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# POTENTIAL TOXICOLOGICAL PROBLEMS ASSOCIATED WITH ANTIOXIDANTS IN PLASTICS AND RUBBER CONSUMABLES

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Antioxidants and stabilisers are of critical importance in the manufacture and use of polymer artifacts. Most conventional additives are readily leached from plastics or rubbers by foodstuffs or body fluids with consequent danger associated with the potential toxicity in the body. Strategy for the development of biologically "safe" stabilisation systems for polymers are discussed and it is concluded that the attachment of the appropriate reactive functional group to the polymer backbone by "reactive processing" provides the best means of immobilising the functional group to leaching fluids without sacrificing its protective action.

KEY WORDS: Antioxidants, stabilisers, packaging, migration, reactive processing, polymer-bound antioxidants.

## THE ROLE OF POLYMERIC MATERIALS IN PACKAGING AND CONSUMABLES

The discovery of rubber as a technological material marked the beginning of the modern polymer industry. Many of the early uses of rubber which relied on its flexibility and resilience are still as important today as they were one hundred years ago. For example, the name of McIntosh, who discovered the rubberisation of fabrics, has now become part of the English language. The emergence of the rubber tyre made possible the development of the modern motor car and many smaller items from hot water bottles to rubber gloves which are an everyday part of modern living, would not have been possible without rubber.

The rubbers themselves whether natural or synthetic are, in pure form, generally biologically inert, but to make them into useful products involves the incorporation of considerable qualities of other chemicals, some of which are far from being harmless in biological environments. Apart from fillers and reinforcing agents, rubber requires vulcanising ingredients, lubricants and antioxidants to make them suitable for long-term service.[1]

Vulcanising agents, which include a variety of sulphur compounds including sulphur itself, have in general not caused too much concern over the years and have been used without problems in such sensitive items as babies bottle teats. However, some commercial antioxidants came under severe criticism in the 1960s and 70s as a

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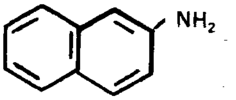

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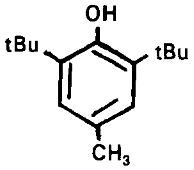
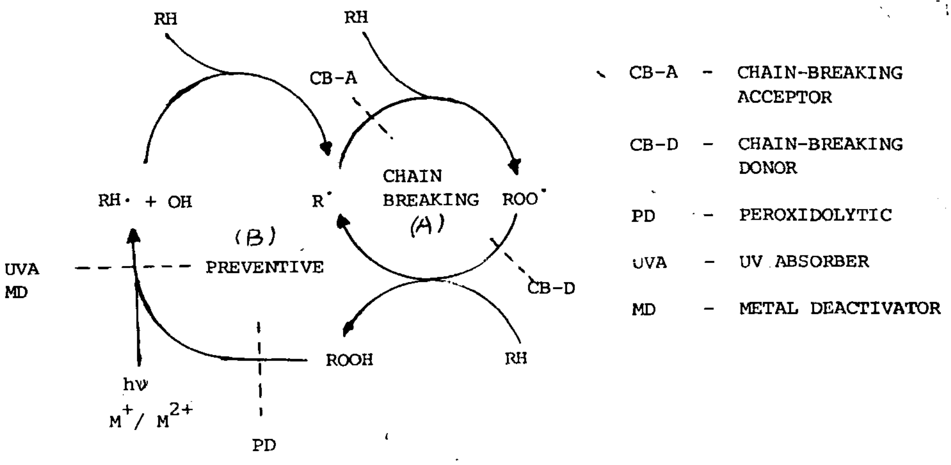


II, BHT

potential cause of cancer. β-Naphylamine (I) and its derivatives were particularly impugned and were eventually banned. The phenolic antioxidants, of which the food additive BHT (II) is most widely used, have not been implicated so strongly from the point of view of toxicity but recently it has been suggested that even BHT itself can cause cancer under certain conditions. The plastics industry is now moving away from low molar mass compounds of this type which leach readily from the polymer[2] to additives which migrate much less readily into the human environment. However, this is a self-defeating stratagem since it results in a decrease of solubility of the additive in the polymer with associated reduction of antioxidant activity. The present trend then is toward antioxidants which are chemically bound to the polymer substrate and hence "infinitely soluble" and which cannot be removed even under the most severe leaching conditions.[2]

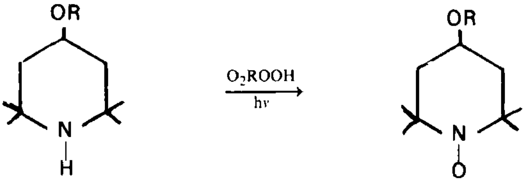
## OXIDATIVE DETERIORATION OF POLYMERS AND ITS INHIBITION

Before discussing in detail the problem of antioxidant migration from polymers it is appropriate to outline briefly why they are required. All polymers degrade in the presence of oxygen either during processing and conversion to consumer products or during use.[3,4] The same basic mechanism is involved in all cases and is essentially the same as that for the oxidation, of the lipids. The central feature of this is the radical



