Synergism of Free Radical Initiators with Self-Extinguishing Additives in Vinyl Aromatic Polymers*

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Synopsis

Vinyl aromatic polymers such as polystyrene can be made nonflammable by the addition of halogen compounds. The amount of halogen required to make such polymers nonflammable can now be greatly reduced by the addition of small amounts of certain free radical initiators. Normally about 5 phr of acetylene tetrabromide (parts of additive per hundred parts of polymer) must be added to polystyrene to obtain a self-extinguishing polymer. Only 0.5 phr of acetylene tetrabromide is required if 0.5 phr dicumyl peroxide is added. This synergistic effect has been observed with a series of peroxides, hydroperoxides, azo compounds, quinone imines, benzothiazole sulfenamides, disulfides, and a bibenzyl compound. The synergistic mechanism seems to be based on a series of reactions involving attack of the polymer by the initiator and subsequent reaction between polymer fragments and the halogen compound. The result is a delay in the loss of halogen from the polymer mass and thus a more efficient use of the halogen additive for flame quenching. Known inhibitors of free radical reactions have a detrimental effect on the synergistic mechanism.

I. INTRODUCTION

The flammability of many organic plastics has been a deterrent to their wider acceptance in many applications. This fact has been recognized for some time, and methods based on the use of additives, polymer reactions, and monomer modifications have been utilized to obtain nonflammable products. No single approach has proved to be the answer for all flammable polymers. The present study will stress additive methods for obtaining self-extinguishing polymers. The choice of a particular flame retardant system depends in part on the polymer. The use of halogenated compounds as additives for obtaining self-extinguishing polymers has been reviewed in a recent publication.[1] Certain polybromohydrocarbons have been reported to be especially effective self-extinguishing additives for polystyrene.[2] Although effective, such compounds when added in sufficient quantity to make the polymer self-extinguishing affect to a varying

degree heat distortion, tensile strength, and impact strength of the plastic. It has now been observed that the amount of halogen required to make polystyrene and related alkenyl aromatic polymers self-extinguishing can be greatly reduced by the addition of small amounts of certain free radical initiators such as organic peroxides.[3]

II. EXPERIMENTAL METHODS AND MATERIALS

A. Sample Preparation

All of the experimental data reported here were obtained by mixing the additives and polymer in liquid methyl chloride, flashing off the solvent, and testing the resulting foam for flammability. Volatile additives cannot be checked by this method, but can be screened either by an impregnation technique[3a] or by direct addition to continuously extruded molten polymer.[3c] The commercially available peroxides checked for synergism were used as received. Samples of N-isopropyl bis(2-benzothizolesulfen)amide and N-tert-butyl bis(2-benzothiazolesulfen)amide were obtained through the courtesy of Naugatuck Chemicals.[4] The bibenzyl compounds were prepared within The Dow Chemical Company.[5] Many of the hydrazones were prepared from the corresponding hydrazine and ketone.[6] Those hydrazones which did not crystallize were concentrated and used in the crude state. No attempt was made to determine the exact analysis of the oil. The halogen compounds were technical grade. All the polymers were prepared within The Dow Chemical Company. The samples of isopropylated polystyrene were prepared by the copolymerization of styrene and p-isopropylstyrene.[7] The p-isopropylstyrene was synthesized from cumene by means of previously reported intermediates.[8] Cumene was reacted with acetyl chloride to form the ketone. The ketone was reduced to the carbinol by reaction with hydrogen at 1000 psi in the presence of 5 wt.-% copper chromite at 160°C. for 4 hr.[9] Dehydration of the carbinol was done over alumina at 300–325°C. Infrared indicated a trace of the *meta* isomer. The polymerization was carried out on a 94-hr./85°C. schedule with 0.2 phr azobisisobutyronitrile.

B. Self-Extinguishing Test

Polymer samples $1/4$ in. in thickness, $1/2$ in. in width, and about 5 in. in length were checked for flammability by holding the sample at 45° in the flame of a microburner for 4 sec., removing the sample, and noting the time for the sample to extinguish. Times longer than 20 sec. were noted as "Burns." The effect of polymer viscosity is of particular importance in self-extinguishing tests as shown in Figure 1. At the low polymer viscosities the hot polymer drips so rapidly that the entire flame front is very quickly detached from the polymer. Such a sample will actually test "self-extinguishing" by the microburner method. A polystyrene viscosity of at least 5 cpoise is required for meaningful self-extinguishing tests.
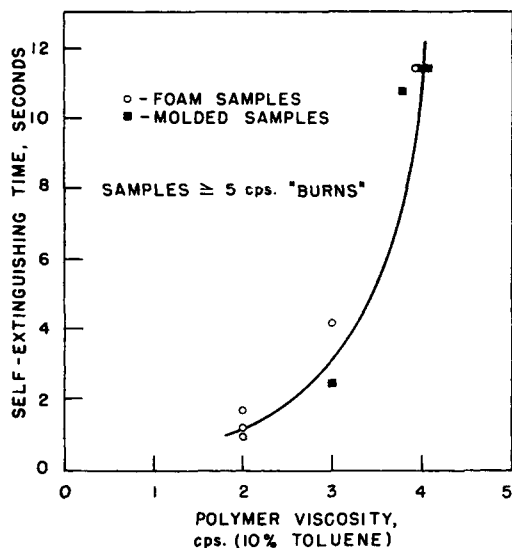
Fig. 1. Effect of polymer viscosity on the apparent self-extinguishing time of polystyrene.

III. EXPERIMENTAL RESULTS AND DISCUSSION

An examination of all the effective compounds which show a synergistic action with halogen compounds indicates that these compounds (or their reaction products) can, to varying degrees, initiate reactions believed to follow a free radical mechanism. The pronounced synergistic effect which can be obtained with a very effective free radical initiator such as dicumyl peroxide in combination with an organic halogen in polystyrene is shown in Figure 2. With no dicumyl peroxide about 5 phr (parts per hundred parts
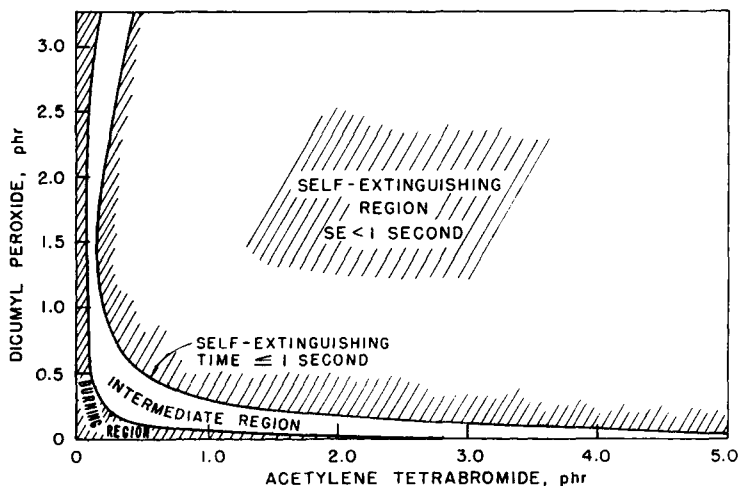

Fig. 2. Self-extinguishing diagram for polystyrene.

