CHAPTER - 1

INTRODUCTION

The degradation of polymers under normal use conditions is a major factor limiting application of these remarkable and versatile materials. Without exception, all polymers are degraded eventually within the environment to which they are exposed during their life cycle. Though there is considerable variation among polymers in their resistance to degradation, eventually important properties of every polymer are affected adversely as those chemical reactions responsible for degradation proceed.[1]

Oxidation of polyolefins in the absence of any additives results in rapid chain scission, cross-linking and formation of oxygen containing functional groups in polymers.[2-4] The typical manifestations of oxidation are summarised by the term ageing phenomena. On one hand, the manifestations of oxidation concern polymer appearance or aesthetics, eg., discolouration (yellowing), loss of gloss or transparency, chalking and surface cracks. On the other hand, there occurs more or less simultaneously, loss of mechanical properties such as impact strength, elongation, tensile strength, etc. With on going ageing, the characteristics of plastic articles are modified in such a way that they loose their usefulness.

The protection of polymers against atmospheric ageing and degradation is a pre-requisite for their successful technological development and application. Fundamentally, there are various means available to retard oxidation Out of these, addition of antioxidants is the most commonly used method of stabilisation. Antioxidants are chemical entities which retard oxidation and thus retard the resulting ageing of the polymer. Although plastics such as polyvinyl chloride (PVC), polyethylene (PE) and polystyrene (PS) have been produced on a large scale for more than fifty years, the efforts in research and development in the additives field are still quite intensive[5]

"**Antioxidants** " can be defined as substances capable of slowing the rate of oxidation in autoxidizable material. When antioxidants are added at the latex stage, as solutions, dispersions or emulsions, they are generally referred to as **stabilisers**

Such antioxidants are designed to inhibit specific steps in the free radical chain oxidation process. A simplified scheme for auto-oxidation is described by equation[6,7] (1-7).

Initiation $\longrightarrow$ Productions of radicals ....(1)

$nRO_2H \longrightarrow RO^{\cdot} + RO_2^{\cdot} + HO^{\cdot}$ ...(2)

Propagation :

$RO_2^{\cdot} + R - H \longrightarrow RO_2H + R^{\cdot}$ ....(3)

$R^{\cdot} + O2 \longrightarrow .RO_2^{\cdot}$ ....(4)

Antioxidants :

Termination :

$$\left.\begin{array}{l}2R^{\cdot}\\ RO_2^{\cdot} + R\\ 2RO_2^{\cdot}\end{array}\right]\text{stable products}\quad\begin{array}{ll}R - R & .\ (5)\\ R - O - O - R & .(6)\\ R - O - O - R + O_2 & ....(7)\end{array}$$

Equation 1 is important only during the very early stages of auto-oxidation. Radicals formed here gradually produce hydroperoxides,[8] which become the kinetically important initiators (eq. 2). Possible examples of early initiation steps include stress induced bond rupture as in polymer processing and fatigue,[9-12] bimolecular reactions of hydrocarbons with oxygen[13] and various photochemical processes.[14]

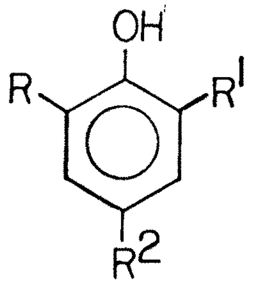
Auto-oxidation can be inhibited at the initiation and propogation steps. Antioxidants are often classified on the basis of their ability to do either or both.

Two General classifications can be made to categorize antioxidants :

(a) primary (chain terminating) antioxidants
(b) secondary (peroxide decomposing) antioxidants.

(a) Primary Antioxidants :

Antioxidants that interrupt the propagation step (eq.3) markedly reduce the oxidation rate The most important commercial antioxidants that function in this way are (i) hindered phenols, and (ii) secondary alkyl, aryl and diaryl amines, eg. structure **1** represents an important class of propagation inhibitors.



$R = R^1 = R^2$ = alkyl (same or different)

$R = R^1$ = tert-butyl.

They act as primary antioxidants by donating their reactive hydrogen (O-H, N-H) to free radicals, particularly to peroxy radicals.

$$ROO^{\cdot} + AH \longrightarrow ROOH + A^{\cdot} \qquad ....(8)$$

AH = Hydrogen donating antioxidant

To sufficiently terminate the oxidative processes, the antioxidant radical ($A^{\cdot}$) must be rendered stable to prevent the continuation of propogation of new radicals. These radicals, in most cases, are stabilized via their electron delocalization, or resonance, as is indicated in case of hindered phenolics like 2,6-di-tert-butyl-4-methyl phenol (BHT)[15] (Figure 1.1)

(i) Phenolic Antioxidants :

Hindered phenolics are most preferred type of primary antioxidants for thermoplastics. This group can be further categorised into the forms showed in Figure 1.2 Simple phenolics **2**, bis phenolics **3**, poly phenolics **4**, and thiobisphenolics **5**.

(ii) Amines :

Secondary aryl amines (Figure 1.3) function by hydrogen donation similar to the phenols However, at higher temperatures, they are also capable of decomposing peroxides[16]

Although members of the amine class of primary antioxidants are usually more effective than the chain terminators and peroxide decomposers, their use is limited to applications in which their discolouring characteristic can be tolerated or masked. Amines are perhaps most used

