiticica, dehydrated castor, and isomerized linseed acids by mass methods at 145°C., using 3% of benzoyl peroxide based on the styrene in all cases. Their attempts to styrenate linseed acids resulted in heterogenous products whereas Powers by dropwise addition of styrene at higher temperatures succeeded in obtaining homogeneity. Most important, Bhow and Payne report that satisfactory styrenated alkyds were made from their styrenated dehydrated castor alkyds and give details of the alkyd preparation and of the evaluation in white air-drying and baking enamels.

Drying Oil Monoglycerides. Monoglycerides may be prepared by more or less conventional alcoholysis procedure by heating styrenated oils with glycerol in the presence of an alkaline catalyst. Young (92) gives a typical procedure for an intermediate step in making an alkyd. An alternate procedure would be to react the styrenated fatty acids with polyhydric alcohol. The direct method of reacting styrene with a preformed monoglyceride is a third possibility for preparing an alkyd intermediate which appears to be as conveniently formed as by the styrenation of the corresponding oil itself. In the preparation of many alkyds it appears that a stop-over at this stage may hardly be necessary.

Alkyds. 1. *Classification of Possible Methods.* The making of styrenated alkyds does not appear to be difficult once the choice is made of suitable reaction methods, convenient for existing plant equipment and inventories. In the preparation of styrenated monoglycerides there are three possible procedures. Now for making the alkyd by the direct method of reacting pre-styrenated oil radicals, it is possible to use any of these three procedures for making the styrenated monoglycerides and then subsequently add the polybasic acid either with or without solvent and process to desired viscosity and acid value. This so-called direct method is based upon the premise that a known and certain amount of styrene should be first satisfactority tied up with the drying oil radicals either in the form of the oil itself, its fatty acids, or its monoglyceride before attempting to make the alkyd. There are obviously many possible variations of the direct method: the oil may be prebodied, or a mixture of oils may be used, or even copolymerized; the fatty acids may be isomerized or selected; the "monoglyceride" may not be a monoglyceride at all but an alkyd intermediate from oil and some other polyhydric alcohol.

A second method is the styrenation of a preformed alkyd and stems from the premise that the alkyd should be well made to the proper viscosity and acid value before attempting to copolymerize its drying oil component with the monomeric styrene. This method in a sense is just as direct as the other. A third possible method is the simultaneous styrenation of the alkyd during its preparation.

With the scant amount of competitive experience in the industry as yet, it is premature to venture which of these methods has the most survival value or whether all three will co-exist together. In general, the same precautions for color preservation (34) for making customary alkyds are also of value for styrenated alkyds.

2. *The Direct Method.* The example of Young (92) gives a typical procedure for making an alkyd from a monoglyceride of a prestyrenated drying oil. The examples of Bhow and Payne may be classified as being the same as alkyds from the monoglycerides formed by glycerol and prestyrenated fatty acids although no distinct stop was made at the monoglyceride stage. Some of Bobalek's (6) products used a combination of prestyrenated oil and fatty acids at the monoglyceride stage. The preparation of a styrenated monoglyceride of a drying oil with subsequent reaction with phthalic anhydride has been given as suggested starting points by both Monsanto Chemical Company (54) and Dow Chemical Company (15).

The main argument for this direct method is that only a few carefully planned and processed styrenated intermediates could suffice to make all the different oil length alkyd requirements.

3. *Styrenation of a Preformed Alkyd.* The disclosures of Wakeford, Hewitt, and Armitage (81) and of Hewitt and Armitage (31) are the earliest ones on the styrenation of a preformed alkyd. Perhaps the most remarkable point of both of them is that their styrenated alkyds were based on preformed linseed alkyds whereas difficulty had been frequently reported with the styrenation of linseed oil itself. A Monsanto (54) starting point gives a typical procedure for styrenating preformed alkyds made from dehydrated castor oil. Because of the relative ease of the styrenation of dehydrated castor derivatives, quite a number of preformed alkyds for styrenation contain some dehydrated castor or tung oils to insure against heterogenous products by providing sufficient conjugated structure to ward off troubles encountered using less expensive oils such as linseed or soya. The direct method permits the use of non-conjugated oils such as soya or linseed when the styrenation can be performed on the "blown" oil. However the styrenation of preformed alkyds can be aided greatly by the dropwise or installment addition of the styrene and catalyst.

The argument for the styrenation of preformed alkyds is similar to that advanced for the prestyrenated intermediates for the direct method, i.e., that only a few carefully planned and processed alkyds could suffice for copolymerization not only with varying amounts of styrene, depending upon the various characteristics of hardness and air-drying and baking properties desired, but also with varying amounts of other copolymerizable monomers such as cyclopentadiene, butadiene, acrylonitrile, etc. Either one of these arguments is about equally logical for the gist of one is that it takes so long to obtain satisfactory styrenation before forming the alkyd that the styrenated products ought to be standardized and therefore made in as large quantities as possible the least number of times, while the gist of the other is that the alkyd takes so much time and effort it ought to be standardized.