TABLE I. Polystyrene Self-Extinguishing Data For Peroxides With Acetylene Tetrabromide (ATB)

Compound	10-hr. half-life temp., °C.ª	ATB, phr	Self-extinguishing time, sec.				
			Mole equivalence, mole peroxide/mole ATB		Weight equivalence, phr peroxide/phr ATB		
			0.5	1.0	0.5/1	1/1	1/2
Peroxides							
Dimethane sulfonyl	<54	1	Burns	Burns	Burns	19	7
		2	12-Burns	8.8			
Lauroyl	62	1	Burns	Burns	Burns	Burns	Burns
		2	"	13			
Caprylyl	63	1	6.2	3.2	6	1	<1
		2	1	<1			
Succinic	66ᵇ	1	Burns	Burns	Burns	Burns	Burns
		2	"	"			
Acetyl	69	1	Burns	10-Burns	6.5	2.5	1.2
		2	7.5	2			
Benzoyl	72	1	Burns	Burns	Burns	10-Burns	3.2
		2	10				
p-tert-Butyl benzoyl	~72	1	Burns	Burns	Burns	Burns	5.8
		2	8.5				
Hydroxyheptyl	85	1	Burns	Burns	Burns	Burns	7.0
		2	8.5				
Cyclohexanone	91	1	Burns	12	Burns	Burns	2.2
		2	1.5	<1			
tert-Butylperoxy isopropyl carbonate	97	1	5.4	1.2	2.3	<1	<1
		2	<1	<1			
2,5-Dimethylhexane-2,5-di(peroxybenzoate)	100	1	6.5	3.8	7	2	<1
		2	<1	<1			
tert-Butylperacetate	102	1	5.2	3.8	3	<1	<1
		2	<1	<1			
Di-tert-butyl diperphthalate	105	1	4.2	1	3.2	1.2	<1
		2	<1	<1			

Compound	t, °C	Amt.					
tert-Butyl perbenzoate	105	1	7.2	2.5	2	1.5	<1
		2	<1	<1	9	2.5	<1
Methyl ethyl ketone	105	1	16	10	9	2.5	<1
		2	4	<1			
Dicumyl[c]	117	1	1.2	1	<1	<1	<1
		2	<1	<1			
Bis(α,α-dimethyl, *p*-methyl benzyl)	~117	1	5.2	1	2	1.5	—
		2	<1	<1			
Bis(α,α-dimethyl, *p*-phenyl benzyl)	~117	1	2.5	<1	3	—	16
Trityl	No data	1	17–Burns	11–Burns	Burns	Burns	1
		2	12	2.8			
2,5-Dimethyl-2,5-di(*tert*-butyl peroxy)hexane	121	1	1.2	1	1.2	1	<1
		2	<1	<1			
Bis(*tert*-butyl peroxymethyl)durene	126	1	4.8	2.2	3	1.4	<1
		2	1	<1			
2,2 Bis(*tert*-butyl peroxy)-butane	~126	1	9.5	3.8	3.8	1.8	<1
		2	3.8	<1			
2,5-Dimethyl-2,5-di(*tert*-butyl peroxy)-hexyne-3	130	1	1.8	1	1	<1	
		2	<1	<1			
Hydroperoxides — Tetralin	No data	1	Burns	Burns	Burns	Burns	19
		2	Burns	13–Burns			
tert-Butyl (contains 30% di-*tert*-butyl peroxide)	121	1	10–Burns	7	4	2.5	1
		2	3.2	2.5			
p-Menthane	133	1	12	10	11.6	6.4	<1
		2	2.8	<1			
2,5-Dimethylhexane-2,5-dihydroperoxide	154	1	Burns	Burns	7.4	6.4	<1
		2	6.5	2			
Cumene	158	1	Burns	Burns	Burns	6.4	1
		2	Burns	Burns			
Special peroxides — Ascaridole	No data	1	—	—	Burns	Burns	Burns
		2	—	—			
Dimeric benzaldehyde	No data	—	—	—	Burns	10	4.2

[a] Half-life in benzene unless otherwise indicated. [b] Half-life in acetone. [c] Di-*tert*-butyl peroxide (10 hr. half-life, 126°C) equivalent to dicumyl peroxide by method of reference 3a. High volatility of di-*tert*-butyl peroxide necessitates pressurization technique for addition to polymer.

of polymer) of acetylene tetrabromide have to be added to obtain a self-extinguishing polymer. The halogen additive can be reduced to 0.5 phr with 0.5 phr of the peroxide. Increasing the dicumyl peroxide beyond about 2 phr at the low acetylene tetrabromide level seemed to decrease the self-extinguishing effectiveness.

A. Synergists

Peroxides

Data showing the effectiveness as synergists of peroxides and hydroperoxides in combination with acetylene tetrabromide in polystyrene are listed in Table I. Self-extinguishing data are presented on both a molar and weight basis. Peroxide mole equivalence was based on the number of [O—O] groups in the peroxide. All weight additive loadings are expressed as parts per hundred of polymer (phr). Half-life data for the peroxides are also listed.[10] Most of the compounds showed some synergistic activity. In general, those peroxides having the greater thermal stability were the most effective. The choice of a particular peroxide will depend in part on time–temperature stability considerations either in processing or in eventual product use. Peroxide half-life data in benzene are probably directly comparable with those in polymers only above the glass temperature of the polymer. Below this temperature peroxide half-life will be considerably greater. This increase in half-life has been explained on the basis of a cage effect in the solid polymer similar to that suggested earlier for reactions in liquid media.[11]

Chemical stability of the peroxide synergist is also important. Both cumene and *tert*-butyl hydroperoxide have a greater half-life than their peroxide analog. The hydroperoxides are subject, however, to acid-catalyzed decomposition.[12] Such reactions are ionic and not radical decompositions and result in synergist wastage. Results for experiments in which self-extinguishing combinations of peroxide and acetylene tetrabromide in polystyrene were exposed to hydrogen bromide vapors for 20 min. at 20°C. are shown in Table II. This treatment resulted in complete loss of self-extinguishing effectiveness for the dicumyl peroxide and cumene hydroperoxide containing polymers Hydrogen chloride vapor had a lesser effect. Samples containing trityl,. 2,5 dimethyl-2,5-di(*tert*-butyl peroxy)-hexane, and 2,5 dimethyl-2,5-di(*tert*-butyl peroxy)hexyne-3 peroxide were essentially unaffected by either the hydrogen bromide or hydrogen chloride. The two samples containing benzoyl peroxide were partially affected. These tests admittedly were somewhat severe since in practice dicumyl peroxide is a very effective synergist. Evidently even with the dicumyl peroxide some wastage takes place.

The breakdown of peroxides is not necessarily limited to ionic means. A vapor-phase attack by halogen acids under conditions of burning would also accelerate the decomposition of the peroxide. Hydrogen chloride reportedly sensitizes the vapor phase decomposition of di-*tert*-butyl and di-

TABLE II
Effect of HBr and HCl Vapor on Self-Extinguishing Polystyrene[a]

Peroxide	Peroxide, phr	ATB, phr	Mole ratio peroxide/ATB	Self-extinguishing times, sec.		
				Initial	After HBr	After HCl
Benzoyl	1.4	2	1:1	<1	4	8.5
Trityl	3.0	2	1:1	<1	<1	1.6
Dicumyl	1.6	2	1:1	<1	Burns	<1
Cumene hydroperoxide	1.2	2	1.4:1	<1	Burns	7
2,5-Dimethyl-2,5-di(tert-butyl peroxy) hexane	0.85	2	0.50:1	<1	—	1.5
2,5-Dimethyl-2,5-di(tert-butylperoxy)hexyne-3	1.3	2	0.80:1	<1	1	1

[a] Polymer contacted for 20 minutes at 20°C. Samples were screened to −20 + 65 mesh.

tert-amyl peroxides while hydrogen bromide does not.[13]   The postulated radical mechanism indicates that one active peroxide fragment rather than two would result from such an attack.   The true extent of peroxide wastage by either ionic or radical attack under actual burning conditions has yet to be established.   There seems to be sufficient reason to expect wastage with some peroxides.

