

**SYNTHESIS, CHARACTERISATION AND USES
OF POLYMER- BOUND ANTIOXIDANTS**

Thesis submitted to the
**COCHIN UNIVERSITY OF
SCIENCE AND TECHNOLOGY**

by

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*in partial fulfillment of the requirements
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DOCTOR OF PHILOSOPHY

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TECHNOLOGY
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KOCHI - 682 022**

MARCH 2002

Certificate

This is to certify that this thesis entitled "Synthesis, Characterisation and Uses of Polymer-bound Antioxidants" is a report of the original work carried out by Smt.Sulekha P.B. under my supervision and guidance in the Department of Polymer Science and Rubber Technology. No part of the work reported in this thesis has been presented for any other degree from any other institution.



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20th March 2002

DECLARATION

I hereby declare that the thesis entitled "Synthesis, Characterisation and Uses of Polymer-bound Antioxidants" is the original work carried out by me under the supervision of Dr. Rani Joseph, Professor, Department of Polymer Science and Rubber Technology, Kochi 682 022, and no part of this thesis has been presented for any other degree from any other institution.



Sulekha P.B.

Kochi-22
20th March 2002

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PREFACE

We have entered the 21st century, rather the new millennium, with tremendous growth prospects in rubber industry. Vast internal market, rapid industrialisation, improved living standard of the masses and the availability of all types of raw materials from within the country and the emergence of IT revolution etc have paved the way for the phenomenal growth of the rubber industry. With this growth the need for longer service life of rubber goods has become a challenge. A new class of antioxidants namely polymer -bound antioxidants have shown great potential in this regard. This thesis is about the synthesis, characterisation and uses of novel polymer -bound antioxidants.

This thesis is divided into eight chapters as follows:

Chapter 1 presents a review of the literature in this field and the scope of the present investigation.

Chapter 2 deals with the materials used and the experimental procedures adopted for the study.

Chapter 3 is divided into four parts. Part I is concerned with the preparation and characterisation of polyisobutylene-bound paraphenylene diamine antioxidant. Part II deals with the preparation and characterisation of chlorinated paraffin-wax bound paraphenylene diamine antioxidant. Part III covers the preparation and characterisation of polyethylene glycol -bound paraphenylene diamine antioxidant. Part IV includes the preparation and characterisation of polyisobutylene-bound diphenylamine antioxidant.

Chapter 4 is divided into two parts. Part I deals with the efficiency of polyisobutylene-bound paraphenylene diamine and chlorinated paraffin wax-bound paraphenylene diamine antioxidants in NR, NR modified bitumen, SBR, IIR and NBR. Part II deals with the use of polyisobutylene-bound diphenylamine and

polyethylene glycol-bound paraphenylenediamine antioxidants in NR. The accelerated ageing studies of these vulcanizates are also discussed in each part.

Chapter 5 is divided into two parts. Part I includes the preparation, characterisation and application of polyisobutylene -bound phenol in NR. Part II deals with the preparation, characterisation and application of 4-octadecyl phenol in NR.

Chapter 6 includes the ozone and flex crack resistance of NR, SBR, IIR and NBR vulcanizates and NR/BR and NR/SBR blends containing polymer -bound antioxidants in comparison with those with and without conventional antioxidant.

Chapter 7 deals with the effect of polyisobutylene-bound paraphenylene diamine and chlorinated paraffin wax -bound paraphenylene diamine antioxidants in NR/BR and NR/SBR blends in comparison with corresponding blends with and without antioxidant.

Summary and conclusions of the present investigation is described in the last chapter, **Chapter 8**.

At the end of each chapter a list of references has been given. A list of abbreviations used in this thesis is also cited.

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Chapter 1

INTRODUCTION

The technological performance of various types of rubber depends on their ability to withstand the effects of the service environment. The development of rubber for many modern uses would not have been possible without the discovery of chemicals to prevent their degradation during service.

The deterioration in the useful properties of rubber products with time is a serious problem involving the oxidation of polymers by the oxygen of the atmosphere.¹ Natural and synthetic polymers deteriorate on ageing in varying degrees as a result of the combination of a number of factors like heat, light, oxygen and ozone. The irreversible nature of the oxidative processes to which industrial polymers are subjected during high temperature processing and under aggressive conditions during service has intensified the search for improved stabilising systems. This has resulted in the development of antioxidants, antifatigue agents, melt stabilisers, uv-stabilisers and fire retardants.

1.1 Antioxidants - Historical Background

Natural rubber latex contains a small percentage of non-rubbery materials, which function as antioxidants. These materials effectively protect the rubber during

coagulation and storage, but they are destroyed during the processing and curing operations.² Thus, it is not surprising that the earliest manufacturers of rubber products who knew nothing of oxidation, were plagued by the problem of deterioration. Hofman in 1861 was credited with being first to discover the oxygen absorption involved in this degradation, and the first patent, concerned with the use of phenol and cresol as antioxidants was issued by Murphy in 1870.³

Until about 1910 the materials chosen to reduce this oxidative degradation were natural products, such as coal tar resins, coumarone resins, paraffin, creosote and inorganic and organic reducing agents. The stability of the rubber product was not greatly improved when these additives were used.

