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NON-MIGRATORY ANTIOZONANT SYSTEM FOR NATURAL RUBBER.

by

MACLEAN. J. BHALA  MSc. MIM

A Doctoral thesis submitted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy of the Loughborough University.

November, 1997

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I extend my gratitude to my sponsors, the Commonwealth, for the financial support for this study programme and remain equally grateful to my employer, National University of Science and Technology, for affording me the three-year study leave.

I dedicate this thesis to my parents whose sacrifices towards my academic achievements have for long been a beacon in all my scholarly endeavours.

I dedicate the same, to my wife Tryphen and our lovely children whose unwavering support and patience during my absence from home has kept me tugging on, even when there seemed to be no light at the end of the tunnel.
ABSTRACT

The current research on non-migratory antiozonant systems for natural rubber follows a tripartite study involving the formulation of a coating compound with static and dynamic ozone testing of the coatings, a review of some commercial in-mould coating techniques and analysis of diffusion of a commercial antiozonant through a coating. An outline of the mixing of Nipol 1312, a low molecular weight nitrile butadiene rubber grade produced by Zeon Chemicals Inc., with other ingredients to produce a coating composition is also given.

Test pieces of the natural rubber substrate were placed in pre-coated mould cavities and cured under compression to achieve covalcanisation between the substrate and the coating. All ozone tests were carried out under standard ASTM D1149-91/D518-91 conditions. Results show that the formulated nitrile rubber coating compound is able to protect natural rubber from ozone attack with no migration of the antiozonant as in classical chemical antiozonant systems.

An up to date patent search on in-mould coating techniques and systems was carried out and evaluated in conjunction with some current commercial coating methods. In this overview, more emphasis is laid on the nature of the coating material which subsequently determines the appropriate coating technique, than on the specific in-mould coating process applied. Post-mould coating work with polyvinyl chloride (PVC) on natural rubber substrate was also assessed.

An experimental and theoretical study of the diffusion of the antiozonant N,Isopropyl N-phenyl-p-phenylenediamine (IPPD) through a protective coating on a natural rubber substrate is made in the project. This study shows that the protective coating is able to reduce the loss of antiozonant through diffusion while giving the rubber adequate protection from ozone. The study also demonstrates that the combination of a commercial antiozonant and a protective coating gives enhanced product service life and provides protection to damaged regions of the coating.
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CDT* continuous dynamic testing
IDT** intermittent dynamic testing
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CHAPTER 1.

INTRODUCTION AND OBJECTIVES

1.1 Problem outline

Antidegradants rank second after vulcanizing agents as the most important ingredients in rubber compounding without which the final product would have an extremely short life span. The continued research activities and recorded financial commitments channelled into the field of antidegradants and indeed other rubber additives have made it possible for the rubber industry to expand its vast product range while also improving the life span of these products. Due to the current standard practice of incorporating antidegradants in the production of rubber articles, general premature failure which occurs through oxidation or ozonation in service has been reduced drastically in many rubber products. Once compounded into the rubber during mixing, the antidegradant is expected to fulfil its role of protecting the product from premature ageing through a specific mechanism depending on its chemical nature and environmental conditions under which the product has to operate.

The effectiveness of an antidegradant can therefore be assessed by the length of time the product remains useful in what it was designed to do. More often than not an antidegradant “disappears” from the bulk of the product resulting in a rapid decline in functional properties of the product concerned and this scenario has to be avoided at all costs. In antioxidants the problem has been largely overcome by the introduction of the so called bound antioxidants which remain permanently linked to the rubber structure while performing their protective functions.

Besides the general protection against oxygen and ozone attack, rubbers (both natural and synthetic) also require specific protection against aggressive chemical and physical environments. In each case the nature of the protective additive is usually determined by both the surroundings within which the rubber is to be used and the basic inherent properties of the rubber in question. Whatever approach is taken in the protection of rubber products against early ageing, the mechanisms of protection need to be well
1.2 Current views on antiozonant protection

Ozone ($O_3$), as stated above, is one of the many problems that confront rubber compounders because it causes a breakdown of the double bond system of the rubber chain. As a result of ozone attack on the rubber structure, the rate of ageing of the rubber product is accelerated through gradual loss of the basic properties of the rubber. It is an established fact that most rubbers which are exclusively backbone saturated like ethylene propylene copolymer (EPM) and other unsaturated backbone elastomers like chloroprene rubber (CR), ethylene propylene diene terpolymer (EPDM) and nitrile butadiene rubber (NBR) are inherently or fairly resistant to ozone while natural rubber ranks the worst in susceptibility to ozone attack among all unsaturated rubbers. It should be noted however, that chemical saturation is a necessary but not sufficient condition for inherent ozone resistance since some known saturated elastomers like polysulfides are prone to ozone cracking.

Research has shown that ozone attacks the surface of the rubber resulting in surface discoloration and subsequent development of characteristic cracks growing perpendicular to an applied stress. At low extensions of about 10%, few cracks tend to develop but these grow large and deep resulting in severe ozone effect. Higher extensions on the other hand normally result in large numbers of cracks which due to mutual interference and stress relaxation do not go deep into the rubber. In all cases the cracks tend to expose more rubber double bonds to the invading ozone leading to further breakdown of the rubber matrix. Once this process of macromolecular scission has been initiated, it eventually leads to the final failure and inevitable replacement of the product.

Rubber industries world-wide use different methods of protecting their products from ozone attack. Generally these methods can be classified as either physical or chemical in nature. While physical means, which include the use of waxes and blending, are less expensive and easy to apply, the type of protection they give is only effective under
static conditions. Chemical antiozonants on the other hand are generally expensive but effective under both dynamic and static conditions. In both chemical and physical means of protection, the formation (by different means) of a protective film on the surface of the rubber is accepted as an integral part of the mechanism of protection by the protective additive.

1.3 Project aims and objectives

The migration of an antiozonant within the bulk of a rubber product, though a necessary process towards its protective function, can be a cause for concern if the expected lifespan of the product falls short of the target mark. Such concerns form the basis for research into non-migratory antidegradants as indicated by the success of bound antioxidants. Notably, no such thing as "bound antiozonant" has been reported to date. In the light of current diverse research interests in antiozonants, the specific objectives of the following project are three fold, namely:

i) to formulate a non-migrating antiozonant coating compound for a natural rubber substrate using inherently ozone resistant rubbers or any other ozone resistant polymer materials that can with reasonable ease be coated and adhere to the substrate.

ii) to study the effectiveness of a combined antiozonant system made up of an antiozonant coating and a commercial chemical antiozonant in the protection of natural rubber against ozone.

iii) to review and evaluate potential methods of in-mould coating for production processes in the rubber industry.

The idea of working on a non-migrating antiozonant system comes in the wake of a realization that, all commercial antiozonants currently being used in most spheres of rubber production are migratory in nature and as such have all the shortcomings that are common with such systems: i.e. they are prone to leaching by different solvents, they cause discoloration of products, they require uniform dispersion to ensure uniform protection and most crucial of all, their ability to protect is dependent on parameters like temperature, solubility and their rate of migration through the rubber matrix. The general effectiveness of classical antiozonants is also limited with time.
The plan of investigations in this project is envisaged to follow the flow chart given below.

![Flow Chart](image)

Figure 1.1- Plan of Investigations

A non-migrating system will not be affected by the above mentioned disadvantages. The other driving force for this project is the dismal gap between the research so far done in antioxidants which boasts achievements in "bound antioxidants" while little of that has been done with antiozonants. There is also a growing demand for rubber components for use in ozone aggressive environments such as the vicinity of vehicle engines/spark plugs and non-migrating antiozonants would be most appropriately used here. In order to achieve the stipulated objectives, an appropriate selection of ozone resistant materials will be made and systematic trials from compounding to ozone testing will be carried out. More than one 'ozone resistant material' will be used in this work so that a basis for material comparison as regards ozone resistance, adhesion to substrate and general quality of coating can be made.
CHAPTER 2.

ANTIDEGRADANTS FOR THE RUBBER INDUSTRY.

2.1 History of antidegradants for rubber.

The rubber industry as we know it today has grown by leaps and bounds since the discovery by Charles Goodyear and others that a pinch of sulphur changes the properties of rubber through vulcanisation. Even as early as the Goodyear times of the 1840s, other additives besides sulphur were also incorporated into rubber mixes in order to achieve ultimate results. Among these were stabilisers that were taken as ingredients that protect the rubber from ageing. Records show that waxes of one sort or other have been used to prevent rubber deterioration since the 1880s.\(^1\) It is unlikely though that the users then recognised the capacity of waxes to protect against ozone attack as is accepted today. Because rubber was fast growing as a commercial commodity in the mid-nineteenth century, the deterioration of its properties was studied with great interest and it was in such work that the ageing phenomenon was shown to coincide with oxygen absorption. Phenolic substances were recommended for use to combat these problems which tended to recur after short periods of successful control. Further studies reported that ageing was a result of peroxide intermediates which could be treated by using aromatic amines.\(^2\)

As is known today, the life span of rubber products then remained alarmingly short mainly due to the fact that the available protective materials were not very effective. It was not until 1921 that antidegradants were introduced into the rubber industry in an industrial scale, after extensive work on antioxidant action by Mouren and Dufraisse.\(^3\) Today, more than seventy years after that vital launch, the industry still cannot boast the existence of an additive agent that can protect rubber from all the unfavourable effects to which it is exposed during storage and use. However, it remains clear that free radicals and hydroperoxides are the key intermediates in hydrocarbon oxidation and this fact has
made it much easier for researchers to focus on appropriate antidegradants for different forms of rubber ageing.

2.2 Ageing characteristics of rubber.

Ageing is a collective term for changes in properties of materials that occur during long term static conditions of storage and likewise during product service without the action of chemicals. These changes lead to partial or complete degradation of the product concerned. It should be noted from the onset that ageing is an irreversible process in which useful polymer properties degenerate when exposed to the environment, resulting in ultimate failure of a product. Product transformations as a result of ageing can appear as rotting, softening, frosting and chalking or even fatigue with static crack formation. Both cured natural and synthetic rubbers are known to be prone to such ageing effects. Uncured natural rubber contains very effective natural antioxidants that preserve it from premature ageing on storage but during processing and vulcanisation these natural protective substances are considerably depleted, thus creating a need for protection of the rubber by means of external antidegradants.

Through ageing, a number of properties important in practice change irreversibly; e.g. tensile strength, elongation at break, modulus, hardness and general surface changes as mentioned above. The actual course of ageing of rubber is affected by the nature of the elastomer used, the vulcanisation system and indeed other components of the compound. The reactivity of oxygen and other gases like ozone in the presence of rubbers is also determined by the chemical structure of the elastomer and this results in various rubbers showing different resistance to ageing. The nature and rate of change on the other hand is affected by other factors such as heat, light, mechanical energy and atmospheric effects. As noted above, chemical reactions during ageing result in structural changes which culminate in polymer failure and subsequent product replacement. Noted among the common changes are the following:

- scission of the cross-links leading to a decrease in the network density (softening),
• formation of additional cross-links with an increase in network density (hardening),
• random scission of network chains on reaction with oxygen and
• chemical modification of the polymeric chains- isomerisation.

Because polymers vary widely in their vulnerability to deterioration when exposed to the same environment, such ageing changes are unlikely to overlap in any one given material.¹⁶)

2.3 Classification of antidegradants.

Antidegradants are mainly refined petroleum products or other chemical materials that are compounded with rubber so as to protect it from premature ageing in the presence of oxygen, heat, ozone or light during storage or service of the rubber product.¹⁷) These materials are normally added to rubber mixtures in amounts of 1-3 parts per hundred parts of rubber (phr), and sometimes up to 5 phr. The degree of protection depends primarily on the composition of the antidegradant and there is no known antidegradant that gives maximum protection against all ageing processes without causing some other side effects like discolouration. More often than not each antidegradant has a certain "activity spectrum" of protection against mentioned processes with specific discolouration behaviour and therefore making selection much easier.¹⁸)

Antidegradants are normally classified into two functional groups,⁴,⁶,⁸,⁹) namely:

a) antioxidants:- those antidegradants that give protection against ageing caused by oxygen, steam and light, and

b) antiozonants:- those that protect the rubber from cracking as a result of ozone attack.

Despite this breakdown, antidegradants are also known to be complex and multifunctional with a majority of antioxidants exhibiting very strong antiozonant characteristics and vice-versa. This relationship is to be understood in the light of the fact that most chemical antidegradants used in the rubber industry are derived from the same basic materials and this leads to the following chemical classification.⁹)
i) aromatic amines from where ketone amine condensates, substituted mono-arylic amines and substituted p-phenylenediamines are produced. These are mainly very effective but staining antiozonants some of which have high levels of antioxidant activity.

ii) sterically hindered substituted phenols which provide mono-phenols, polyhydroxyphenols, bisphenols and thiobisphenols. Phenols have a lower protective effect than amines but their oxidation products are less coloured and with minimum staining. Some of these groups produce good to very good antioxidants which also exhibit antiozonant characteristics. (see appendix)

2.4 Oxidation and ozonation in rubber.

The classification of antidegradants as antioxidants and antiozonants requires that the main roles and mechanisms of protection of each group be defined even though it is recognised that their basic functions tend to overlap.\textsuperscript{[7,8]} It is important to note that antiozonants, are with exception of the waxes, generally also protectors against oxygen and heat but not every antioxidant is effective against ozone crack formation. The reaction of rubber with oxygen is of a chain character with an autocatalytic course. In order to retard or even to suppress its course, the free radicals formed should be bound or the peroxides and hydroperoxides formed should be decomposed to innocuous products and this is the role of the antioxidant. Indeed the effects of oxidation and ozonation in rubber have been confused by a majority of rubber users for many years, compelling researchers to clarify the main differences between the two processes.\textsuperscript{[10]}

The table below summarises the differences as observed:
Table 2.1- Distinction between ozonation and oxidation.\textsuperscript{[10]}

<table>
<thead>
<tr>
<th>FACTOR:</th>
<th>OZONATION</th>
<th>OXIDATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cause</td>
<td>Ozone (O\textsubscript{3})</td>
<td>Oxygen (O\textsubscript{2})</td>
</tr>
<tr>
<td>Affected area</td>
<td>surface of rubber</td>
<td>throughout rubber</td>
</tr>
<tr>
<td>Effect on rubber</td>
<td>cracking, frosting</td>
<td>hardening, softening</td>
</tr>
<tr>
<td>Effect of temperature</td>
<td>no effect</td>
<td>doubles with 10\degree C increase</td>
</tr>
<tr>
<td>Effect of cure</td>
<td>no effect</td>
<td>slight protection</td>
</tr>
<tr>
<td>Effect of strain</td>
<td>increases cracks</td>
<td>no effect</td>
</tr>
</tbody>
</table>

In the same light, the mechanisms of attack by oxygen and ozone on rubber can be contrasted. While oxidation involves the basic formation and consumption of radicals in a process of either polymerisation or depolymerisation, ozonolysis entails the breakdown of the double bond system of the rubber chain leading to premature failure of the component. While the key to the process of oxidation is the initial formation of a free-radical species in a process involving initiation, propagation and termination (Figure 2.1), the ozone reaction with unsaturation, on the other hand, results in the formation of an ozonide from the recombination of a double ion and a carbonyl compound through an electrophilic mechanism. At high temperatures free radical formation by cleavage of carbon-hydrogen and carbon-carbon bonds becomes likely during oxidation. The resultant free radicals formed during processing react with the oxygen to form deleterious peroxides.