SCHEME 1 Mechanism of oxidation and the role of antioxidants.

chain reaction, scheme 1, cycle A.[4] The primary product of this process is the hydroperoxide (ROOH) which due to its weak 0–0 bond is the source of further initiating radicals in cycle B which feed back into the main cycle. Antioxidants can act in two ways. They can interfere with the main cycle by either oxidising alkyl radicals (CB-A mechanism), or by reducing alkylperoxyl radicals (CB-D mechanism). They may remove hydroperoxides or retard their breakdown to new initiating radicals (preventive mechanism). The arylamine and hindered phenols already referred to are examples of the chain-breaking hydrogen donor class. The chain -breaking hydrogen acceptor antioxidants are less well known but examples include processing stabilisers and UV stabilisers (e.g. III) which are oxidised to nitroxyls (IV) in polymers during UV exposure.



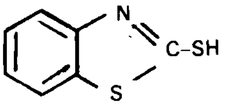
III IV (1)

The stable radicals of which the nitroxyls are typical, act as catalytic antioxidants by reversible reduction and oxidation between the reduced and oxidised forms (see scheme 2).[5]

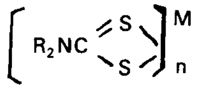
The peroxidolytic antioxidants are either stoichiometric reducing agents for hydroperoxides (e.g. phosphite esters) or they are sulphur compounds (e.g. V, VI) which are converted to low molar mass sulphur acids by oxidation with hydroperoxides,[4,6,7] so that like the hindered amines, they are converted to secondary products during use

$(ROCOCH_2CH_2)_2S$

V

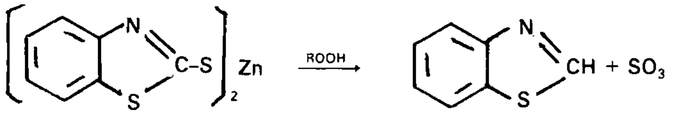


VI

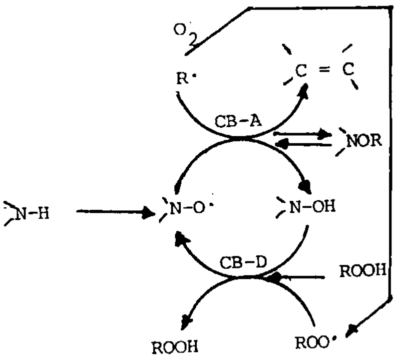


VIII

(e.g. zinc mercaptobenzothiazolate (VI). The latter are present as antioxidants in many rubber vulcanizates and are oxidised to other products during use. In general the toxicity of these derived products has not been examined.

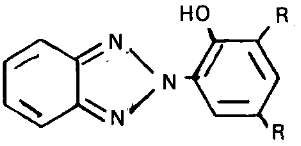


VI (2)

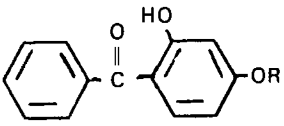


SCHEME 2 Catalytic antioxidant mechanism of 'stable' nitroxyls.

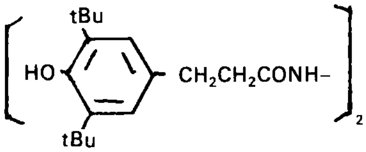
Similarly it is known that the UV absorbers IX and X and metal deactivators (e.g. XI) are oxidised during use and little attention has been paid to the toxicity of their oxidation products.



IX



X



XI

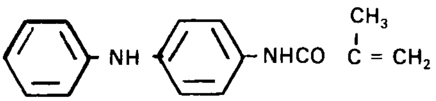
## THE DEVELOPMENT OF 'SAFE' ANTIOXIDANTS AND STABILISERS FOR FOOD CONTACT AND PROSTHESES

At present, every new antioxidant or stabiliser which is intended for use in an application where it may end up in the human body (including all food packaging materials) has to be exhaustively tested for toxicity. As indicated above, clearance in this test does not in itself guarantee that transformation products formed in the normal performance of its function will also not enter the body but so far this aspect of additive toxicity has been largely ignored.

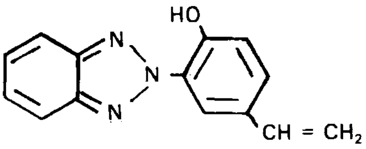
These circumstances together with other technical considerations arising from the relative ineffectiveness of low molar mass additives in polymers, has led to an intensive search in many countries for practical ways of combining antioxidants and stabilisers as part of the polymer molecule so that it cannot subsequently be lost to the environment of the artifact.

### *(a) Co-polymerisation of antioxidants and stabilisers.*[9]

Recently polymers have been produced commercially which contain randomly copolymerised antioxidants such as XII[10] and an extensive investigation is in progress in the USA on the copolymerisation of UV absorbers such as XIII with vinyl monomers to give vinyl polymers with built-in UV stability.[11,12] Although this approach is technically effective, its disadvantage is the high cost of the resulting polymers which put them beyond price range of conventional packaging.