The first antioxidants made their appearance in 1924 and slowly gained acceptance. Within a few years, their true value in rubber industry became apparent and the resulting search for new antioxidants led to the patenting of hundreds of materials. The first two widely used antioxidants were the reaction product of aniline and acetaldehyde and aldol naphthylamine. Hydroquinone and pyrogallol were patented in 1901,⁴ resorcinol and 2-naphthol in 1920,⁵ 1-naphthol and aldehyde condensation products in 1922,⁶ and mercaptobenzimidazole in 1931.⁷ In 1957, a new way to manufacture 2,6-di-*tert*-butylphenol in high yield and purity was discovered.⁸ The attachment of methylene bridged groups to the *para* position of this phenol by condensation reactions with formaldehyde and acrylates led to the discovery and commercialisation of a number of new antioxidants. Currently, bound antioxidants are being developed to give maximum resistance to losses by extraction and volatilisation.

1.2 General Aspects of Polymer Degradation and Stabilisation

All hydrocarbons are vulnerable to deterioration caused by heat, light and oxygen. These polymers vary widely in their susceptibility to oxidative degradation. It is well-known that the relationship between polymer structure and ease of oxidation depends primarily on the relative C-H bond dissociation energies of the various polymers. Polymers with C-H bonds of low dissociation energies are more readily oxidised than polymers with higher C-H bond dissociation energies. Consequently, branching and unsaturation lower bond energies and increase the polymer's susceptibility to oxidation.⁹ The amount of unsaturation present in a

polymer is also important. The rubber with low olefinic content, such as EPDM(ethylene propylene diene terpolymer), is more resistant to oxidation than the highly unsaturated rubbers, such as SBR (styrene - butadiene rubber) and NR (natural rubber).¹⁰

The chemical structure of the polymer not only determines the rate of oxidation but also the physical changes that can occur during oxidation. Hardening of the polymer occurs when oxidative crosslinking pre-dominates in the degradation process. Most rubbers, such as SBR, NBR (nitrile-butadiene rubber) and BR (cis-polybutadiene) harden during oxidation, while rubbers derived from isoprene, such as NR, IR (cis-polyisoprene) and IIR(isobutylene isoprene rubber), soften on oxidation due to chain scission.¹¹ It is not surprising, then, that an antioxidant which affords excellent protection in one rubber is not the most effective stabiliser for another.

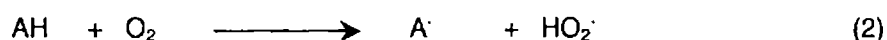
A broad distinction is generally made between materials, which can protect raw synthetic rubber, and those, which protect vulcanised rubber products. Synthetic rubbers are very susceptible to oxidation and must be protected with an antioxidant immediately after they are formed by polymerisation in order to prevent oxidative degradation during the high temperature drying step and during the subsequent storage.

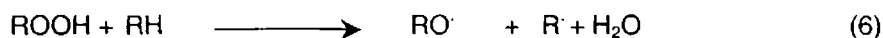
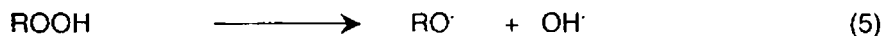
Tyres account for the largest volume of antioxidants used each year,¹² they are primarily the amine staining antioxidants. A wide variety of light coloured vulcanised products are protected with non-staining antioxidants.

1.2.1 Mechanism of polymer oxidation

Oxidation of polymers can lead to chain scission, crosslinking or formation of oxygen containing functional groups in the polymer or its degradation products. In order to understand the antioxidant inhibition mechanisms, a brief outline of the oxidation process is given below.^{13,14}

Initiation



Propagation**Chain transfer****Termination****Scheme1**

RH = polymer molecule or portion thereof, AH = antioxidant, A[·] = antioxidant radical, RO₂[·] = polymer peroxy radical, and ROOH = polymer peroxide.

1.2.2 Basic classification of antioxidants

Rubber antidegradants included in this classification are divided into six classes as shown below.¹⁵ The classification in general is based on chemical structure and application on rubber.

- a) Class 1. p-Phenylene diamines (PPDs) - This group of additives represents the primary materials used in tyres and other mechanical goods to impart ozone protection. These additives are also used as antioxidants and antiflex agents in a number of applications but are considered to be strongly staining and thus limited to black rubber applications. They can also be used as raw polymer stabilisers.
- b) Class 2. Trimethyl-diquinolines (TMQs) - These materials are primarily used to protect rubber articles from degradation by atmospheric oxygen at higher temperatures. They are moderately staining.

- c) **Class 3. Phenolics** - Phenolic antidegradants represent a group of nonstaining and non discoloring additives used primarily in light colored mechanical goods and tyres. They can also be employed as raw polymer stabilisers. In general they are weaker antioxidants than amine types.
- d) **Class 4. Alkylated diphenylamines (DPAs)** - This class of additives generally represents substituted amine antioxidants and it is used as raw polymer stabiliser in vulcanizate applications. These additives are moderately discoloring and staining.
- e) **Class 5. Aromatic phosphites** - These are phosphorus containing fully non-staining, non-discoloring additives used as stabilizers for synthetic elastomers in 'white rubber' applications. They also have applications as peroxide decomposers and radical traps in polymer systems.
- f) **Class 6. Diphenylamine - ketone condensates** - This group of additives is used primarily in carbon black loaded compounds to protect them against oxygen and heat deterioration.

1.2.3 Classification of antioxidants based on their mode of action

Two main groups of antioxidants are distinguished according to their mode of action: primary or chain breaking, and secondary or preventive antioxidants.