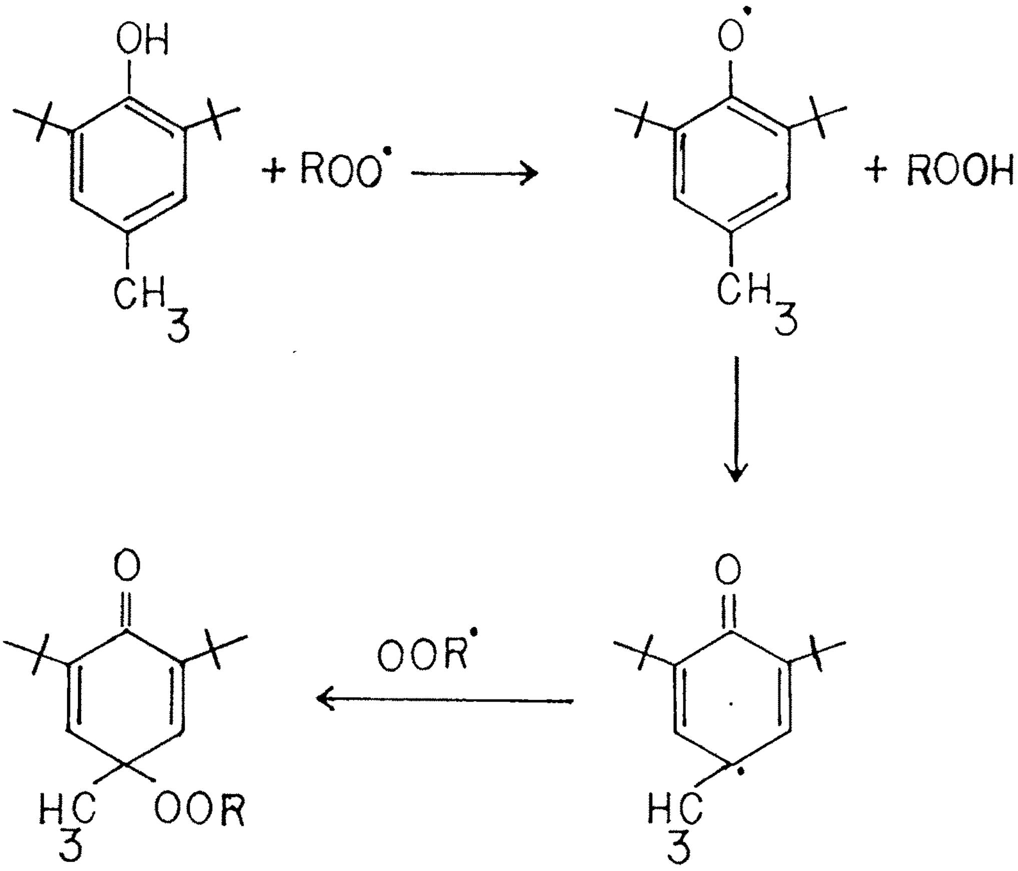
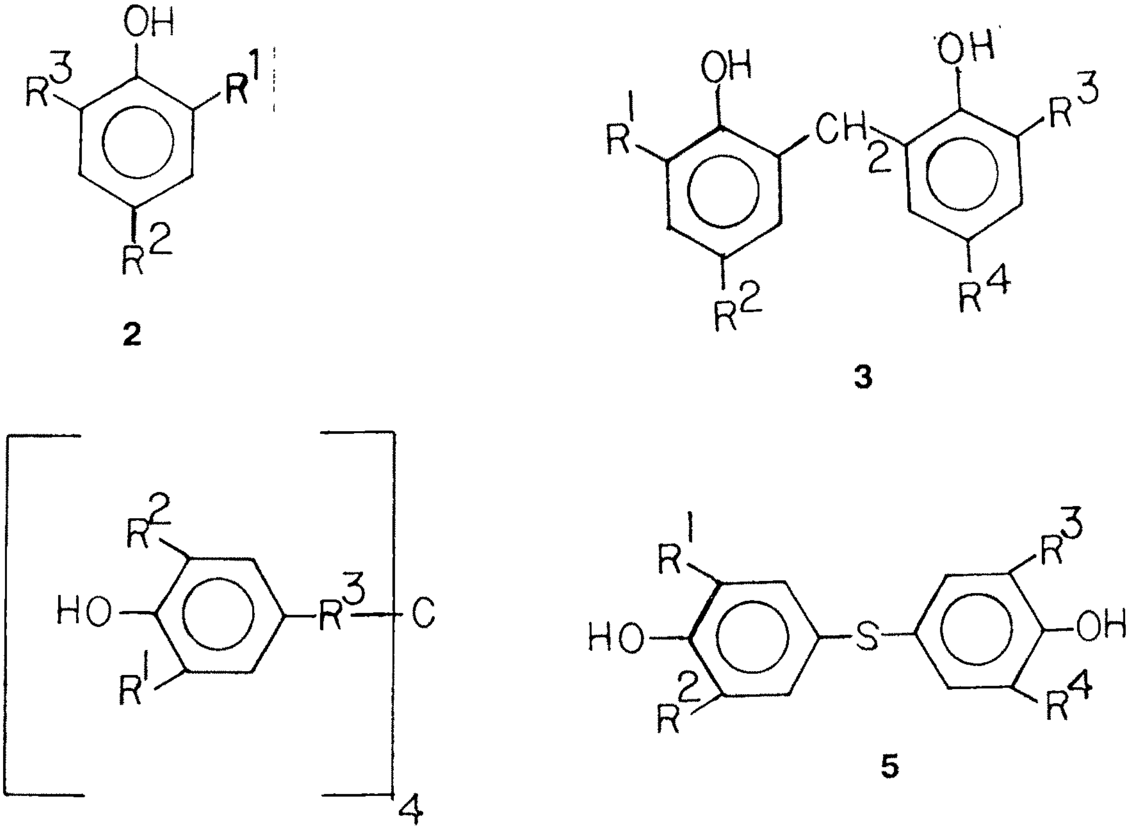


Figure 1.1 The Chain terminating mechanism of BHT, a hindered phenolic.



2

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4

5

Figure 1.2 Hindered phenolic types : Simple Phenolics 2 bisphenolics 3, Polyphenolics 4, thiobisphenolics 5,

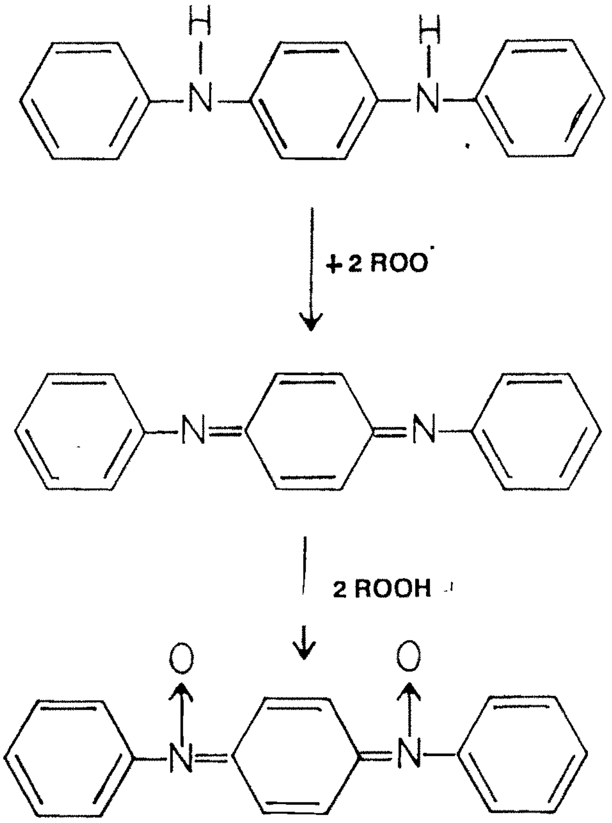


Figure 1.3 Antioxidant mechanism of secondary aryl amines

in unsaturated polymers containing carbon black. (Figure 1.4) e.g., diphenyl amine **6**, N,N'-diphehyl-p-phenylene diamine **7**, phenothiazines **8**.