By making the assumption that peroxides are present in even the most carefully prepared raw rubber, the ease of oxidation of rubber at low to moderate temperatures is understandable. At low temperature oxygen absorption is roughly linear to reaction time and yet at elevated temperature the originally linear reaction changes to an auto catalytic

\textsuperscript{1} Ozonolysis is the specific process of attack by ozone on unsaturation as distinguished from general ozonation which implies reactions in which ozone is involved.
Relatively small amounts of bound oxygen lead to deep seated changes in the structure of the vulcanizate, not only on the surface but also in the bulk of the vulcanizate. Depending on the type of rubber involved, oxygen through an ageing process, can lead to all and more of the structural changes mentioned in section (2.2) and in this the oxidation process follows the mechanism steps of initiation, propagation and termination. All these changes can be prevented by the use of specific antioxidants for different rubbers in different applications.

The mechanism of oxidation as expressed in the Bolland Scheme \cite{111} is shown below.

![Figure 2.1- Mechanism of Oxidation process\cite{13}](image)

Radicals that initiate oxidation in polymers are formed by thermal energy, ultraviolet radiation, bombardment by high energy particles, mechanical stress, metal catalysis and the addition of initiators. When polymer bonds are ruptured under any of these conditions and oxygen is present in the environment, oxidation can easily occur.

Following the work by Bolland and similar studies by Dunn\cite{12}, it is now accepted that the basic functions of antioxidants should include the following:
• suppression of initial free radicals that initiate degradation of the rubber;
• deactivation of the chain propagation step of degradation;
• decomposition of peroxide intermediates that produce free radicals.

The three basic requirements for antioxidants mentioned above form the basis for current research and development into more effective industrial antioxidants. A parallel can be made with a case for antiozonants and it will no doubt be accepted that their basic function is to prevent ozone from attacking rubber by means of a system which is either:

1) naturally (inherently) impermeable to ozone, or
2) reacts with ozone to produce a product impermeable to ozone.

This analogy does tally well with the findings of researchers regarding the nature of antiozonants be they of physical or chemical nature. However, the parallel given above does not offer any clues on the essential mechanisms involved in antiozonant action. In some literature and research studies carried out,[16,13-15] suggests that antiozonants act by two different mechanisms:

a) by increasing the critical stress required to cause cracking. Antiozonants in this group provide mainly physical protection against ozone.[14,16,17]

b) by reducing the rate of growth of cracks which have already been formed. Antiozonants in this group provide chemical protection for the rubber.[18-20]

The general consensus currently held is that an antiozonant reacts with ozonides formed on the rubber surface producing a protective film that prevents the access of ozone to the rubber. The ozone attack on unsaturated rubber is basically similar to the ozone attack of model olefins originally proposed by Criegee.[21]
The sequence of events outlined by this model starts with the contact between the rubber double bond system and ozone from where the so called primary ozonides or molozonides are produced. In the presence of oxygen these ozonides change to oxides like ketones, aldehydes and other carbonyls which become the core of the ozonation process. The initial step in the mechanism as shown in (Figure 2.3.) involves nucleophilic attack of a resonance form of ozone on the olefin to form a cyclic ozonide or molozonide (III). This is rapidly rearranged by heterolytic cleavage of the oxygen-oxygen bond resulting in the formation of an unstable zwitterion (IV). This first stage zwitterion breaks down to form another ion (V) together with an aldehyde or ketone (VI) and it is this new ion (V) which becomes the key to the ozonation process.

The reaction of ozone with olefins is known to be extremely rapid, with a low activation energy. The fact that ozone attack on olefins occurs very rapidly implies that the attack by ozone on unsaturated rubber occurs at the exposed surface and olefins in the interior of the sample would be attacked only after all of the surface olefins had been consumed.
This being right therefore, the ozonation of unsaturated rubber appears to follow the mechanism steps of: consumption of double bonds, decrease in molecular weight, formation of carbonyl compounds and the ultimate formation of ozonides.

\[
\begin{align*}
&\text{I} \quad \begin{array}{c}
\text{C} \quad \text{O} \\
\text{C} \\
\end{array} \\
&\text{II} \quad \begin{array}{c}
\text{C} \\
\text{O} \\
\end{array} \\
&\text{III} \quad \begin{array}{c}
\text{O} \\
\text{O} \\
\end{array} \\
&\text{IV} \quad \begin{array}{c}
\text{O} \\
\text{O} \\
\end{array} \\
&\text{V} \quad \begin{array}{c}
\text{O} \\
\text{O} \\
\end{array} \\
&\text{VI} \quad \begin{array}{c}
\text{O} \\
\text{O} \\
\end{array}
\end{align*}
\]

Figure 2.3 - Ozonation of olefins.\textsuperscript{[11]}

It is generally accepted in theory and for most practical purposes that both antioxidants and antiozonants require a certain amount of migration within the rubber product in order to fulfill their protective functions.\textsuperscript{[22]} The question of migration of these antidegradants has not always been gratifying for most practical applications. It had been noticed with dismay that due to this migration, some antidegradants had gradually disappeared from the areas that needed protection resulting in an escalation in premature failure.\textsuperscript{[23]} In some instances the reasons for the disappearance of the additives would remain a mystery, and yet in the majority of cases leaching out through some solvent or even evaporation at high temperatures were given as the rationale. Antidegradant migration has also been blamed for extensive staining resulting in unmarketable products.
2.5 Bound antioxidants

Due to the problems faced with migration of antidegradants in general, the urge to "bind" them to substrates has lingered long in the minds of most researchers in this field. As early as 1964, Sir Harry Melville, speaking at the Natural Rubber Producers' Research Association (NRPRA) Jubilee Conference, said the problem of retaining antidegradants in the rubber would be a thing of the past if it became possible "to attach the rubber molecule at the vulnerable points, without affecting other properties, specific groups that would effectively diminish the severity of the attack by both oxygen and ozone."[24]

It was therefore no surprise when Cain and co-workers made a breakthrough with "tying up the antioxidant" in 1968.[25] The incidental finding was made during an experiment on the oxidation of squalene at 100°C in the presence of an aromatic nitroso compound N,N'-diethyl-p-nitrosoaniline (DENA) when it was noted that the normal reaction tended to stop after a period of time. Analysis led to the discovery that during the oxidation process, p-phenylenediamine was formed and subsequently joined to the isoprene units leading to the termination of the reaction. A potential rubber bound antioxidant had been produced. The bound antioxidant proved to be inextractible, non-migratory, non-staining and above all showed no signs of blooming in storage. It was from this research that the term 'network-bound antioxidants' developed and from this initial discovery a whole spectrum of research activities in binding different antidegradants to rubbers were pursued relentlessly.[23,26]

It has been demonstrated in other research work that the synthesis of rubber-bound antioxidants and indeed that of antiozonants, follows an almost charted route of reacting a rubber containing a reactive pendant group with an antidegradant containing a substituent group capable of reacting with the one attached to the rubber.[27] Obviously the choice of the appropriate antioxidant or antiozonant for the relevant rubber type remains of paramount importance if positive results are to be achieved.
In 1972 Cain and co-workers\textsuperscript{28} demonstrated that bound antioxidants, completely resistant to extraction by water or organic solvents, could be produced through an initial 'ene' reaction of either natural rubber and synthetic rubbers with 4-nitroanilines or 4-nitrosophenols. Among these, 4-nitrosodiphenylamine (NDPA) was found to be the most effective of the 4-nitroanilines while nitrosophenols gave much less effective antioxidants and showed considerable variations with substitution in the aromatic ring. In some cases bulky substituents were found to completely prevent the formation of effective bound antioxidants. However, the method used showed that almost any unsaturated material may be converted to an antioxidant by this reaction.

The antioxidant activities observed here were comparable with those of many commercial materials and, where measured, the resistance to leaching by water and some oils was greater. Undoubtedly the most outstanding property of the formed bound antioxidants was their ability to survive an extremely exhaustive extraction process. On the other hand this work by Cain and co-workers also revealed that the lack of mobility of bound antioxidants (Figure 2.4) may be responsible for their inactivity against ozone attack in natural rubber since it is known that surface diffusion of \textit{p}-phenylenediamine type antiozonants occur on exposure to ozone. Besides natural rubber, unsaturated synthetic rubbers such as styrene butadiene rubber (SBR), polybutadiene rubber (BR), nitrile butadiene rubber (NBR) and chloroprene rubber (CR) were reported to have formed rubber bound antioxidants with NDPA during normal vulcanisation.\textsuperscript{29} Evaluation tests done on the new products showed that the rate of change of some physical properties of interest, like storage hardening, was controlled; rate of crystallisation of natural rubber at \textit{-26°C} was reduced; while tensile strength retention and plasticity retention index (PRI) were equally enhanced by the binding.
Following shortly on Cain's work, Kline and Miller introduced a new concept of polymerizable antioxidants\[^{30}\] for emulsion rubbers, whereby units of an antioxidant are chemically attached to a polymerizable segment of the same molecule. Like most previous work in this area, this research was an attempt to avoid the serious disadvantage of conventional antioxidants i.e. their detrimental disappearance from rubber during service because of volatility and extractability. Since attachment of an antioxidant to rubber had been achieved by reacting a rubber containing a reactive pendant group with an antioxidant containing a substituent group capable of reacting with the one attached to the rubber, this research with emulsion rubbers had all the marks of success. The antioxidant functions used in this work were the 4-anilinophenyl group (I) and the 3,5-di-t-butyl-4-hydroxyphenyl group (II) while the polymerizable functions were $\alpha$-$\beta$ unsaturated acryl groups such as acryloyl (III) and methacryloyl (IV).
These compounds and many more from the \( \alpha-\beta \) chlorides of unsaturated acids and phenolic antioxidants were designed to be used as co-monomers in the preparation of selected emulsion rubbers in which the antioxidant components would remain bound to the rubber and still perform their protective functions effectively. Both phenolic and amine polymerizable antioxidants produced exhibited characteristic properties typical of their original classes.

Copolymerized antioxidants in polyether-ester elastomers were studied by Wolfe \(^{31}\) and published in one of his many articles on additives. The polymeric substrates employed in this study of copolymerized antioxidants belong to a class of segmented polyether-ester polymers which have found commercial use as thermoplastic elastomers. The polymers are composed primarily of a random sequence of amorphous poly(tetramethylene ether) segments, which provide elasticity, and crystallizable tetramethylene terephthalate polyester segments, which act as virtual crosslinks providing high melting points and rapid crystallisation rates. It should be noted that as a prerequisite, copolymerizable antioxidants must react strictly bifunctionally with the chosen ester and hydroxyl groups since monofunctional reactions result in weak low molecular weight polymers while polyfunctional reactions result in chain branching with gel formation.

Effective antioxidant protection is essential for polyether-ester elastomers as they are frequently exposed to high temperatures not only during synthesis by melt-condensation copolymerization but also during isolation, fabrication and end-use application. Only phenolic antioxidants were chosen for synthesis in Wolfe's work since severe reaction
conditions and the chemistry of the melt-condensation process impose stringent limitations to the nature of the antioxidant to be used, although some amine linkages were incorporated to enhance the general combination. This research showed that antioxidants copolymerized into polyether-ester elastomers increase the resistance of the elastomer to degradation by heat ageing. It was also concluded from this work that dimethyl-3,5-di-t-butyl-4-hydroxybenzenepropanamido isophthalate (BPI) antioxidant structure gave the best results with polyether-ester elastomers.

Wolfe, like other researchers, found that polymer-bound antioxidants have less freedom of movement within the substrate they are protecting than do conventional antioxidants. If this is taken as a disadvantage, then it could be alleviated by adding small amounts of conventional antioxidants to systems only protected by polymer-bound antioxidants. The more mobile conventional antioxidants could migrate between the area where it acts to inhibit polymer degradation and the next bridge formed by the bound-antioxidant. Parallel to this assertion, further research has shown that a small amount of non-bound amine antioxidant increases further the resistance to heat ageing of elastomers protected by copolymerized phenolic antioxidants. It has been noted that this functional relationship between bound and conventional antioxidants might be attractive for polymers in which large amounts of conventional antioxidants cause extensive blooming and staining.

Recently Al Mahdawe and Stuckey showed that polychloroprene rubber (CR) type-W (the mercaptan modified homopolymer) reacted with some amines to form rubber bound antioxidants, following the discovery that the allylic chlorine atoms of the mercaptan-homopolymer have a tendency to react with amine antioxidants. Three amine antioxidants were used in this study and they included N-Isopropyl-N'-phenyl-p-phenylenediamine (IPPD) and N,1,3-dimethylbutyl-N'-diphenyl-p-phenylenediamine (DMBPD) both products of Monsanto and N,N'-diphenyl-p-phenylenediamine (DPPD) supplied by Vulnax International Ltd. Of these, IPPD was found to give the best results
as a bound antioxidant with polychloroprene. The study showed that IPPD reacts with CR type-W during which 6.35 phr of antioxidant, an amount equivalent to each 37 chlorine units, remains bound into the polymer during mixing and yields about 1.4 phr of bound antioxidant during vulcanisation. When a small amount of IPPD was used (up to 3phr), there was an increase in the modulus which gradually decreased as the concentration increased. The initial increase was probably due to the fact that the basic IPPD acts as an accelerator but increasing amounts block the reactive chlorine atoms and effectively reduce their overall reactivity. It was also demonstrated that the protection given by IPPD bound by processing before vulcanisation was very inferior to that produced when the antidegradant was bound in situ during vulcanisation.

Al-Malaika[14] notes that chemical agents that interfere with polymer degradation reactions provide the ultimate antioxidant for the protection of the polymer during processing and service. In order to achieve the highest degree of antioxidant substantivity, a novel reactive processing procedure that aims at in situ modification of the polymer backbone while mixing has been proposed. The end result of this process is the production of protective polymer-bound adducts that are fully compatible with the unmodified elastomer. The advantages of rubber bound-antioxidants over conventional antioxidants are discussed through all the references quoted above and these can not be over emphasised. These advantages include the resistance of bound antioxidants to extraction or volatilisation, the inability to bloom, no migration to result in discoloration or staining, user friendliness (no direct dealing with powders and chemical dusts) and an overall total protection as opposed to mere surface protection.

Despite all these positive attributes of rubber-bound antioxidants, the contemporary rubber industry remains in favour of conventional antioxidants because of their very low costs. More and more suppliers are coming into the market with improved or new brands of antioxidants and thus cutting down the prices of the materials. Undoubtedly,

1 The ability of an antioxidant to remain in a polymer through aggressive conditions.
more needs to be done to raise the image and reduce the price of bound antioxidants to the level enjoyed by conventional ones if all the merits enumerated above are to be enjoyed by the consumers. The escalating demands on rubber products for enhanced service life in increasingly more hostile environments may well be another relevant motivation for the use of bound antioxidants.

