  Bull. Chem. Soc. Jpn., 61, 165—170 (1988)

Invited Paper

Antioxidants

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(Received September 3, 1987)

Antioxidants can be classified by the way in which they interfere with the process of autoxidation. Two main types can be identified; the chain-breaking antioxidants which either reduce the alkylperoxyl radical or oxidise the alkyl radical and the preventive antioxidants which either retard the breakdown of hydroperoxides (metal deactivators, UV absorbers) or destroy them by non-radical mechanisms. Synergism results from the complementary action of antioxidants when used together. Recent studies of antioxidant mechanisms have led to the discovery of "stable" redox systems which are able to catalytically scavenge alkyl and alkylperoxyl radicals in competition with the normal reactions of these species in autoxidation. The physical behaviour (solubility, volatility etc.) of antioxidants can dominate their behaviour under certain conditions and the development of polymer-bound antioxidants is believed to be a solution to antioxidant migration and loss.

The Significance of Autoxidation in Technological and Biological Processes. Most carbon-based materials deteriorate as a result of chemical reaction with oxygen of the environment. During the past century autoxidation has been shown to be a common factor in the loss of physical properties of rubbers and plastics, in the rancidification of fats and oils, in the deterioration of lubricating properties of hydrocarbon oils[1] and more recently reactive species involved in autoxidation have been implicated in a variety of diseases in vivo.[2–12]

The phenomenon of rubber "ageing" and the effects of very small amounts of added chemicals which were given the name "antioxygens" or "antioxidants" in inhibiting this process were observed at an early stage in the development of rubber as a technological material. Ageing of rubber was recognized by Ostwald to be associated with the absorption of oxygen in the early 1900's.[13] However, the understanding of the mechanism of oxidative deterioration remained obscure until the free radical chain reaction of autoxidation was proposed by Bäckström for benzaldehyde in the mid 1920's.[14] A key feature of the process (reactions (1)—(6)) is the formation of an intermediate peroxide[15] since this provided an explanation for the autoaccelerating oxidation rate curve which had first been observed by Genthe in 1906 in a study of the autoxidation of linseed oil.[16] The rate of autoxidation is now known to be directly related to the concentration of this species in many organic substrates and once it is present in the autoxidising system, no other initiator is required (reaction (1)).

Initiation

$$\mathrm{ROOH} \xrightarrow[(a)]{\Delta,\,h\nu} \mathrm{RO}\cdot + \cdot\mathrm{OH} \qquad (1)$$

$$\mathrm{RH} + \left.\begin{matrix}\cdot\mathrm{OH}\\ \cdot\mathrm{OR}\end{matrix}\right] \xrightarrow[(b)]{} \mathrm{R}\cdot + \left.\begin{matrix}\mathrm{H_2O}\\ \mathrm{ROH}\end{matrix}\right]$$

Propagation

$$\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{ROO}\cdot \qquad (2)$$

$$\mathrm{ROO}\cdot + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R}\cdot \qquad (3)$$

Termination

$$2\mathrm{R}\cdot \longrightarrow \mathrm{R\text{-}R} \qquad (4)$$

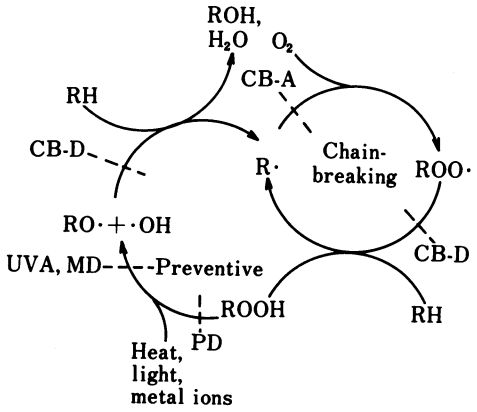
$$\mathrm{R}\cdot + \mathrm{ROO}\cdot \longrightarrow \mathrm{ROOR} \qquad (5)$$

$$2\mathrm{ROO}\cdot \longrightarrow \text{Disproportionation products} \qquad (6)$$

Since reaction (3) is normally rate determining, termination generally occurs by reaction (6) but important exceptions to this will be discussed below.