(b) Secondary Antioxidants :

This class of antioxidants consists of various trivalent phosphorous and divalent sulphur containing compounds, most notable of which are organophosphites and thioesters The secondary antioxidants are also termed as preventive stabilisers, because they prevent the proliferation of alkoxy and hydroxy radicals by destroying hydroperoxides Two main classes of antioxidants inhibit the initiation step in thermal oxidation.[17]

(i) The peroxide decomposers :

Antioxidants that decompose hydroperoxides include sulphides, such as dialkyl thiodipropionates **9**, aryl phosphites **10** and metal salts of certain dithio acids such as zinc dithiocarbamates **11**, xanthates **12** and dithiophosphates[18-20] **13**.

$(RO_2CCH_2CH_2)_2S$ **9**

$(RO)_3P$ **10**

$(R_2NCS_2)_2Zn$ **11**

$(ROCS_2)_2Zn$ **12**

$[(RO)_2PS_2]_2Zn$ **13**

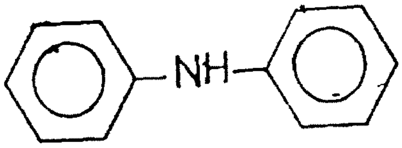
Phosphites function by reducing hydroperoxides to alcohols and thus, converting themselves to phosphates

$$(ArO)_3-P + ROOH \longrightarrow ROH + (ArO)_3-P \qquad ..(9)$$

Among the phosphites, most popular stabiliser is tris (nonyl phenyl) phosphite (TNPP) A serious drawback of phosphite is its sensitivity to hydrolysis. Hydrolysis of phosphites ultimately leads to the formation of phosphorous acid, which can cause corrosion of processing equipment.

(ii) Metal deactivators : (Preventive Antioxidants)

The ability of metal ions to catalyse oxidation can be inhibited by deactivators.[21] Homolytic decomposition of hydroperoxides is catalysed by traces of metal ions which are capable of undergoing one-electron, oxidation - reduction reactions.[22-25] (eq 10,11)



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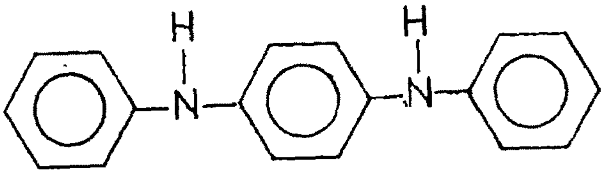

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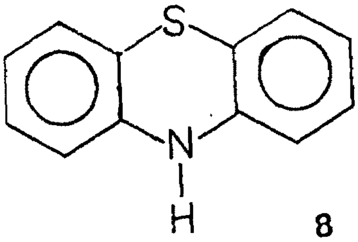

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Figure 1.4 Examples of Amine antioxidants

$$ROOH + M^{n+} \longrightarrow RO^{\cdot} + M^{(n+1)+} + HO^{-} \qquad ....(10)$$

$$ROOH + M^{(n+1)+} \longrightarrow ROO^{\cdot} + M^{n+} + H^{+} \qquad ... (11)$$

These additives chelate metal ions and increase the potential difference between the metal to produce radicals from hydroperoxides by oxidation and reduction.

The deactivation of metal ions by chelation operates by :

(i) Steric effect which blocks the hydroperoxide from the coordination sites on the metal ion
(ii) An electronic effect which preferentially stabilises one of the metal oxidation states [21]

However, chelation is not always effective and can sometimes enhance metal ion activity. The most effective metal ion deactivators are often polydentate chelating agents capable of forming very stable chelates in which all the coordination sites are occupied.[21,26]

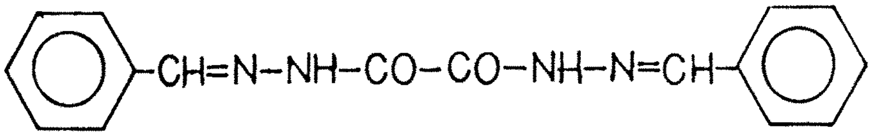
Examples of commercial metal deactivators used in polymers are oxallyl bis (benzylidene hydrazide) **14**, N,N' - bis (3, 5-di-tert-butyl-4-hydroxy hydrocinnamoyl) hydrazine **15**, 2,2'-oxamidobis ethyl (3, 5-di-tert-butyl-4-hydroxy)–hydrocinnamate **16** and ethylene diamine tetra-acetic acid **17**, and its sodium salts Figure 1.5.

Photo-oxidation and Stabilisation :

Hydroperoxides are important initiators in photo-oxidation. They are decomposed by solar radiation both photochemically (eq. 12) and thermally. A number of photochemical reactions can produce hydroperoxides early in the photo-oxidation process

$$RO_2H \longrightarrow RO^{\cdot} + HO^{\cdot} \qquad (12)$$

These include radical production from hydrocarbon oxygen charge transfer complexes,[27] Norrish scission of photoexcited carbonyls,[28] scission through photoexcited conjugated and isolated double bonds,[29] and from photoexcited catalyst residues.[30] Hydroperoxides can also form directly through an "ene" reaction of olefins with photochemically generated singlet oxygen. [31] Therefore, agents that protect substrates from photo-oxidation include those that reduce the amount of damaging radiation entering the substrate (uv-absorbers) and those which deactivate photoexcited chromophores by energy transfer (quenching agents) Most hindered phenols alone provide little protection, probably because they are rapidly decom-



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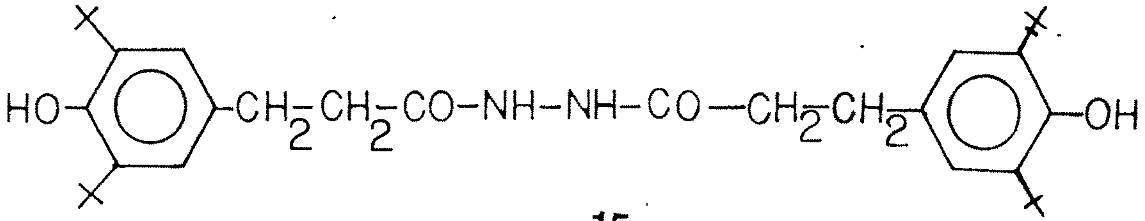