4. *Simultaneous Styrenation While Forming the Alkyd.* Constructively viewing the two arguments as to whether a styrenated intermediate or a preformed alkyd should be standardized, one point seems to be very evident, and that is the great length of time for performing either step. Both the styrenation and the alkyd preparation usually require at least a full working day. With double the working hours for styrenated alkyds' production costs tend to soar, and advantage is lost in competitive fields in which their properties justify use.

A few alkyds have been made by simultaneously styrenating during regular alkyd processing. In parallel experiments two 45% oil length dehydrated castor oil fatty acid alkyds were made. The control alkyd was made in the customary azeotropic fashion using xylol as a solvent to a viscosity of Z_1 (Gardner Holdt) at 50% non-volatile. It was subsequently styrenated the next day with an amount of styrene equal to half of the solid alkyd content and using 2% of ditertiary-butyl peroxide on the styrene content. The resulting resin made a clear solution at 50% in xylol with a viscosity of Z and baked out to a clear film having a Sward Hardness of 35 when baked 30 minutes at 300°F. at .0015″ film thickness. In the other experiment the alkyd ingredients were loaded into the flask and brought to 195-200°C. using xylol as an azeotrope, at which point the catalyst dissolved in the styrene was added dropwise over a period of 3½ hours as the alkyd was processed. After 4½ hours the styrenated alkyd had an acid number of 6.6 and was substantially equivalent in properties to the control. It should not be concluded from this one set of experiments that this method is a panacea for making styrenated alkyds, and these results will have to be carefully checked. However the method resulted in a styrenated alkyd in one working shift instead of two or more. The methods of control and reproducibility for such a process will have to be carefully checked before it can be considered safe. Even the addition of ditertiary butyl peroxide catalyst in xylol to the alkyd alone without the presence of styrene has a strong tendency to advance the viscosity of the unstyrenated alkyd.

Cyclopentadiene. This is obtained by heating the dimer. If it is distilled from the dimer at a temperature of approximately 180°C. so that the vapor temperature at the top of the column is held at 39-42°C., it may be condensed with an ordinary water condenser, but the receiver must be surrounded by ice to retard polymerization. Cyclopentadiene repolymerizes rather rapidly to dicyclopentadiene. In drying oil copolymerization reactions using dicyclopentadiene, the freshly generated cyclopentadiene gas, in something like a nascent state, reacts with the oil radicals instead of reverting to the dimer. In an autoclave none of the cyclopentadiene gas can be lost and if the heating is not too strong, the reaction with the oil radicals removes the gas as it is formed from the dimer and helps to regulate the pressure. Most commercial dicyclopentadiene has been 65% actual content but has been used as is for most polymerization work. Gerhart and Adams (26) purified it from drip oil by polymerizing it to a slush, then filtering off the unpolymerized solvent, or distilling off the solvent in vacuo. Recently dicyclopentadiene of 90-99% purity has been available.

Drying Oils. Since cyclopentadiene will give diene type polymerization whereas styrene can only give vinyl type polymerization, the reactions of dicyclopentadiene are generally much more vigorous and require less catalyst or often none at all. The available literature on cyclopentadiene drying oil copolymers consists chiefly of the patent disclosures of Gerhart (23, 24), Adams (25), Lycan (27), and the paper by Hansen (28), Konen, and Formo. The procedure by both groups of investigators has been somewhat similar, i.e., copolymerizing the cyclopentadiene and drying oil in a mechanically agitated autoclave between 200-300°C. until a homogeneous resinous material is formed which is soluble in hydrocarbon thinners. Apparently no catalyst is necessary under these conditions. Lycan and Gerhart (27) found the best uniformity resulted by bringing the oil to 580°F. and introducing the dicyclopentadiene then. The data of Hansen, Konen, and Formo describe the preparation and properties of several linseed oil copolymers. The series from 7.5 to 60% dicyclopentadiene combined was kept, with a few exceptions, very constant in temperature at 540-550°F.(282-288°C.). The viscosity at 100% non-volatile content increased from 44.3 Stokes at 7.5% of dicyclopentadiene to 3,600 Stokes at 38.5%. At 60% dicyclopentadiene the copolymer was completely gelled in a short time, as might be expected from the increasingly large proportions of diene component.

The processing in the autoclave is continued, with occasional sample testing until the desired viscosity is obtained. At the conclusion of the reaction any unreacted monomer and incidental hydrocarbon solvents are stripped off by the application of vacuum, with or without steam. This removes odor as well as the unwanted volatiles. The yields are in close agreement with the total weight of drying oil and 100% basis dicyclopentadiene charged into the autoclave.