2.6 Research in antiozonants.

2.6.1 Theories of antiozonant protection

It is fair to say that the actual mechanism of protection by antiozonants has for some time eluded researchers, who have been content with some acceptable theories which endeavour to explain the process. Be that as it may the extent of research in this field has led to several theories being proposed and currently three main ones are extant. These include:

2.6.1.1 The relinking theory;

This theory assumes that the major role of an antiozonant in a given compound is to relink ozonized rubber fragments resulting from ozone attack on the surface. Braden and Gent\textsuperscript{135} observed that when severed molecular ends move apart relatively sluggishly, the general attack by ozone on the underlying material is delayed. They suggested in their discussion that the sluggish separation of the newly formed molecular end groups allowed for some recombination to take place. It should be noted that findings from this work were particular only to the use of N,N'-dioctyl-p-phenylenediamine (DOPPD) as an antiozonant which supposedly reacted with ozonized rubber to yield a "strong material R." Despite the fact that the researchers noted that severed molecular ends separate due to the deformation at the tip of the growing crack, their hypothesis of relinking remains very much alive.

Andrews and Braden\textsuperscript{141} pursued the issue of relinking culminating in an equation with no direct chemical evidence i.e.

\[
\text{Rubber + DOPPD + Ozone} = \text{brittle layer material}
\]
This work cast more and more doubt on the feasibility of relinking as a mechanism theory while strengthening the effectiveness and formation of surface reaction products as means for ozone protection. Razumovskii and Batashova thus convincingly showed that under normal circumstances olefins and double bond systems of rubber chains do not react with ozone as long as IPPD or some such antiozonant is present in the system. The researchers went further to demonstrate that even IPPD-Ozone reaction products could not react further with other ozonides and thus the crosslinking between rubber chain fragments was untenable.

The relinking theory has not been accepted because of many obvious flaws in it. Among these is the fact that it has been established beyond any doubt that when rubber chains are cleaved by ozone, they immediately separate due to retractive forces and therefore no type of relinking would prevent exposure of the underlying double bonds. Studies have also shown that ozone reacts exclusively with the antiozonant on the surface and that the rubber is not involved.

2.6.1.2 The scavenging theory;

The scavenging theory can be traced back to the early work done by Cox in which he proposed that for an additive to protect a rubber compound from ozone degradation it must function in one or more of three possible ways:

- form a physical barrier over the rubber surface and therefore prevent contact between rubber and ozone,
- react preferentially with the ozone before an attack is made on the unsaturation system of the rubber,
- react with the rubber ozonide or a precursor in such a way as to prevent chain scission even though ozone reaches the double bond system.

All in all the theory looks at the antiozonant as a scavenger of ozone due to its exceptional reactivity and equally assumes that the antiozonant functions by migrating to the surface of the rubber where it has a chance to react with the ozone before it attacks the double bond system. Research has since shown that antiozonants react much more rapidly with ozone than do the double bonds of the rubber they protect, while ozonized products react much more slowly. This has given a lot of credibility to the theory and
made researchers look more critically at the solubilities and rates of diffusion of antiozonants, specific reactivities of antiozonants with ozone and also to study the reactivity of ozone in relation to the concentration of double bond systems on the rubber surface.

In an earlier paper Biggs[40] referred to work done by the Augustana Research Foundation in which experiments with models of unsaturated rubber (mixtures of unsaturated hydrocarbons and antiozonants) showed the preferential reaction of the antiozonant with ozone. This work concluded that the amount of antiozonant at the surface at any time is a function of a number of factors prime of which are:

- its concentration and solubility in the polymer;
- its rate of diffusion through the polymer;
- previous contact of the surface with ozone and;
- the volatility of the antiozonant.

The scavenging theory remains credible despite the fact that the general rate of diffusion of antiozonants to the surface has been found to be too slow to support the possibility of total scavenging all the ozone on the surface.

2.6.1.3 The protective film theory;

This theory states that an antiozonant protects rubber from ozone attack by reacting rapidly with ozone to produce a film on the surface of the rubber which prevents penetration by free ozone. Earlier proponents of this theory include Erickson[41] and co-workers who observed that SBR vulcanizates in a relaxed state and exposed to low concentrations of ozone eventually formed a film on the surface. The film so formed proved to be a barrier against any further reaction with ozone. The researchers also noted that rupture of the protective film resulted in immediate cracking. Following this work, a report was issued to the effect that where an antiozonant is present, protection against cracking is possible when the following criteria are met:

- there is a specific reaction between the antiozonant and ozone,
- the initial concentration of the antiozonant on the surface is enough to form a film barrier of oxidized residue and
there is a continuous migration of fresh antiozonant from within the rubber to the outer surface of the film.

Lorenz and Parks\textsuperscript{[39]} showed through microscopy studies that a film had been formed on the surface of test pieces with the result that consumption of the antiozonant was not proportional to the initial concentration. Lake\textsuperscript{[42]} went further in his investigations of the protective film and made an analysis of the constituents of the layer. He pointed out that the protective layer formed on the rubber surface was composed of predominantly unreacted antiozonant and polar ozonized products. These could be removed either mechanically by scraping or chemically by swabbing off with an appropriate solvent. The need for an antiozonant to be soluble in the rubber is also discussed and contrasted with the essential insolvability of its reaction products.

Using attenuated total reflectance (ATR) spectroscopy, Andries\textsuperscript{[43]} and co-workers studied the surface film formed by ozonation of DOPPD and observed that the film produced compared well with one produced from the liquid form of the antiozonant. This proved to be evidence of diffusion of the antiozonant to the surface. At the end of this debate on the mechanism of antiozonant action, the position held by researchers in this field of study has been to accept a combined "scavenger-protective film" theory which stipulates that an antiozonant migrates to the surface of the rubber and preferentially reacts with ozone to produce a layer of polar ozonized products impenetrable to ozone.

### 2.6.2 General research interests

While so much was going on in the field of antioxidants, research in antiozonants took a somewhat unimpressive and low profile. It is a fact that research in antioxidants has generally been done parallel with that of antiozonants although altogether in different areas of operation. Where results have been outstandingly positive for antioxidants, very little or nothing at all is recorded as a means of contrast or comparison with antiozonants despite the sometimes overlapping functions of the two antidegradants. If the differences between oxidation and ozonation are fully upheld, then it is logical that
research involving any of these antidegradants can be carried out independently of each other. Within the past twenty five to thirty odd years, research in antiozonants for natural and synthetic rubbers has had a bias towards the following areas of interest:

a) **Use of blends for ozone protection of NR**,  
b) **Improving the ozone resistance of NBR by blending with EPDM and PVC**,  
c) **Effectiveness of different types of waxes as antiozonants**,  
d) **Replacement and/or combination of waxes and chemical antiozonants**,  
e) **Products of ozonation from different chemical antiozonants**,  

In a recent review on blends for ozone protection of natural rubber by Lattimer and Layer\textsuperscript{137}, the two authors correlate their findings with those made earlier by Andrews\textsuperscript{144} on the same topic. It was noted in these studies that blends of natural rubber with different levels of EPM showed different intensities of cracking while the crack density was observed to increase as the proportion of EPM decreased. A further interesting and crucial observation was that, while many cracks terminated at the unreactive EPM particles others appeared to jump and continued to grow without rupturing the obstacles. The notion of crack circumvention was dismissed in this research as its realisation would involve cracks propagating parallel to the applied stress.

Consequently, the current accepted position is that the ozone-inert phase in an elastomer blend imparts necessary protection to the material in that it raises the critical stored energy required to initiate macroscopic ozone cracking. The role of the inert phase appears to be to hinder the development of macroscopic cracks from microscopic ones by providing physical barriers to crack propagation. These barriers may be overcome by the crack jumping and bridging the inert particle and all this depending on the proportion of the inert material in the blend and the stored energy density in the specimen. Under dynamic service conditions, where flexing by itself supplies the energy to disturb the surface and thus no critical energy is required\textsuperscript{144,45}, polymer blends do not completely
prevent cracking but help to slow down the rate of crack growth by reducing the segmental mobility of the rubber chains.

Materials that have been used extensively in blends for ozone protection of natural rubber are polyvinylchloride (PVC), EPM and EPDM.\textsuperscript{[46]} Loadings of 20 to 40 parts of EPM or EPDM produce positive results although it is apparent that the higher the loadings the poorer the properties of the blends become. Amounts above 50 parts of the blending material do not improve the protection level any better than lower loadings do. It is also important to note that blending is referred to as the only effective non-discolouring method of protecting rubber against ozone under dynamic conditions.\textsuperscript{[47]}

A good deal of research\textsuperscript{[48-50]} has been done on blending of NBR with saturated polymers such as PVC and EPDM as a means of improving its ozone resistance without discolouring. Through these investigations it has been demonstrated that the ozone resistance of NBR can be improved by blending the elastomer with EPDM without a reduction in the original desired properties of the unblended polymer. The addition of EPDM to NBR at various levels ranging from ratios of 50:50 to 70:30 has yielded variable results depending on the different curing systems being used. Poor physical properties in blends have been attributed to improper partitioning of curatives between the rubber phase. Researchers however, agree that a combination of appropriate mixing procedures and compounding systems may be the key to obtaining ozone resistance with 25% or less of EPDM. Such a low level of EPDM is necessary to ensure fair retention of the basic property of NBR which is oil resistance.

NBR-PVC blends were dealt with much earlier\textsuperscript{[51-50]} than the NBR-EPDM types and the early discovery of their economic significance resulted in extensive commercialisation and academic attention focused on them. A prime objective of these studies has been to establish the best grades of NBR and PVC that would provide the best property combination. NBR of medium acrylonitrile content together with a high molecular
weight PVC resin at a ratio of 70:30 have so far given the best ozone resistance while properties like oil resistance and ageing resistance have been well maintained. It has been demonstrated that blending NBR with PVC necessitates a trade off in properties whereby nitrile rubber contributes low temperature flexibility and resistance to crack growth on flexing while the PVC contributes to abrasion and ozone resistance. The chosen acrylonitrile content should in turn reflect a compromise between low temperature flexibility and oil resistance.

Protective waxes are broadly classified into two types: paraffin and microcrystalline waxes. The former are predominantly straight-chain hydrocarbons of relatively low molecular weight and large crystals whose melting points range from 38 to 74°C. On the other hand microcrystalline waxes are produced from high molecular weight petroleum residues and have smaller irregular crystals which melt from about 57 to 100°C. This temperature difference between paraffin and microcrystalline waxes has necessitated the use of blends of these waxes in order to guarantee protection over the widest possible temperature range since these antiozonants protect the rubber through temperature-dependent solubility.

![Electron micrograms of wax bloom at magnification of 1000x](image)

**Figure 2.5**-Electron micrograms of wax bloom at magnification of 1000x
At dosages ranging from 1 to 3 phr, waxes dissolve in the hot rubber during compound mixing but exceed their solubility limit at ambient exposure conditions. This drives the wax to diffuse to the surface (bloom) where it creates a protective ozone barrier. The migration occurs continuously until an equilibrium is reached between the wax on the surface and the rest in the bulk of the rubber. If effective protection against ozone attack is to be achieved, the fragile balance created between solubility and migration of the wax must be upheld. Layer and Lattimer\textsuperscript{[53]} also noted that effective protection is only attained when the film (bloom) is thick enough to constitute a barrier to ozone.

It has also been reported in a separate research on waxes that the ability of a wax to migrate to the surface depends upon the specific wax type, the rubber composition, and the time and temperature before and during exposure to ozone.\textsuperscript{[54]} All these factors together with bloom density, wax continuity, flexibility and wax adhesion to the rubber influence the ability of the wax to protect. Waxes, although cheap and easy to incorporate into rubbers through compounding, are effective only under static conditions. This inadequacy is alleviated by combining or totally replacing them with chemical antiozonants.

The weaknesses of wax protection against ozone have been studied by a number of researchers who have concluded unanimously that waxes can not protect rubber under dynamic conditions due to the inextensibility of the wax film.\textsuperscript{[44,46]} Normally during flexing in dynamic applications, the "film" or wax bloom is broken and this allows ozone to attack the underlying rubber since no other mechanism or material is in place to replenish the damaged protection. This then is one of the main disadvantages of waxes which has confined them to protection only under static conditions while chemical antiozonants take over the protection in dynamic conditions.

Unlike waxes, chemical antiozonants react with ozone much faster than do the double bonds of the rubber they protect and in this way are therefore able to deal with the
ozone before it gets to the rubber. The polar ozonized products of the reaction between the chemical antiozonant and the ozone remain on the surface and act as a barrier to further ozone attack. The unique feature of chemical antiozonants is that when the protective barrier is damaged during flexing and general application, the initial reaction is restarted by the migrating antiozonant and this process generates more ozonides to replenish the broken barrier.

The combination of a wax and a p-phenylenediamine (PPDA) comprises a common antiozonant system in which the wax acts either as a diluent leading to a slower rate of cure or as an internal lubricant reducing the heat history of the compound. Based on the premise that wax is the dominant factor in static ozone protection, it is theorised that the addition of a PPDA to an elastomer may cause the development of a higher level of wax bloom. The results from tests based on this assumption indicate that at 1 phr wax, an increase in PPDA concentration from 1 to 3 phr causes the wax bloom to increase from approximately 15 to 30 mg/cm². (Figure 2.6)

![Figure 2.6- Wax bloom with addition of chemical antiozonant, Santoflex 13](image)

\[\text{Figure 2.6- Wax bloom with addition of chemical antiozonant, Santoflex 13}^{[55]}\]

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1 Santoflex 13, antiozonant N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (HPPD)-Monsanto
It is also noted that as the level of wax increases, protection against intermittent ozone exposure also increases indicating that a higher level of wax bloom develops for improved static ozone resistance. A combination of wax and PPDA, however, gives a level of protection under intermittent ozone exposure that is higher than either material by itself. This result therefore conclusively points out the major reason for using a wax/PPDA combination, which is to combine the static protection afforded by wax with the dynamic protection given by a PPDA. This work by Dimauro et al. further demonstrated that at practical levels of antiozonant, no synergism between wax and PPDA is possible in static or continuous dynamic ozone exposure tests. Significant synergism was however, observed only under intermittent dynamic conditions.

The research on products of ozonation from different chemical antiozonants has for the past fifteen or so years, been dominated by publications from Lattimer and co-workers.\cite{37,53,55-57} Ozonation of PPDA antiozonants gives rise to a multitude of surface products making separation and characterisation of the individual components extremely difficult. Since the interest in this field started, different methods of polymer characterisation including infrared spectroscopy, chromatography (gas and liquid), spectroscopy and micro-attenuated total reflectance infrared spectroscopy, have been used to identify the tens of different products formed during ozonation of different PPDAs.

Prior to all the recent work on the subject, Lorenz and Parks\cite{39} applied the technique of gas chromatography to follow the reactions of ozone with a model polyisoprene in a bid to identify the ozonides produced. Among other findings, they reported that the action of two different p-phenylenediamines during ozonation of cis-polybutadiene vulcanizates included chemical reactions with ozonized rubber: a claim disputed by latter day researchers who consider the relinking theory untenable. In one of their earlier papers, Lattimer et al.\cite{57} concluded that a number of predominantly low molecular weight species found on the rubber surface (e.g. amides, nitrones, nitrosoaryls) made up the
bulk part of the surface film. These species were said to be quite polar and relatively non-volatile due in part to intermolecular hydrogen bonding. Because of low solubility, diffusion of these species into the bulk of the rubber was unlikely; thus they remained on the surface to act as a barrier to ozone. The researchers also concluded that three principal mechanisms appear to govern the ozonation of PPDAs in general namely:

*amine oxide formation* which leads to the observed nitrosoaryl and nitroaryl products,

*side chain oxidation* which leads to several low molecular weight products while

*nitroxide radical formation* leads to the production of a nitrone which is the most abundant ozonation product. Furthermore, the result of these studies confirm that the combined "scavenger-protective film" theory of antiozonant protection of rubber compounds can be relied upon. No evidence has been shown that ozonized rubber reacts with antiozonants during the ageing of rubber vulcanizates thus ruling out the possibility of a relinking theory.