Azo Compounds

Azo compounds such as azobisisobutyronitrile are used as free radical polymerization catalysts and might be expected to show a synergistic effect similar to that of the peroxides.   Experimental data for the two azo initiators tested are shown in Table III.   Both azo compounds show some synergistic activity.   The better activity shown by the azobiscyclohexanenitrile can probably be attributed to the greater temperature stability of this compound.   A study of the effectiveness of the azonitrile from cyclobutanone which has a reported half-life of 1100 hr. at 80°C. would be of interest here.[14]

TABLE III
Polystyrene Self-Extinguishing Data for Azo Compounds with Acetylene Tetrabromide
(ATB)

| Initiator | Half-life, hr. at 80°C. | ATB, phr | Self-extinguishing time, sec. | | | | | |
| | | | Mole equivalence, mole initiator/mole ATB | | Weight equivalence, phr initiator/phr ATB | | | |
			0.5	1.0	0.5/1	1/1	1/2	2/2
Azobisisobutyro-nitrile (AZBN)	2.1[a]	1	Burns	Burns	Burns	Burns	Burns	12
		2	9.5	12				
Azobiscyclohex-anenitrile	31[a]	1	Burns	Burns	Burns	15	2	1
		2	7.2	4				
Acetyl peroxide	2.0[b]	1	Burns	10–Burns	6.5	2.5	1.2	—
		2	7.5	2.0				

[a] In toluene.
[b] In benzene.

A comparison of the AZBN and acetyl peroxide data in Table III indicates that although both initiators have the same half-life, the AZBN is not as effective as the peroxide.   The possibility that this reduction in effectiveness could be caused by acid attack of the AZBN was checked by Jahn.[15]   His work indicated no acceleration in decomposition of the initiator by hydrogen bromide at 70°C. in carbon tetrachloride.   The relatively poorer synergistic results obtained with AZBN can probably be attributed to the non-reactivity of the resonance-stabilized 2-cyano-2-propyl radicals.   This stabilization of the $Me_2\dot{C}CN$ radicals has been used as an explanation for the inability of AZBN to initiate graft polymerization in a   benzene   solution   of   *trans*-1,4-polyisoprene–methyl   methacrylate.[16]

Benzoyl peroxide is an effective initiator for this graft polymerization reaction.

Quinone Imines

Certain quinone imines have also been found which show synergistic activity with acetylene tetrabromide in polystyrene. Data for p-quinone dioxime, p-dibenzoylquinone dioxime, and 2,6-dichloroquinone chlorimide are shown in Table IV. The reported use of N-chloro-p-benzoquinone

TABLE IV
Polystyrene Self-Extinguishing Data for Quinone Oxime Initiators with Acetylene Tetrabromide (ATB)

Synergist	ATB Phr	Self-extinguishing time, sec.		
		No synergist	1.0 phr synergist	2.0 phr synergist
p-Quinone dioxime	1	Burns	19	—
	2	Burns	1.2	<1
p-Dibenzoylquinone dioxime	1	Burns	16	8
	2	Burns	1.4	1.0
2,6-Dichloroquinone chlorimide	1	Burns	11.4	7.6
	2	Burns	1.2	<1

imine and a dichlorosubstituted derivative as vulcanizing agents for ethylene–propylene elastomers[17] would indicate that N-chloro-p-benzoquinone imine and related derivatives should also be effective synergists for self-extinguishing polystyrene.
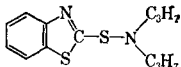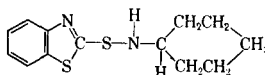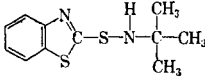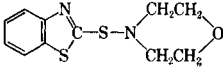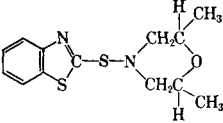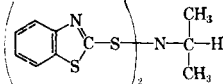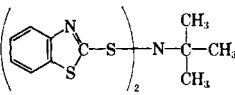
Sulfur Compounds

A number of investigators have reported that organic sulfur compounds dissociate to produce free radicals.[18] A large number of sulfur compounds were checked as synergists. The most effective compounds were either benzothiazole sulfenamides or disulfides. Data for these are shown in Tables V and VI.

Sulfenamides of benzothiazole are used commercially as delayed action accelerators for the vulcanization of rubber. Not all delayed action accelerators, however, proved to be effective synergists. Both 2-benzothiazyl-N,N-diethylthiocarbamyl sulfide and 1,3-bis(2-benzothiazolyl mercaptomethyl)urea, typical delayed action accelerators,[19] were not effective. However, sulfenamides derived from 4-methyl-5-substituted 2-thiazolethiols might be effective synergists.[20] The morpholinyl, $tert$-butylamido, and hydroxy $tert$-butylamido derivatives in particular have a delayed vulcanization action as great as N-cyclohexyl-2-benzothiazole sulfenamide.[20]
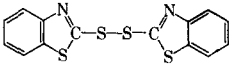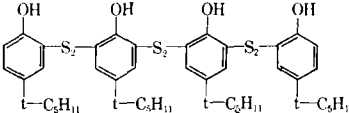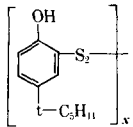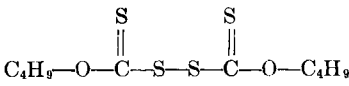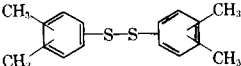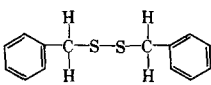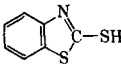
In addition to the sulfenamides, a number of disulfide compounds also exhibited synergistic action. Attempts to correlate synergism with structure were complicated by the fact that many disulfides were totally ineffective. A correlation of self-extinguishing results (SE) with the disulfide

TABLE V
Effectiveness of Benzothiazole Sulfenamides As Synergists in Polystyrene Containing
Acetylene Tetrabromide (ATB)

Sulfenamide	Self-extinguishing time, sec., at various phr sulfenamide/phr ATB		
	$^1/_1$	$^1/_2$	$^2/_2$
Diisopropyl benzothiazyl	Burns	19	8.4
N-Cyclohexyl-2-benzothiazole	Burns	1.6	1.2
N-tert-butyl-2-benzothiazole	11	1.4	0.9
2-(Morpholinothio)benzothiazole	Burns	2.4	1.9
2-(2,6-Dimethyl-4-morpholinothio)	12.8	2.3	2.6
N-Isopropyl bis(2-benzothiazole-sulfen)amide	17	2.8	1.4
N-tert-Butyl bis(2-benzothiazole-sulfen)amide	14	1.0	<1

chain transfer constants (C_s) for the polymerization of styrene is shown in Table VII. These data show that the effective and ineffective disulfides group into two rather well-defined categories. Those disulfides with chain transfer values greater than 0.5 (50°C.) were the most effective synergists. A number of mercaptans were also investigated as synergists. This group consisted of 2-mercaptobenzothiazole, 2-benzimidazolethiol, benzyl mercaptan, and ethyl mercaptoacetate. The mercaptan chain transfer con-

TABLE VI
Effectiveness of Disulfides As Synergists in Polystyrene Containing Acetylene Tetra-
bromide (ATB)

Disulfide	Self-extinguishing time, sec., at various phr disulfide/phr ATB		
	$^1/_1$	$^1/_2$	$^2/_2$
Benzothiazyl disulfide	11	2.1	1.0
Alkylphenol disulfide (Vultac 2)[a]	—	8.0	<1
Alkylphenol disulfide (Vultac 3)[a]	Burns	1.8	1.6
Butylxanthic disulfide	Burns	1.2	2.0
Mixed dixylyl disulfides (RR10)[b]	Burns	2	<1
Dibenzyl disulfide	Burns	6.6	2.0
2-Mercaptobenzothiazole	Burns	Burns	15

[a] Pennsalt Chemicals Corporation.
[b] E. I. du Pont de Nemours and Company.

stants (99°C.) for the polymerization of styrene ranged from 0.27 to 27.6.
None of these compounds were effective synergists.