The oxidation of fats and oils has been studied by chemists for almost as long as polymeric materials. The pure linoleate esters were frequently used as chemical models of more complex oils and fats and indeed the understanding of the chemistry of cross-linking of drying oils and the deterioration of food stuffs resulted from early observations of the effects of oxygen on the 1,4 unsaturated fatty acids and their esters.[17,18] In recent years the full significance of this chemistry has begun to be appreciated by biologists and biochemists and to the scientist concerned with the durability of relatively stable systems it is a cause of wonder that nature has been able to develop such highly effective antioxidant systems in vivo. The chemical constituents of the lipids when isolated from their natural antioxidants undergo oxidative breakdown and cross-linking extremely rapidly and it is clear that man has much to learn from nature about the preservation of organic materials. Nevertheless, evidence is accumulating that the natural antioxidant defences of the body become less effective with age.[11] This results in increasing free radical activity in the cells and associated loss of elasticity of the cell tissues. There is strong evidence too that many of the diseases of old age, notably Alzheimer's disease,[10] Parkinsons disease,[12] artherio-sclerosis[12] and cancer[12] are associated with decreased oxidation resistance of the organisms involved.

There is clearly then a powerful motivation on the



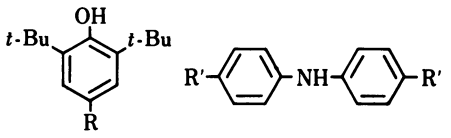
CB-A	Chain-breaking acceptor
CB-D	Chain-breaking donor
PD	Peroxide decomposer
UVA	UV absorber
MD	Metal deactivator

Scheme 1. Antioxidant mechanisms.

part of both technologists and biologists to a better understanding of how destructive oxidation processes may be inhibited. The following review aims to bring together the most important developments in antioxidant mechanisms that have occurred during the past thirty years.

Inhibition of Autoxidation. The autoxidation chain reaction outlined in reactions (1)—(6) can be conveniently reformulated in a way (Scheme 1) that illustrates in principle the means by which the kinetic chain can be inhibited.[19] It is clear from Scheme 1 that the process of autoxidation involves two distinct but interacting cyclical processes. The primary kinetic chain reaction involves the continuous regeneration of the chain propagating species, R· and ROO· but this cycle is continually replenished with new alkyl radicals as a result of homolysis (which may be light or metal ion catalysed) of hydroperoxides. From this formulation antioxidants may be broadly categorised into those which intercept the primary chain reaction, the chain breaking (CB) antioxidants, or those which prevent or retard the formation of initiating radicals, the preventive (P) antioxidants.[20]

Chain-Breaking Mechanism of Antioxidant Action. The alkyl and alkylperoxyl radicals display complementary behaviour.[21] Alkylperoxyl, ROO·, is an electron acceptor and can be readily reduced by hydrogen (or electron) donors. Provided the radical species produced by oxidation is stable and cannot continue the kinetic chain, this constitutes the chain-breaking hydrogen (or electron) donor (CB–D) mechanism of antioxidant action. Most CB–D antioxidants are hindered phenols or aromatic amines and representative examples used in technological systems are the 2,6-di-tert-butyl phenols (**1**) or diphenylamine derivatives (**2**).



1 **2**

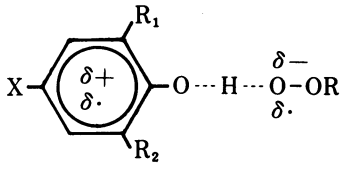
In the former, -R varies from a simple alkyl group as in BHT (R=methyl) to the much more complex multifunctional group (e.g. $C(CH_2OCOCH_2CH_2-)_4$ designed to meet the physical requirements (solubility, low volatility) of a polymeric substrate. In the diphenylamines, again the group -R′ varies widely and is frequently attached through nitrogen or oxygen.

A large amount of semiempirical information based on studies in hydrocarbon substrates has provided the following generalisation on the relationship between CB–D activity and structure.[20]

1. Electron releasing groups in the aromatic ring increase antioxidant activity, whereas electron attracting groups decrease it.

2. Substituents that delocalise the electron in the aryloxyl or arylaminyl radicals increase antioxidant activity.

These "rules" can be rationalised on the basis of the transition state (**3**) involved in hydrogen abstraction



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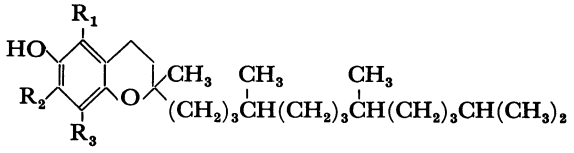
by alkylperoxyl. There is both partial separation of charge between the alkylperoxyl and the aromatic ring and partial delocalisation of the electron in the π bond system. Thus, groups in X and R_1,R_2 which release electrons or delocalise the impaired electron decrease the transition state energy.