A number of review papers [110,57] have also appeared to compliment the ongoing research process. It seems from the above mentioned areas of research interests in antiozonants that the call for binding these additives like antioxidants was not taken as warranting equal attention. One author went on to defend the somewhat negative response to binding antiozonants by saying: "...bound-antiozonant is a contradiction in terms since ozone attack is essentially a surface reaction and its prevention depends on the concentration of an antiozonant at the surface." [121]

Such statements might have suggested to some aspiring researchers, that there was no need to try binding antiozonants if the term 'binding' only referred to the interlinking of the antidegradant to the chain structure of the rubber. There is however, a lot of research scope in this area and a well chosen topic in trying to bind antiozonants in the same manner that has achieved positive results for antioxidants will not be found wanting.
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CHAPTER 3.

DIFFUSION IN ELASTOMERS.

3. General concepts.
Diffusion in elastomers is the process by which matter is transported from one point of a piece of rubber to another.\textsuperscript{[1]} The driving force behind this transportation system is the absence of equilibrium caused by the difference in concentration coupled with the tendency to eliminate these differences through molecular motion. It is of fundamental importance to note that in diffusion through rubber, it is not only Brownian motion of the penetrant molecules that is involved, but also a micro-Brownian motion of segments of the rubber molecules. The rate of diffusion is generally controlled by the constant formation and concentration of “holes” big enough to allow passage of the diffusing molecules. From diffusion data information on the strength of intermolecular interaction forces of the elastomer, the relationship between molecular structure and various physical properties can be deduced.

The practical importance of diffusion in elastomers cannot be over emphasised since numerous examples can be given. It is well known that during vulcanisation the various compounding ingredients dissolve and diffuse through the rubber, and only form a homogeneous dispersion through diffusion.\textsuperscript{[2]} The overall useful properties of a rubber article can be traced back to this initial diffusion process of the various ingredients within a compound and a good example of one such property is optimum ozone protection. Most elastomeric products are used in contact with foreign molecules which may be gases, liquids or solids that can easily diffuse into the elastomer resulting in some form of material accumulation, oxidation or ageing on the surface. It should be noted therefore that in some cases the diffusion process can be a cause for concern if the distribution of matter results in a negative change of physical properties like loss of antidegradant protection, loss of tackiness and staining of light coloured compounds.
3.1 Diffusion coefficients

In elastomers, diffusion can be considered as a process which seeks to balance the level of substance distribution by assuming that the rate of transfer of the diffusing matter through a unit section area of the elastomer is proportional to the normal concentration gradient produced. This can be expressed mathematically from Fick's first law\(^3\) as follows:

\[
R = -D \frac{\partial c}{\partial x}
\]  

(3.1)

where \(R\) is the rate of transfer of the diffusing matter,

\(D\) is the diffusion coefficient or proportionality constant and

\(\frac{\partial c}{\partial x}\) is the concentration gradient.

The diffusion coefficient also known as *diffusivity* gives information on the nature of the transport process and on the interaction of the molecules involved. For the movement of gases and simple liquids through polymers, the diffusion coefficients have been measured widely\(^{1,4}\) while data for such coefficients for polymers through polymers is not readily available. Depending on the concentration of the diffusing molecules, diffusion can either be a concentration-independent process whereby the diffusion coefficient remains unchanged by variations in concentration or a concentration-dependent process where the diffusion coefficient is variable.

More often than not, problems concerning constant diffusion coefficients are tackled by solving differential equations for one or three dimensional diffusion with appropriate boundary conditions. The diffusion coefficients of concentration-independent diffusion have been determined by a variety of methods each with its own error margins. From Fick's second law, valid for one dimensional diffusion, the concentration of the diffusing substance in an infinite medium can be expressed as a function of time and distance.\(^{5,6}\)
\[ c = \frac{m}{2\pi Dt^{1/2}}\exp\left(-\frac{x^2}{4Dt}\right) \]  

(3.2)

where \( m \) is the total amount of diffusing substance at time \( t \) and in plane \( x \).

An expression in terms of the mean square displacement and time can be derived for the diffusion coefficient \( D \) and this is given as:

\[ D = \frac{\langle \Delta x^2 \rangle}{2t} \]  

(3.3)

Equation (3.3) has been noted\(^7\) as very useful for the estimation of \( D \) vis-à-vis the depth of penetration of a diffusing substance in rubber and is particularly applicable to the Brownian movement of small particles. Over and above this dependence on the diffusing molecules, diffusion coefficients in rubber materials have been shown to be equally dependent on the type of curatives used for vulcanisation purposes. It should be noted also that diffusion is very much dependent on the nature and structure of the elastomer i.e. its molecular weight and chemical structure as well as on the size, concentration and solubility of the diffusing molecules. The determination of the diffusion coefficient of concentration-dependent diffusion offers considerable difficulties emanating from the vapour pressure of the penetrant as it swells the rubber during the diffusion process.

3.2 Diffusion of Antidegradants

Diffusion plays a vital role in the action of conventional antidegradants, whose protection mechanisms depend on their ability to migrate to the affected parts of the product. It has been noted that the diffusion of antidegradants in rubber articles is normally dominated by the emphasis on the process of material blooming which is fundamentally also a diffusion process.\(^8\) The theory behind blooming of antidegradants starts during compounding or mixing when, with an increase in compound temperatures to above the melting temperature of the antidegradants, the solubility of the ingredients in rubber increases considerably.\(^9\) During vulcanisation the dissolved antidegradants remain in solution and on cooling, their solubility decreases abruptly.
causing the materials to be supersaturated in the rubber and therefore reducing their dissolved concentration to an equilibrium value. A concentration gradient is therefore set up in the rubber forcing the dissolved material to diffuse to the surface where, in case of chemical antiozonants, the reaction with constituents of the environment (oxygen, ozone, etc) results in the formation of a protective bloom.

Although the basic causes of material blooming can be explained acceptably, the detailed mechanism of the process has remained very much unresearched. It is however, accepted that the general diffusion of conventional antidegradants i.e. the time taken by the antidegradant to migrate to the surface of the elastomer, can be taken as a function of the following parameters:

- concentration of the antidegradant;
- temperature of the elastomer;
- the solubility of the antidegradant in the elastomer;
- physical and chemical state of the elastomer, and
- physical and chemical state of the antidegradant.

Taking into account the above parameters, general research in this field has shown that the rate of diffusion of an antidegradant usually determines the thickness of the protective film or bloom formed on the surface of the elastomer. Curative migration is of particular concern in uncured tyres as these normally contain many interfaces between different rubber compounds with differing cure systems. Many curatives used in such studies\(^{[10,11]}\) have been shown to diffuse across a rubber-to-rubber interface.

![Direction of diffusion](image)

Figure 3.1-Arrangement for transfer diffusion
Diffusion of curatives has also been studied using transfer measurements\textsuperscript{[4]} (Figure 3.1) in uncured rubber and results have shown that curatives in general will readily migrate within the rubber following the classical laws of diffusion. In this classical diffusion study Lederer et al. monitored the diffusion process of several curatives in respect to temperature, distance of diffusant from initial point after a given time and the amount of the diffused material in the initially curative-free compound. It was clear from the many diffusion profiles, that the absolute change in curative concentration diminishes with increasing distance from the interface. (Figure 3.2) The diffusion coefficients were shown to be dependent on the curative type.

![Figure 3.2 Curative diffusion across an interface\textsuperscript{[4]}](image)

The magnitude of change in curative concentration generally increases with increasing storage time and or temperature while the rate of diffusion decreases with increasing molecular weight of the diffusing material. Most curatives are however, unlikely to play a major role in diffusion after vulcanisation has taken place as they are directly involved in the chemical formulation of the new rubber structure and thus diffusion of antidegradants is more of a concern in cured rubber articles. Due to lack of a cross-linked structure in uncured rubber, it is fair to assume that the rate of diffusion in an
uncured structure is much faster than in cured material. The higher the crosslinking density, the slower the diffusion rate is likely to be and vice versa.

3.3 Measurement of Diffusion.
Gardiner\textsuperscript{[12]} used microinterferometry to measure the curative diffusion between rubbers. Through this unique method he showed that diffusion coefficients do change with curative concentration and concluded that during vulcanisation, a complete diffusion zone gradient is set up long before any significant crosslinking reactions occur. This development results in the change of the cure rate and mechanical properties. This work also expressed diffusion across an interface as similar to diffusion in a homogeneous rubber where a characteristic S shaped curve is obtained with inflection at the interface. (Figure 3.3)

![Figure 3.3- Diffusion of sulphur from NR to SBR\textsuperscript{[12]}](image)

Nah and Thomas\textsuperscript{[9]} worked on a wax blooming model and noted that during the initial stages of blooming, the system may be treated in the same way as that of an antiozonant diffusing out from a semi-infinite medium and the concentration of the antiozonant at the surface being given by its equilibrium solubility. This approach

\textsuperscript{1} The concentration of the antiozonant that finally remains in the rubber after all the blooming has stopped.
makes it possible to express the described process in the following mathematical relation[31 leading to the determination of the rate of material blooming.

\[
\frac{M_t}{t^{1/2}} = 2(w_o - s_o)(D/\pi)^{1/2}
\] (3.4)

where \(M_t\) is the amount of antiozonant bloomed per unit area
\(t\) - is the time taken by the antiozonant to bloom
\(D\) is the diffusion coefficient of the antiozonant
\(s_o\) is the equilibrium solubility and
\(w_o\) is the initial concentration of the antiozonant

Equation (3.4) can easily be rearranged as an expression of concentration when only the positive direction of material movement is considered and the end result gives a useful method of estimating the diffusion coefficient from the slope of the \(M_t\ vs\ t^{1/2}\) plots[3] in Figure 3.4.

\[
c_{x=0} = \left[ \frac{m}{D\pi t} \right]^{1/2}
\] (3.5)

\[
D = \left( \frac{m}{c} \right)^2 \left( \frac{1}{t \pi} \right)
\] (3.6)

where \(m\) is the total amount of the diffusing substance.

The theory of antiozonant diffusion and migration has also been viewed in respect to the reaction of ozone with an antiozonant at the surface of the rubber substrate where the surface is taken as a plane sheet.[3] In this case the mathematical expression of the process involves the following relation:

\[
dC/\ dt = -k_a C
\] (3.7)

where \(C\) is the concentration of the antiozonant at a given time \(t\),
Figure 3.4: $M_i$ vs $t^{1/2}$ (Reference: 9)

\[ a \text{ is the concentration of the ozone and} \]
\[ k \text{ is the bimolecular rate constant of the reaction.} \]

The solution to this diffusion problem is reached after an assumption that the concentration of the ozone at the surface of the rubber remains constant since the self-diffusion coefficient of the gas greatly exceeds the diffusion coefficient of the antiozonant in the rubber. The assumption leads to the rewriting of the equation as Fick's second law valid for one-dimensional diffusion which includes the diffusion coefficient.

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \]

(3.8)

This work by Braden led to the conclusion that the diffusion rate of an antiozonant decreases quite rapidly with time after the maximum rate has been reached. (Figure 3.5)
All in all, research work done over the years shows unequivocally that diffusion in elastomers plays a vital role in day to day operations. In tyre manufacture for example, various compounds with different curing systems are used in the making of the various components. Diffusion of additives in this case occurs from component to component and for each specific compound, the diffusion profiles and coefficients can be determined by using analytical and mathematical techniques.
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CHAPTER 4

COVULCANISATION AND ADHESION BETWEEN COATING AND SUBSTRATE.

4.1 Definitions

4.1.1 Covulcanisation

Covulcanisation can be defined as simultaneous vulcanisation of two polymers in order to improve specific properties of interest in one or the other polymer. The term implies the formulation of a single network structure including crosslinked macromolecules of the two elastomers through which equal vulcanisation across the microdomain interface must be achieved. Theoretically, covulcanisation can be accomplished when the chosen components of the polymer-polymer system are compatible, when the polarities of the polymers are closely related and when the cure rates of the polymers are distinctly similar. These indeed, are accepted necessary requirements for covulcanisation to occur but they are by no means sufficient conditions since other factors like curative solubility and migration are also determinant in achieving the process.

4.1.2 Adhesion

Several definitions of "adhesion" have been proposed over the years although no single one of these is completely satisfactory or generally accepted. An earlier definition from ASTM describes adhesion phenomenon as "the state in which two surfaces are held together by interfacial forces which may consist of valence forces, interlocking action or both." One of the more acceptable definitions is given by Wu who states that adhesion refers to the state in which two dissimilar bodies are held together by interfacial contact such that mechanical force or work can be transferred across the interface. The interfacial forces holding the two phases together may arise from van der Waals forces, chemical bonding or electrostatic attraction. Wu goes further and explains that the mechanical strength of the system is determined not only by interfacial forces but also by the mechanical properties of the interfacial zone of the two bulk phases. The underlying prerequisite to adhesion given by the above definition is for the
materials to approximate one another sufficiently to facilitate an interaction. Adhesion can also be looked at and discussed as either thermodynamic, chemical or mechanical in nature depending on the state of the interfacial energies at the interface.

When covulcanisation and adhesion occur during a single operation, there arises need to explain the mechanism of the occurrence while retaining the identity of each concept. A number of theories\(^4\) have since been proposed in an attempt to explain the interactions and adhesion between resin-based surface coatings and solid polymeric substrates at low and high temperatures. Four of the most prominent of these theories are summarised below.

4.2 Theories of Adhesion.

4.2.1 Adsorption theory:
The adsorption theory\(^5\) proposes that two materials adhere, at least initially, due to the presence of van der Waals's forces which act between the atoms in the two surfaces. Since these forces operate over small distances, the atoms in the two surfaces must be brought close enough for the forces to be effective. In a more extended review of this theory Kinloch\(^6\) further looks at two types of bonds (secondary and primary) being formed at the interface as a measure of strength for the adhesion. He expresses this as the work \(W_A\) of adhesion by the expression:

\[
W_A = \gamma_a + \gamma_b - \gamma_{ab} \tag{4.1}
\]

where \(\gamma_i\) is the surface free energy of each component.

The basic requirement for one or both of the materials is to conform better to the surface roughness of the other and thereby increase the interfacial area of contact. This is expressed as wetting\(^7\) and relates to thermodynamics of adhesion. Researchers here conclude that the positive aspect of the adsorption theory of adhesion is that it describes the essential process of wetting the adherend by the adhesive and shows that this does have a very definite correlation with the possibility of making a good interfacial joint.
4.2.2 Electrical theory:
The electrical (electrostatic) theory, in essence, treats the adhesive-adherend system as a capacitor which is charged due to the contact of two different substances. Adhesion is presumed to occur due to the existence of attractive forces across the electrical double layer at the interface. Deryagin\(^8\) and co-workers, the originators of the theory, suggested that the electrostatic forces arising from such double layer contact may contribute significantly to intrinsic adhesion. The mathematical basis of this theory is taken from Coulomb's Law of electrostatic forces between objects with different material properties and is expressed by the following equation:

\[
F = \frac{Q_1 Q_2}{4\pi \varepsilon r^2}
\]

where \(F\) is the electrostatic force,
\(Q_1\) and \(Q_2\) are point charges,
\(r\) is the distance separating \(Q_1\) and \(Q_2\) and
\(\varepsilon\) is the permittivity, characterizes the polarity of the medium.