The colors of the dicyclopentadiene copolymers are disappointing in comparison with those of the styrenated copolymer drying oils, but there is hope for improving the color of both.

Gerhart *et al.* not only disclosed cyclopentadiene drying oil copolymers but also several varnishes and varnish gums coreacted with the monomer. References in the literature seem to be completely lacking or else very obscure on any copolymers with fatty acids, monoglycerides, and alkyds corresponding to the styrene copolymer products just described. Cyclopentadiene has entered into alkyds for sometime through its maleic adduct, which has been shown by Cosgrove and Earhart (10) to be oil-reactive. It would not be surprising to see announcements of commercial cyclopentadiene alkyds any day now. Suggested starting points are already given for making cyclopentadiene alkyds from monoglycerides of cyclopentadiene-fish oil copolymers (87). Ternary systems of styrene, cyclopentadiene, and drying oil copolymers have been proposed (48, 64). Truly there is no beginning and no end to the possibilities. Certainly the field of copolymers has advanced a long way since Konen's prediction of their coming importance at a meeting in 1943 (44).

Evaluation

Oils. Copolymerization of oils with styrene and cyclopentadiene in general tends to upgrade the oils to a point where they approach many of the properties of the alkyds. Likewise, copolymerization of the same monomers with alkyds tends to give an approach to many of the properties formerly attained only by "fortified" alkyd enamels through the use of amine-aldehyde resins. In making that general statement, it must not be inferred that copolymerization is the panacea for all evils in the finishing game. The copolymer-oil ratio bears a close relationship between the older concepts of hard resin and oil length in judging properties, even though not identical.

1. *Advantages.* Styrenated oils have many valuable properties for the coatings field for they have increased hardness, drying speed, water and alkali resistance over the corresponding oils achieved at low cost, and apparently with no sacrifice in color, color retention, gloss and gloss retention, flexibility, or exterior durability. The increase in hardness is outstanding; some air-dried enamels now reach a hardness in less than a week equal to or greater than many of the best high baking industrial enamels. The longer oil types are not difficult to brush. The pigment stability is at least as good because the acidity of the vehicle has been lowered by dilution. The anti-skinning properties have been enhanced by the lowered proportion of oxygen sensitive double bonds.

Cyclopentadiene-drying oil copolymers as a rule exhibit similar properties to the styrene-oil copolymers, producing fast and hard drying, fair flexibility, freedom from pigment reactivity, good water and alkali resistance, brushing ease, and weather resistant features. The fish oil copolymers form elastic polymers, light in color, free from after tack, and rapid-drying. The linseed copolymers are particularly useful for varnishes and for fortifying softer oils. The cyclopentadiene copolymers at short oil lengths are not quite as good on color as the styrene copolymers but have been used for both colored enamels and whites at the lower levels of addition. The cyclopentadiene-oil copolymers have good adhesion, a somewhat broader range of compatibility, and faster film cure compared to the styrene copolymers. At low levels of addition and low viscosities, the fish oil copolymer oils are recommended for alkyds.

2. *Disadvantages.* The only important objections raised to copolymer oils are lack of resistance to solvents and lack of mar-proofness.

Fatty Acids and Monoglycerides. Since these are intermediates for alkyds or reconstituted oils, they need no discussion here.

Alkyds. 1. *Advantages.* Styrenated alkyds have been on the market (56) for less than three years, yet their use is rapidly growing. The quick solvent release makes a properly styrenated alkyd "free of dust" in 10-45 minutes and allows quick handling in less than 2½ hours. The films set up quickly and are soon to a point where accidentally touching them causes no harm. The hardness is generally much greater than the unstyrenated alkyds and approaches those enamels usually fortified by urea or melamine resins. The baking schedules may be speeded up and lower temperatures used. This means again faster production and less danger of rejects. Gloss and gloss retention, color and color retention are excellent. The water, soap, and alkali resistance is generally improved, providing the alkyd itself has been well formulated and carefully processed before or during styrenation. Greater ease of brushability has been claimed for the long oil styrenated alkyds. Styrenated alkyds have been the base of exceptionally fine hammer finishes and novelty coatings.