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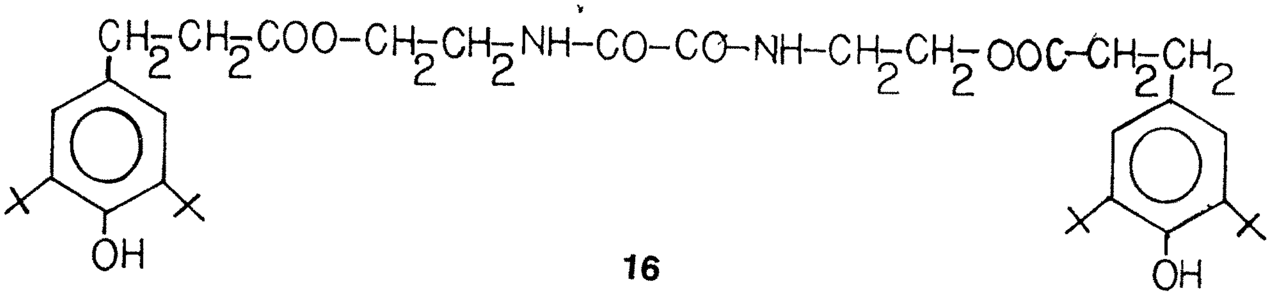

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$_2$(HOOCH$_2$C) N–CH$_2$–CH$_2$–N(CH$_2$COOH)$_2$

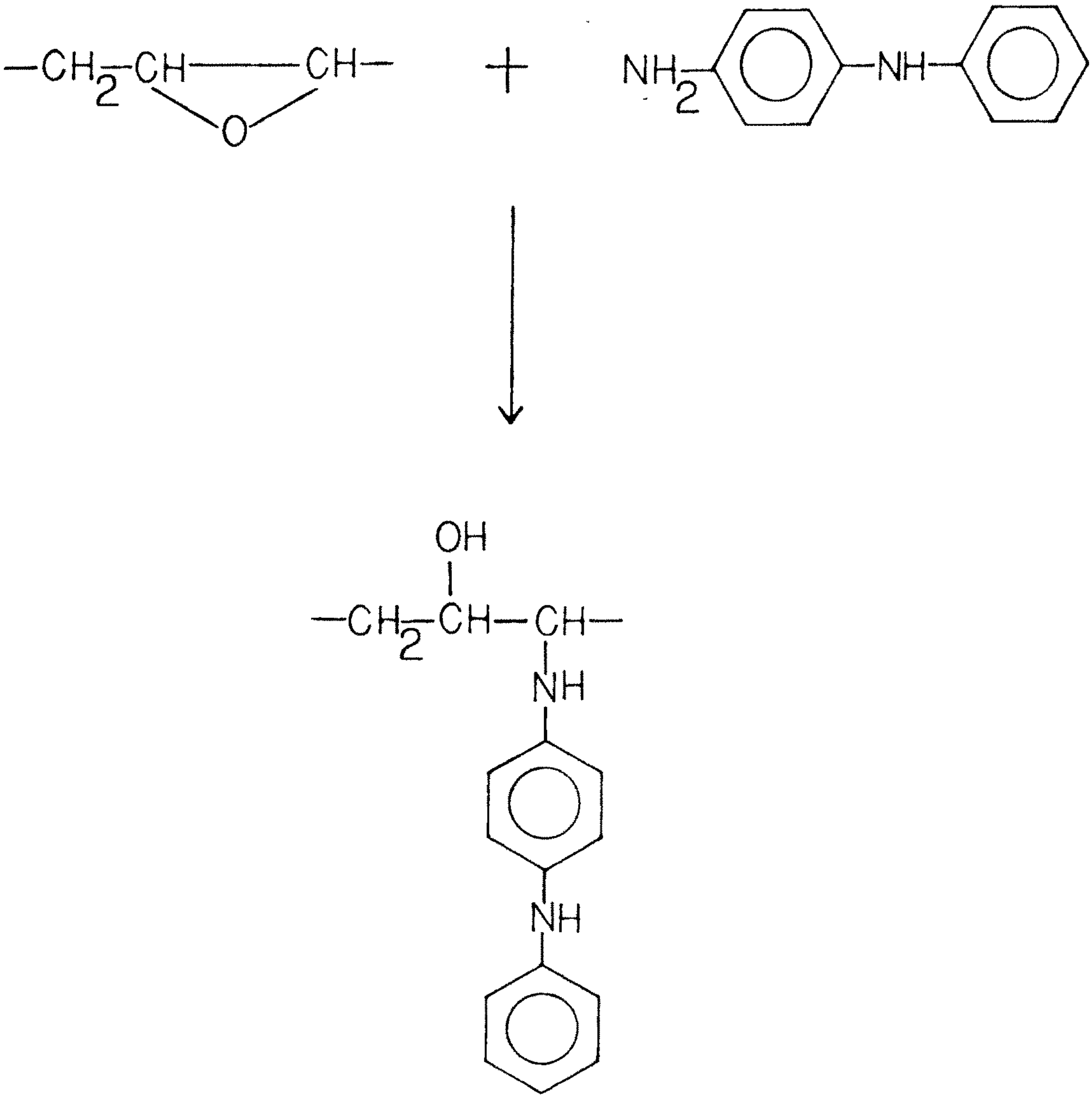
17

Figure 1.5 Examples of Metal deactivators.

posed under uv irradiation.[32-34] Nevertheless, combinations of uv absorbers (qv) and phenolic antioxidants can be synergestic and are commercially important.

Bound Antioxidants :

The chemical bonding of antioxidants onto polymer molecules would prevent migration and the accompanying loss of stabilizers. Antioxidants bound in this way would not be lost either through evaporation or solvent extraction Antioxidants have also been developed that are copolymerised into the elastomer chain.[35] Unexpected advantages of bound antioxidants have been observed due to the selective protection of the most oxidatively sensitive resins of the polymer in rubber modified polymer blends. The product formed in the following reaction is a typical sec-alkylamino diphenyl amine which is characteristic of the best rubber antidegradants. [36]



Antioxidant Combinations :

It is possible to obtain a high level of protection by using combination of two or more different stabilisers. In thermal oxidation the proper selection of antioxidants can provide very high level of protection. Combination of antioxidants may result in :

(i) a simple additive effect
(ii) antagonism
(iii) synergism.