A third generalization which has proved useful is that bulky groups which hinder the group from which hydrogen abstraction occurs improve antioxidant activity. This has been related to the steric stabilisation (non-reactivity) of the radical produced.[22]

The biological antioxidants, the tocopherols

Tocopherols	R_1	R_2	R_3
α	CH_3	CH_3	CH_3
β	CH_3	H	CH_3
γ	H	CH_3	CH_3
δ	H	H	CH_3



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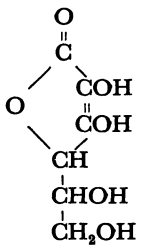
Ascorbic acid



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(Vitamin E) (**4**) and ascorbic acid (**5**) both act by the CB–D mechanism.

Although the aryloxyl derived from α-tocopherol is not as stable as many hindered phenoxyls, there is evidence that it can be readily reduced back to the parent phenol by ascorbic acid[23,24] and this cooperative interaction is believed to account for the synergism that has been obseved between these two CB–D antioxidants in the unsaturated fatty esters. Similar synergism has been observed in technological media.[25]

Although the chain-breaking donor mechanism of antioxidant action has been known for many years following the pioneering studies in the 1930s of Lowry and his co-workers,[26] very little attention was paid to the complementary chain-breaking acceptor mechanism until relatively recently. The main reason for this is that any oxidising agent for alkyl radicals is in competition with oxygen (see Scheme 2) and the CB–A process will only occur if alkyl radicals are present in the system at a concentration that makes this competition possible. CB–A antioxidants involve essentially the same radical trapping chemistry as polymerization inhibition in the absence of oxygen.[27] Among the more effective are quinones, nitro compounds and "stable" radicals; they are effective electron acceptors. These are precisely the species now recognised to be important as CB–A antioxidants.[28,29]

It was suggested some years ago[30] that an antioxidant which was capable of reversible oxidation and reduction could in principle behave as a catalytic antioxidant. The example quoted was the Cu^{2+}/Cu^{+} system since cupric salts were known to be antioxidants in some substrates. This antioxidant mechanism was subsequently shown to occur in paint media[31] where cupric acetate, which is used as a blue-green pigment, was shown to lead to the formation of conjugated polyunsaturation and brown discolouration in the paint medium.

The mechanism proposed is summarized in reactions (7) and (8) and was subsequently shown to

$$R\cdot + Cu^{2+} \longrightarrow [RCu^{+}] \longrightarrow \text{>C=C<} + Cu^{+} + H^{+} \quad (7)$$

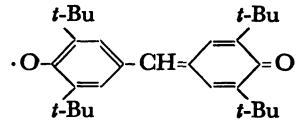
$$ROO\cdot + Cu^{+} + H^{+} \longrightarrow ROOH + Cu^{2+} \quad (8)$$

operate in polypropylene subjected to oxidation in a high shearing mixer when the oxygen concentration is low.[32] A side reaction which competes with this process and limits its practical usefulness at higher oxygen pressures when the hydroperoxide concentration is appreciable, is the well-known redox sequence involving hydroperoxide.

$$Cu^{+} + ROOH \longrightarrow Cu^{2+} + RO\cdot + OH^{-} \quad (9)$$

$$Cu^{2+} + ROOH \longrightarrow Cu^{+} + ROO\cdot + H^{+} \quad (10)$$

Nevertheless, the catalytic cycle summarised in reactions (7) and (8) has proved to be a useful model to explain the behaviour of a variety of oxidising species as antioxidants in oxygen deficient systems. Particularly interesting is the very high efficiency of "stable" oxyl radicals as melt stabilisers for polypropylene.[27] Galvinoxyl (**6**) and the nitroxyls derived from "hindered" piperidines (**7**) have been studied in



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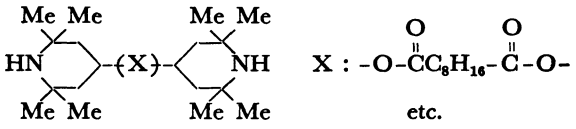

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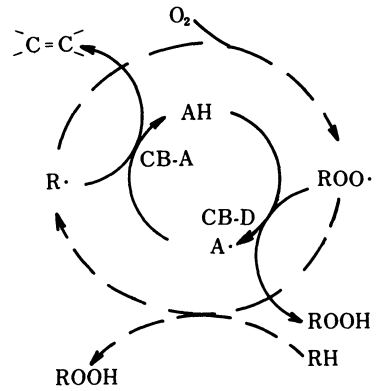

A· = Phenoxyl, nitroxyl, quinone, Cu^{2+}, I_2, ETC

Scheme 2. The chain-breaking antioxidant mechanisms.

