

STABILIZATION OF POLYOLEFINS BY PREVENTIVE ANTIOXIDANTS AND SYNERGISTIC EFFECTS

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Summary

A mechanism for stabilizing polyolefins has been developed in the last few years.

The key initiators in thermal and UV initiated oxidation and degradation processes are hydroperoxides, and the key anti-oxidants are phenolic compounds.

The action of phenolic antioxidants consists of trapping free radicals or destroying hydroperoxides. Compounds containing sulphur, phosphorus and, in special cases, nitrogen exert synergic effects and govern the length of the induction period.

Complexing agents avoid the rapid and sometimes catastrophic degradation brought about by ultra-violet radiation in the presence of metal ions. Chain terminators, peroxide decomposers and complexing agents form synergic systems, and the maximum efficiency would be obtained if they were all present in the one molecule or in the one mixture.

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1. INTRODUCTION: NECESSITY OF STABILIZING

Organic polymers may well have admirable properties; but, unlike the pyramids, they have not been designed to last for ever.

Their great advantages are their low density, the great scope that they allow in processing, the wide range of applications open to them, and the ease with which their properties can be engineered to meet specific requirements. Thus polymers are very versatile and allow conformance to a wide variety of demands on their mechanical strength, dielectric properties, appearance, resistance to chemicals, or on any combinations of these properties.

Their disadvantage is that their properties may deteriorate in various environments. The variations in stability can primarily be ascribed to the chemical configuration, although the physical structure or morphology may also be responsible.

There are two sets of conditions under which degradation is most likely to occur.

1. During processing, when the polymers are exposed to high temperatures for short intervals of time.

- 1a. In some cases, a deterioration in properties may be traced as far back as the polymerization process itself. It may result from the incorporation of certain impurities, e.g., oxygen, or undesired monomers; these sensitizing groups often accelerate degradation of the polymer during its subsequent service.
2. Long-term aging. This phase embraces storage. By the time that the effects of long-term aging become visible, the polymer may already have failed to meet the demands imposed in the intended application.

Failure in this case is defined as the alteration of a given property beyond a specified limit, and it is this particular property that is taken as a criterion in tests for polymer stability or stabilizer efficiency.

The life and thus the serviceability of polymers can be considerably lengthened by means of stabilizers, e.g., substituted phenols, and other additives. In selecting the stabilizer system, however, allowance must be made for both sets of conditions under which degradation may occur, i.e., processing and long-term aging^(a). Another fact to be considered is that, obviously, the very complexity of oxidation degradation mechanisms rules out the possibility that any one stabilizer could act as a panacea. In actual fact, there are numerous antioxidant and auxiliary systems, each of which pertains to a particular case of stabilization.

Antioxidants prevent or inhibit oxidation, particularly that caused by the oxygen in the atmosphere. They are mostly aromatic compounds with at least one hydroxyl or amino group. Some of the best known are monocyclic and polycyclic phenols with one or more hydroxyl groups, and they can be used in foodstuffs and pharmaceuticals. A number of aromatic amino compounds are used besides phenols for industrial applications in plastics, lubricants, rubber, etc.

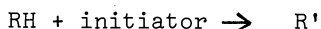
For the most part, antioxidants are used together with synergists, stabilizers and chelating agents. All the mixtures thus formed are intended to improve the efficiency, expand the field of application and simplify handling. Various types of chemical substances are represented in the synergists: acids, salts, bases and reducing agents. The feature that they share in common is the boost that they impart to primary antioxidants.

Antioxidants have existed since time immemorial. The methods of preserving foodstuffs that were adopted in ancient times also embraced the use of vegetable products that acted as antioxidants.

The chemistry of autoxidation^(b)

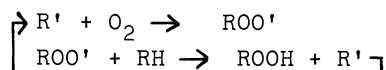
The conclusions and hypotheses presented by various authors on autoxidation of unsaturated fatty acids at low temperatures have been reviewed by Scott^(c). His work gives a good idea of the current situation. Autoxidation, or oxidation caused by molecular oxygen, is also referred to as atmospheric oxidation. It is initiated by the formation of free radicals and proceeds as a radical chain reaction. In the various reactions that ensue, the radicals formed are finally converted into inactive substances, and oxidation is thus terminated. Hence the stages in autoxidation are initiation, propagation and termination. This is shown schematically below.

a) Initiation



RH = autoxidizable molecule, e.g. hydrocarbon, saturated fatty acid, ester, aldehyde, etc.

b) Propagation



c) Termination



Under normal atmospheric conditions, the last reaction predominates.