(i) Additive Effect :

Usually when two or more antioxidants of the chain breaking type are used in combination, it results in simple additive effect. This effect, however, may exceed that obtained when the concentration of either component is increased two-fold. Two or more chain breaking antioxidants could provide better retention than higher concentration of either components. The combination of a short-term or processing antioxidant with one designed for long-term protection would be an example of such a combination.

(ii) Antagonisitic Effects :

Antagonism between antioxidants would be expected if interactions occur which would destroy or reduce the effectiveness of either component. Hawkins and coworkers,[37] observed an antagonistic effect when carbon black, used to protect against outdoor weathering, was combined with secondary amines or certain hindered phenols.

(iii) Synergism :

When combination of two or more antioxidants provide more protection than would be expected from the sum of that provided by the individual components, the phenomenon is refered to as synergism.

The most common synergistic combinations are mixtures of antioxidants, operating by different mechanisms. For example combinations of peroxide decomposers with propagation inhibitors are used in certain elastomers.

When a synergistic combination consists of two or more antioxidants, each functioning by the same mechanism but of an unequal activity, the phenomenon has been referred to as homosynergism. [38]

Example of homosynergism :

If AH is a highly reactive hindered phenol and A'H a less hindered phenol, hydrogen abstraction by peroxyl radicals is particularly fast with A'H. The phenoxy radical A' is rather reactive and may participate in chain transfer reaction such as given below.[39] (eq. 13 & 14)

$$A'^{\bullet} + RH \longrightarrow A'H + R^{\bullet} \qquad \text{... (13)}$$

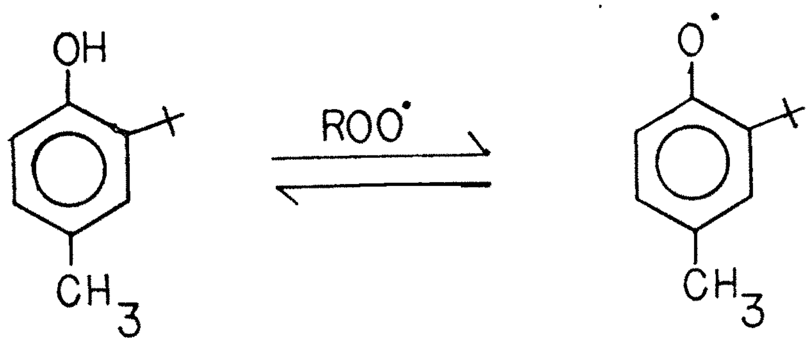
$$A'^{\bullet} + ROOH \longrightarrow A'H + RO_2^{\bullet} \qquad \text{...(14)}$$

In the presence of more hindered phenol AH, $A^{\bullet}$ can also enter the exchange reaction 15.

$$A'^{\bullet} + AH \longrightarrow A'H + A^{\bullet} \qquad \text{....(15)}$$

In reaction 15, the equilibrium is displaced to the right- hand side, because the highly hindered phenoxy radical $A^{\bullet}$ is less reactive than the less hinered phenoxyl radical $A'^{\bullet}$

Homosynergism has been observed [40] with combination of two hindered phenols, acting as chain-breaking antioxidants. The more effective phenol (I) is the primary deactivator of propogating radicals. The less active phenol (II) acts as a reservoir for labile hydrogen to regenerate the primary antioxidant. Here two phenols differ in the size and number of the ortho substituents which effect the ease of hydrogen abstraction. Phenol (I) has less hindrance adjacent to the labile hydrogen and is therefore more effective. Since it is regenerated from its radical by abstraction of hydrogen from (II) it is not depleted as rapidaly.



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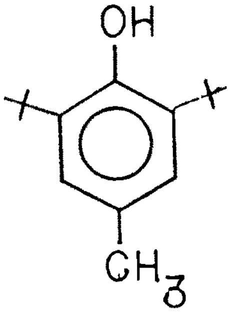

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Heterosynergism involves two or more antioxidants acting at different steps in the degradation mechanism. Most combination of this type consists of a preventive and a chain-breaking antioxidant.

The Degradation and Stabilization of Polymers :

Polymeric degradation typically occurs via a free radical process.[41] Chemical bonds whether they are within the main chain of the polymer or in the side groups, can be dissociated by energy resulting from heat, mechanical shearing or radiation to create a free radical ($R^\bullet$) This "initiation" of ($R^\bullet$) can occur in any one of the various phases of a polymer's life cycle polymerization, processing, and end use.

Propogation occurs when atmospheric oxygen reacts with ($R^\bullet$) to form a peroxy radical ($ROO^\bullet$). This peroxy radical can further react with labile hydrogens of the polymer to yield an unstable hydroperoxide followed by homolysis of the O-O bonds to give two radicals which lead to autocatalysis (eq. 16-21)

$$R^\bullet + O_2 \longrightarrow ROO^\bullet \qquad ...(16)$$

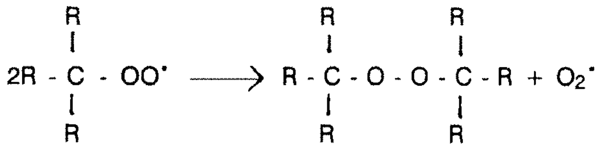
$$ROO^\bullet + RH \longrightarrow ROOH + R^\bullet \qquad ....(17)$$

$$ROOH \longrightarrow RO^\bullet + OH^\bullet \qquad ....(18)$$

$$RO^\bullet + RH \longrightarrow ROH + R^\bullet \qquad ....(19)$$

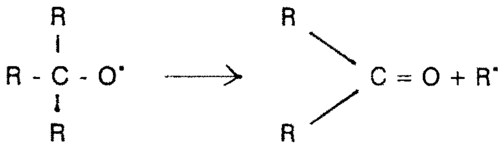
$$HO^\bullet + RH \longrightarrow HOH + R^\bullet \qquad ....(20)$$

Auto-oxidation will progress until termination results from the formation of stable products such as in the following :



$$2R-\overset{R}{\underset{R}{C}}-OO^\bullet \longrightarrow R-\overset{R}{\underset{R}{C}}-O-O-\overset{R}{\underset{R}{C}}-R + O_2^\bullet$$

....(21)



..(22)

Equation 21 represents crosslinking, which increases the molecular weight of the polymer; this type of degradation manifests itself as brittleness, gelation and decreased elongation Chain scission (eq. 22) results in a decrease in molecular weight, leading to increased meltflow and reduced tensile strength.