Bibenzyl Compounds

A group of bibenzyl type compounds were checked for synergism. These
alkoxy compounds (I–IV) are of interest in that they decompose at ele-

TABLE VII

Correlation of Disulfide Chain Transfer Constants (C_s) and Self-Extinguishing (SE) Rating

Disulfide	C_s	Temp., °C.	SE rating	Comments
Diethyl	0.0045[a]	99	(Poor)	Dimethyl tested
Dibenzoyl	<0.0050[b]	50	Fair	
	0.1100[a]	99		
Di-*tert*-butyl	<0.0050[b]	50	Poor	
Di-*N*-morpholyl	0.0050[c]	50	Fair	
Tetramethylthiuram	0.0136[d]	70	Poor	
Dibenzyl	0.020[b]	50	Good	
Diphenyl	0.060[b]	50	Poor	
Di-*p*-tolyl	0.110[b]	50	Poor	
Di-2,6-dimethyl phenyl	0.690[c]	50	Good	Mixed dixylyl tested
Benzothiazyl	2.1[c]	50	Good	
	2.7[a]	99		
Diisopropylxanthogen	5.3[c]	50	(Good)	Butyl derivative tested

[a] Data of Dinaburg and Vansheldt.[21]
[b] Data of Costanza et al.[22]
[c] Data of Pierson et al.[23]
[d] Data of Ferington and Tobolsky.[24]

vated temperatures to yield methyl radicals capable of initiating free radical reactions.[5]

CH$_3$O   OCH$_3$

I

H   OCH$_3$

II

CH$_3$O   OCH$_3$

CH$_3$ CH$_3$

III

CH$_3$O   OCH$_3$

H   H

IV
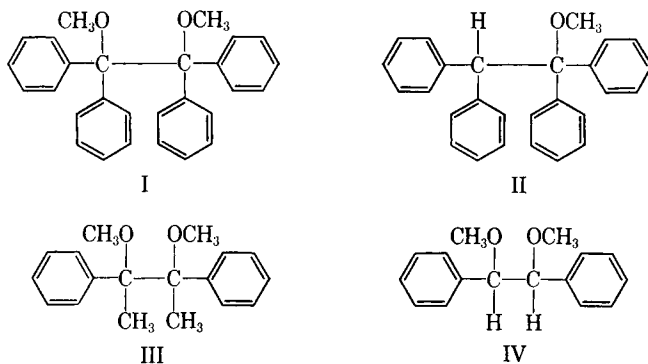
The self-extinguishing results for these compounds are listed in Table VIII. Only Compound II showed any synergistic activity. Compounds III and IV may be too stable for effective synergistic action. Compound I is believed to be ineffective largely because of side reactions.[5] Additional related compounds tested but not active included 1,1,2,2-tetraphenylethane, benzopinacol, acetophenone pinacol, hydrobenzoin, and diphenylmethyl methyl ether.

Hydrazones

All the previously reported synergists are capable of initiating free radical reactions. The hydrazones as such cannot. They do, in fact, effectively

TABLE VIII

Effectiveness of Several Bibenzyl Compounds as Synergists in Polystyrene Containing Acetylene Tetrabromide (ATB)

Synergist	10-hr. half-life temp., °C.[a]	ATB, phr	Initiator, phr	Self-extinguishing time, sec.
α,α'-Dimethoxy-α,α'-diphenyl-bibenzyl (I)	114	1.0	1.0	Burns
α,α'-Diphenyl-α-methoxybi-benzyl (II)	164	0.5	0.5	10.4
		0.5	1.0	1.8
		1.0	0.25	Burns
		1.0	0 50	2.2
		1.0	1.0	<1
		2.5	0	Burns
		0	3	Burns
α,α'-Dimethoxy-α,α'-dimethyl-bibenzyl (III)	226	1.0	0.8	Burns
		1.0	1.5	Burns
		2.0	3.0	Burns
α,α'-Dimethoxybibenzyl (IV)	ca. 300	2.0	1.0	Burns
		2.0	1.4	Burns

[a] Measured in diphenylmethane.[5]

inhibit the polymerization of styrene. Many hydrazones, however, proved to be effective self-extinguishing synergists as shown in Tables IX and X. The effectiveness of certain hydrazones as synergists is probably associated with their ability to react with oxygen to form peroxides. This reaction

TABLE IX

Synergistic Effectiveness of Hydrazones Derived from Phenylhydrazine and a Series of Ketones (in Polystyrene)

Ketone	ATB phr	Initiator phr	Self-extinguishing time, sec.
Acetone	1.0	1.0	9.4
	2.0	0.5	1.2
	2.0	1.0	<1
Methyl ethyl ketone	2.0	1.0	5
3-Pentanone	2.0	1.0	7.6
2-Pentanone	2.0	1.0	4.6
Hexanonephenone	2.0	1.0	8.6
2,3-Pentanedione	2.0	1.0	4.4
2,4-Pentanedione[a]	2.0	1.0	Burns
2,5-Hexanedione[a]	2.0	1.0	Burns
Acetophenone	2.0	1.0	4.6
Benzophenone	2.0	1.0	4.2
Dibenzyl ketone	2.0	2.0	Burns
Cyclohexanone	2.0	2.0	Burns

[a] These ketones probably form pyrazole derivatives rather than hydrazones.
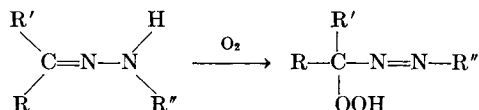
TABLE X
Self-Extinguishing Times for a Series of Hydrazones (in Polystyrene)

	Self-extinguishing time, sec.[a]		
Hydrazine	CH₃ \ C=O / CH₃	CH₃ \ C=O / C₆H₅	C₆H₅ \ C=O / C₆H₅

Hydrazine	$\begin{array}{c}CH_3\\ \diagdown\\ \quad C=O\\ \diagup\\ CH_3\end{array}$	$\begin{array}{c}CH_3\\ \diagdown\\ \quad C=O\\ \diagup\\ C_6H_5\end{array}$	$\begin{array}{c}C_6H_5\\ \diagdown\\ \quad C=O\\ \diagup\\ C_6H_5\end{array}$
$H_2NNHC_6H_5$	9.4[b] <1 Sec.	4.6	4.2
$H_2NNHC_6H_3Cl_2(2,5)$	7.6	9.4	6–Burns
$H_2NNHC_6H_3(NO_2)_2(2,4)$	Burns	—	—
H_2NNHCH_3	Burns	—	—
$H_2NN(CH_3)_2$	Burns	Burns	Burns
$H_2NN(CH_3)C_6H_5$	4[b]	<1	5
$H_2NN(C_6H_5)_2$	7[b]	<1	2.4

[a] Data for 2 phr ATB and 1 phr hydrazone unless otherwise indicated.
[b] 1 phr ATB and 1 phr hydrazone.

was first described by Busch and Dietz.[25] Subsequent work by Criegee[26] and Pausacker[27] indicated that the following overall reaction takes place:

$$\begin{array}{ccc}
\begin{array}{c}R'\\ \diagdown\\ \quad C=N-N\\ \diagup \qquad \diagup\\ R \qquad\quad R''\end{array}\;\begin{array}{c}H\\ \diagup\\ \\ \end{array} & \xrightarrow{\;O_2\;} & \begin{array}{c}R'\\ |\\ R-C-N=N-R''\\ |\\ OOH\end{array}
\end{array}$$

where R′ can be hydrogen.