Scheme 3. Mechanism of catalytic chain-breaking antioxidants.

some detail.[28,33–35] and the mechanism proposed is generalised in Scheme 3. Scheme 3 shows the competition between oxygen and the CB–A antioxidant (A·) for alkyl radicals and between the CB–D antioxidant (AH) and the substrate for alkylperoxyl radicals. The catalytic CB–A/CB–D mechanism has been shown to occur in polymeric substrates when the diffusion of oxygen into the system is limited and the oxygen concentration is therefore low.[28] The general conditions for its operation are:

(i) The antioxidant has two relatively stable oxidation states which can coexist in the substrate. These include aryloxyl and their cognate phenols, nitroxyls and their cognate hydroxylamines, quinones and their cognate semiquinones, iodine and hydrogen iodide and cupric, and cuprous ions.

(ii) Termination can occur through alkyl. It has been known for many years, since the pioneering studies of Bateman and his co-workers,[36] that hydrocarbons which oxidise to give resonance stabilised radicals terminate in part by reactions (4) and (5) up to relatively high oxygen concentrations. Limitation of oxygen diffusion which occurs widely in polymeric substrates also increases termination through alkyl radicals so that in photo-oxidation at ambient oxygen pressure, termination of macroalkyl by nitroxyl can readily occur.[28,37] A high rate of initiation by UV light may also lead to a higher macroalkyl concentration, again favouring the CB–A/CB–D process.

Nitroxyl radicals can be generated in situ in polymers by the spin trapping procedure.[38] Mechanical shear in polyolefins during processing gives rise to macroalkyl radicals which subsequently react with spin traps.[39,40] Thus 2-methyl-2-nitrosopropane (NTB) processed into polypropylene is an effective light stabiliser. Its photoantioxidant activity is directly related to the amount of nitroxyl produced in the polymer.[40]

The Preventive Mechanism. Scheme 1 indicates three main mechanisms of preventive antioxidant action. Two of these, the deactivation of metal ions and the absorption of UV light, are palliative and are therefore of limited effectiveness since they retard rather than inhibit the generation of free radicals from hydroperoxides. Many such compounds are in commercial use but most of them operate by more than one mechanism, thus displaying the phenomenon of autosynergism (i.e. they contain two complementary inhibitory functions in the same molecule). Thus the copper deactivator, **8**[41] and the UV stabiliser, **9**[42] are both CB–D antioxidants and the

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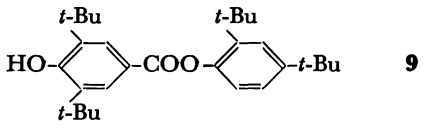

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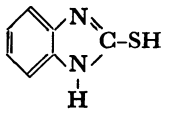
copper deactivator **10**[43] and the UV stabiliser **11**[44] are



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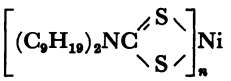

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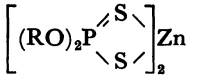
both effective peroxide decomposers. The decomposition of hydroperoxides by chemical reactions which do not lead to the formation of free radicals is by far the most important preventive mechanism of antioxidant action. It was first observed in hydrocarbon oils[45] and most modern lubricating oils contain a zinc dialkyl dithiophosphate (**12**) as a key stabilizing component. The mechanism of the metal dithiolates of which the dithiocarbamates (**11**) dithiophosphates (**12**) are typical has been extensively investigated in recent years[44] and they have been shown to function by being oxidised by hydroperoxides formed in the substrate to sulfur acids which in turn act as ionic catalysts for the further and complete destruction of hydroperoxides. Simple aliphatic sulphides (**13**) also act



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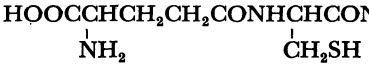
$(ROCOCH_2CH_2)_2S$

13

in the same way.[46] The chemistry is complex and the generation of the antioxidant species is preceded by the formation of intermediates which destroy hydroperoxides in a free radical process (Scheme 4). The early stages of the action of peroxide decomposing antioxidants are therefore often associated with prooxidant effects. Other sulphur antioxidants including the dithiolates, generate sulphinic, sulphonic and sulphuric acids in analogous processes.[44] Prior oxidation of the sulphur precursors has been shown in some cases to give rise to more effective stabilising systems.[47,48] Glutathione peroxidase (**14**) is a