Polymers are normally processed in the molten state and thus are exposed to elevated temperatures, albeit for only short intervals. Sites of incipient degradation, formed during processing, lead to eventual failure under conditions of normal use. Short-term or processing antioxidants are designed to provide protection during processing or fabrication into finished products. [42]

The Degradation and Stabilization of Isotactic Polypropylene :

Since our study pertains to hindered phenolic antioxidants useful for stabilisation of isotactic polypropylene, we discuss here the mechanism of degradation and stabilisation of IPP

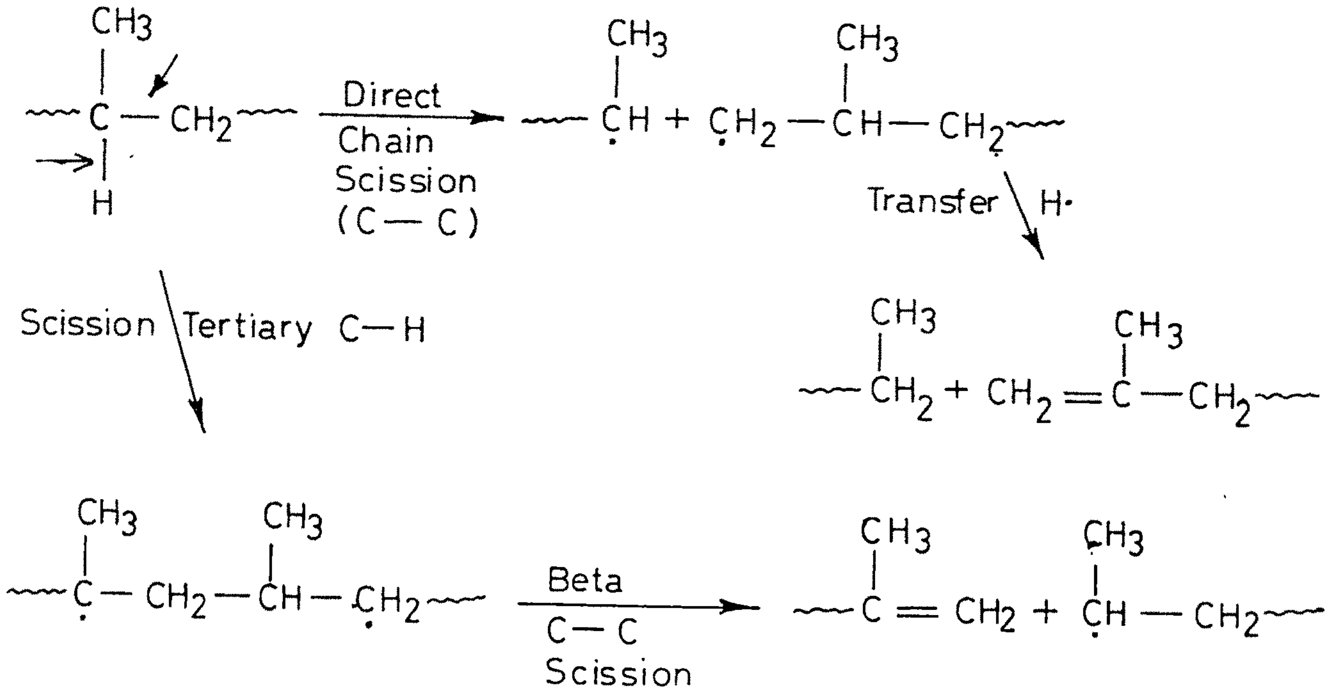
Thermal Degradation of Polypropylene (in abscence of oxygen)

The relative ease with which polypropylene suffers chain scission on thermal treatment, e.g during processing, depends to a large extent on their basic structure. In the complete absence of oxygen, purely thermal degradation in polypropylene is significant at temperatures above 270 °C. However, even when an extruder is operating at normal temperatures of well below 300 °C, the shearing action will cause local 'hotspots' that could easily be 50°C higher.[43] Thermal degradation could take place either by direct C-C bond scission and subsequent hydrogen transfer (Scheme 1) or via β-scission after C-H rupture. A relatively small number of alkyl radicals will be directly formed in an extruder by shear processes.

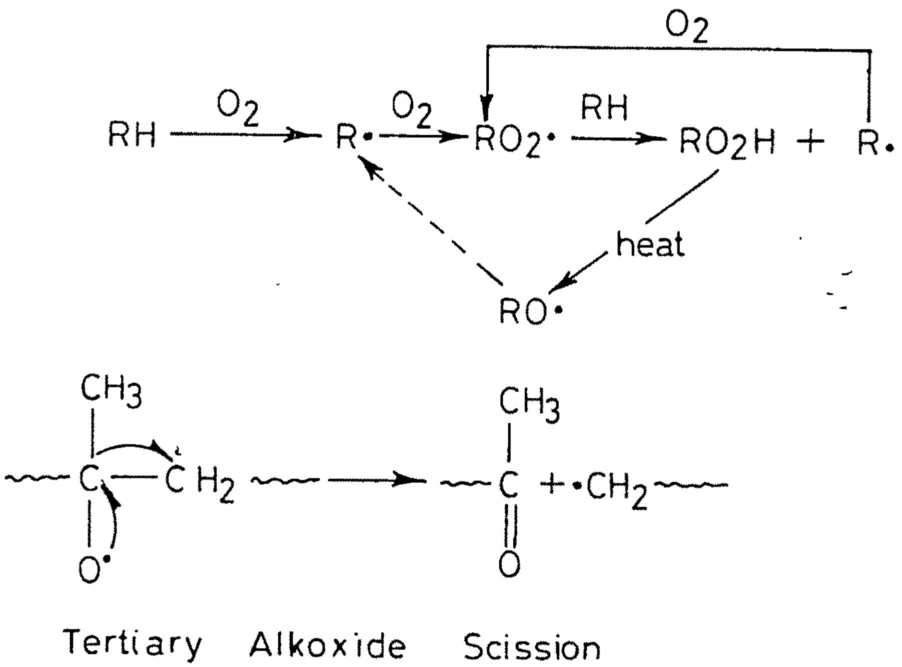
Thermo-oxitative Degradation of Polypropylene : (In presence of oxygen).

In presence of measurable amounts of oxygen, which applies to the present work, the well known[44-45] initiation, propogation and termination sequences occur, as summerised in Scheme 2.

Once an alkyl radical is formed, it will react with oxygen, even at very low partial pressure, to give the alkylperoxy radical. This is converted by radical exchange to give a hydroperoxide, which in turn will cleave to an alkoxy radical. In polypropylene, reduction in molecular weight



Scheme 1 Thermal secission of Polypropylene



Scheme 2 Degradation of Polypropylene (RH) in an Extruder.

is caused principally by fragmentation of this tertiary alkoxide radical to give a ketone, regenerating a primary alkyl radical which after rearrangement can once again take part in the original scheme.