During the initiation phase, the products of the oxidation reaction collect slowly and in small amounts. The phase, also referred to as the induction phase, is represented by a section with a low slope in the curve for the peroxide values. Since antioxidants inhibit the propagation of oxidation, they prolong the induction phase, the length of which can thus be taken as a measure for the oxidation stability. Initiation requires a very high activation energy. Heat, light and, in particular, ultra-violet radiation exert an exogenous effect on the reaction, and dyes and many metals including the highly effective salts of iron, copper and cobalt act as endogenous catalysts.

Singlet oxygen (1O_2) can react with, say, methyl linoleate at a rate that is 10^3 to 10^4 times greater than that attainable with normal triplet oxygen (3O_2), from which it is formed photochemically^(d). Triplet oxygen plays a decisive part in autoxidation, and singlet oxygen initiates the photooxidation reaction that sensitizes colorants^(e). In both cases, allyl hydroperoxides are formed that have the same constitution but differ in abundance. Volatile carbonyl compounds are formed by lipoxygenases and singlet oxygen during the oxidation of, say, linoleic acid in the presence of haemoglobin. A study of these reactions has revealed that singlet oxygen can split unsaturated fatty acids at the C = C double bond. The volatile aldehydes thus formed may affect the aroma in foodstuffs of vegetable origin.

Traces of metals, which are always present in adequate amounts in any substrate, act as catalysts and are of great practical significance. Hence the inactivation of these metals by chelating agents is an important measure in inhibiting autoxidation.

Oxygen attacks the preferentially energized hydrogen attached to the allyl group. In other words, oxidation commences at a carbon atom in the alpha position relative to a C = C double bond. The ratios of the rates of oxidation for stearic, oleic, linoleic and linolenic acids are 1:1000:1200:2400. These figures^(e) reflect the increasing activation of methylene groups for hydrogen abstraction^(f).

The radicals formed trigger off the chain reaction. Extremely small amounts of substances that promote or oppose oxidation in the substrate may tremendously accelerate or inhibit propagation of the chain reaction. Under the influence of traces of the metals previously mentioned, particularly copper, more radicals may be formed from the peroxides. Theoretically, the chain reaction could proceed until the entire substrate is consumed or no more oxygen is available.

The peroxides may be fragmented into aldehydes, ketones, carboxylic acids and other decomposition products. During these secondary processes, the amount of "active" peroxide oxygen is reduced, with the result that the peroxide number is no longer a suitable measure for the degree of oxidation. As opposed to this, the carbonyl compounds formed can be taken as a parameter that can be determined quite easily analytically.

2. RADICAL REACTIONS

Do radical reactions initiate oxidative degradation, and are they thus responsible for it?

All organic substances are liable in various degrees to oxidation, which can be initiated by radicals set free from peroxides or by mechanical shear, high-energy radiation, ultra-violet light, thermal decomposition at weak bonds, radical precursors and the radical chain mechanisms described below.

There are two major types of stabilizer.

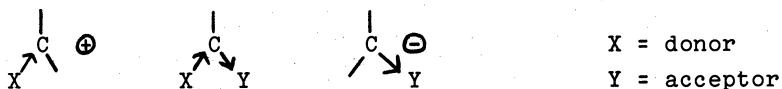
- (1) Preventive antioxidants, which inhibit or retard in some way the formation of free radicals in the initiation stage, i.e., they act as scavengers.
- (2) Chain-breaking antioxidants, which interrupt the propagation cycle by reacting with the free radicals, R· or $RO_2\cdot$, thus introducing new termination reactions.

It is evident that the first type will slow down oxidation without altering the mechanism but that the second type will introduce competition reactions that change the sequence of the reactions. Thus the mechanism of retarded autoxidation is considerably more complex than that of the uninhibited reaction(a),(c).

2.1 CAPTO-DATIVE SYSTEMS^(g)

Capto-dative systems explain the stabilization of carbon radicals by scavengers. The underlying principle is described below.