From the onset, this theory met fierce criticisms from proponents of alternative theories like Vuyutskii\(^9\) and Vasenin\(^10\) who argued that the electrical double layer arises because of different pressures of electron gas in the two surfaces and not in the difference between the charges of the surfaces. They stressed that if the theory were to stand, adhesion should be least between similar materials and should therefore increase as the two become more and more different. In the same vein, Hays\(^11\) noted that the electrical theory missed the point when it looked at adhesion from a separation standpoint rather than from the forces that bring about the resultant bonding. Despite all the inconsistencies in the interpretation of this theory, in practice a number of technologies\(^12\) are based on electrostatic adhesion of particles.

4.2.3 Mechanical theory:
This theory has its origins from the work done by M'Bain and Hopkins\(^13\) who were at pains to distinguish between what they termed specific adhesion and mechanical adhesion. As it stands today, the theory\(^6\) proposes that mechanical keying, or interlocking of an adhesive into the irregularities of a substrate surface is the major
source of intrinsic adhesion. While the theory presupposes that the greater the surface irregularity and porosity the greater the joint strength, research work and the attainment of good adhesion between smooth surfaces exposes the theory as not being of general aptness.

Reports and results compiled by de Bruyne\textsuperscript{[14]} have raised doubts as to whether any significant penetration of adhesive into some configurations of irregular cavities can actually lead to the formation of a mechanical keying. Nonetheless, there are recorded instances where the applicability of this theory has been demonstrated to contribute significantly to intrinsic adhesion. Borroff and Wake\textsuperscript{[15]} showed in their research that the most important single feature in the adhesion of simple rubber to an uncoated fabric is the penetration of the protruding fibre ends of the spun yarn into the rubber. The intrinsic adhesion between the fibre and rubber arises from primary or secondary forces, i.e. either van de Waals or chemisorption bonds. In the final analysis, there is an attempt by researchers to quantify the strength of the bond formed at the interface by expressing it as a product of both mechanical and topographical components.\textsuperscript{[16]}

\[ J_s = m_c s_c \]  

(4.3)

where \( J_s \) is joint strength,

\( m_c \) is the mechanical component and

\( s_c \) is the surface component.

In a recent review of this theory Allen\textsuperscript{[17]} observed that the concept of interlocking can be considered on two different scales viz. macro scale and micro scale. The former scale refers to original and classical work like that of Borroff and Wake which still has a degree of acceptability, while the latter view refers to research by Packham and co-workers\textsuperscript{[18-20]} which has drawn the theory into the spotlight of adhesive technology. While on a macroscopic scale interlocking may be of little relevance, progressive work in this field has shown that at the microscopic scale it plays a vital role in adhesion.
4.2.4 Diffusion theory:
The diffusion theory proposed by Voyutskii\textsuperscript{21} states that intrinsic adhesion of high polymers to themselves (autohesion) and to each other, is due to mutual diffusion of surface layers of polymer molecules, each into the other to form an interwoven network across the interface. In order to achieve the above, a process of interpenetration of molecular chains must take place at the interfacial contact of two polymers governed by diffusion of segments of the macromolecules. The macromolecules or chain segments of both the adherent (substrate) and the adhesive must possess sufficient mobility and be mutually soluble i.e. they should possess similar or close values of their solubility parameters leading to thermodynamic compatibility.

Both one-way and two-way diffusion of the system should bring about the ultimate disappearance of any boundary between the two phases being replaced by a continuous transition layer from one polymer to the other. The strength of the bond $F$, formed at the interface can be assessed by taking into account three factors which have proved complex\textsuperscript{22} to quantify in practice.

\[ F = fQn \]  
(4.4)

where $f$ is the strength of a single intramolecular bond

$Q$ is the number of molecular chains crossing the boundary and

$n$ is the depth of the penetration of a unit

As it stands, the theory cannot explain the adhesion of polymeric materials to metals, glass or other hard solids since it is difficult to see how adhesion of these materials results from diffusion of the polymer into them. However, the limited diffusion observed by Vuyutskii and confirmed by Wake\textsuperscript{71} is all that is needed to bring about adequate adhesion between the surfaces.

Like all the other theories therefore, the diffusion theory has had its fair share of criticism\textsuperscript{10} and further research work continues to be carried out in this area.\textsuperscript{23,24} It is
also important to note that some researchers have further looked at the adhesion phenomenon as an occurrence that combines all the above theories and that it could be expressed as follows:

\[ \Psi = \alpha \Psi_M + \beta \Psi_A + \gamma \Psi_D + \delta \Psi_E + \ldots \ldots + \omega \Psi_\infty \]  

(4.5)

where: \( \Psi \) is total adhesion

\( \Psi_M, \Psi_A, \Psi_D \) and \( \Psi_E \) are mechanical, adsorption, diffusion and electrostatic components of adhesion respectively and \( \alpha, \beta, \gamma \) and \( \delta \) are their respective mixing constants.

Notably, all these theories cover the essential aspects like wetting and wettability of interfaces, solubility and compatibility of the polymer phases and ultimate adhesion of the materials on contact at the interface. There are however, no precise theories of interfacial actions or explanations about the development of network structures which appear during covulcanisation of elastomers in which one of the rubbers involved acts as the substrate (adherend). It is apparent though that the above mentioned theories are equally at play during covulcanisation but the analysis of events is more complex due to additional independent parameters like vulcanising agents, elastomer polarity and differences in cure temperatures between the bonding materials.

For all intents and purposes the adsorption theory remains by far the most generally accepted of the theories although a substantial amount of research work has been reported on the effects of diffusion across the polymer-polymer layer during vulcanisation of blends.

4.3 Assessment of covulcanisation.

Researchers have noted that the various theories of adhesion have each a vital role during covulcanisation of polymers in both solid/solid combinations and solid/liquid systems. The interpretations of how bonding occurs at the interface remain as varied as the number of researchers who care to discuss the issue. All however, are agreed that the ultimate measure of covulcanisation is interfacial network formation.

Shershnev suggests that a transition layer is formed on the phase interface as a result of segmental solubility. It is at this layer that the nature of vulcanisation will determine
the network structure formed. The composition of individual vulcanising systems (if independently compounded) and the solubilities of the curing agents within the transitional layer considerably affect the covulcanisation process while the nature of the polymer determines their ultimate reactivity. Tests for mechanical properties have been used to assess the effects of covulcanisation and network formation between the phases. An increase in mechanical strength and network density of a vulcanisate is indicative of successful covulcanisation while the worsening of properties is a manifestation of lack of covulcanisation.

While studying the migration of curatives in vulcanizates, Gardiner\textsuperscript{[26]} noted that the diffusion gradient at an interface between two different rubbers was not the same as that at an interface in the same rubber despite the use of an identical vulcanising system. Determination of such a gradient was useful since exact concentrations of the curatives could be given at any distance from the interface resulting in a good assessment of the effectiveness of the covulcanisation process. Gardiner emphasised on the need for control of curative diffusion at all times if the polymer-polymer interface was expected to produce a layer conducive for the bonding of the phases. One way of controlling the diffusion was to carry out separate mixing of specific curative combinations into individual polymers. Curative migration was regarded as related more to diffusion during curing than a material transfer process during mixing.

Corish and Powell\textsuperscript{[27]} reported that co-curing could be achieved if the cure rates of the elastomers were virtually identical and the expected crosslink structure was predominantly polysulfidic. This proposal was not long standing as it was established through chemical probe analysis that interfacial bonds are associated with a preponderance of monosulfidic crosslinks formed during the initial stages of vulcanisation rather than the maturation of polysulfidic crosslinks.\textsuperscript{[28]} In a test for covulcanisation, other researchers\textsuperscript{[29,30]} demonstrated that the development of interphase crosslinking caused a merging of the dynamic mechanical loss peaks characteristic of the individual elastomer. Separate loss peaks observed in uncured blends of the polymers, merged on progressive vulcanisation to provide a pseudo-single phase system.
In the final analysis it is evident that, in order for covulcanisation to be achieved between the interfaces of contact polymers, intrinsic adhesion should also be the positive result of that process. The reverse of that is however not true as it is possible to achieve some form of surface adhesion without passing through covulcanisation. The ultimate proof of covulcanisation has been assessed through mechanical tear tests and the following conditions can be said to be necessary for covulcanisation to take place between a substrate material and a coating layer:

- Complete wettability between the surfaces. This can be assured through the use of pressure during the vulcanisation process.
- The covulcanising polymers should have cure rates as close as possible if not identical. Their vulcanisation temperature should also be the same.
- There must be some degree of solubility between the polymer systems to allow for interpenetrating of the molecules at the working temperature. The interchange of molecules at the interface also provides with conditions suitable for covulcanisation to occur.
- Curative diffusion is expected across the interface if cross-linking is to be achieved. There is therefore a need to control curative migration to avoid a one sided cure process in which one of the polymers ends up with adequate cure while the other remains undercured.

The latter recommendation can be achieved through a careful selection of curative materials taking into account their solubility in both polymers and their general rate of diffusion at their working temperature. Where possible, the amount of curatives within the polymers should be balanced in accordance with the concentration content of each polymer.
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CHAPTER 5

REVIEW OF IN-MOULD COATING PATENTS AND OTHER METHODS OF COATING APPLICATION.

5.1 Introduction.

The last fifteen to twenty years has seen a boom in patent submissions in the areas of coating in general and in-mould coating in particular. Despite all these inventions, in-mould coating remains unexplored in many production areas where its application would result in improved quality products. A considerable amount of work has however been done with polyurethanes and other thermoplastic elastomers where in-mould coating has shown positive results.[1] Generally, any method of moulding (i.e. compression, injection or reaction injection) whereby the surface of the mould unit (cavity) is "coated" with one type of material prior to moulding a subsequent material in the same unit, can be referred to as in-mould coating. The form in which the coating material is used (i.e. liquid, powder, paste or solid) exclusively determines the method of its application onto the mould.

In-mould coating describes the coating of a substrate by first applying the coating material onto the surface of a mould after which the substrate is introduced into the mould for covalcanisation i.e. both the substrate and the coating material are simultaneously cured to achieve the required bonding between them.[2] The coating operation is usually accomplished by either brushing or spraying the liquid coating material onto the surface of the mould prior to introducing the substrate through injection or other means. This practice allows for partial setting of the coating material on the mould surface before the substrate is introduced. If the substrate is a low molecular weight material, the rate of its injection has to be controlled so that the film already formed by the coating material on the mould surface is not broken before the curing process begins.

Moulding techniques used for in-mould coating include reaction injection moulding (RIM) in which the substrate, normally a two component low molecular weight
system, is allowed to react in a mould previously coated with a coating material; injection moulding-in which a single component substrate is injected into mould cavities previously coated with a coating material and compression moulding which follows the coating of either the substrate surface itself or the mould surface. Compression moulding can also be done after dip coating of a substrate. In all the moulding cases mentioned above, the application of coating material onto the substrate or onto the mould cavities is carried out through classical coating methods like spraying, brushing, dipping and powder coating. These methods are discussed in some detail later in section (5.3) of this chapter.

5.2 Patents.

5.2.1 Coating with unsaturated polyester/polyurethane resin

This invention aims at producing an in-mould coating composition with a stable and extended shelf life. The single mix composition has stability for six or more months when stored under normal conditions and requires no accurate mixing of ingredients prior to use. This invention also provides a method of forming a compression or injection moulded, fully cured, reinforced thermoset article with a compression or injection moulded coating, resulting in a smooth surface, superior adhesion and adequate hardness. According to this invention, the coating composition comprises a homogeneous liquid mixture of an unsaturated polyester or polyurethane resin, a copolymerizable monomer and a functional-group-terminated liquid polymer. Suitable coatings containing 20-50% by weight of the unsaturated polyester or polyurethane component; 2-15% by weight of the functional group terminated liquid polymer and 30-60% by weight of the copolymerizable monomer have been produced. The blend may also contain antioxidants, mould release agents, adhesion promoters, pigments, fillers, dispersing agents and catalysts; i.e. both translucent and pigmented coatings can be produced.

The resin (substrate) is passed into the mould in the form of either a sheet moulding compound (SMC), bulk moulding compound (BMC) or dough moulding compound (DMC) and moulded to a thickness of about 6.4 mm at a temperature of
between 135 and 150°C under pressure of 2.7 MPa. After about two minutes the mould is opened and 5-10 grams of peroxide catalysed coating composition are added from a syringe or automatically. Once more the mould is closed while gently squeezing the coating uniformly over the surface and curing the coating over the SMC part. Cured coatings are tested for adhesion to the cured substrate following standard test ASTM-3359-74.

5.2.2 Improved shelf life of coating compound.

This patent was founded on the basis of the patent in this previous section and involves the production of a stable liquid coating composition with an extended shelf life. The resin compound mixed with reinforcing fibres in the form of SMC or BMC is injected into a mould cavity. The mould is compressed to form the desired part while heat is applied to cure the resin. On slightly opening the mould the coating compound is injected to fill the space between the substrate and the mould face. The mould is finally closed slowly to squeeze the coating uniformly over the surface to a thickness less than 0.5 mm while curing.

5.2.3 Aromatic, polycarbonate and ABS coating systems.

This patent relates to the in-mould coating of a thermoplastic aromatic polycarbonate resin and thermoplastic acrylonitrile butadiene styrene (ABS) polymer resin structural foams with an in-mould thermosetting coating composition. According to this invention, it has been found that thermoplastic structural foam mouldings or parts made from polycarbonate resins or ABS polymer resins can be in-mould coated at low curing temperatures and pressures to provide an adherent, glossy, hard and smooth thermoset coating or layer on the structural foam part. To make the structural foam part, pellets, granules or whatever form material of the polycarbonate resin or ABS polymer resin are mixed with a blowing agent additive system, fed to a compression or injection moulding machine and moulded to form the article.

The thermosetting coating compound comprises an unsaturated polyester resin and an unsaturated crosslinking monomer including a peroxide initiator and an
accelerator for the initiator. The in-mould coating covers up the surface defects of the substrate. The in-mould coating composition is applied by spraying, brushing or by injection onto the surface of the structural foam part in the injection mould after the part has been cooled. The mould is then closed with pressure and heat supplied to cure the coating. Alternatively, the moulded part is removed from the mould after cooling and placed into another mould already coated with the coating composition or the surface of the moulded part is charged with the coating composition and then placed into the mould for curing. By use of appropriate amounts of polyester and monomer(s) desirably including filler, it is possible to obtain in-mould coatings which have good to excellent adhesion to the substrate.

While this process is especially useful in improving the surface appearance of low pressure moulded structural foam, it is also applicable for coating surfaces of high pressure moulded structural foam. The process and products of the present invention can be used in the manufacture of vehicle parts such as grille and head lamp assemblies, deck hoods, fenders, door panels and roofs as well as in the manufacture of food trays, appliance and electrical components, office machine covers and other structural panels.