The auto-oxidation of polyolefin is a branch chain reaction in which the chain carriers are alkyl and alkyl-peroxy radicals whose relative concentrations depend upon temperature and oxygen pressure. In principle this chain can be interrupted by components which trap either alkyl or alkyl-peroxy radicals. A very wide range of conventional radical trapping agents is effective in melt stabilisation[43]

As might be expected alkyltraps are relatively poor antioxidants in oxygen-rich end-use conditions where alkyl- peroxy radicals are expected to dominate. In such cases alkyl-peroxy traps are widely used, the commonest being those based upon 2,6-di-tert-butyl phenol. These and related antioxitants function by donation of the hydroxyl hydrogen to the peroxy radical to produce a radical which is too stable to reinitiate oxidation.[46]

It has been reported that tert-butyl group in the ortho position and alkyl group at the para position results in the most effective antioxidant activity in the alkyl phenolic type of antioxidants of which 2-6-di-tert-butyl-4-methyl phenol (BHT) is one of the best known[47]

Several methods are reported for the synthesis of BHT.[48-54] Out of these, the most commonly used method is alkylation of p-cresol with $Me_2C = CH_2$ generated by catalytic decomposition of $ROCMe_3$ ($R = HMe$, Me_2CHCH_2). By passing $MeOCMe_3$ at 140°C through a phosphate catalyst, cooling the products, and feeding the nonocondensing gaseous component at 80°C into p-cresol in presence of H_2SO_4 gave 80% BHT In a parallel experiment approximately equal BHT concentration in the product was obtained by alkylating p-presol with $Me_2C\ CH_2$

Applications of Antioxidants :

Antioxidants are widely used in elastomers, plastics, gasoline, synthetic lubricants, adhesives, food products, animal feed etc.[55]

Elastomers :

The use of antioxidants in raw and cured rubber is essential in order to retard oxidative deterioration promoted by heat, light and oxygen. Styrene-butadiene rubber (SBR) must be protected with an antioxidant in the polymerisation step. This ensures easy processing, good storage stability, and high quality cured end products. Phosphites and p- phenylenediamines are used as stabilisers for both SBR and butyl rubber. Cured and uncured rubbers insufficiently protected with antioxidants differ considerably in the manner by which they degrade oxidatively. Isoprene and butyl rubber soften by chain scission or depolymerisation, whereas SBR, neoprene, butadiene and acrylonitriles become stiff and brittle because of cross linking or polymerisation. However, there are speciality antioxidants, such as the mercaptobenzimidazoles for nitrile rubbers and nickel dimethyldithiocarbamate for epichlorhydrin rubber. In general, phenolics are not used in cure recipies for dry rubber because of their low activity. However, they are employed when minimum discoloration is required. Diphenylamine and phenylene diamine types are particularly important because of their ability to retard fatigue or flex- cracking in tires and belts.

According to Babayan et al.[56] the heat resistance to rubber based composition could be improved by the use of N,N'-bis (3,5-di-tert-butyl-4-hydroxy benzyl) methyl amine.

Plastics :

The commercial success of most plastics depends on proper stabilisation by antioxidants or other additives incorporated by extrusion or of powder blends or by milling. Low-density polyethylene used for making disposable garment bags does not require the use of an antioxidant. A general purpose antioxidant, such as 2,6-di-tert-butyl-4-methyl phenol (BHT), is adequate for low-density polyethylene. Relatively nonvolatile polynuclear phenols, phenylene diamines or bisphenol sulfides are frequently used for electrical application such as wire and cable insulation.

Polypropylene or propylene copolymers are far more difficult to stabilise than polyethylene because of the presence of an easily oxidised tertiary hydrogen. In general, antioxidants recommended for polypropylene and copolymers include phenolics, thiodipropionates, phosphites, phenylenediamines and dithiocarbamates.[57]

Polyvinyl chloride (PVC) can be protected adequately with a wide variety of stabiliser systems which are comprised primarily of acid acceptors such as metallic soaps.[58]

Other important plastics are stabilised by a variety of systems. Impact polystyrene is best protected with BHT Although acrylonitrile butadiene-styrene (ABS), is produced in smaller volume [59] than any of the four resins, the total antioxidant requirement is largest.[60]

Sterically hindered amines have been used as stabilisers against thermal oxidation of low density polyethylene at high temperature as reported by Dobrescu and coworkers.[61]

Boehshar and Coworkers [62] synthesised tetrakis (2,4-di-tert- butyl phenyl) 4,4'-bis phenylene diphosphonite and used as stabiliser for polypropylene.

Chemeta et al.[63] reported the use of organic phosphites combined with hindered amine light stabilisers (HALS) as stabilisers in the photo and thermal oxidation of isotactic polypropylene.

3-Phenyl-benzofuran-3-ones, prepared by reaction of mandelic acid with 2-(1-hexadecylethyl) phenol at low pressure were used as polymer stabilisers by Dubs and Pitteloud. [64]

Gasoline :

Unprotected, stored gasoline discolours slowly and gums are deposited because of oxidation and polymerisation. Gasoline containing such gums causes valve sticking, plugged fuel jets, and in general, lowered motor efficiency. The effect of copper on gasoline is particularly deleterious since only trace amounts promote oxidation via peroxide decomposition The combination of an antioxidant capable of decomposing peroxides and a metal deactivator are the prime requisites for optimum stabilisation of gasoline BHT and N,N'-di-sec-butyl-p-phenylenediamine are widely used for gasoline. The salicylidene is an effective copper inhibitor for gasoline

α-Methylbenzylideneoctadecylamine as antiwear and antioxidation for hydrocarbon fuel was reported by Bebikh et al.[65]

Morris and Coworkers [66] showed the effects of stabiliser additives on the thermal stability of jet fuel. The behaviour of several types of fuel stabilisers like phenylenediamine, an aliphatic tertiary amine and metal deactivator was examined in thermal stress of a jet fuel in modified JETOT.

Lubricants :

Next to fuels, lubricants and lubricating oils are the second most important class of material which require antioxidant protection. Many of them function at high temperatures and are best protected by phenolic and aromatic amine antioxidants such as dioctyl diphenyl amine and phenyl α - naphthyl amine. Hydraulic fuels are protected by phenolic antioxidants such as BHT or aromatic amines. Synergic effects are also obtained by mixture of antioxidants. At the same time gear oils are protected by sulphur or sulphur-phosphours containing additives, although at a greater concentration, greases are protected by phenolic amine or multipurpose sulphur containing compounds such as metal dialkyl dithiocarbamate, gasoline or disel engine oils are adequately protected by zincdithiophosphate **13**.