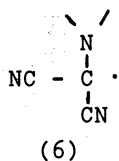
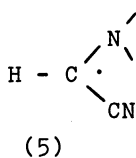
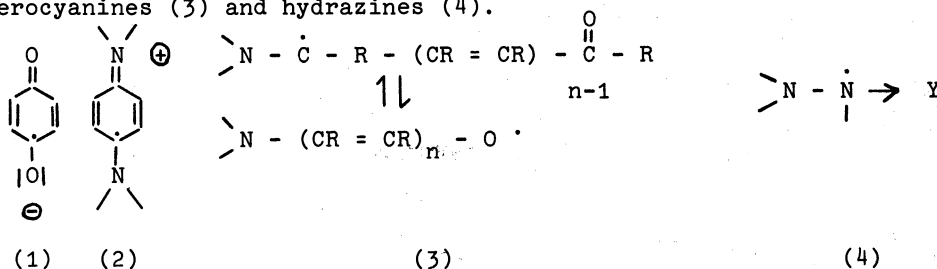
Since carbanions are stabilized by electron acceptors and carboniums by electron donors, radicals between both types are stabilized by the simultaneous presence of both donor and acceptor substituents.



Viehe calls this particular effect capto-dative stabilization^(g). Although it has been the subject of discussion^(g), it does not seem to be generally known and has remained unexploited.

The efficiency of CD substitution in stabilizing radicals is evident from the canonical structures shown by Jellinck^(b) and is confirmed by ab initio calculations.

Examples of persistent radicals with CD substituents that have been known for some time are semiquinones (1), Wurster salts (2), those derived from merocyanines (3) and hydrazines (4).

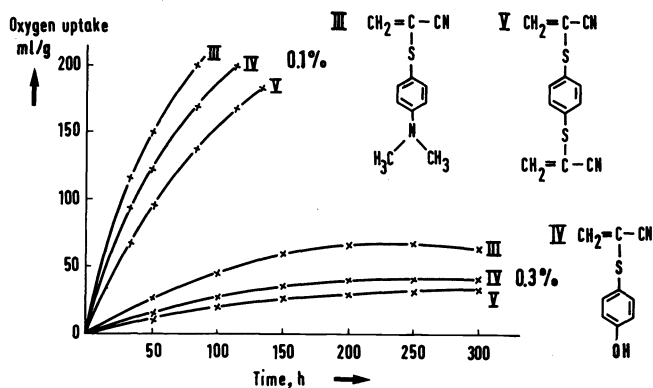


In these radicals, the donor and acceptor groups are generally in vinylogous positions, and delocalisation across the polyenic systems is enhanced by the capto-dative stabilization. Other capto-dative radicals enjoy additional stabilization owing to the presence of an aromatic system. Research is directed at those simple systems in which the donor and acceptor groups are bonded to the same carbon, in which the additional stabilizing factors of polyene delocalisation and steric hindrance are absent or minimized.

The only well-documented radicals that satisfy this criterion are (5) and (6).

Viehe et al discovered that in contrast to typical monomers such as styrene, acrylonitrile and vinyl ethers, CD-substituted olefins (7) do not polymerize with isobutyronitrile (IBN) radicals but enter into addition reactions with them to form new persistent radicals (9).

Fig. 2



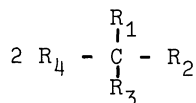
Stabilization of branched polyethylene by varying different CD-compounds (140°C, 1 bar O₂); % = percent by weight

2.2 INSTABLE C-C SYSTEMS CONTAINING SULPHUR^(m)

Our interest is attracted by instable C-C compounds containing freshly formed thio bridges. The general formula is shown below (12). In the formula, R₁, R₂ and/or R₃ and R₃ stand for S-alkyl, S-cycloalkyl, S-aralkyl or S-aryl groups.

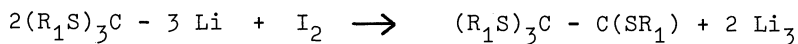


An example of the initiator's structure would be



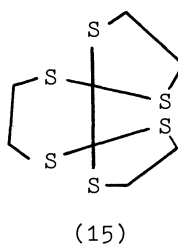
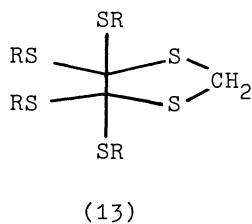
Two groups in Formula (12) may also join together to form a ring.