Chain breaking antioxidants

Chain breaking antioxidants interfere with the chain propagation steps of polymer oxidation. These antioxidants can terminate the kinetic chain by,

- a) **Free radical traps** which interact with chain propagating $RO_2\cdot$ radicals to form inactive products. Quinones and conjugated molecules (e.g. anthracene) can function as free radical traps.
- b) **Electron donors** give electron to peroxy radical and thus stabilising the system.
- c) **Hydrogen donors** are the most commonly used chain terminating antioxidants. Inhibitors of the aromatic amine (InH) type interfere with oxidative chain propagation by competing with the polymer for peroxy radicals:



Preventive antioxidants

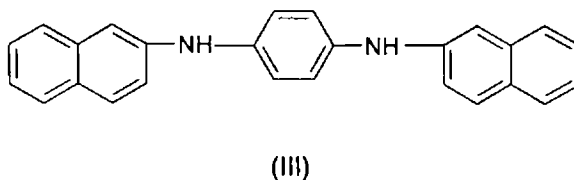
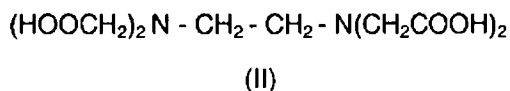
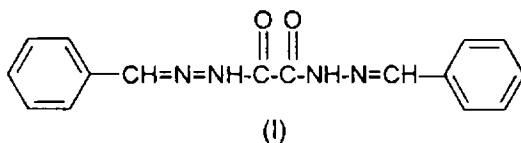
a) Light absorbers

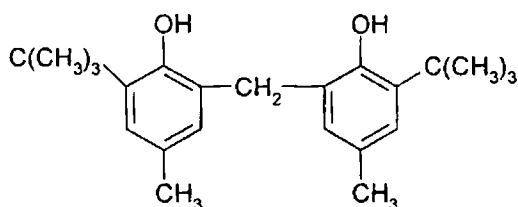
Processes operative in environmental ageing of hydrocarbon polymers include transformations induced by light. Commonly used photostabilisers are hydroxybenzophenone derivatives, substituted benzotriazole derivatives, metal complexes of different ligands and different metals etc.

The oxidation mechanism developed by Bolland¹³ to explain the thermal oxidation of rubber has been applied successfully to thermal oxidation of other substrates and also to photo-oxidation.

b) Metal deactivators

They are strong metal ion complexing agents that inhibit catalysed initiation. The most effective groups are polydentate chelating agents capable of forming very stable chelates in which all the co-ordination sites are occupied. Examples are oxalyl bis- benzylidene hydrazide (I), ethylene diamine tetra acetic acid(II), N,N'-di-naphthyl-p-phenylene(III), 2,2¹methylene-bis (4-methyl-6-tert-butylphenol) (IV).¹⁵⁻¹⁶

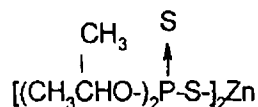




(IV)

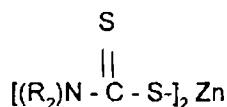
c) Peroxide decomposers

Peroxide decomposers have proved to be very important in rubber. The main requirement of compounds falling into this class is that they should substantially reduce hydroperoxides to alcohols without substantial formation of free radicals. Several organic sulphur compounds, including zinc dialkyl dithiophosphates (V) were found to decompose hydroperoxides and the mechanism of inhibition by the latter has been reviewed.¹⁷

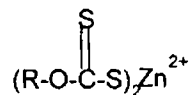


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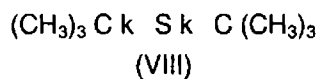
Compounds containing an imino group have also been found to be effective antioxidants. In certain cases peroxide decomposers decompose hydroperoxides through polar reactions, thereby inhibiting initiation. This class includes metallic salts of certain dithioacids such as zinc dithiocarbamates (VI), xanthates(VII), di-tert - butyl sulphide (VIII), tert-butyl thio sulphonylic acid(IX).¹⁸⁻²⁰ etc.



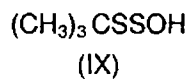
(VI)



(VII)



(VIII)



(IX)

1.2.4 Important characteristics of antioxidants

There are a number of properties that antioxidants must possess besides good antioxidant activity if they are to be widely used in rubber applications. They should be inexpensive and should not interfere with the cure characteristics of the rubber. They should be non-toxic, non-fugitive, handy, compatible with the rubber and for certain applications, non-discolouring and non-staining.

Service requirements placed on finished rubber products demand improved polymer stabilization. The effectiveness of antioxidant depends on two factors. 1) intrinsic activity of the antioxidant and 2) permanence of the antioxidant in the polymer.

1) Intrinsic activity of the antioxidant

This is the fundamental ability of the antioxidant and its transformation products to interfere with and retard the radical chain oxidation process, which in turn depend on the chemical structure of the antioxidant.

2) Permanence of the antioxidant in the polymer

The concentration of the antioxidant in a polymer decreases during long term use as a consequence of the following processes: (1) chemical loss of antioxidant and (2) physical loss of antioxidant from the polymers.^{21, 22}

Chemical loss of antioxidant as a result of their mechanism of stabilization is summarised by Vink.²³ Physical loss of antioxidant mainly depends on (a) distribution of antioxidants in polymers, (b) compatibility of antioxidants in polymers, (c) volatility of antioxidants, (d) diffusion of antioxidants in polymers and (e) extractability of antioxidants from polymers.