5.2.4 Coating with reactive plastic material

This patent is based on two earlier patents\[7,8\] both of which relate to the process of in-mould coating for a moulded part produced from reactive plastic material. It is demonstrated in this invention that an in-mould coating technique may be used to produce a smooth surface on a plastic moulded part containing a filler which is present at least in part in proximity to the surface of the substrate. The in-mould coating process permits transfer of the coating to the substrate during the time the plastic substrate solidifies and while the filler is being locked in place at or near the surface of the substrate. By transfer of the coating from the mould surface to the plastic substrate during the moulding operation and prior to solidification of the substrate, a completely smooth surface on the moulded part can be obtained. Subsequent finishing of the moulded part is therefore not necessary.
The moulded part is produced by coating the surface of the mould, prior to moulding the part, with a coating composition containing a reaction promoter for the reactive plastic moulding material, introducing the reactive plastic moulding material and the filler into the mould and moulding the part. The amount of reaction promoter, which acts as a courier of the coating composition to the substrate during the moulding operation, is sufficient to both transfer the coating composition from the moulded surface to the moulded part and bond the two surfaces together. The normal amount of reaction promoter used is about 10% based on the total coating weight.

Substrates for this invention are defined as reactive plastic moulding materials which include materials that undergo polymerization and/or crosslinking during the moulding cycle. Included in this definition are the reactant isocyanate and polyol components of polyurethane moulding systems. Both the coating and the reactive promoter are conveniently applied to the mould surface by spraying the coating at a pressure of about 0.21-0.41 MPa in a solvent at about 10 to 35% solid content. In compression and injection moulding, the mould surface temperature may range from below ambient temperatures to as high as 232°C.

5.2.5 In-mould powder coating

In-mould coating with powder is illustrated in this patent. The powder is required to be stable in storage without clotting and must flow out well after application as well as be able to harden quickly. All known coating powders do not fulfil these requirements. In this invention, it has been found out that by using crystalline unsaturated polyesters, powders can be obtained having an increased storage stability.

The polyesters to be used in this invention must show a melting point of between 40°C and 175°C. The melting point should preferably be above 70°C and it depends on the temperature at which the powder is to be used. Preference is given to using a polyester with a melting point about 25°C below the processing temperature. In order to meet the required criteria, the powder should consist of
one or more copolymerizable unsaturated components which jointly form the bonding agent, a curing system for the bonding agent, and if so desired, other non-copolymerizable components such as release agents, flow agents, pigments, fillers, stabilisers, etc. A catalyst is certainly required for the curing process to materialise and a conventional accelerator may also be added.

The powder is applied to the wall or walls of the mould where it melts and forms a continuous layer at temperatures between 75°C and 200°C. The polymer is allowed to cure to such an extent that the layer can withstand some mechanical load and yet not fully cured for good adhesion with the polyester moulding compound. Alternatively the powder is electrostatically sprayed onto the surfaces and a coating between 0.05 and 0.8 mm thick is eventually obtained.

5.2.6 Post-mould coating

In accordance with the present invention there is provided a method of in-mould coating of a moulded article with a coating to eliminate surface defects. The in-mould coating aspect of this invention involves placing a charge of thermosetting coating composition on the outer surface of a moulded article so as to produce a coating of a thickness no less than 0.5 mm. Sufficient pressure is then applied to the charge so as to cause the coating composition to substantially and uniformly cover and penetrate the surface of the article.

The coating composition comprises of a polymerizable ethylenically unsaturated urea-urethane polymer, a catalyst, and a mould release agent. There are many catalysts which are conventionally utilised in moulding compositions but typically a free radical generating catalyst such as peroxide is preferred for cross linking purposes. The mould release agent is a common additive under standard moulding practice. It functions as an external lubricant so that after moulding is completed and the mould is opened, the coated article can be removed with minimum handling and a reduced incidence of scratching or abrasion.
In this invention, the in-mould coating composition is applied to the outer surface of the moulded articles to cover surface defects like sink marks, porosity, microcracks and open knit lines. Once the mould is closed, sufficient pressure (from about 0.34 to 20.6 MPa, depending on the size of the article) is applied to cause the coating to cover and penetrate the article surface. Curing takes place at temperatures between 50°C and 200°C for about 15 seconds to 5 minutes before the mould is finally opened and the article is released. It is a claim of this invention that articles coated in this manner exhibit excellent surface quality free of defects, good chip resistance, good adhesion of coating to substrate and good intercoat adhesion between the moulded coating and subsequently applied coating positions. Besides use in in-mould coating compositions, the dispersions of this invention are useful in the formulation of injection moulding compositions and also can be used in conventional compression moulding where high viscosity can be tolerated.

5.2.7 Electrodeposition process

This patent describes an in-mould electrodeposition process the objective being to enable the rapid moulding of static free plastic parts, more particularly, plastic parts having a conductive or semi-conductive coating formed in the mould by electrodeposition. The present invention tackles a method for the production of static free plastic parts with a coating or a film of conductive or semi-conductive polymeric material on their surface.

A film of conductive or semi-conductive polymer material is electrodeposited onto a platinum treated surface of a mould cavity. The platinum facilitates for both the polymerization and electrodeposition of the conductive film. After sufficient film has been deposited onto the mould, a viscoelastic moulding material is injected or compressed into the mould to form the plastic part. The moulding material can alternatively be melt-fused with the conductive or semi-conductive polymeric film. Rapid electrodeposition onto the mould surface is carried out using high current densities and a turbulent flow of electrocoating solution between the electrode and the mould surface.
Application of this technology includes the manufacture of catalytic electrodes. When the conductive or semi-conductive polymeric film such as pyrrole is electrodeposited, dopants such as iron phthalocyanines can be incorporated electrochemically into polypyrrole during polymerization. The resulting film formed as a surface part of a moulded part would have electrocatalytic activity for reduction of oxygen.

5.2.8 Coating of fibre-reinforced plastics[12]

The patent relates to in-mould coating of compression moulded and fibre reinforced plastics from SMC and BMC. Reference to other patents[13,14] is also made in the development of this process. In accordance with the present invention, a method of applying a composite coating to a fiber-reinforced plastic substrate is provided. The method involves applying a primer coating composition made up of a polyepoxide and a polyacid curing agent directly to a surface of the substrate. The primer composition provides excellent sealing properties to the fibre-reinforced plastic substrate giving it high gloss and distinctiveness of image.

The primer coating composition can also be applied to the substrate by any of the conventional coating techniques such as spraying, brushing and dipping but preference is given to the use of compressed air spraying and electrostatic spraying. If spraying is used, the viscosity of the primer coating composition should be adjusted with additional solvent if necessary. The substrate may be coated at elevated temperatures to release volatiles which are often entrapped in substrates. The primer coating is heated and cured after which a topcoat of the required coating material is applied directly onto the primer coat through the same coating method. When heat is introduced, the finish coat coalesces and in the process binds with the primer coating. Typically, heating is from 82°C to 163°C for about 15 to 60 minutes depending upon the nature of the resin and curing agent in the finishing coat. Film thicknesses for the finishing coat are typically on the order of 0.025 to 0.130 mm. The finishing coat can be applied as a one-coat system or alternatively it can be applied as a so-called colour-clear system in which the pigmented or
coloured basecoat is first applied to the primer followed by the application of a clear topcoat over the coloured basecoat.

5.2.9 Weather resistant coatings

The objectives of this invention are:
- to provide a method for producing a weather resistant composite moulded material comprising a ring-opened polynorbornene base or core with a weather resistant polymer film material on its surface;
- to provide a reaction injection moulding (RIM) method for producing an integrally moulded composite product having superior weatherability and surface smoothness and
- to provide a polymer composite having an integrally formed weather resistant film surface without the need for special adhesives.

A weather resistant film forming polymer is applied to the inside of a mould subsequently fed from a bulk-polymerizable reaction solution of norbornene monomer with a metathesis catalyst dissolved in the monomer system. Any norbornene monomer can be utilised as the base material in this invention, as long as it has a norbornene ring. Preference is however, given to those monomers with three or more rings since they impart better heat resistance in the composites. As far as the weather resistant polymer is concerned, there are no particular restrictions except that it has to have the ability to form a film, it does not inhibit hardening of the norbornene monomer and its film must be capable of forming an integral body with the base polymer. Polymerization of the base polymer and the weather resistant polymer in situ gives a base of norbornene having an integrally bound weather resistant surface.

Initially the weather resistant polymer is dissolved or dispersed in a solvent or dispersant with optional improving agents prior to spraying or brushing it onto the mould surface. The temperature of the mould should be kept at the moulding temperature of the polynorbornene resin. The base material is moulded through conventional RIM by feeding and hardening the reaction mixture inside the mould.
Feeding can take any of the two methods i.e. either reaction mixtures are instantaneously mixed within the RIM mixing head and then injected into the mould at high temperature or the materials are mixed in a mixer after which they are injected into a preheated mould where the reaction takes place at once.

By means of the manufacturing method of this invention it is possible to manufacture three dimensional composite moulded articles of complex shapes where a film of a weather resistant polymer adheres firmly at the interface. This invention further claims that composite moulded articles of good appearance can easily be obtained without using the many complicated processes of undercoating and topcoating which increases the risks of surface roughness and discolouration of the articles. Articles produced by this invention find application as automobile parts, electrical components, construction panels, etc.

5.2.10 Powder coating of polyesters

The outline of this patent is similar to that described in reference [8]. The invention relates to a powdered unsaturated polyester resin formulation useful for coating reinforced polyester articles in the mould. The in-mould coating method employed results in the hardening and scratch resistance of the surface of the moulding. The polyester resins useful in this invention work best in combination with copolymerizable, ethylenically unsaturated monomers and/or oligomers. It is preferred that these monomers or oligomers have two sites of unsaturation per molecule. Powder coating is applied electrostatically onto the walls of the mould with a temperature above 130°C and as it melts and coalesces on the hot mould, it produces a uniform coating.

The inner surface of the coating is then charged with a partially cross-linked unsaturated polyester fill resin in the form of a sheet moulding compound (SMC) or dough moulding compound (DMC). The coating and the fill resin are kept within the closed mould at a temperature from about 140°C to about 170°C with a pressure of above 4.5 MPa for a period of between 1 minute to 12 minutes or until
the fill resin has flowed to its final dimensions with curing having been sufficiently achieved.

The mouldability of in-mould coating composition is determined by evaluating the surface of an article coated therewith after demoulding. Mouldability is considered good if the coating separates cleanly from the mould surface and adheres tightly to the article over the entire coated surface without any defects. Bubbles and inadequate adhesion between the coating and the substrate are a manifestation of incompatibility between the coating composition and the fill resin.

5.3 Coating Techniques.

There are several tried and tested methods and techniques of applying a coating layer to a substrate surface with the objective of achieving lasting protection or decoration of a product. Different moulding methods in conjunction with classical coating techniques[16-18] have over the years been used in industry to process coatings as a result of which drastic technological changes to the current scenario are unlikely in the near future. The ultimate choice of a method depends on many factors foremost of which is the state of the coating material i.e. solid, liquid or powder. Once the coating material has been applied onto the surface of the substrate, the process of "curing" follows to ensure some degree of adhesion is achieved between the surfaces.

5.3.1 Brush coating:

Application of coating material through brushing is recorded as the oldest and simplest method used manually.[17] The process of brushing may be divided into two stages. In the first stage referred to as "brushing out", the coating material is put on the surface to be coated and then spread into a film of more or less even thickness by using powerful brush strokes. Following this stage the brush is lightly skinned over the surface first in one direction and then in a direction at right angles. This is known as "laying-off". The success of this method depends to a great extent on the physical quality of the brush, the rheological properties of the coating material and equally to the steadiness of the applicator. The type of brush and the nature of the coating
material will determine how easily the application process will go and to what degree the surface will show residual brush marks.

While rheological properties are known to control the flow and the appearance of material, the end product is as well dependent on the cure conditions of the process. It should be noted that brush coating is also possible where flow of the coating material is induced through increase in temperature. Although an increase in temperature reduces viscosity and facilitates brushing, in solvent free coating the wet-edge time becomes almost impossible to determine.

Brush coating is a slow method whose position in today’s high production lines has been relegated to small items with unique configurations. Many jobs done through brushing of coating material reveal human inadequacies through uneven film distribution on the surface of the substrate. This mode of coating also tends to leave contour markings in the direction of painting and these lines may be a source of stress flows on the surface.

**5.3.2 Dip coating: (cold and hot)**

In cold dip coating, the object (substrate) is totally or partially immersed into a bath of coating then removed at a controlled rate to allow part of the material to drain while some is retained on the substrate surface. This controlled withdrawal technique keeps the lower parts of the article beneath the surface of the coating while excess material is draining back into the tank from the upper parts. The technique of slow withdrawal of the substrate from the coating tank also improves the appearance of dip finishes and enhances the chances of obtaining thicker films.

This method is generally used either in the coating of large objects where protection rather than decoration is the main objective, or for obtaining a high class decorative finish on small objects with irregular shapes. The size and shape of the article to be

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1 The interval during which it is possible to restart coating from a previously coated edge without leaving a visible joint when the film dries.
dipped greatly influence the appearance of the finish i.e. the larger the article and more irregular its shape, the more difficult it is to produce a satisfactory finish.

Dip coating normally results in the formation of flow lines and runs on the coated surfaces and therefore it has been used mainly in the application of primer coatings. Notably, this method can only be applied in cases where solvents have been used to reduce the viscosity of the coating material or where polyvinylchloride (PVC) plastisols are used as coatings. In the case of plastisols, the substrate is warmed in an oven for a few minutes prior to dipping in order to improve the adhesion of the coating material onto the substrate surface. This is referred to as hot dip coating. To obtain the required thickness of the coating, the adherend is left for a while in the dipping tank after which it is suspended to allow for excess paste to drip off. The coating material is constantly stirred to avoid gelling and lumping. Once a fairly uniform coating is obtained on the substrate, curing in an oven is allowed to take place at about 160°C for up to ten minutes depending on the coating thickness.

5.3.3 \textit{Spray coating}:

Spray coating is the most common industrial method of applying coating using manual, semi-automatic and robotics techniques.\cite{16,19} The spray gun is a device used to atomise up a stream of coating material into fine mist which will coat any object at which it is directed. Varieties of spray systems are used in industry and each method well suited for specific coating requirements. An example of a spray gun is shown in Figure 5.1.

Because of its speed of application and adaptability to almost any condition, shape or size of article, the method is applicable to obtain smooth coatings from rapid setting paint compositions and organic coatings which dry solely by solvent evaporation.

The viscosity of the coating material, the selection of the proper spray tips and the holding, moving and triggering of the spray gun all have an important bearing on the production of satisfactory finishes. Spray coating is also noted for wastage of coating material through overspray in which the material does not fall on the surface of the substrate. These stray particles are a potential health hazard to operatives on the shop floor.
5.4 Other application methods:

5.4.1 Flow coating,

In this method a coating is applied to the surfaces as they are carried through an enclosure. The coating material is showered from all directions in the enclosure via nozzles which act as outlets of a pumped recirculating system. Only externally exposed surfaces can be coated by this method. The method is designed to coat objects which might otherwise be difficult to dip coat and in cases where the likelihood of air-pocket formation is high. Flow coating requires far less coating material than does dip coating yet coating efficiencies are high.