The instable C-C compounds may be formed by reactions of the type illustrated by the equation below, in which R₁ is again one of the groups mentioned above.

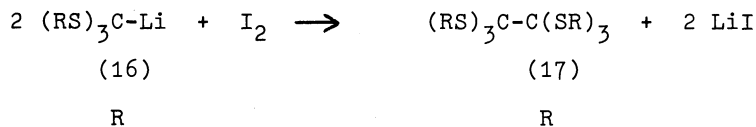


The only representatives of this type of compound have at least one -[CH₂]_n- bridge between two of the six sulphur atoms.

Derivatives are obtained by the action of diazomethane on trithiocarbamates⁽ⁿ⁾,^(o). Structure (15) was assigned to the substance formed by oxalyl chloride and ethanedithiol. Coffen^(p) assumed that the first step in the degradation reaction is the homolysis of a C-S bond.

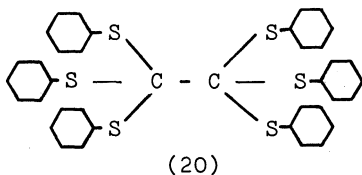
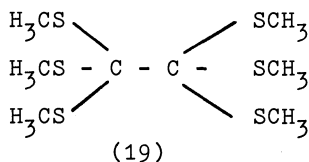
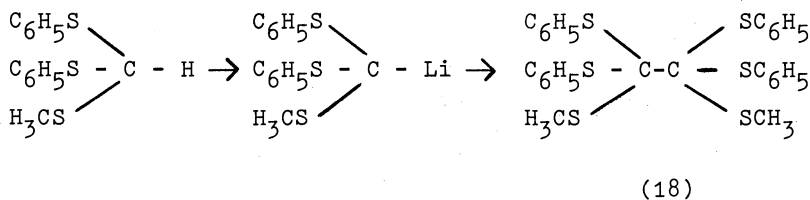


It has been demonstrated that sparingly soluble ethanes (17a - 17h) are isolated when metal triaryl trithio-o-formates (16) react with iodine. For instance, if iodine is added in tetrahydrofuran (THF) to a solution of (16a) that is kept stirred at -80°C , each drop added will be decoloured until the end point is reached. Shortly after all the iodine has been added, a colourless solid will separate from the mixture of reactants. The yield is more than 95%. The solid can be recrystallized at 100°C from abundant pyridine, and it decomposes at temperatures of 200°C or more. Elementary analysis reveals the composition expected for (17a).



<p>a C_6H_5</p> <p>b $\text{p-H}_3\text{C-C}_6\text{H}_4$</p> <p>c $\text{o-H}_3\text{C-C}_6\text{H}_4$</p> <p>d $\text{p-tC}_4\text{H}_9\text{-C}_6\text{H}_4$</p>	<p>e $\text{p-CH}_3\text{O-C}_6\text{H}_4$</p> <p>f $\text{p-F-C}_6\text{H}_4$</p> <p>g $\text{p-Cl-C}_6\text{H}_4$</p> <p>h β-naphthyl</p>
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Replacing two of the six $\text{C}_6\text{H}_5\text{S}$ groups in (17a) by CH_3S groups tremendously improves the solubility. Eight of the dimers obtained from the corresponding trithio-o-formates have solubilities of 5 g/100 ml of THF at 20°C . The solubility of (17a) is less than 0.02 g/100 ml.



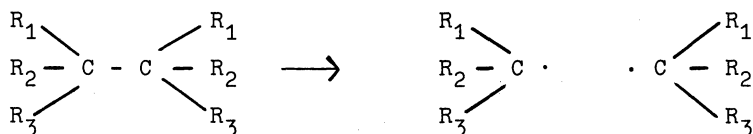
The NMR spectrum for (18) shows a CH_2S singlet and an aromatic multiplet in a ratio of 3:10. The molecular mass determined by osmosis agrees with the results of the elementary analysis.

Purely aliphatic substituted ethanes of the (17) type can also be obtained by this method. Hexakis(methylthio)ethane is unstable in air, very readily soluble in pentane and difficult to isolate in the pure form. The cyclohexyl derivative (10) is easier to handle.