(a) Distribution of antioxidants in polymers

In general, it may be assumed that the distribution of antioxidants is uniform in amorphous polymers where the antioxidants form micro heterogeneous phases uniformly dispersed in a polymer according to their compatibility with the polymer.²⁴ In semicrystalline polymers, the distribution of antioxidants is not uniform owing to the presence of crystalline and amorphous phases. The distribution of several types of low molecular weight compounds in different polymers was investigated by Billingham

et al.²⁵ They also ascertained that the distribution of stabilisers in spherulitic polymers depended on the conditions of crystallisation and on the total amount of the atactic polymer concentrated at the boundaries of spherulites.

Irrespective of the problems of solubility and migration of the antioxidants, such distribution of antioxidants in polymers appears to be advantageous because the amorphous portion of most of the polymers is the region most sensitive to degradation. The uneven distribution of an antioxidant raises the concentration in the amorphous phase thus protecting it more effectively against degradation.

(b) Compatibility of antioxidants in polymers

One of the factors which affect the effectiveness and permanence of antioxidants in polymers is compatibility, which represents the totality of effects which are involved in the polymer additive interaction. If polymers are modified by antioxidants, a physical mixture characterised by certain degree of homogeneity or heterogeneity arises. The degree to which this occurs depends mainly on the cohesion and adhesion forces between the components and their bulk or surface interactions.

The theory of solutions of macromolecular substances²⁶ is most frequently applied to mixtures of polymers with low molecular weight substances or to polymer — polymer mixtures. This theory predicts that the compatibility of components in mixing may be approximately estimated from the squared difference of the values of solubility parameters of the components ($\Delta\delta$).² The solubility parameter δ represents the density of cohesion energy and is numerically equal to the potential energy of a unit volume of a material,

$$\delta = \frac{E}{V} = \frac{N_0 v}{V} \dots\dots\dots(14)$$

where E is the potential energy, V is molar volume, N_0 is the Avogadro number and v is the potential energy of one molecule. The greatest difference between the solubility parameters of the polymer (δ_p) and the second component (δ_a) defines the critical value:

$$(\Delta\delta)_{\max} = (\delta_p - \delta_a)_{\max} \dots\dots\dots(15)$$

If the experimental or calculated value of $(\Delta\delta)^2$ is less than the critical value $(\Delta\delta)^2_{\max}$, the components are able to form a homogeneous mixture. If the value $(\Delta\delta)^2$ exceeds the maximum value, the formation of a heterogeneous mixture is to be expected.²⁷

c) Volatility of antioxidants

One of the causes of the physical loss of stabilisers in polymers is their volatility which in turn is a manifestation of thermal motion of molecules on the surface of a sample. It is related to the heat of evaporation of antioxidant in the sense of the Clausius Clapeyron equation (16) and dependent on the interactions in the polymer - stabiliser system.

$$d \ln p / dT = \Delta H / RT^2 \quad \dots\dots\dots(16)$$

The solubility of an additive in a polymer is a thermodynamic equilibrium property of the additive polymer combination and the diffusion coefficient is a kinetic parameter defined for closely controlled conditions. In contrast, the rate of evaporation of an additive is a kinetic quantity which is sensitive to the conditions of measurement. Spacht et al.²⁸ measured the vapour pressures of a series of phenolic and amine antioxidants by a direct manometric measurement at temperatures above the melting points. Angert et al.²⁹ showed that the loss of amine antioxidant from a thick rubber sample follows the first order kinetics and concluded that the rate constant is related to the volatility of the pure additive. These authors showed that the presence of carbon black or chalk as fillers significantly reduces the loss rate although they did not interpret this result. The introduction of an amine or hydroxy group into the para position of diphenylamine reduces the volatility almost by an order of magnitude, the formation of intermolecular hydrogen bonds leads to an increase in intermolecular attraction forces and thus lead to volatility.³⁰

(d) Diffusion of antioxidants in polymer

The diffusion of antioxidant in polymer does not itself produce any loss of antioxidant from the polymer. The diffusion processes play an important role in the evaporation and leaching of antioxidants from polymers. The diffusion of gases, solvents and hydrocarbons in rubber has been extensively studied.³¹⁻³³ The nature of the polymer and the size of the diffusant appear to be the main factors that govern the rate of diffusion.

In most cases, the method employed for diffusion coefficient determination is a radio isotope labelling technique³⁴. The attempt to correlate the antioxidant diffusivity to rubber crosslink densities was done by N. C. Billingham et al.³¹ Carlsson et al.³³ believe that the optimum stabilisation may be achieved by using a very low concentration of the antioxidant in the bulk of the polymer but a higher concentration in the surface layer. Nevertheless, evaporation of the low molecular weight antioxidants washing with water or organic solvents and mechanical abrasive wear of the surface layers in long term use results in an overall decrease in stabiliser content in the polymer and hence a decrease in its resistance to degradation.

(e) Extractability of antioxidants from polymers

Another factor causing the physical loss of antioxidants in polymers is extraction. This plays a part wherever the polymer articles come into contact with water or organic solvents. The extraction reduces the antioxidants in the polymers especially in the surface layers which are the most sensitive to degradation during ageing. The extractability can be estimated. (1) by determining the stabiliser concentration in the polymer after extraction,³⁴ (2) according to the content of antioxidant in the extraction medium³⁵⁻³⁶ and (3) by comparing the stability of non-extracted and extracted samples.³⁷

Cain et al.³⁸ have observed that diethylaniline bound to rubber, although less effective than its low molecular weight analogue, N-phenyl-N'-isopropyl-p-phenylene diamine becomes more effective with water at 100°C and its antioxidant activity does not decrease.