TYPICAL COMMERCIAL PRODUCTS

Name	Manufacturer	Type of Copolymer	Uses
Admerol 101	Archer Daniels Midland	Styrene vegetable oil copolymer	Semi-industrial baking enamels
Admerol 251	Archer Daniels Midland	Vegetable oil copolymer	Exterior trims and trellis paints
Admerol 301	Archer Daniels Midland	Vegetable oil copolymer	Architectural enamels of fast through dry and good brushability
Admerol 351	Archer Daniels Midland	Vegetable oil copolymer	Hard fast dry general purpose vehicle
ADM 75-5 Oil	Archer Daniels Midland	Dicyclopentadiene-linseed oil	Varnishes, enamels, interior and exterior, aluminum
Dryfol M	Archer Daniels Midland	Dicyclopentadiene-fish oil	For alkyds by monoglyceride method
Dryfol T	Archer Daniels Midland	Dicyclopentadiene-fish oil	For alkyds by monoglyceride method
Dryfol W	Archer Daniels Midland	Dicyclopentadiene-fish oil	House paint, flats, enamels, sealers, decorative coatings
Dryfol Z3	Archer Daniels Midland	Dicyclopentadiene-fish oil	House paints, flats, enamels, sealers, decorative coatings
Dryfol Z6	Archer Daniels Midland	Dicyclopentadiene-fish oil	All flats
Keltrol 15	Spencer Kellogg & Sons	Styrene-soybean oil	General purpose vehicle
Keltrol 60	Spencer Kellogg & Sons	Styrene-soybean oil	Traffic paint and general purpose
Keltrol L	Spencer Kellogg & Sons	Styrene-linseed oil	General purpose vehicle
Bakelite BJS-502	Bakelite	Oil modified polyester styrene copolymer	Fast air drying and baking enamels
Cyclopol S101-1	American Cyanamid	Styrene-alkyd	Very rapid air drying finish
Cyclopol S102-5	American Cyanamid	Styrene-alkyd	Low temperature and fast baking enamels
Styrosol 4250	Reichhold	Styrene-alkyd	Low temperature and fast baking enamels
Styresol 4400	Reichhold	Styrene-alkyd	Baking primers

Cyclopentadiene alkyds have not been commercially available, but they are reported to possess fast drying speed, excellent water resistance, durability, rapid processing time, fast oven bake, and other desirable properties.

2. *Disadvantages.* As in the case of the copolymer oils, the copolymer alkyds have the same two points of sensitivity: aromatic solvents and lack of mar-proofness, also lowered impact and flexibility as might be expected from the extreme hardness. The factor of mar-proofness has been the most serious of these objections, but many steps in formulation of enamels are possible to prevent it or minimize the effect.

Uses. 1. *Styrene-soya oil copolymers.* Styrenation of soybean oil is particularly advantageous since it upgrades an abundant and economical oil which is inherently a poor film-former by itself to vehicles which will perform very efficiently for many purposes. Obviously, no single copolymer will perform successfully in all the uses in the list, but the styrene-soybean oil system in some proportions can be used in one or more of the following:

- Industrial baking enamels
- Floor enamels
- Rust-inhibitive primers
- Wood primers
- Exterior trim and trellis paints and maintenance enamels
- Architectural enamels (long oil) fast drying and easy brushing
- Floor and deck paints
- General purpose vehicles
- Traffic paint
- Emulsion paint
- Fast printing inks
- Overprint varnishes and paper coatings
- Quality drum enamels
- Ready mixed aluminum enamels
- Enamel undercoats
- Non-penetrating clear vehicles

2. *Styrene-linseed copolymers.* These may in general be used for much the same purpose as those just listed for the soya copolymer, but since linseed is a "stronger" drying oil for a starting point, generally increased viscosity, higher speeds, and lower penetration may be expected. Of the uses listed above, the linseed copolymers may be better adapted to paper and fabric coatings, traffic paint, and emulsion paints.

3. *Cyclopentadiene-soya oil copolymers.* While generally adaptable to most of the same uses as the styrene-soya copolymers, they are particularly suited for hard tough resistant varnishes and aluminum vehicles.

4. *Cyclopentadiene-linseed oil copolymers.* These are particularly for use in varnishes, furniture finishes, rubbing finishes, clear enamels, floor enamels, interior wall enamels, ready mixed aluminum vehicles, and exterior colored enamels.

5. *Cyclopentadiene-fish oil copolymers.* The following uses have been proposed: exterior paints, decorative interior flats, non-penetrating flats, primer-sealers, semi-gloss finishes, high lustre finishes, deep tone flats, stipple finishes, and for alkyd monoglycerides (87).

6. *Styrenated alkyds* (56). While there are several commercial products on the market and a large number of experimental products being tested, it is premature to generalize on the infinite number of possible styrenated alkyds. The field of usefulness appears to include:

- General industrial finishing
- Replacement for some amine-aldehyde fortified alkyds systems
- Washing machines
- Venetian blinds
- Refrigerators
- Kitchen utensils
- Hospital fixtures
- Toys
- Office furniture and business machines
- Hammer and novelty finishes
- Baking primers
- Lacquers
- Lacquer replacement

7. *Cyclopentadiene-alkyds.* While no commercial products of this class have been announced as available, this class may be expected to perform as useful vehicles for industrial enamels and fast air-drying

long oil alkyds for maintenance. It has been claimed that they are to be particularly useful for oxygen stable dip tank and flow coat enamels.

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