If a vigorously stirred suspension of finely ground (17a) is heated in the following solvents under reflux in an atmosphere of argon for the following periods of time, a deep red solution will be obtained: in pyridine, 10 hours; in chlorobenzene, 1.5 hours; and in mesitylene, 0.3 hours.

The new unstable C-C compounds represented by Formula (12) are suitable initiators for the radical polymerization of vinyl monomers and for grafting and crosslinking polymers. One reason for this is their favourable half-life, e.g., 0.1 to 10 minutes at 100°C , the actual time depending on the medium.

Another is that they allow the sulphur group to be introduced simultaneously during polymerization or into the polymer after it has been formed, because the instable compound decomposes according to the following equation.



General instructions for the preparation of hexakis(arylthio)ethanes (17), e.g. hexakis(phenylthio)ethane (17a)

A solution of tris(phenylthio)methyl lithium (16a) with a concentration of 10 mmol in 50 ml of THF and 7 ml of n-hexane is treated at -78°C with 1.20 grams of iodine dissolved in about 10 ml of THF. As the last of the iodine is being added, a fine precipitate is formed in the stirred solution. After 0.5 hour, the bath is removed, and the mixture is allowed to attain room temperature. It is poured into an Erlenmeyer flask containing 150 ml of water, some sodium hydrogensulphite (enough to cover the tip of a spatula), and 75 ml of chloroform. The mixture is shaken up and sucked through a G4 frit glass filter. The residue is washed with water and chloroform and dried (oil pump vacuum over phosphorus pentoxide). The yield is 3.10 g (91 %) of a colourless powder that decomposes on melting between 184 and 189°C . It is recrystallized as follows. One litre of pure pyridine is kept stirred in a bath thermostatically controlled at 95°C , and (17a) is run in until no more can be dissolved (after about 3.5 grams).

The solution is filtered and allowed to cool as slowly as possible to 0°C . A fine crystalline substance is thus obtained with a yield of about 70 %. If it is heated at a rate of $1^{\circ}\text{C}/\text{min}$, it decomposes at 202 - 205°C . Further data are listed in the table.

The other aryl derivatives (17) are obtained in the same way. At -78°C , the (16a, e) lithium compounds are not completely dissolved in 70 ml THF and 7 ml of hexane. In this case, the iodine is added to the suspension. The t-butyl-substituted (17d) is somewhat soluble in chloroform, with the result that the combined solutions obtained on washing must be concentrated to attain the yields listed in Table 1.

The new instable C-C compounds can also initiate radical reactions as is demonstrated below. Styrene that has been freshly distilled under white spot nitrogen is degassed in a vacuum for three hours at 50°C and 0.1 mm Hg; 100 parts are treated with one part of initiator and heated for five hours at 100°C . The yields and the molecular masses of the polymers obtained with the new initiators are listed in Table 2.

The analytical specimens of the polymers listed in Table 2 were prepared by dissolving in toluene, precipitating with methanol and drying for eight hours at 80°C and 2 mm Hg. The proportion of sulphur remains constant, even after the polymers have been reprecipitated twice. In other words, the sulphur has been incorporated in the polymer molecule.

A surprising fact is that the yields obtained with the new initiators are all higher than that attained in the blank experiment and that the molecular masses are of the same order. In other words, the sulphur exerts practically no controlling effect in this case.

TABLE 1. Yields, analyses and spectrometric data for hexakis(organylthio)ethanes (17-20)