Leachability decreases with increasing molecular weight of the stabiliser. Another factor which influences extractability is the relation among the interactions of stabiliser, extraction medium and polymer.

Accelerated solvent extraction of antioxidants in linear low density polyethylene was studied by M. Waldeback et al.³⁹ A method for quantitative supercritical fluid extraction of Ethanox 330 antioxidant from high-density polyethylene was studied by A M Pinto et al.⁴⁰

As a result of the above processes, the decrease in concentration of the antioxidants in polymers affects the resistance to degradation. Basically there are two approaches in increasing the persistence of an antioxidant:

- (1) to produce antioxidant of high molecular weight.
- (2) to chemically attach the antioxidant to a polymer, thereby guaranteeing its persistence in the final product i.e. polymer-bound antioxidants.

1.2.5 Mechanism of antioxidant action

Oxidation inhibition processes have been classified into two main types: kinetic chain-breaking processes and initiation prevention mechanisms. The first type embraces the traditional rubber antioxidants, the aromatic amines and phenols, and the second includes the hydroperoxide decomposers, the transition metal deactivators and u.v. stabilisers acting by the light absorption mechanism.

Chain-Breaking (CB) mechanism

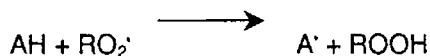
This was the first antioxidant mechanism to be investigated in detail.⁴¹ The free radical oxidation chain reaction indicates two ways in which the chain might be interrupted. These may be summarised in scheme 2.



Scheme.2

Chain-Breaking Donor Mechanism (CB-D)

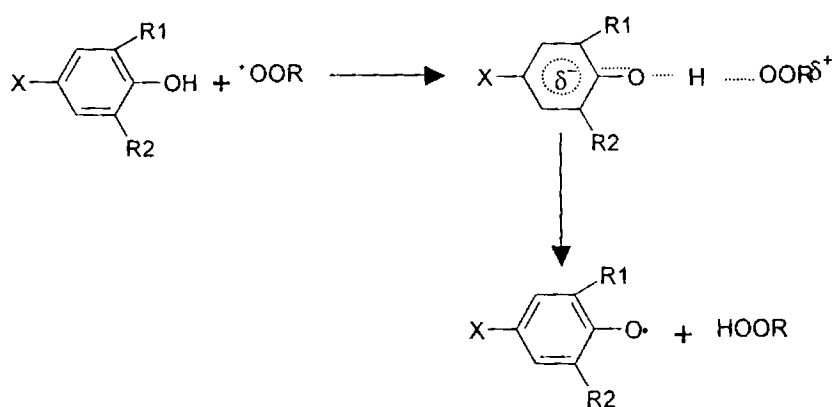
Chain breaking antioxidants act according to the following general reaction.



where AH is the antioxidant. The chain breaking antioxidants are frequently called as primary antioxidants. The geometry of the reaction is influenced by the steric environment of the reaction site of the antioxidant (OH or NH).⁴²⁻⁴⁴ From a sterically hindered 'AH', H is transferred in a direction perpendicular to the plane of the aromatic ring. If at least one ortho substituent is not very bulky, the process is most likely a coplanar one, a longer life may be assumed for the resulting transition

state.⁴⁵⁻⁴⁶ Depending on the nature of the AH, the radical A[•] may be either phenoxyl or amino radical. Transformation products of phenoxyl and amino radical are summarised by Pospisil.⁴⁷

Both amine type and phenolic type antioxidants can donate hydrogen to an alkylperoxy radical. The effects of substituent groups in the aromatic rings is to reduce the energy of the transition state (II) which involves electron delocalisation in the aromatic ring (scheme3).

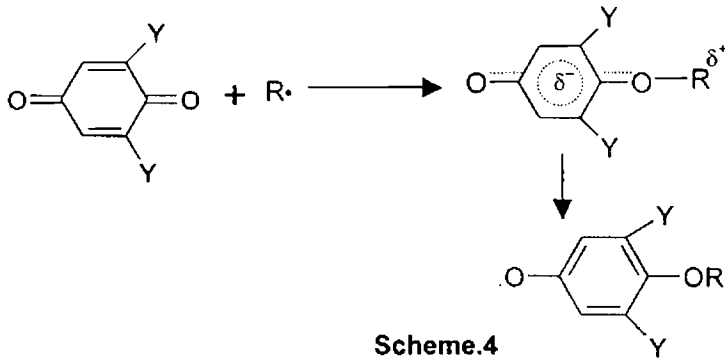


Scheme. 3

The products formed by further reaction of the initially formed phenoxyl radical are complex and may have either antioxidant or pro-oxidant activity.⁴⁸

Chain - Breaking (Acceptor) Mechanism (CB- A)

Macro-alkyl radicals, unlike alkylperoxy radicals, are not powerful oxidising agents, but they are themselves readily oxidised by electron acceptors. A variety of oxidising agents are capable of removing alkyl radicals from an auto-oxidising system and if they are able to do this in competition with alkylperoxy radicals, they have antioxidant activity.⁴⁹ In general, the molecular requirements for a CB-A antioxidants are the same as for polymerisation inhibitors. This class includes quinones, nitro compounds and stable \cdot free radicals of which nitroxyls⁵⁰ and phenoxyls⁵¹ have been most studied.