5.4.2 Curtain coating

Curtain coating was developed as a substitute for spray application methods which were considered both wasteful and expensive to sustain. The technique involves the metering of liquid through a slot to form a continuous curtain of material which is able to give an even coating to flat objects when passed through. The pouring head containing the slot at the bottom is fed by a pump and a reservoir mounted at the side or bottom of the machine. Objects to be coated are carried by a two-part
conveyor system with variable speed adjusted according to the weight of the different coatings. The slower the conveyor speed, the heavier the coats and vice-versa.

![Diagram of a curtain coating system](image)

**Figure 5.2- Diagram of a curtain coating system**

### 5.4.3 Roller coating

Roller coating is the most widely used method for coating flat surfaces. Two different processes of this method can be described i.e. hand roller coating and machine coating.\(^{[17]}\)

![Diagram of a roller coating system](image)

**Figure 5.3- Roller coating system**
Machine coating is a highly commercialised method for coating coiled material of varying gages. A series of drive rollers are used to guide and move the material to be coated in a continuous process. (Figure 5.3) Hand roller method replaces the brush coating method with greater uniformity and little specialised skill. It is used mainly by wall painters and decorators.

5.4.4 Knife coating

Knife coating method is used to apply a coating or dyes to a continuous web of paper or textile material. Two processes can be described i.e. blanket spreaders and bowl spreaders. In blanket spreaders the material to be coated is carried along by a continuous belt conveyor while the knife is pressed against the surface with the coating material behind it. The film thickness is regulated by varying the tension in the belt. In bowl spreaders the web is carried forward by a cylinder with the knife suitably placed at the required angle. The film thickness is regulated by the positioning of the knife and also by the adjustment of the properties of the coating. (Figure 5.4)

![Figure 5.4- Knife coating processes](image)

5.5 Post-moulding Coating:

Post-moulding (post-mould) coating refers to the coating of an earlier cured substrate with material which is then vulcanised so as to form a film on the substrate surface. The time difference between total cure of the substrate and the introduction of the
coating material is of no consequence as long as the substrate is accepted as cured when the coating is introduced.\textsuperscript{[21-23]} Although there is a clear distinction between post-mould coating and in-mould coating, some of the patents\textsuperscript{[21,22]} describe industrial processes which overlap the two methods. Normally post-mould coating would be preferred in cases where the substrate and the adhesive have very different curing rates for which simultaneous vulcanisation would result in poor adhesion at the interface. Because the coating is usually placed on previously cured articles, the moulding that follows results in "skin" formation of the coating material on the surface of the substrate. The mechanical strength of the interfacial bonding depends to a large extent on the following factors:

- the general adhesion properties of the bonding materials resulting from appropriate surface preparation of the substrate;
- the nature of chemical and physical reactions at the interface of the bonding materials, and
- the compatibility of the bonding materials.

In principle all the main methods of coating application described for in-mould coating can be used on substrates for post-moulding coating depending on the physical state of the coating material.

5.6 General comment on in-mould coating method.

The general view from the summarised patents is that in-mould coating is normally carried out in conjunction with compression moulding, injection moulding or more often with reaction injection moulding (RIM). Coating of the mould is usually done through spraying or brushing and the deposited material is allowed to (partially) set as the solvent is evaporated by the mould heat. The base material, fill resin or substrate material is either injected into a tightly closed mould, or simply placed into an open mould in a manner that allows for the coating film on the mould surface to remain unbroken. On application of heat and pressure the coating material and the substrate interact at the interface forming a strong bond. When the mould is opened, the moulded item comes out with a film coating on its surface.
The basic parameters needing special attention during in-mould coating include the following:

- control of mould temperature which is determined by the nature of material used for making the mould and the nature of polymer material being used;
- thickness of the coating on the mould surface or on the surface of the substrate normally controlled by the moulding pressure applied;
- the rate of cure of the coating material which should determine the pre-heating period prior to the injection of the substrate;
- general reactivity of the moulding material which controls the final cure time and
- the compatibility between the coating and moulding materials which finally defines the ability of the two materials to adhere to each other.

It is a general observation that all the patent references given above are applicable to thermoplastics, thermosetting and composite materials. In all cases where powders are not involved, the materials had to be dissolved in some solvent(s) prior to applying them onto the mould surfaces through conventional means like brushing and spraying. The use of in-mould coating with rubber materials is not given in any of the reviewed patents. It can, however, be noted that in-mould coating with low molecular weight (liquid) rubber materials is possible as described in the succeeding chapters.
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CHAPTER 6.

SOLVENT FREE COATING MATERIALS.

6.1 Introduction
Solvent-based coatings have long been the choice for industrial finishing because of their inherent ease of application, excellent coating performance and continued technical development over many years. However, with the introduction of Environmental Protection Act 1990 which legislates on strict licensing of industrial processes and demands high standards of pollution control, the operation of solvent based processes in the UK faces a real decline in the next few years. The coating industry is targeted to control and where possible eliminate altogether the use of organic solvents which have been for years a subject of environmental debates. It can be noted that other countries like the United States of America, Germany and most EEC countries already have operating statutes regarding the general use of solvents in their industries.

In the coating industry, solvents may be defined as volatile liquids which are used to dissolve solid, or highly viscous resins or binders to produce a homogeneous phase or solution. Toxic fumes and emissions of these solvents and their vapours have affected the health of a lot of shop-floor workers most of whom have been left nursing chronic ailments with little or no compensation from the industries concerned. It is to this cause therefore that research and development units of many coating industries have launched investigations into uses of solvent-free coating materials. This chapter seeks to give only an overview of three of the many materials and means used in the field of solvent-free coatings i.e. polyurethanes, polyvinyl chloride and thermoplastic elastomers. A comprehensive review of the subject is presented by Paul et al.

6.2 Basic requirements for rubber coating materials.
In 1992 Klooster presented a paper on the development of solvent-free polyurethane coating materials used in plastics, wood and metal finishing. No mention is made in this paper and indeed in any other reference, about the applicability of the discussed materials as coatings for elastomeric substrates although the fundamental requirements
for such materials can easily be extended to cover some rubbers. For a material to be used as a coating for a rubber substrate, certain minimum requirements on the part of the material have to be complied with and these include the following:

6.2.1 Achievement of low viscosity

A coating material meant for a rubber substrate should be able to achieve low viscosity at the desired application temperature without the use of a solvent. The molecular weight of such materials is a determining factor since low molecular weight products are easier to attain low viscosity than materials with higher molecular weights. It is possible with the bulk of these materials to attain low viscosity through the use of primary plasticisers. More often than not the application of these plasticisers allows for the use of higher molecular weight materials while temperature techniques are positively applied for low molecular weight materials. Besides their ability to swell compound resins and reduce their viscosity, plasticisers also lower the glass transition temperature of the materials concerned resulting in direct physical changes. Whatever method is therefore used towards achieving low viscosity, the final viscosity should be such as to allow the use of techniques like roller, brush and spray applicators to introduce the coating on the substrate surface. It is important to note that this “necessary viscosity” should be achieved by a compound comprising of the coating material and other additives as these will also affect the coating and adhesion of the material at the interface with the substrate.

6.2.2 High extensibility

One of the main properties of elastomeric materials is their ability to “extend” more than several times their original length when a force is applied in the appropriate direction. A good coating material, when placed on the surface of a an elastomeric substrate should be one that gives minimum or no restriction to the extensibility of the elastomer. This can be achieved only when the respective coating material has also the capacity to extend equally with the rubber while adhering firmly on the surface. A coating material of low extensibility will reduce the elongation of the substrate and negatively affect the modulus and tensile properties of the product. Materials with relatively high elongation and low modulus can be used for coating purposes provided
their adhesion characteristics are good with the substrate. High extensibility compared to that of the rubber substrate should therefore be expected of all coating materials to be used with elastomers.

6.2.3 Ability to adhere to a rubber substrate

Coating materials for rubber substrates should be capable of adhering onto the surface of the substrate material preferably as a result of a covulcanisation process. Based on the theories of adhesion as discussed in Chapter 4, the basic requirements for adhesion to occur between two materials include:

- the establishment of total wettability between the contact surfaces and
- the possibility of an adsorption process taking place at the interface with possible diffusion of ingredients across the interface to enhance the bonding through intermolecular exchange.

The above requirements can only be achieved if the method of vulcanisation and other vulcanisation requirements such as rate of cure, temperature and time of cure applicable to the substrate are also feasible for the coating material. It is therefore a requirement that the rate of cure of the coating material should be commensurate with the rate of cure of the rubber substrate if the two are to covulcanise. The use of pressure during covulcanisation helps to improve the degree of wettability between the contact surfaces and therefore increases the chances of bonding.

6.2.4 Compatibility

A degree of compatibility between the coating material and the rubber substrate is necessary if minimum bonding is to be achieved. To a greater extent this requirement depends more on the polarity of the materials than on the state in which the respective materials are being processed. More often than not, a theoretical indication of possible solubility between the materials can be estimated by determination of their respective solubility parameters. Similar or very close values of these parameters are usually an indication of possible compatibility. As far as compatibility is concerned, polar materials are usually more compatible with other polar materials and in the same way, non-polar materials more compatible with materials of low polarity. However, it is
possible to enhance polarity either way to improve compatibility and adhesion at the interface.

6.3 Polyurethanes

The general term "polyurethane" (PUR) is used as reference to a multitude of polymers prepared according to the diisocyanate polyaddition principle and characterised by the urethane group structural element shown below.

\[
\begin{align*}
O \\
\mid \\
R'\text{NCO} + R''\text{OH} & \rightarrow R'\text{-NH-C-O-R}''
\end{align*}
\]

Broadly speaking, even polymers containing very low amounts of urethane groups have been classified as polyurethane as long as their products are derived from difunctional or polyfunctional isocyanates. The functionality of the reactants largely determines the linearity or branching of the product polymer. Examples of such materials include polyureas, polyetherureas and polyisocyanurates. Polyurethanes are polar materials whose compatibility depends on the polarity of the urethane.

It is worth noting from the onset that polyurethanes are commercially produced both for use as substrate and or coating materials. The choice of a polyurethane coating product system depends upon the performance required of the coating and therefore the nature of the basic materials. Polyester based polyurethane coatings are known to have the highest toughness and resistance to abrasion while polyether based coatings have the highest resistance to hydrolysis and microbiological attack. If polyurethanes are categorised according to the basic requirements of solvent free coating materials, they no doubt qualify as possible coating materials for rubber substrates. Depending on the nature of the raw materials used and the purpose for which the product is designed to perform, polyurethanes can be produced as low and high molecular weight materials with controllable viscosity. As such, classical coating techniques such as rollers and brushes can be used over substrates with ease. Furthermore, polyurethane materials can be flexible and have high extensibility which meets the requirements for rubber substrate coatings.
6.3.1 Classification of polyurethane coatings:
In the coating industry, the term "polyisocyanate" is used to describe adducts containing more than two NCO groups per molecule, prepared from lower molecular weight diisocyanates. Polyurethane coatings can therefore be defined as materials that contain a minimum of 10% by weight of a polyisocyanate monomer reacted so as to yield polymers containing any ratio of urethane linkages, active isocyanate groups or polyisocyanate monomers.\(^7\) Such a system allows for the classification of polyurethane coatings into five groups based on the medium (polyol) and reaction mechanism involved in the linkage production. Both solvent-containing and solvent-free coatings can be enlisted into these groups. While the ASTM classification was popular in the early 1970s to the mid 1980s, the current trend is to classify polyurethane coatings by the number of isocyanate components in the coating system leading to one and two component coating systems. Because many polyurethane products are film forming and cure on the substrate through specific chemical reactions, polyurethane coatings can generally be referred to as reactive coatings.\(^5,6,8\)

6.3.1.1 Two component coating systems
Branched polyethers are normally used as primary ingredients in two component coating systems because of their low viscosity, while the isocyanate component is usually 4,4'-diphenylmethane diisocyanate (MDI) in combination with oligomeric or polymeric MDI units. Because of the likelihood of production of carbon dioxide during the reaction process due to the absence of volatile solvents, moisture absorbers like potassium hydroxide are included in most formulations of two component systems. Solvent-free two component coating systems are typically applied by hand using a casting process. The same materials can also be applied using a brush, roller or putty knife techniques. Due to relatively high viscosities and short pot lives of these product materials, spray techniques cannot be used with normal equipment.

Two component solvent-free coatings have very good elastomeric, physical and mechanical properties. They have a very low degree of shrinkage with good adhesion to different substrates which they provide with anti-corrosive properties. Most have excellent resistance to aqueous salts, acids, dilute alkaline solutions and heating oil but
are susceptible to aggressive solvents such as tetrahydrofuran and concentrated alkaline solutions. Thick two-component coating systems combine toughness and high elasticity with the capability of bonding onto various substrate materials and as such, find use in numerous industrial applications. Coatings based on MDI tend to yellow and exhibit relatively fast chalking upon outdoor exposure. The bulk of these coating materials find applications in food processing plants, offices, hospitals, exhibition halls, industrial flooring for machine foundations and many other places.

6.3.1.2 One component systems

Three grades of one-component systems are commonly used as polyurethane coating and these are:

- moisture-curable coatings;
- fully reacted coatings from unsaturated fatty acids or esters, and
- coatings where the functionality of the isocyanate is blocked.

The two main diisocyanates used in these grades of coating materials are toluene diisocyanate(TDI) and MDI. In all cases, the finished coatings exhibit a microporous structure which tends to allow for the diffusion of available moisture into the coating and diffusion of carbon dioxide out of the film. One-component coating systems in aqueous dispersions of cross-linkable elastomers are widely used to avoid the use of solvents which are generally expensive and difficult to recover. Most one-component coating systems have a longer shelf-life and low stoving temperatures as compared to two component systems. One other advantage of one-component systems is that, other than carbon dioxide, they do not release any low-molecular weight compounds during cure which tend to interfere with the adhesion between interfaces. One component polyurethane coatings are used to protect outer surfaces of fire hoses against wear and rotting and their application significantly increases the life span of the hoses even under harsh operating conditions.

Both one- and two-component systems are capable of giving coatings of either hard or soft elastomers. Based on the typical properties of some of these coating materials, it is appropriate that they are found useful as coatings on rubber substrates.
Table 6.1- Properties of some coating polyurethane materials\(^9\) contrasted with natural rubber properties.

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
<th>Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-component dispersion-aliphatic isocyanate based.</td>
<td>31</td>
<td>400</td>
<td>6</td>
</tr>
<tr>
<td>One-component dispersion-aromatic isocyanate based.</td>
<td>30</td>
<td>700</td>
<td>2</td>
</tr>
<tr>
<td>Natural rubber substrate*</td>
<td>28-30</td>
<td>&gt;450</td>
<td>3.6-4</td>
</tr>
</tbody>
</table>

* From own records

From the short review of one- and two-component polyurethane coating systems it can be concluded that these coating materials can be used as rubber coating systems as long as a feasible way of covulcanisation is found.

6.4 Polyvinyl chloride (PVC)

Polyvinyl chloride is currently the cheapest and largest produced polymer in industry. The history of this very common material dates back to 1835 when the vinyl chloride monomer (VCM) was discovered by Leibig while he reacted ethylene dichloride with alcoholic potassium hydroxide.\(^{10}\) It was not until some forty years later when the polymer itself was incidentally discovered by Baumann during a study of UV-induced reactions on materials. Records show that intensive commercial production of PVC and its other similar vinyl polymers occurred first in England by ICI and the Distillers Co. in the years 1942 and 1943\(^{11}\) and since then the expansion in production and use of this polymer has been monumental. There are four commercial ways of polymerising PVC and each method, due to the particle sizes produced, determines the final area of application for the resin. (Table 6.2)

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Polyvinyl chloride is extensively used as a coating material in the plastics industry where it finds application in upholstery, footwear, tool handles, toys, conveyor belts, flooring etc. In the rubber industry PVC has featured among other applications in blends with nitrile rubber and natural rubber as an antiozonant material. This versatility of PVC makes it a strong candidate in coating areas where rubbers are the substrates.