Name and formula number	Yield (%) ^a Decomposition point (sol- vent for re- crystallization)	Molecular formula (molecular mass)	Elementary analysis ^b C H S
Hexakis(phenyl- thio)ethane (17a)	91 201-205° (pyridine)	C ₃₈ H ₃₀ S ₆ (679.1)	Calc. 67.22 4.45 Actual 67.62 4.41
Hexakis(p-tolylthio)- ethane (17b)	91 193-197° (toluene)	C ₄₄ H ₄₂ S ₆ (787.2)	Calc. 69.24 5.55 25.21 Actual 69.61 5.64 24.82
Hexakis(o-tolylthio)- ethane (17c)	88 165-173°	C ₄₄ H ₄₂ S ₆ (787.2)	Calc. 69.24 5.55 25.21 Actual 69.03 5.70 25.20
Hexakis(p-tert-butylphenyl- thio)ethane (17d)	98 219-221° (toluene)	C ₆₂ H ₇₈ S ₆ (1015.6)	Calc. 73.31 7.74 18.94 Actual 72.86 7.69 19.20
Hexakis(p-methoxyphenyl- thio)ethane (17e)	90 184-185° (CHCl ₃)	C ₄₄ H ₄₂ O ₆ S ₆ (859.7)	Calc. 61.50 4.93 22.39 Actual 61.38 4.75 22.34 Calc. 011.17 Actual 011.34
Hexakis(p-fluorophenyl- thio)ethane (17f)	90 203-209°	C ₃₈ H ₂₄ F ₆ S ₆ (787.0)	
Hexakis(p-chlorophenyl- thio)ethane (17g)	93 171-181°	C ₃₈ H ₂₄ Cl ₆ S ₆ (885.8)	
Hexakis(2-naphthyl- thio)ethane (17h)	70 193-196°	C ₆₂ H ₄₂ S ₆ (979.4)	
1,2-Bis(methylthio)- 1,1,2,2-tetrakis- (phenylthio)ethane (18) ^b	94 139-142° (THF/ pentane)	C ₂₈ H ₂₆ S ₆ (554.9)	Calc. 60.60 4.73 34.67 Actual 60.59 5.07 34.52 Mol. mass 496 (by osmosis in CHCl ₃)
Hexakis(methyl- thio)ethane (19) ^b	50 125.0-125.5° (pentane) (melts without de- composing)	C ₈ H ₁₈ S ₆ (306.6)	Calc. 31.34 5.92 62.75 Actual 31.22 5.76 62.67 Mol. mass 292 (cryoscop. in benzene)
Hexakis(cyclohexyl- thio)ethane (20) ^b	68 151-152.5° (CCl ₄ /pentane)	C ₃₈ H ₆₆ S ₆ (715.3)	Calc. 63.80 9.30 26.89 Actual 63.01 9.14 27.77 Mol. mass 687 (by osmosis in benzene)

^aThe figures for the yield are valid for the crude products. If no solvent is cited, the substance could not be recrystallized.

^bNMR spectrum for 18 (in CHCl₃): τ = 2.65 (m of aromatic protons) and 7.87 (s of SCH₃)

NMR spectrum for 19 (in CCl₄): τ = 7.63 (s)

NMR spectrum for 20 (in CHCl₃): τ = 6.7 (wide s, 6H), 7.8 (wide s, 12H) and 48 H multiplet between 3.0 and 9.0

TABLE 2. Results of Styrene Polymerization

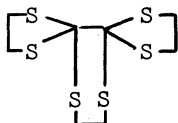
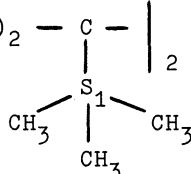
Initiator	Formula number	Yield (parts)	Molecular mass by osmosis in Mechrolab
$(\text{CH}_3\text{O}-\text{C}_6\text{H}_4\text{S})_3 \equiv \text{C} \begin{array}{l} \\ 2 \end{array}$	17c	25	6 000
$(\text{CH}_3\text{S})_4 \text{C}$		26	5 700
	15	33	6 100
$(\text{C}_6\text{H}_4(\text{CH}_3)\text{S})_3 \equiv \text{C} \begin{array}{l} \\ 2 \end{array}$	17c	35	4 600
$(\text{C}_6\text{H}_4\text{S})_4 \text{C}$		42	6 100
$(\text{CH}_3\text{-S})_2 - \text{C} - \begin{array}{l} \\ 2 \end{array}$ 		66	7 100
$(\text{C}_6\text{H}_4\text{S})_3 \text{C} - \begin{array}{l} \\ 2 \end{array}$	20	75	8 100
9. Without initiator		12	6 900
10. Lauroyl peroxide		49	5 800
11. Azodiisobutyronitrile		75	6 400

Table 3 lists the results that would be obtained if the same procedure were to be adopted and the styrene were to be replaced by the monomers listed.