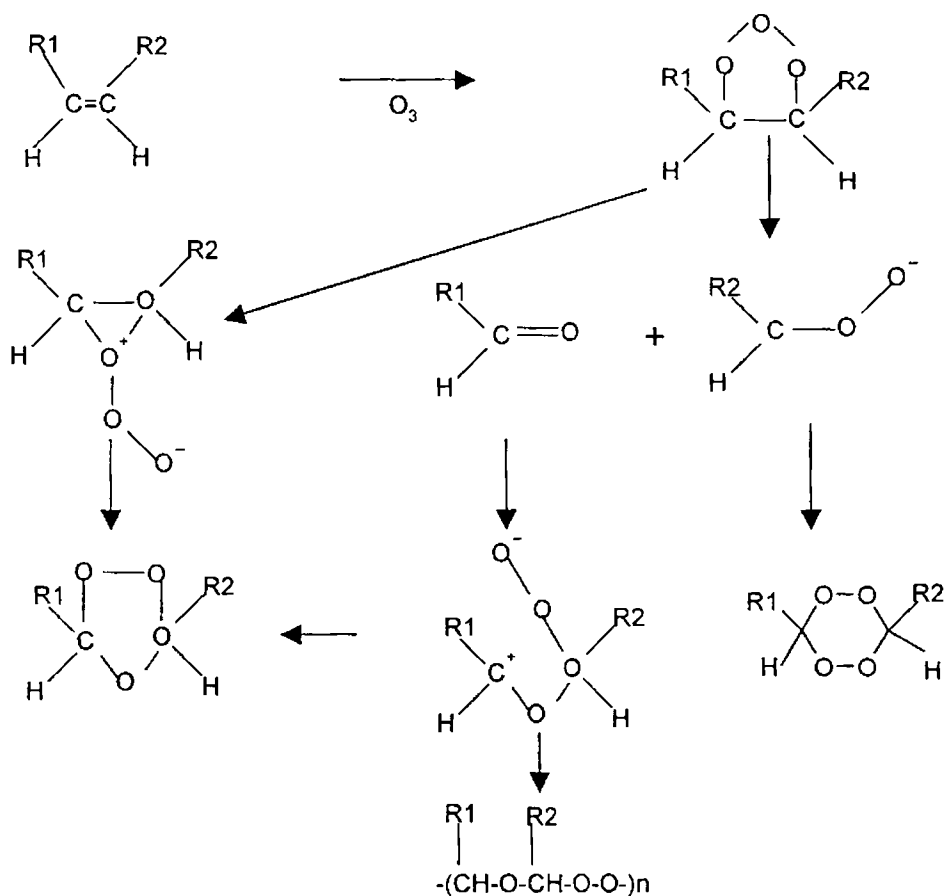
1.3 Polymer Degradation Caused by Ozone

Ozone, a degradant of vulcanized rubber, occurs naturally and is formed in the earth's stratosphere by the action of sun's ultraviolet light on atmospheric oxygen. Even though ozone is only present in the atmosphere at concentrations normally in the range 0-7pphm⁵² it can severely attack non-resistant rubbers when these are in strain. The interaction of rubber with ozone during the process of fatigue is the most destructive and dangerous mode of ageing. Ozone directly destroys the surface of rubber. The use of antiozonants is an effective means of protecting stressed rubber against surface cracking.

1.3.1 The mechanism of ozone attack on elastomers

The unsaturation in diene based elastomers accounts for their high sensitivity to ozone attack. Ozone causes cracking of stressed or flexed vulcanized rubber as a result of chain scission and formation of polymeric peroxide.

Ozonation may be interpreted as shown in scheme 5.⁵³⁻⁵⁵



Scheme. 5

1.3.2 Theories of antiozonant action

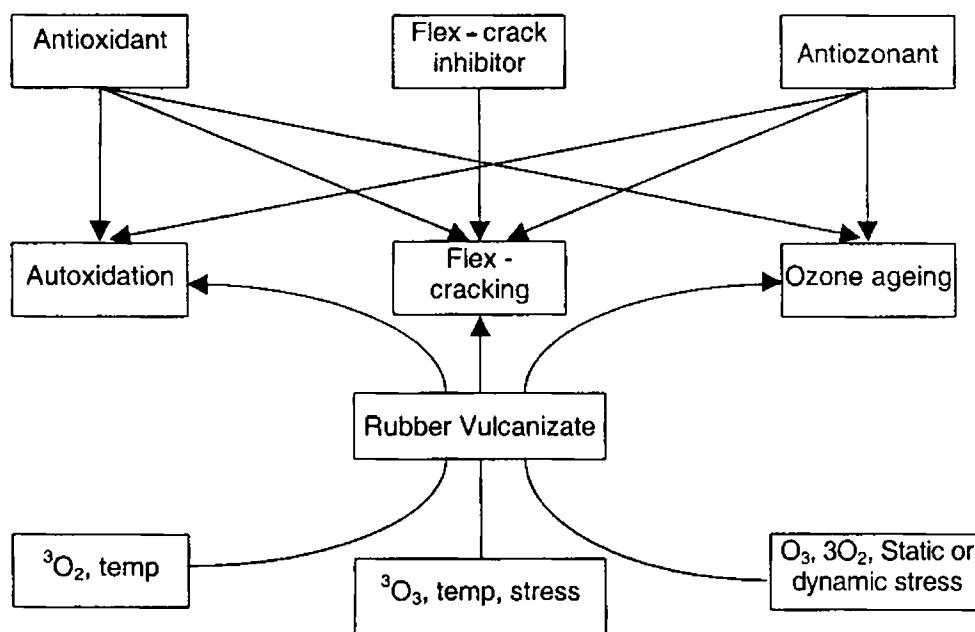
The process of ozone ageing of vulcanizates is extremely complicated and no simple model approach to the explanation of protection against O₃ attack can explain all the important factors involved. The simplest mechanism involves diffusion of antiozonant into the rubber surface and preferential reaction with O₃.⁵⁶⁻⁵⁹ The rubber matrix therefore remains protected until all the antiozonant in the rubber is depleted.