The rate-determining step is that of hydrogen abstraction.[27] Both authors reported that hydrazones of the type RR′C=N—NR″R‴ (where R′ only can be hydrogen) do not react with oxygen to form peroxides. Busch, however, reported reaction of benzaldehyde benzylphenylhydrazone with oxygen under pressure. We have noted that hydrazones containing the groups —N(CH₃)C₆H₅ and —N(C₆H₅)₂ are active synergists, but that the —N(CH₃)₂ hydrazones are not.

The plausibility of hydrazone *in situ* oxidation to peroxide in polystyrene during polymer ignition was substantiated by oxidizing acetone phenylhydrazone and using the reaction product directly as a synergist. The hydrazone in benzene was contacted with oxygen at one atmosphere for 72 hr. at 28°C. Analysis indicated that a minimum of 93% of the hydrazone had been converted to peroxide. A polystyrene sample containing 1.2 phr of the oxidized hydrazone and 2 phr acetylene tetrabromide had a self-extinguishing time of 5.0 sec. The *in situ* autoxidation similar to that obtained with hydrazones has been reported for 1,2,3,4-tetrahydrocarbazole.[28] The carbazole was prepared by the method of Rogers[29] but showed no activity as a synergist with acetylene tetrabromide in polystyrene.

Related nitrogen containing compounds other than the hydrazones were also investigated. These included hydrazines, aldazines, ketazines, and

hydrazides. None of those tested showed any synergistic action. Recently Ingram has reported that certain N-chloro and N-nitroso compounds such as N,N-dichlorotoluene sulfonamide and N-nitroso-N-methylaniline can be used as synergists.[30]

B. Halogen Additives

Numerous halogen containing compounds have been reported as self-extinguishing additives for polystyrene.[1] Self-extinguishing data for a series of representative halogen compounds with dicumyl peroxide as synergist are shown in Table XI. Similar results have been noted for effective synergists other than peroxides. Bromine containing compounds are as a rule more effective than the corresponding chlorine compounds. Not all bromine compounds are of equal effectiveness. The pre-

TABLE XI
Effectiveness of Various Halogens with Dicumyl Peroxide in Polystyrene

Halogen	Halogen, phr	Dicumyl peroxide, phr	Self-extinguishing time, sec.
Acetylene tetrabromide	1.5	0	Burns
	1.0	0.5	<1
Hexabromoethane	1.0	0	Burns
	1.0	0.5	<1
Dibromotetrachloroethane	1.5	0	Burns
	1.0	0.5	<1
Tetrabromoethylene	1.0	0	Burns
	1.0	0.5	16.5
Hexabromoethane	1.0	0	Burns
	1.0	0.5	<1
1,2,3,4-Tetrabromobutane	1.0	0	Burns
	1.0	0.5	<1
Dibromoacetic acid	1.5	0	Burns
	1.0	0.5	1
Pentabromoethylbenzene	1.0	0.5	2
ar-Pentabromoethylbenzene	1.0	0.5	Burns
Hexabromobenzene	10	0	Burns
	10	1.0	<1
Pentabromomonochlorocyclohexane	1.5	0	Burns
	1.0	0.5	<1
Tris(2,3-dibromopropyl) phosphate	4	0	Burns
	4	0.5	<1
Tris(2,4-dibromophenyl) phosphate	10	0	Burns
	10	1	1.4
	4	0.5	Burns
Hexachloroethane	10	0	Burns
	10	1	1
Diiodomethane	3	0	14
	3	1	1.5
Ammonium bromide	2	0	Burns
	2	1	6

ferred organic bromine derivatives contain bromine in an aliphatic or cycloaliphatic radical.

Unsaturated aliphatic compounds with bromine substitution on the ethylene carbons and aromatic ring substituted compounds are much less effective. In general, if the halogen compound shows some effectiveness as a self-extinguishing additive, then a suitable free radical initiator will enhance the effectiveness of the compound.

C. Polymers

Most of the experimental self-extinguishing work reported here was done with polystyrene. The synergistic concept has proved to be effective with a number of other alkenyl aromatic polymers. Data for these are listed in Table XII. The possibility of enhancing the capture of volatile halogen additives by introducing reactive vinyl groups into the polymer structure was also examined. Copolymers of styrene and butadiene containing as much as 10% butadiene when tested with acetylene tetrabromide (but no peroxide) showed no improvement over the homopolymer. These copoly-

TABLE XII
Self-Extinguishing Data for a Series of Alkenyl Aromatic Polymers

Polymer	ATB, phr	Dicumyl peroxide, phr	Self-extinguishing time, sec.
Polystyrene	2.5	0	Burns
	3.5	0	12
	4.0	0	7.5
	5.0	0	1.4
	0.5	0.5	1
	1.0	0.05	Burns
	1.0	0.07	17
	1.0	0.15	12
	1.0	0.20	2
	1.0	0.5	<1
Copolymer of 79% styrene and 21% α-methyl styrene	6	0	Burns
	4	2	<1
Copolymer of 72% styrene and 28% methyl methacrylate	2	0	Burns
	4	0	18
	2	0.5	1
Copolymer of 72% styrene and 28% acrylonitrile	4	0	Burns
	2	1	6
	2	2	3.2
Copolymer of 95% styrene and 5% of a rubbery copolymer of approximately 76.5% butadiene and 23.5% styrene	3	0	Burns
	4	0	19
	2	0.5	10
	2	1.0	1.6
	2	2.0	<1
Polyvinyltoluene (meta–para mixture)	4	0	Burns
	6	0	Burns
	4	2	<1

mers react rapidly with bromine but evidently the compounds so formed are not appreciably more stable than the original halogen additives.

The possibility of developing a polymer which could be readily autoxidized to form *in situ* peroxides was also investigated. Such a polymer should require only the halogen additive and no free radical initiator. Metz and Mesrobian reported that autoxidation of isopropylated polystyrene yields polymeric peroxides much more readily than polystyrene.[31] Copolymers containing 20 and 32 mole-% isopropylstyrene were prepared by the method discussed previously. These polymers when tested with acetylene tetrabromide showed no improvement in flammability over polystyrene. The results indicate that either very few of the isopropyl groups are oxidized to peroxides at ignition conditions (which seems doubtful) or that such polymeric peroxides if formed are not as effective as organic peroxides added directly. The position of the reactive groups in the polymer structure no doubt is quite important. Of related interest is the fact that polystyrene containing 2 phr acetylene tetrabromide and initially rated as a material which burns was made self-extinguishing by hot milling in the presence of air. The data are shown in Table XIII. Hot milling in a nitrogen atmosphere did not improve the flammability of the samples. Evidently *in situ* peroxide formation resulted when the hot milling was done in air. Such peroxides were not stable, however, since after a period of time the polymer again burned. This effect was simulated by an accelerated aging test as shown in Table XIII.