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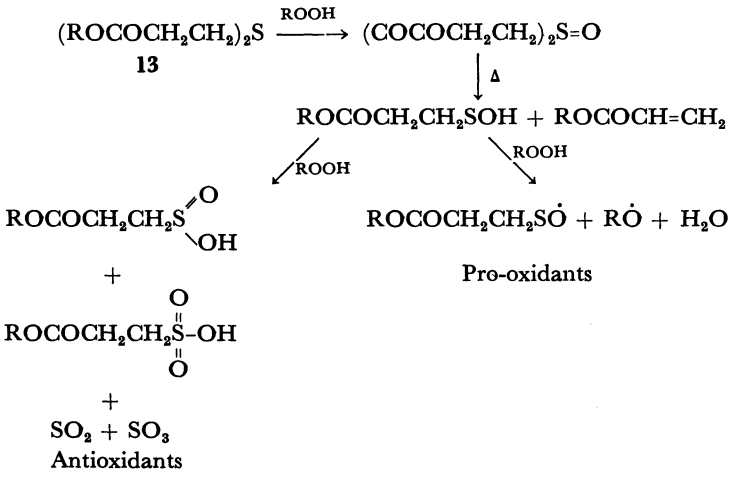
biological antioxidant with a formal resemblance to the synthetic peroxidases. However, it seems that its hydroperoxide decomposing mechanism is quite different from the latter, involving coupled single electron-transfer steps which reduce hydroperoxides to alcohols.[49]

Synergism. Reference to Scheme 1 suggests that preventive antioxidants and chain-breaking antioxidants should have a mutual protective effect on one another. This phenomenon, commonly referred to as



Scheme 4. Mechanism of sulfide antioxidants.

"synergism" has in practice proved to be of considerable importance in technological systems. A typical synergist used in the thermal-oxidative stabilisation of polypropylene is a combination of a typical high molecular weight hindered phenol (**1**) and a 3,3′-thiodipropionate ester.[50] However, synergism can also occur between preventive antioxidants. Thus, for example, it is known that the primary initiator in photo-oxidation is the hydroperoxide which is inevitably present as a result of the processing operation.[51] The generation of radicals by this process (reaction (1)) places a very severe strain on other antioxidants present. However, many peroxide decomposers and chain-breaking antioxidants are photolytically unstable and cannot survive for very long unless they are themselves protected against UV light.[52] UV absorbers have the ability to protect chain-breaking and peroxidolytic antioxidants against photo-oxidation and some of the most effective systems condtain a combination of peroxide decomposer, chain-breaking antioxidant (sometimes as in the case of the nitroxyls, catalytic) and a UV absorber.[53]

Physical Aspects of Antioxidant Action. In recent years, attention has turned from the organic chemistry to the physical chemistry of antioxidant behaviour. Homologous antioxidants containing the same functional group frequently behave very differently in technological systems and this phenomenon can be related to their physical behaviour, particularly solubility and volatility which determine their effectiveness.[54] In order to minimise such effects a good deal of attention is being directed to the chemical attachment of antioxidants and UV stabilisers to the polymer backbone. This can be done conveniently by copolymerization or by grafting of antioxidants to the polymer chain.[55,56] Considerable success has been achieved in producing polymers which are much less susceptible to high-temperature oxidation but which will also stand up to the rigorous conditions of oil or solvent extraction to which rubbers and plastics are often exposed in the technological environment.[56,57]

An important by-product of research into polymer-bound antioxidants is the discovery that in rubber modified plastics (e.g. ABS), antioxidants chemically attached to the more oxidisable rubber phase are several times more effective than conventional antioxidants. This is due to the fact that the antioxidants are located in much higher concentration in the rubber domains where they are required to act.[57]

Future Perspective. The study of antioxidants which began as an empirical art has now become a systematic scientific discipline to interpret disparate technological phenomena by unified chemical and physical concepts. The mechanisms elaborated over the past twenty years permit the selection of antioxidants to solve specific technological problems.

As polymers and other technological media are used under more and more severe conditions, it seems inevitable that durability will in the future be an important design factor. In the field of biology too, the prevention of random oxidation is seen to be increasingly desirable in the fight against disease. In the design of synergistic antioxidant mixtures and in the targeting of antioxidants to specific sites, the biochemist can profit from research in vitro. However, man has yet to learn how to mimic the complex single electron transfer peroxidases developed by nature.

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