Essentially three theories of antiozonant action have been developed:

- (1) The antiozonant blooms to the surface and preferentially reacts with the ozone so that the rubber is not attacked until the antiozonant is exhausted and reacts preferentially with the incident ozone (Ozone scavenging).
- (2) The antiozonant blooms to the surface of the rubber and forms a protective film on the surface.
- (3) The antiozonant reacts with the intermediates formed in the ozonation of rubber preventing chain scission or rubber chain relinking.

The antiozonant efficiency is dependent on the rate of reaction of antiozonant with O_3 , on the initial antiozonant concentration in the rubber surface and on the rate of diffusion of fresh antiozonant on the outer surface. The antiozonant effect was found to increase with the initial surface concentration of antiozonant⁶⁰ and the reaction rate was reported to be related to antiozonant efficiency.⁶¹

The schematic representation (scheme.6) of involvement of antioxidants in different aspects of rubber degradation mechanism is given below:



Scheme. 6

1.4 Use of Antioxidants in Elastomer Blends

Owing to economic and technical uncertainties associated with synthesizing polymeric materials, the utilization of polymer blends to achieve a desired combination of properties has obvious attraction. Blending of two or more rubbers is carried out for improvement in technical properties, better processing and to lower compound cost.

Many products in rubber industry are based on blends in all or part of their construction. Tyres are typical examples of products in large-scale volume production. The introduction of cis- 1,4 - polybutadiene [butadiene rubber (BR)] during the late 1950s is probably the single most important development relating to the use of elastomer blends in tyres. Blends of NR with BR has enabled significantly improved tread wear and groove cracking resistance without reduction in resilience.⁶² Better oil extension and higher black loadings are additional benefits made possible by the development of BR, along with less dependence on the availability of NR.

Evstratov et al⁶³ evaluated the tread wear performance of NR/BR and NR/SBR blends under different road conditions. Under test conditions with considerable braking and turning, the wear advantage of treads containing BR was found to increase. Milner and Windibank⁶⁴ showed that the state of degradation of NR is reduced in blends with BR. Corish⁶⁵ reviewed different aspects of elastomer blends. A. K. Bhowmick and S. K. De⁶⁶ studied the effects of curing temperature and curing system on structure property relations of NR/BR, NR/SBR and NR/SBR/BR blends.

Rubber blends used in industrial products have a complex and multifunctional nature. Vulcanizate properties can be optimised by proper selection of rubber types, including viscosity considerations and by control of the distribution of insoluble and soluble compounding ingredients, the latter with particular emphasis on achieving good 'infra'- and, 'inter'-phase crosslinking.⁶⁷

Even though elastomer blends have been in use for several decades, a clear understanding of their rheological and physical properties in relation to the properties of constituents and morphology is still limited.⁶⁸ Physical properties of cured polymer blends are generally inferior to those predicted from the properties

of the component polymers. This behaviour is especially seen in the cured blends of dissimilar polymers having large differences in polarity and unsaturation. In polymer blends of similar polarity and unsaturation, the cured blends exhibit additive properties and so-called covulcanized state is realized.⁶⁹

A major cause for the inferior properties exhibited by the cured elastomer blends is that its constituents are incompatible on the molecular scale and exist in the form of separate phases.⁷⁰ It is found that the mechanical properties of elastomers depend very strongly on crosslinks density.⁷¹ Practical information regarding processing and vulcanization of NR/SBR blends was reported by Springer.⁷² Mastication of NR⁷³ is necessary prior to blending with SBR. Shundo⁷⁴ has compared the use of roll mill and Banbury mixer for the preparation of NR/SBR blends and found that mill mixing furnishes more uniform compounds.

1.5 Polymer-Bound Antioxidants

The antioxidant action depends mainly on three factors. The first is the intrinsic activity of the antioxidant itself. This is the fundamental ability of the antioxidant or its transformation products to interfere with and retard the radical chain oxidation process. The second factor is the compatibility or solubility of the antioxidant in the polymer matrix. Polarity changes will result in aggregation of the stabiliser, insolubility in the matrix, spewing or blooming of the material, or preferential absorption on the filler. All these factors result in the stabiliser not being present uniformly in the polymer.

The third factor is the volatility or fugitive nature of the antioxidant. Losses due to extraction or volatility immediately affect the ultimate performance of the final product. Of the three factors, the third factor is the most important, since it affects the antioxidant's persistence directly. Basically, there are two approaches for increasing the persistence of an antioxidant. One is to produce antioxidants of high molecular weight and therefore, of low volatility or extractability. The other is to chemically bind the antioxidant to the polymer i.e. polymer-bound antioxidant, thereby guaranteeing its persistence in the final product.