TABLE XIII
Aging of Self-Extinguishing Polystyrene Hot-Milled in Air

Preparation	Time	Self-extinguishing time, sec.
Polystyrene, 25 cpoise (10% toluene), milled in air with 2 phr acetylene tetra-bromide for 10 min.; roll temperature 320°F.	Initially	6
	6 days	4
	28 days	9
	46 days	12
	74 days	Burns
Polystyrene, 25 cpoise (10% toluene) milled in air with 2 phr acetylene tetra-bromide for 10 min.; roll temperature 360°F. Polymer dissolved in methylene chloride. First sample devolatilized and tested. Second sample heated and de-volatilized.	Initially	8
	Methylene chloride solution	10
	Heated at 80°C. for 30 min.	17

D. Mechanism

Various explanations for the observed synergistic effect have been considered. The following possibilities will be discussed here.

1. The free radical initiator thermally decomposes and by some mechanism increases the rate of decomposition of the halogen compound or initi-
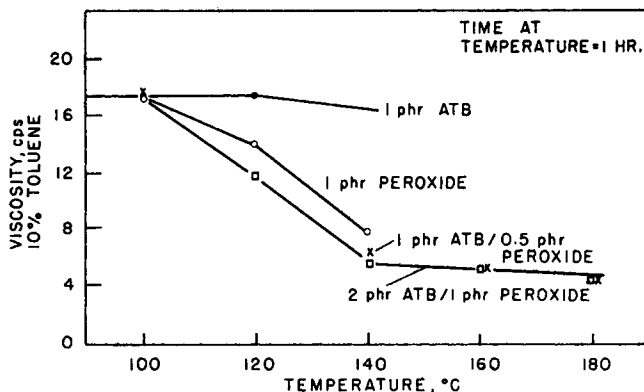
Fig. 3. Thermal degradation of polystyrene containing acetylene tetrabromide and dicumyl peroxide.

ates the decomposition at a lower temperature. There seems to be some evidence that the decomposition of organic halides can be accelerated by free radical initiators. A thermogravimetric study in air of the system 1 part dicumyl peroxide and 7 parts of 1,2-dibromotetrachloroethane showed that the temperature at 50% decomposition of the halogen compound was 12°C. lower than in the absence of the peroxide. At 90% decomposition the temperature was 20°C. lower. Similar observations have also been noted for combinations of halogens and dicumyl peroxide in polystyrene.[32]

2. The free radical initiator, the halogen, or both interacting, lower the temperature at which oxidation of the polymer occurs. In this way the decomposition of the polymer might be more advantageously matched with the decomposition temperature characteristics of the effective halogen compounds. Some support for such a concept can be found in the reported effect of di-*tert*-butyl peroxide on the vapor phase oxidation of benzene.[33] The addition of 5 mole-% of peroxide lowered by 150°C. the temperature at which 0.5% of the benzene had oxidized. The effectiveness of hydrogen bromide in lowering the oxidation temperature of hydrocarbons has been reported earlier.[34] Recent work on the hydrogen bromide-catalyzed vapor-phase oxidation of isobutane showed that di-*tert*-butyl peroxide had a marked synergistic effect in this system.[35] Various polymer degradation studies were carried out as part of the present study on synergistic self-extinguishing polymers. No grossly accelerated oxidation of polystyrene was noted when halogen compounds, peroxide, or both were present in the polymer. Differential thermal analysis[36] and thermogravimetric methods were used. Ignition studies based on the Setchkin method[37] likewise showed no difference for polystyrene samples with and without halogen and peroxide additives. The samples contained a maximum of 1 phr organic halogen and 0.5 phr dicumyl peroxide. At higher additive loadings evidence of accelerated oxidation might be more pronounced.
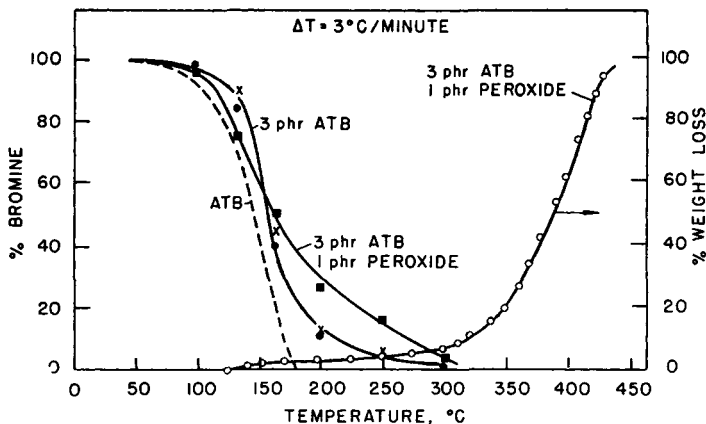
Fig. 4. Thermogravimetric analyses of the polystyrene–acetylene tetrabromide–dicumyl peroxide systems.

3. The free radical initiator thermally decomposes, accelerates the breakdown of the polymer, and promotes reaction between polymer fragments and halogen containing material. This leads to a delay in loss of halogen from the polymer mass. The support for this concept is based on the following observations. Polystyrene containing a peroxide additive will degrade in molecular weight upon heating.[11] Organic halogen compounds likewise promote the degradation of polystyrene. Combinations of peroxide and halogen are even more effective in this respect. Such degradation effects are illustrated in Figure 3. Panayotov has reported the effect of benzoyl peroxide on the bromination at 76°C. of polystyrene with *N*-bromo-succinimide (NBS) in carbon tetrachloride.[38] In the absence of benzoyl peroxide no reaction was observed between the polymer and NBS. Addition of peroxide produced higher reaction rates but had no effect on the final bromine content of the brominated polymer. A sharp drop in polymer viscosity was reported. No evidence of polymer cross-linking was observed.

Polystyrene containing acetylene tetrabromide and dicumyl peroxide was heated in air at a constant rate in a thermogravimetric apparatus. Samples were withdrawn at various temperatures and analyzed for bromine. The data are shown in Figure 4. It is significant that an appreciably greater amount of bromine was present throughout the 150–300°C. range in the samples containing dicumyl peroxide. This suggests that a halogen derivative(s) more stable than the original additive had been formed by peroxide–halogen–polymer interaction. The resulting halogen–polymer combination retains more of the halogen than a system containing no initiator. The net result is a more efficient use of the halogen additive for flame quenching.

A schematic representation of polymer combustion is shown in Figure 5. Fuel and oxygen must be present in the flame front to sustain the combus-
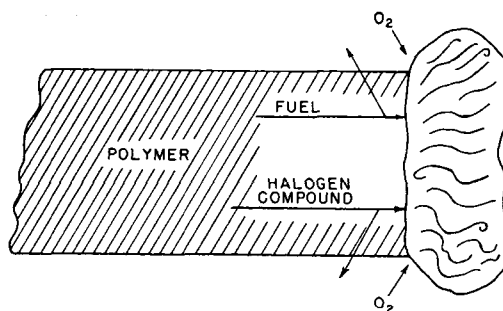
Fig. 5. Polymer combustion.

tion. Burning will be hindered if the transport rate of either the fuel or oxygen is reduced. The transport rate of the fuel into the flame front will be reduced if insufficient heat is available for degradation of the polymer into volatile fragments. Polymers such as polyesters, phenolics, epoxies, and polyurethanes produce char on combustion. Char production hinders the rate of heat transfer from the flame front to the underlying polymer. Combustion is hindered by the subsequent insufficient volatilization of fuel. Polymers such as polystyrene and polyethylene burn with no char build-up. One method of retarding the combustion of such plastics is to inhibit the fuel oxidation reactions. The addition of halogen compounds to the polymer undoubtedly hinders the combustion by interfering with the free radical chain reactions in the flame front. In a hydrocarbon flame, the scheme of reactions shown in eqs. (1)–(4) has been postulated for combustion and inhibition.[39]

Exothermic propagation:

$$\cdot OH + CO \rightarrow CO_2 + H \cdot \tag{1}$$

Chain branching:

$$\cdot H + O_2 \rightarrow \cdot OH + O \cdot \tag{2}$$

Inhibition:

$$\cdot OH + HBr \rightarrow HOH + Br \cdot \tag{3}$$

Regeneration:

$$\cdot Br + RH \rightarrow HBr + R \cdot \tag{4}$$
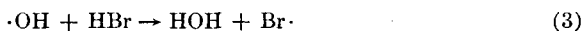
Here RH is any hydrogen-containing species in the flame.