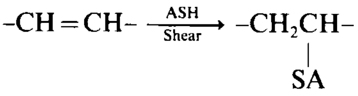
XII



XIII

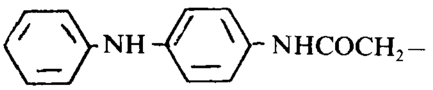
### *(b) Adduct formation in polymers by "reactive processing".*[13]

A much more convenient and economical way of achieving the same result is to attach antioxidants and stabilisers to the polymers through a reactive anchoring group by "reactive processing". Such a procedure is now being developed commercially involving addition of thiols to reactive double bonds in the presence of radicals formed in the polymer as a result of shear;[13] reaction.



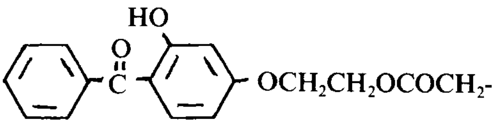
$$-CH{=}CH- \xrightarrow[\text{Shear}]{\text{ASH}} -CH_2\underset{\displaystyle SA}{\underset{|}{C}H}- \tag{3}$$

where A is an antioxidant group such as



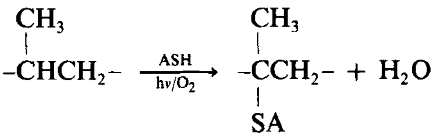
XIV

or a UV stabiliser group such as



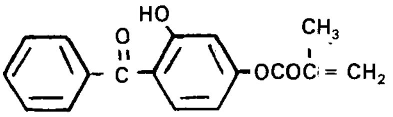
XV

This process is particularly convenient for rubbers and rubber modified plastics and under conditions of UV irradiation it can also be used in the saturated polymers such as polypropolene.[14] This process is summarised in reaction 4

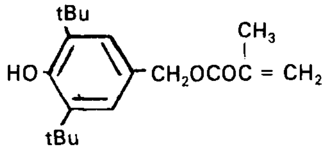


$$-\overset{CH_3}{\overset{|}{C}}HCH_2- \xrightarrow[h\nu/O_2]{ASH} -\underset{\underset{SA}{|}}{\overset{CH_3}{\overset{|}{C}}}CH_2- + H_2O \qquad (4)$$

Another reactive processing procedure which is the subject of intensive investigation, is the grafting of antioxidants containing a reactive vinyl group (e.g. XII, XIII), to



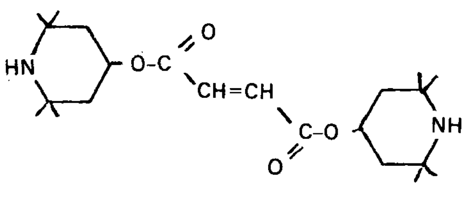
XVI



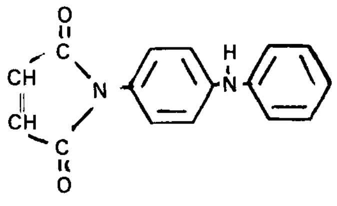
XVII

polymers in the prescence of a radical generator.[15] Many examples have been reported in the literature (e.g. XVI, XVII) but in general only a minor proportion of the active functional group becomes chemically attached to the polymer. The remainder homopolymerises and is much less effective as a stabiliser because it is present in an incompatible separate phase.

However, monomers containing a vinylene group tend to homopolymerise much less readily than vinyl compounds and it has been found that very high levels of adduct formation (>95%) can be obtained from bis maleic esters or amides[16] (e.g. XVIII, XIX).

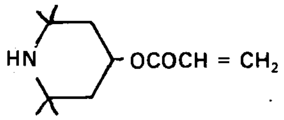


XVIII

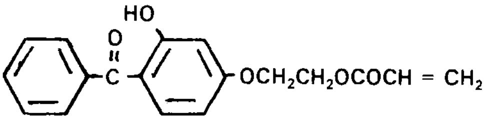


XIX

Very similar results have been obtained with the UV stabilisers XX, XXI, under special conditions.[17]



XX



XXI

A general advantage of the reactive processing procedure is that high concentration of bound stabilisers can be obtained in commercially available polymers and these can be used subsequently as normal additives during compounding and fabrication.[13,16] This procedure can in principle be applied not only to engineering polymers but to polymers normally used in packaging applications so that there is no danger of either the additive used or its transformation products being leached from the polymer by foodstuffs or biological fluids.

For particularly critical applications such as the use of polymers inside the body where absolutely no contamination from low molar mass chemicals can be tolerated over a period of many years, it is entirely feasible to exhaustively extract the concentrate before it is added to the host polymer. The evidence suggests that under these conditions, the artifact will be biologically inert as the virgin polymer without additives and experience to date suggests that for all practical purposes, polymer bound antioxidants and stabilisers are as effective and in some cases much more effective than conventional additives.[13,16,18,19]

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