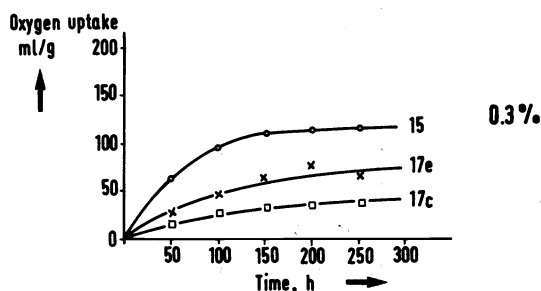
TABLE 3. Results of Different Monomer Polymerization

Monomer	Yield (parts)	Molecular mass*
Styrene	75	8 100
n-Butyl acrylate	82	9 400
1-Ethylhexyl acrylate	81	9 600
Methyl methacrylate	79	8 000

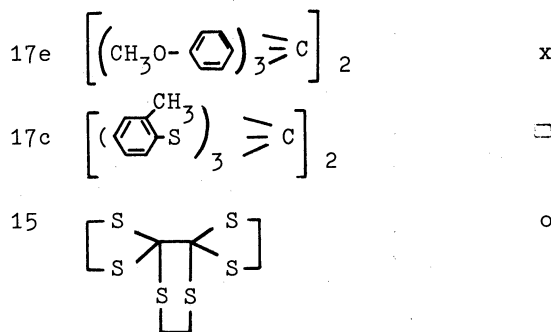
*Determined in the Mechrolab by vapour pressure osmosis

The efficiency of various instable C-C systems containing sulphur is shown in Fig. 3.

Fig. 3



Stabilization of branched polyethylene by varying different S-containing C-C label systems (140°C, 1 bar O₂); % = percent by weight



3. SYNERGISM - INCREASING EFFICIENCY BY MEANS OF SPECIFIC ADDITIVES

The effect of specific additives is boosted, in some cases quite drastically, by small amounts of certain auxiliaries. Well-known examples are flame retardants (cf. Fig. 4).

The amounts of flame retardants required to make polypropylene self-extinguishing are shown in the diagram. They can be greatly reduced by synergists. The highest efficiency in this respect (final column in Fig. 4) is shown by synergists that release radicals (instable C-C compounds). Many examples of synergism involving combinations of stabilizers have been reported (d), (e), (p), (q).

Scott et al discovered that sulphur dioxide is an effective catalyst for the decomposition of hydroperoxides. Ingold et al studied the effect of bases on the autoxidation of hydrocarbons in the presence and in the absence of inhibitors. Carbon black is also a very effective catalyst, but greater importance is attached to phosphites. In the light of known reactions of phosphorus (III) systems, it seems certain that they exert their antioxidant activity by reducing hydroperoxides stoichiometrically, thus being converted to the corresponding phosphorus (V) compounds.

Two mechanistically distinct types of synergism can be recognized, at least in theory (G. Scott). The first is homosynergism. One of the two compounds involved in this case is a conventional antioxidant, and the other is a weak antioxidant with a similar mechanism. The second is heterosynergism, which is the operative effect of two antioxidants with different mechanisms.

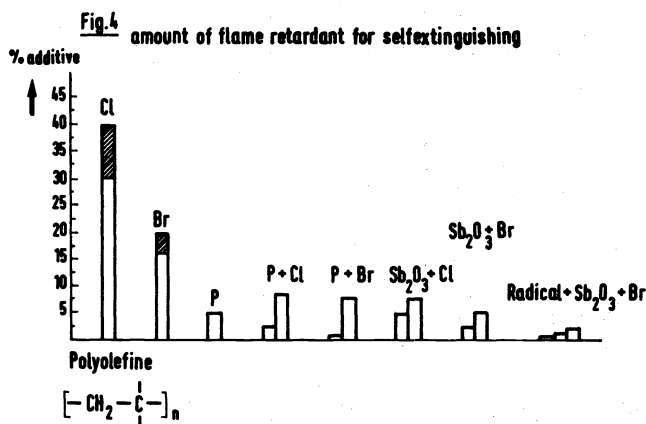


Fig. 4 Efficiency of synergists in flame retardants

TABLE 4

Effectiveness of dialkylphosphonates as synergists with 3-methyl-4-hydroxy-5-t-butylphenyl sulphide^(r)

Dialkylphosphonate	Phosphonate concn. x 10 ² (mol/l)	Phenol/phosphonate (molar ratio)	I.P. (min)
tert.-Butyl	0.526	0.97	208
Isopropyl	0.572	0.90	170
Methyl	0.573	0.90	160
sec.-Butyl	0.582	0.88	143
Isobutyl	0.532	0.96	142
2-Methyl-4-pentyl	0.528	0.97	134
2-Ethylhexyl	0.545	0.94	120
2,6-Dimethylheptyl	0.578	0.89	100

By varying the phosphonate structure, Knepp^(r) showed the importance of steric dependence.