The reduction of OH radicals by reaction with HBr slows the exothermic propagation reaction. This inhibition of reaction (1) results in flame quenching. The synergistic system functions largely outside the flame front but in the polymer zone adjacent to the front. Here the temperature conditions are such that the initiator decomposes, radical attack of the polymer takes place, and the resulting polymer fragments react with the halogen additive. The efficiency of an initiator is thus related to its effectiveness in promoting breakdown of the polymer.

E. Inhibition

The necessity that the synergist be a free radical initiator indicates that the synergistic system probably consists of a series of free radical reactions. If this is so, then the addition of an effective free radical scavenger should interfere with these reactions. A number of possible free radical inhibiting schemes which might affect the synergistic self-extinguishing mechanism are shown in Fig. 6. A free radical scavenger could react with the synergist radicals and thus prevent polymer attack by the synergists, or it might chain transfer with the polymer free radicals and prevent reaction with the halide. This second reaction scheme could conceivably help by slowing polymer decomposition or it might have a negative effect by preventing synergist–halide–polymer reaction.

Fig. 6. Synergistic self-extinguishing mechanism.

Experimental data for three free radical inhibitors at various additive levels in polystyrene are shown in Table XIV. Interestingly enough, none of these additives had a noticeable effect on the self-extinguishing times of polystyrene containing only acetylene tetrabromide and no synergist. Evidently the scavengers do not interfere with the inhibiting reactions in the flame front, but do affect the synergistic reactions. Both p-benzo-quinone and phenothiazine interfere with the peroxide systems. Similar results have also been obtained with quinhydrone, hydroquinone, and 2,2,-diphenyl 1-picryl-hydrazyl. Additional data in Table XV indicate that the phenothiazine has a specific effect on the dicumyl peroxide. The addition of phenothiazine markedly reduced the extent of polymer degradation in the polystyrene sample containing dicumyl peroxide and acetylene tetrabromide.

The mechanism by which phenothiazine inhibits the peroxide synergistic self-extinguishing process has not been established. It has been suggested that the phenothiazine ring structure must first react with oxygen

TABLE XIV

Effect of Free Radical Inhibitors in Self-Extinguishing Polystyrene – Self-Extinguishing Time, Sec.

	p-Benzoquinone[a]					Phenothiazine				Ethyl mercaptoacetate			
	0 phr	0.5 phr	0.75 phr	1.0 phr	5.0 phr	0.1 phr	0.5 phr	1.0 phr	5.0 phr	0.25 phr	0.5 phr	1.0 phr	5.0 phr
Acetylene tetrabromide (5 phr)	1.0	—	—	1	1	2.8	—	—	1.2	2.8	2.4	1.6	1.6
ATB (1 phr)/dicumyl peroxide (0.5 phr)	1.0	1.4	7	Burns	Burns	2.0	6.6	13.2	Burns	1.4	1.8	2.4	16
ATB (2 phr)/Santocure[b] NS (1 phr)	2.4	4.4	—	6	8	—	2.2	—	7.4	8.6	11	Burns	Burns

a Chain transfer constant with polystyrene radical: benzoquinone 566 at 80°C.[40]; ethylmercaptoacetate 27.6 at 99°C.[21]

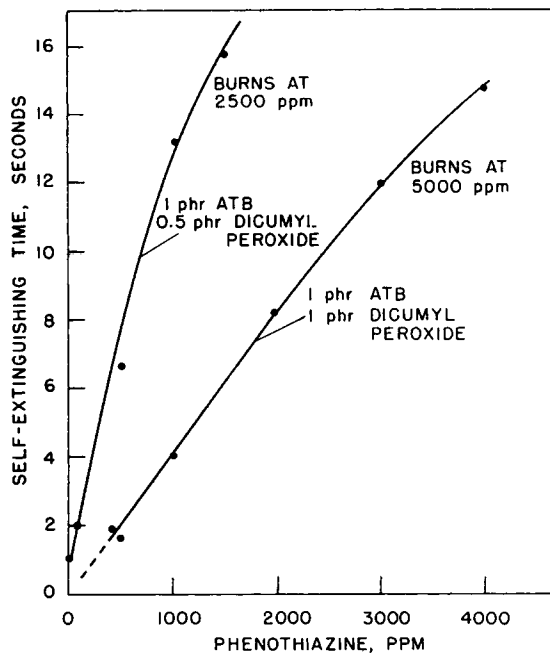b N-tert-Butyl-2-benzothiazolesulfenamide.

Fig. 7. Effect of phenothiazine in self-extinguishing polystyrene.

to form the active inhibitor. The activity ascribed to phenothiazine is postulated to be due primarily to the 3-hydroxyphenothiazine-semi-quinone-phenothiazone-3 system, to which phenothiazine is oxidized through the intermediate phenothiazine-5-oxide.[41] Each phenothiazine molecule could thus be expected to terminate two free radicals. The inhibition data in Figure 7 have been analyzed on this basis in the Appendix to obtain an estimate of peroxide efficiency. The calculations indicate that the effective usage of the peroxide may be no more than 10%.

The scavenger data for the ethylmercaptoacetate in Table XIV are interesting in that they show no effect on the peroxide synergists but a specific effect with N-tert-butyl-2-benzothiazole-sulfenamide. Thiols are sufficiently reactive hydrogen donors to react with a number of free radicals.[18a] It seems that the ethylmercaptoacetate inactivates the benzothiazyl radicals by such a mechanism. The resulting 2-mercaptobenzothiazole compound is a poor synergist (Table VI).

In addition to initiator inhibition reactions, there is also the possibility that the inhibitors chain transfer with the polymer and thus compete for reactive sites with the halide. The transfer constant (C_s) for acetylene tetrabromide with a polystyrene radical is probably no greater than 100.[42] The transfer constant for benzoquinone at 80°C. is 566 (Table XIV). Benzoquinone would be expected to transfer more readily than acetylene tetrabromide with a polystyrene chain. The data in Table XIV for benzoquinone and 5 phr acetylene tetrabromide show neither a beneficial or

TABLE XV
Effect of Phenothiazine on Polystyrene Viscosity[a]

Acetylene tetrabromide, phr	Dicumyl peroxide, phr	Phenothiazine, phr	Polymer viscosity, cpoise[b]
0	0	0	14.7
1	0	0	14.0
1	0.5	0	7.0
1	0.5	0.5	11.0

[a] Samples molded at 200°C. for 5 min.
[b] 10 wt.-% toluene solution.