Dißase and Coworkers [67] reported that sulphur containing compounds are useful as general purpose antioxidants and friction modifiers for lubricating compounds and automatic transmission fluids and as additives especially in metal working lubricants. They prepared lubricant by sulphurizing fatty acid ester of a polyhydric alcohol.

Cardis and Coworkers [68] reported alkyl benzenesulfonyl derivatives of N,N-diorganodithiocarbamic acids as multifunctional additives for lubricating oils.

Adhesives :

The water-based adhesives may be formulated with polymers such as acrylates and carboxylated neoprene which have good inherent stability. Hot-melts are subjected to decomposition as evidenced by the development of discoluration, skinning, charring, or change in viscosity The ideal antioxidant should maintain the original properties of a hot melt, and also be thermally stable, permanent, nontoxic, and meet FDA requirements. Phenolic antioxidants and phosphites or blends there of are apparently preferred for the majority of hot- melt systems. Tri – and tetrafunctional phenolic antioxidants were developed for less stable polyolefin systems, such as amorphous polypropylene based hot melts. The loss of antioxidants from hot melts emphasizes the need for new types of antioxidants.

Food Products :

Flavour and odour of many foods deteriorate rapidly in the presence of oxygen. Again, the flavour and odour of carbonyl compounds, derived from auto-oxidation of food lipids are perceived as rancid.

The selection of the antioxidant is based on the substrate, its method of preparation, packaging, and distribution. It is important that the antioxidant is added to the fats and oils or intact food before oxidation has started. Antioxidants in cooking oils are used primarily for their carry-through and stabilising effect on the fried product. This property of carry through is essential for the success of several commercial fried foods.[69] The most widely used antioxidant in food is BHT. Moreover synergism with mixed antioxidants is frequently demonstrated [70] and standard commercial synergistic mixtures are available. Many also contain chelating agents, such as citric acid for metal ions in fats and oils or sodium tripolyphosphate for meat system.[71,72]

Chiba and Coworkers [73] reported the use of organic acid, salts of amino alcohols $[RCH(NH_3)^+(CH_2OH)]A^-$ (R = lower alkyl, A = organic anion) as highly effective for oils and oily foods. They are highly thermostable and nontoxic compared with other conventional antioxidants.

Noor and Augustin [74] reported the effectiveness of antioxidants on the stability of banana chips. The effectiveness of BHA and BHT in improving the stability of banana chips stored at 65°C was compared. Chips fried in refined bleached and deodorized (RBD) olein containing BHA or BHT were reported to be more stable than chips fried in RBD olein without antioxidant. Antioxidants for foods and edibles have also been reported by Sree and Lal [75], who used BHT to stabilise Ghee (vegetable oil) during its clarification from butter and its storage

Animal Feed :

Antioxidants are used in animal feeds to retard the oxidation of vitamins A and E, carotene, xaninophyll pigments, and to stabilise rendered animal feed fats and vegetable oils commonly used to increase energy density. Codliver oil has been mixed with BHT to prevent the oxidation of vitamin A, present in the fish oil.[76]

Some of the relatively lesser known application of antioxidants are in the medical field. Antioxidants have been found to prevent the oxidative degradation of eye lens and cataract.[77] Lam and Coworkers[78] have shown antitumor properties of 3,5-bis-(3,5-di-tert-butyl-4-hydroxy benzyl)-2,3,6 trimethyl benzyl derivatives. Takahashi[79] reported a decrease in blood coagulation by oral administration of BHT. Antioxidants have also been found to improve cardial resistance. Meerson [80] reported that BHT is effective in preventing heart damage due to acute overload.

Gannushkina and coworkers [81] have shown effectiveness of the versatile antioxidant BHT in reducing cerebral oedema and cerebral ischema.

BHT has also been found to be a potent inactivator of viruses. Reimund[82] suggested that BHT disturbs the lipid envelope of virus, there by inhibiting its absorbance in host cell This is a very important finding because the virus responsible for aids contains a lipid envelope and BHT may prove to be an effective weapon against this dreaded disease.

Naturally occuring antioxidants e.g. phenolic fraction extracted from Arenica foliosa has been found to be effective in reducing the damage to liver on large doses of tetracycline.[83]

Other miscellaneous applications include cosmetics, spice powders and organic extracts reported by House food industries.[84]

The synthesis and application of antioxidants based up on hindered phenols is reviewed in chapter 2.

Proposed Work :

By considering the various applications of antioxidants, it was thought worth while to synthesise new antioxidants and to evaluate the stabilisation efficiency of these antioxidants. The present study pertains to antioxidants based upon hindered phenols which are useful in polypropylene. Of all the known types of antioxidants for PP the 2,4,6-trialkyl phenols appear to have the best combination of properties. They have high potency, good combatibility with the polymer, excellent resistance to gas yellowing, and high degree of chemical resistance to acids, bases, oxidising agents and the like. However, most of the commercial 2,4,6-trialkyl phenol antioxidants are so low in molecular weight that their consequent volatility makes them of little use in high temperature applications.[85] It is already mentioned that out of the hindered phenols, 2,6-di-tert-butyl-4-methyl phenol is one of the best known. However it suffers from a major drawback viz. high volatility. It is reported that the high volatility could be minimised by increasing the length of the side chain at the para position of OH group of BHT[15]. In the present work the structure of BHT is modified by replacing the hydrogen atom of the methyl group at the para position by different groups of high molecular weight. This was achieved by converting the methyl group into an aldehyde by using a method reported in the literature by Coppinger and Campbell.[86] The aldehyde was converted into acid hydrazones,semicarbazone and thiosemicarbazone by reacting with appropriate reagents. Semicarbazone was cyclized to oxadiazole. The aldehyde was also converted into pyrazole derivative.

The performance of some of the synthesised antioxidants with isotactic polypropylene is evaluated by using the following methods.

1. Melt-mixing.
2. Multiple extrusion
3. Melt flow index
4. Differential scaning calorimeter

Mechanical properties like :

(a) Izod impact strength (b) Heat deflection temperature

(c) Tensile strength and modulus (d) Flexural strength and modulus.

The second chapter of the thesis deals with the synthesis and characterisation of some new antioxidants.

The third chapter of this thesis consists of evaluation of antioxidant activity of selected synthesised antioxidants with the stabilised isotactic polypropylene.

The last chapter of the thesis comprises of the study of selected synthesised antioxidants with unstabilized IPP.

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