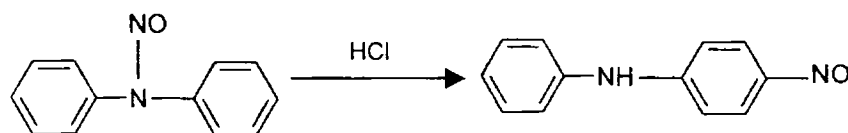
One of the more exciting areas of research during the past decade was the preparation of polymer-bound antioxidant systems. The advantages of bound antioxidants in oil and fuel resistant nitrile rubber have been well documented.⁷⁵

Considerable effort has been expended in the preparation and utilisation of phenolic antioxidants which have pendant unsaturated groups. The utility of such a system was demonstrated by Davy and Williams,⁷⁶ who co-vulcanised 2-allyl - 4 - alkoxy - phenols into natural and synthetic rubber recipes. Excellent nonstaining and anti-flex properties were claimed for the vulcanizates.

The preparation of nitrile rubber containing copolymerized N- (4-anilinophenyl) methacrylamide was reported by Meyer and coworkers.⁷⁷ Several polymerisable amine and phenolic antioxidants were discussed in the literature.⁷⁸⁻⁸⁶

Most versatile method of polymer modification is the direct introduction of an antioxidant function by the reaction of a conventional polymer with a suitable reactive adduct. The advantages of such modification are numerous. These include a multiplicity of polymer choices, a choice on ultimate level of stabiliser loading and the introduction of the stabiliser in a separate step from the production process. An existing commercial polymer is modified inexpensively by a chemical reaction with a polymer reactive antioxidant.

Cain and co workers⁸⁷ found that "ene" addition of nitroso phenols or aniline derivatives produce polymer-bound stabilisers. A commercial preparation of *p*-nitrosodiphenylamine by hydrochloric acid catalysed rearrangement of the *N*-nitrosodiphenylamine was described by Levy and Seif⁸⁸ (Scheme.7).

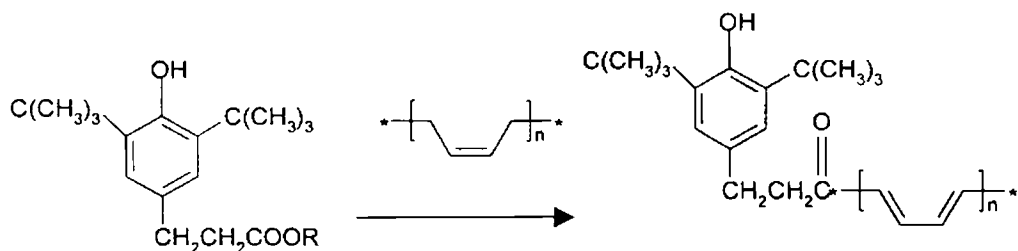


Scheme.7

The preparation of polymer-bound antioxidants by 1,3 - Saltman first described cycloaddition reaction and Auerbach.⁸⁹ They prepared a series of compounds related in structure to 1-(3,5-di-*t*-butyl-4-hydroxyphenyl)-*N*-phenyl-nitrone. This material was found to add readily to unsaturated polymers to provide a bound antioxidant.

One novel process for introducing bound antioxidants was described by Farrar⁹⁰ Living polymers, produced by lithium-catalysed polymerisation of diene monomers were reacted with a variety of commercial antioxidants, which contained ester functionality. Presumably, the polymer behaves as a normal alkyl lithium

reagent, which adds to the carbonyl function. Neutralisation produces the bound antioxidants as a ketone (scheme. 8).



Scheme.8

Although synergism between sulphur compounds such as thiodipropionates and chain breaking antioxidants is well- known and reasonably well understood in polyolefin and in certain non vulcanized rubbers, the synergistic effect is generally not noted in vulcanised rubber.⁹¹⁻⁹² Shelton has attributed this lack of synergism as possibly being due to a masking effect from the presence of other sulphur compounds present in the vulcanizate such as crosslinks and vulcanization fragments.⁹³ Other explanations centre on antagonism between the synergist and the curative system, other antioxidants or fillers. This antagonism leads to synergist destruction, trapping, or absorption.

An additional example of a system which binds into the polymer during cure was described by Dharni.⁹⁴ This material is 2-mercapto-3-allyl-3,4 dihydroquinazoline-4-one. Oxidation-resistant polymers were produced, but no explanation was given as to its method of attachment.

Gregory prepared polymer-bound phenolic antioxidants by alkylation of various alkylated phenols by a variety of polydiene rubbers.⁹⁵⁻⁹⁶ M. S. Al-Mehadawe et al described the preparation of polymer-bound antioxidants by direct hot melt mixing of chlorine containing polymers and a commercial antioxidant.⁹⁷

Scott et al have demonstrated that simple hindered phenols which contain a methyl group in the ortho or para position can react with natural rubber in the presence of oxidising free radicals to yield polymer-bound antioxidants.⁹⁸ Antioxidants like styrenated phenol, diphenylamine etc bound to hydroxy terminated liquid natural rubber by modified Friedel Craft's reaction were also found to be effective in improving ageing resistance.⁹⁹ Natural rubber bound