TABLE XVI
Effect of Polydimethylsiloxane in Self-Extinguishing Polystyrene

Halogen	Halogen, phr	Synergist	Synergists, phr	Siloxane, ppm[a]	Self-extinguishing time, sec.
Acetylene tetrabromide	5	None	0	0	1
"	5	"	0	100	16
"	5	"	0	200	Burns
"	5	"	0	500	Burns
"	5	"	0	1000	Burns
Acetylene tetrabromide	1	Dicumyl peroxide	0.5	0	1
"	1	"	0.5	100	3
"	1	"	0.5	500	9
"	1	"	0.5	1000	Burns
Acetylene tetrabromide	1	Dicumyl peroxide	1	0	<1
"	1	"	1	100	2.5
"	1	"	1	500	9
"	1	"	1	1000	Burns
Acetylene tetrabromide	2	Santocure NS[b]	1	0	2.4
"	2	"	1	200	Burns
"	2	"	1	500	Burns
"	2	"	1	1000	Burns
Hexachloroethane	10	Dicumyl peroxide	1	0	1
"	10	"	1	250	9
"	10	"	1	500	Burns
"	10	"	1	1000	Burns

[a] DC-200 (Dow Corning Corporation).
[b] N-tert-Butyl-2-benzothiazolesulfenamide.

detrimental effect. The addition of 25 phr benzoquinone by itself to polystyrene did not prevent the combustion of the polystyrene. It has been reported that 1,4-diaminoanthraquinone has an inhibiting action in the high temperature degradation of poly(methyl methacrylate). The addition of 60 parts of quinone per 100 parts of poly(methyl methacrylate) reduced the rate of polymer decomposition to 40% of the original rate at 220°C.[43] In the present study, the addition of 25 phr of 1,4-diamino-anthraquinone to polystyrene did not prevent polymer combustion. One

must conclude that these inhibitors do not either noticeably interfere with halide–polymer reactions or decrease polymer degradation.

Finely divided inorganic substances can also have a detrimental effect on the self-extinguishing characteristics of polystyrene containing halogen and peroxide.[44] Table XVI presents quantitative data showing the dramatic effect of dimethylsiloxane polymer added to a number of self-extinguishing polystyrene systems. The action of the siloxane seems to be independent of the particular self-extinguishing system used. It differs in effectiveness from the previously discussed inhibitors in that the self-extinguishing acetylene tetrabromide samples containing no peroxide are also affected. One might surmise that the siloxane at elevated temperatures decomposes to form silicon dioxide which in turn further reacts to form volatile $SiBr_4$ and $SiCl_4$. If as much as 1000 ppm of siloxane reacted to form $SiBr_4$ and this bromine were totally unavailable for flame extinguishing, the loss would amount to about 0.5 phr acetylene tetrabromide. This would not be sufficient to explain the complete loss of nonflammability of the 5 phr acetylene tetrabromide samples. Rather, it seems that the siloxane (as silicon dioxide) has a catalytic effect on the decomposition of either the halogen compound or the polymer. A similar catalysis has been reported for sodium silicate in the combustion of sucrose.[45]

APPENDIX

At a fixed concentration of halogen additive the self-extinguishing time for a polymer containing a synergistic combination will be a function only of the initiator concentration. The initiator added will be consumed by wastage and by synergistic reactions. At any specific value of self-extinguishing time, the following relationship is valid:

$$C_0 = FC_0 + C_A \tag{5}$$

where C_0 = initial initiator concentration, C_A = initiator active as synergist, and F = fraction wasted.

If a free radical inhibitor is added to the system, an increased amount of initiator must be used if the self-extinguishing time of the polymer is to be unchanged. Such a system could be described as:

$$C_T = C_0 + F(C_T - C_0) + C_I \tag{6}$$

where C_T = total initiator added to inhibited system, C_0 = initiator required for a specific self-extinguishing time if no inhibitor were present, and C_I = inhibitor added to obtain the specified self-extinguishing time. If it is assumed that eq. (6) is a valid extension of eq. (5), both equations can be combined to give an expression for initiator efficiency:

$$(1 - F) = C_I/(C_T - C_0) \tag{7}$$

Solutions to eq. (7) for a series of self-extinguishing values are summarized in Table XVII. These calculated point values of initiator efficiency for

both 0.5 and 1.0 phr peroxide decrease with decreasing amounts of inhibitor. A simple linear extrapolation of $(1 - F)$ as a function of inhibitor concentration gave a value of about 10% efficiency at zero inhibitor. Additional treatment of the data are probably not justified in view of the rather simple model assumed for the calculations.

Table XVII
Initiator Efficiency

Self-extinguishing time, sec.	C_T, phr	C_I, phr[a]	$C_0{}^c$, phr	$(1 - F)$, %[b]
8	0.5	0.052	0.18	21
	1.0	0.192	,,	29
12	0.5	0.092	0.15	33
	1.0	0.300	,,	44
Burns	0.5	0.250	0.05	69
	1.0	0.500	,,	65

[a] From Figure 7.

[b] Includes 1.24 conversion factor for phenothiazine–dicumyl peroxide equivalence. Calculations based on 100% utilization of inhibitor.

[c] From Table XII.

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Résumé

Des polymères aromatiques vinyliques comme le polystyrène peuvent être rendus inflammables par l'addition de composés halogénés. On peut réduire la quantité d'halogène nécessaire en ajoutant de petites quantités de certains initiateurs produisant des radicaux libres. Normalement on doit àjouter au polystyrène 5% de tétrabromure d'acétylène (parties d'additif par cent parties de polymère), afin d'obtenir un polymère tel qu'il s'éteigne lui-même. Quand on ajoute 0.5% de peroxyde de dicumyle, 0.5% de tétrabromure d'acétylène suffit. Le synergisme de ces effets a été observé avec une série de peroxydes, d'hydroperoxydes, de dérivés azo, de quinone-imines, de benzothiazol-

sulfénamides, de disulfures et un composé bibenzyle. Il semble que le mécanisme synergique est basé sur une série de réactions impliquent l'attaque du polymère par l'initiateur, suivi par une réaction entre des fragments polymériques et le composé halogéné. Le résultat est un retard dans la disparition de l'halogène de la masse polymérique et il s'en suit un usage plus efficace de l'additif halogéné pour l'extinction des flammes. Les inhibiteurs connus des réactions initiées par radicaux libres ont un effet défavorable sur le mécanisme synergetique.

Zusammenfassung

Vinylaromatische Polymere wie Polystyrol können durch Zusatz von Halogenverbindungen nichtentflammbar gemacht werden. Die zum Nicht-Entflammbarmachen solcher Polymerer benötigte Menge an Halogen kann man durch Hinzufügen von geringen Mengen bestimmter radikalischer Starter sehr verringern. Normalerweise müssen zu Polystyrol ungefähr 5 phr Acetylentetrabromid (Teile Zusatzstoff pro hundert Teilen Polymerem) hinzugefügt werden, um ein selbstauslöschendes Polymeres zu erhalten. Bei Zugabe von 0,5 phr Dicumylperoxyd sind nur 0,5 phr Acetylentetrabromid erforderlich. Dieser synergistische Effekt wurde an einer Reihe von Peroxyden, Hydroperoxyden, Azoverbindungen, Chinoniminen, Benzothiazolsulfenamiden, Disulfiden und einer Bibenzylverbindung beobachtet. Der synergistische Mechanismus scheint auf einer Reihe von Reaktionen, wie Angriff des Polymeren durch den Starter und darauf folgende Reaktion zwischen den Polymerbruchstücken und der Halogenverbindung zu beruhen. Das Ergebnis ist eine Verzögerung des Halogenverlustes aus der Polymermasse und daher eine wirksamere Ausnützung des Halogenzusatzstoffes zur Flammenunterdrückung. Bekannte Inhibitoren für radikalische Reaktionen stören den synergistischen Mechanismus.

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