Other forms of synergism are

- 1) synergism involving metal deactivation,
- 2) autosynergism involving metal deactivation,
- 3) synergism involving ultra-violet absorption, and
- 4) synergism involving peroxide decomposition.

Effective antioxidants for metal-catalyzed autoxidation are chelating agents that can complete the coordination shell of transition metals and thus make further hydroperoxide coordination impossible or difficult. Since their mechanism is preventive, metal deactivators should be synergic with radical-deactivating antioxidants.

An aspect of synergism that is of practical importance occurs if two kinds of antioxidant activity are associated in the same molecule (Kuminskii).

TABLE 5

Synergism of 2-hydroxybenzophenones with chain-breaking and peroxide-decomposing antioxidants in polyethylene (g)

Additive	Concentration (%)	Time to reach 10 units of C=O	Time to 50 % loss of elongation (Weather-ometer) (h)	% Elongation after 14 months outdoor exposure
None		1	120	9
A Dilaurylthiodipropionate	0.5	2		11
B Zinc dibutyldithiocarbamate	0.5	-	400	-
C Bis(2-hydroxy-3-tert.-butyl-5-methylphenyl)methane	0.5	-	-	10
D 2-Hydroxy-4-n-octoxy-benzophenone	1.0	-	-	42
E 2-Hydroxy-4-n-dodecyloxy-benzophenone	1.0	18	700	80
F A + E	1.5	>29	-	110
G C + D	1.5	-	-	100
H B + E	1.5	-	1500	-

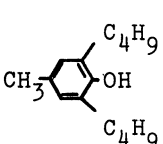
Dialkylaluminium hydrides are extremely efficient systems for reducing all R-O-O- groups (k).

Model reaction to eliminate active functional groups

Reducing model compounds I and II with a highly reactive agent lengthens their induction time (l).

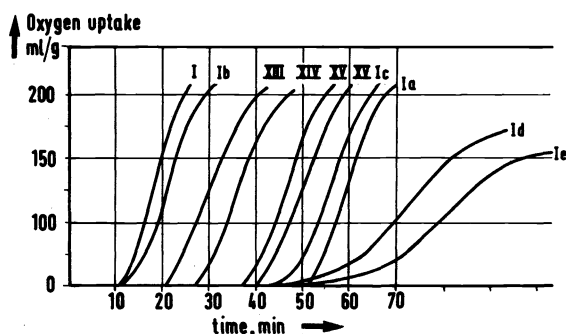
TABLE 6

Induction times for polyethylene containing reducing agents

No.	Type	Specification	Induction time in min
I	Low-density polyethylene		15-20
Ib	High-density polyethylene		20
Ia	Polymethylene	No functional groups	60
XIII	I reduced by SO ₂	Peroxides	25
XIV	I reduced by H ₂	or CO	35
XV	I reduced by H ₂ S	undetectable	40
XVI	I reduced by NaBH ₄	by IR	45
Ic	I stabilized with 0.1 % wt. of		45-50
Id	Ic + 0.1 % wt. (C ₄ H ₉) ₂ AlH		50
Ie	I + 0.1 % wt. of 17c + 0.1 % wt. of (C ₄ H ₉) ₂ AlH		50

*2,6-di-*t*-butyl-4-methylphenol

Fig. 5



Stabilization by different compounds and reactions

4. REQUIREMENTS IMPOSED ON ADDITIVES AND POLYMERS

There is no point in imposing utopian demands that would act only as an impediment, but the following demands are really important.

- 1) The components must be physiologically harmless. This applies not only to the additives themselves but also to their derivatives.
- 2) The additives must have high long-term efficiency.
- 3) They must be stable to heat and not migrate.

The ideal case occurs if the polymer itself has a sufficiently long life for the application concerned and does not require any stabilizer at all.

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