### Properties of PVC

It can be noted from the onset that PVC satisfies the earlier criteria outlined in this chapter as regards solvent free coating materials and a few properties of this polymer can be mentioned to illustrate the point. The melt viscosity of PVC depends on both the molecular weight and molecular weight distribution of the resin and that based on the method of polymerisation. It is necessary to get the viscosity of the resin as low as possible so that coating procedures can be followed. To this end, plasticisers are used and a well chosen plasticiser can change a high molecular weight resin, with high strength and low elongation, into a soft rubbery material having reduced tensile strength but with high elongation.

The usability of a PVC resin also depends to a greater extent on the thermal properties of the resin. At temperatures above 100°C most PVC resins undergo thermal degradation unless otherwise protected by use of stabilisers. Although the mechanism of thermal degradation of PVC is not fully understood\(^{12}\), the effects of this process have been identified in many PVC processing systems. Since the glass transition temperature \(T_g\) of PVC resins depend on the temperature of polymerisation, it is

---

**Table 6.2- PVC production methods**

<table>
<thead>
<tr>
<th>Method</th>
<th>Market (%)</th>
<th>Particle size (μ)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspension</td>
<td>75</td>
<td>75-250</td>
<td>extrusion, calendering</td>
</tr>
<tr>
<td>Emulsion</td>
<td>12</td>
<td>0.5-20</td>
<td>coating, plastisols</td>
</tr>
<tr>
<td>Bulk</td>
<td>10</td>
<td>30-140</td>
<td>moulding compounding</td>
</tr>
<tr>
<td>Microsuspension</td>
<td>3</td>
<td>&lt;0.5</td>
<td>coating plastisols</td>
</tr>
</tbody>
</table>
possible through the use of specific plasticisers to lower or raise that $T_g$ so that an appropriate processing temperature of the resin can be aligned to that of the rubber substrate. Because of the gelation and fusion characteristics of PVC resins, it is also difficult to covulcanise these resins with rubber substrates. Coating with such materials will therefore require that a post-mould process be used to achieve some adhesion between the substrate and the coating material.

6.4.2 Plastisols

A plastisol as defined by Sarvetnick\textsuperscript{[13]} is a dispersion of fine particle size PVC resin in a liquid plasticiser meant to produce a fluid mixture which may range from a pourable liquid to a heavy paste. Not all vinyl resins are suitable for making plastisols but only those that are referred to as dispersion grades. These are mainly fine particle size resins produced through either emulsion or microsuspension polymerisation. The basic properties of plastisol compounds are therefore directly linked to the characteristics of the polymer resin used. The fluidity of a plastisol depends among other factors on:

- the nature and particle size of the polymer resin,
- the nature and amount of free plasticiser used, and
- the resin-plasticiser ratio.

Because of their liquid nature, plastisols can easily be applied onto substrates through a variety of coater line methods or by dip coating prior to being fused.\textsuperscript{[13]}

Brush methods of applying plastisol coatings have also been used with considerable success. Several moulding methods can be applied to plastisols and the most common of these are dip moulding which is carried out after a process of dip coating; slush moulding in which the plastisol is poured into a mould and fused to produce a hollow object; rotocasting which is similar to slush moulding but includes a biaxial rotation of the mould while fusion is allowed to take place.

6.5 Thermoplastic Elastomers (TPE)

Thermoplastic elastomers are materials which combine the processing characteristics of thermoplastics with the physical properties of vulcanised rubbers.\textsuperscript{[14]} The most unique feature of these materials is their ability to provide products with most of the
physical properties of conventional vulcanised rubbers but without going through the process of vulcanisation. The exclusive ability of TPEs to become fluid on heating and then solidify on cooling has given manufacturers the capacity to produce rubber-like articles and coatings using fast processing equipment like injection moulders, blow moulders and extruders. Their ability to adhere to different substrates like wood, metals and other polymers has contributed to the widening of their applications in many industries.

Through their many methods of processing, TPEs have established expanding markets in the footwear industry, wire coating industry, as adhesives or sealants and in many other sectors where they find use as film materials. Thermoplastic elastomers rely on physical crosslinking processes i.e. intermolecular forces of attraction, to form a three-dimensional structure and in this way prevent a viscoelastic flow. However, at sufficiently high temperatures, the physical forces of attraction forming the network can be disrupted and therefore get the polymer to soften and flow.[151] From the basic definition and description of TPEs, it is apparent that they can be used as coating materials without the use of solvents. Due to the fact that TPEs are able to flow at high temperatures, the use of injection moulding for coating purposes becomes a reality with these materials. Coating applications can therefore be done through either in-mould coating or post-mould coating techniques.

6.5.1 General Structure
All thermoplastic elastomers (TPEs) are phase separated systems in which one phase is hard and solid at room temperature while the other phase (soft) is an elastomer. The soft phase normally controls both the stability and the stiffness of the final product. The physical changes of the hard phase at higher temperatures guarantees ease of processing on the elastomer phase and on cooling the material has renewed strength. Most TPEs are block copolymers of thermoplastic materials with suitable counterpart elastomeric blocks. It is important to note that the hard phase/soft phase ratio needs to be proportional if the product material is to exhibit true thermoplastic elastomer properties. Only two of the major groups of TPEs are briefly mentioned below.
6.5.2 Polystyrene/Elastomer Block Copolymers

TPEs based on triblock copolymers of polystyrene and polydienes are the largest commercially produced of all thermoplastic elastomers.\textsuperscript{[16]} Three elastomers are commonly used in the commercial versions of these materials namely; polybutadiene, polyisoprene and poly(ethylene-cobutylene) and the respective blocks produced are styrene-butadiene-styrene (S-B-S), styrene-isoprene-styrene (S-I-S) and styrene-ethylene-cobutylene-styrene (S-EB-S). It is important to be able to differentiate between S-B-S and styrene butadiene rubber (SBR) by noting that the former is a phase separated system and is characterised by two glass transition temperatures since each of the two phase components retain the properties of their respective homopolymers.

Polystyrene/elastomer block copolymer coatings are extensively used in chemical milling of metals.\textsuperscript{[14]} A protective film is first applied to the whole surface of the metal sheet then selectively peeled off from areas from which the metal is to be removed. The sheet is then immersed in an etchant bath, which dissolves away the unprotected areas. Other applications involve roof coatings\textsuperscript{[17]} and can sealants which equally require high strength and elasticity.

6.5.3 Polyurethane/Elastomer Block Copolymers\textsuperscript{[14,17]}

Polyurethane/elastomer block copolymers, commonly known as thermoplastic polyurethanes (TPU) are generally made from long chain polyols, chain extenders and polyisocyanates. It is well established now that TPU owe their unique properties to a domain structure which is achieved by the phase separated system of the multi-block polymers involved in their construction. Their general structure is an alternating series of hard and soft segments. The hard segments are either polyureas or polyurethanes while the soft elastomeric segments are either polyethers or polyesters.

At temperatures above the melting of the hard segment, the polymer forms a homogeneous viscous melt which can be processed by thermoplastic techniques such as injection moulding, blow moulding, extrusion, etc.
The low viscosity, flexibility and controllable cure characteristics of TPU make it possible for these materials to be used as solvent free coating systems. Mechanical properties of TPU are very good and as such offer many opportunities for the materials to be used in wide ranging applications. Their superior adhesive properties make them excellent for use in hot-melt adhesives for running and tennis shoes while their high tensile strength and elongation allow for their use as coatings for meat and poultry wraps. Where canvas or other heavy fabric is used as a base, extrusion coated TPU can provide exceptionally flexible reinforcement. Coating with TPU is also possible through injection moulding as in the production of automotive parts like corner panels, gaskets, seat belts, etc.
References

7. ASTM D16-1974 and 1982a
CHAPTER 7

PRACTICAL WORK AND METHODOLOGY.

7.1 Introduction
An experimental work plan towards the accomplishment of this project is shown in Figure 7.1. The work is divided into four major operations namely, compounding, moulding coating and testing. The final results of these operations are assessed under tensile property investigations, ozone property studies and diffusion studies.

![Diagram showing the experimental work plan](image)

Figure 7.1- Schematic diagram of experimental work.
7.2 Material selection.

7.2.1 Natural rubber

Natural Rubber (NR) compounds used in this work are shown in Tables 7.1 and 7.2. Any grade of natural rubber could have been used for this project since all are susceptible to ozone attack when used in the absence of an antiozonant. In this case, SMR10 was opted for as it was available in sufficient quantities. The recipe given in Table 7.1 is a standard natural rubber formulation for moulding purposes. In order to control the scorching characteristics of the compound, a post-vulcanisation inhibitor (Santogard PVI) was included in the formulation. The two compounds prepared for ozone tests i.e. NR₀ and NRₐ only differed in that the latter compound had an additional antiozonant system of wax and a p-phenylenediamine antiozonant.

Table 7.1 - NR compounds for ozone tests.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>NR₀(phr)</th>
<th>NRₐ(phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR SMR10</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Antioxidant*</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>N660 black</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Accelerator*</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Santogard-PVI*</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Antiozonantd</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>Wax*</td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>

Key:
NR₀ = compound without antiozonant
NRₐ = compound with antiozonant system

*2,2,4 Trimethyl-1,2-dihydroquinoline (TMQ), or Flectol H (Monsanto)
For diffusion studies, five natural rubber compounds with different amounts of the antiozonant, isopropyl-phenyl-p-phenylenediamine (IPPD) were prepared. (Table 7.2) It is important to note that carbon black was not included in these compounds so that the original colour of each compound could be determined by the rubber and the vulcanising system only. No antioxidant was added either so as to ensure that the blooming recorded was largely from the antiozonant IPPD.

Table 7.2 - NR compounds for diffusion studies.

<table>
<thead>
<tr>
<th>Compound (phr)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR SMR10</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Accelerator</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Antiozonant</td>
<td>0</td>
<td>2</td>
<td>5</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

7.2.2 Acrylonitrile-butadiene liquid rubber (NBR-Nipol)

The material used here is a product of Zeon Chemicals Europe Ltd., South Glamorgan, UK. Some general properties of this material are listed in Table 7.3 below. The choice of a coating material was made difficult by the requirement of the project not to use solvents in order to attain the necessary coating viscosity.

Nipol, a copolymer of butadiene and acrylonitrile (nitrile rubber-(NBR)) with a low to medium acrylonitrile content was chosen for this purpose because:
Table 7.3 - Properties of Nipol

<table>
<thead>
<tr>
<th>Acrylonitrile content (%)</th>
<th>28+</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>-39</td>
</tr>
<tr>
<td>Volatiles (%)</td>
<td>0.5 max.</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>0.5 max</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>0.96</td>
</tr>
<tr>
<td>Appearance</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>Viscosity at 50°C (cps)</td>
<td>20000-30000</td>
</tr>
<tr>
<td>Odour</td>
<td>Mild to strong</td>
</tr>
</tbody>
</table>

- it was found to be the only commercially available elastomer with inherently ozone resistant properties and is at the same time produced in sufficiently low molecular weight form to be a low viscosity fluid;
- it is known to be non-extractable, non-migrating and non-volatile in plastisols;
- it would be easy to apply onto a mould due to its low viscosity;
- it can be used without dissolving it in a solvent, and
- it has not been used for this purpose before.

\[
\text{CN} \\
\text{---(-CH}_2\text{-CH-)}_m\text{-(-CH}_2\text{-CH = CH-CH}_2\text{-)}_n\text{---}
\]

Figure 7.2 - Nitrile butadiene rubber (NBR)

Two grades of Nipol i.e. Nipol 1312 and Nipol 1312LV which differ slightly in viscosity were first tried in different tests. The final project work was however, limited to the use of Nipol 1312 only in order to maintain some consistency in the results. Nipol 1312 was chosen because it was much easier to handle during and after compounding. This grade of liquid rubber has a milder odour when applied onto the hot mould than the Nipol 1312LV grade.
7.2.3 N-Isopropyl-N'‐phenyl-p-phenylenediamine (IPPD)
IPPD comes in the form of brown flakes soluble in benzene, acetone, ethanol and oils but with good storability and good mixing into compounds. On longer contact with water, it is partly washed out. IPPD protects against oxidation, ozone, flex cracking and dynamic fatigue. Its melting point is above 75°C. Protection against ozone is achieved under both static conditions in conjunction with waxes and under dynamic conditions without the addition of waxes. This antiozonant also appears on the market under trade names Santoflex IP (Monsanto) and Vulkanox 4010 NA (Bayer). IPPD is applied as an antiozonant at different dosages for different rubbers. While for natural rubber recommended levels of the antiozonant range from 1-3 phr, for synthetic rubbers the required levels might be slightly above that range.

7.2.4 Petroleum Wax Blend (Okerin 1891),
This blend contains both paraffin and microcrystalline waxes and functions as a microcrystalline antiozonant under static conditions. It is classified under saturated petroleum hydrocarbons from both straight and branched chain hydrocarbons. Okerin 1891 appears in white solid flakes with a melting temperature range from 63°C to about 75°C. The material is insoluble in water and has a mild waxy odour. It is a product of Astor Stag Limited (UK).

7.3 Equipment
7.3.1 Mixing of NR compounds:
Natural rubber compounds for ozone testing with or without antiozonants were all mixed using a Francis Shaw K1 Intermix with a capacity of 5.5 litres and a fill factor of 0.55. The water temperature in the Intermix was about 30°C and the rotor speed of the machine was set at 30 rpm. The general mixing regime on the machine was as shown in Table 7.4. At the end of each run, the compound mix was dumped onto a mill and followed by sheeting of the rubber after six to eight runs through different nip openings. The objective of this final exercise was to obtain rubber sheets with a thickness of about 2.5 mm appropriate for moulding purposes.
Table 7.4 - Mixing regime for NR compounds for ozone tests.

<table>
<thead>
<tr>
<th>Component/mix</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>0</td>
</tr>
<tr>
<td>Sweep</td>
<td>180</td>
</tr>
<tr>
<td>Black</td>
<td>225</td>
</tr>
<tr>
<td>Sweep</td>
<td>370</td>
</tr>
<tr>
<td>Curatives</td>
<td>415</td>
</tr>
<tr>
<td>Sweep</td>
<td>475</td>
</tr>
<tr>
<td>Discharge</td>
<td>535</td>
</tr>
</tbody>
</table>

Natural rubber compounds designed for diffusion tests were all mixed in a Haake Rheomix 600 with a capacity of about 79 ml and operating on a fill factor of 0.65. The general mixing regime is indicated in Table 7.5.

Table 7.5 - Mixing regime for the Haake Rheomix 600.

<table>
<thead>
<tr>
<th>Maximum mixing time (m)</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control temperature (°C)</td>
<td>160</td>
</tr>
<tr>
<td>Rotor speed (rpm)</td>
<td>50</td>
</tr>
<tr>
<td>Mixing temperature range (°C)</td>
<td>110-120</td>
</tr>
</tbody>
</table>

The sequence of mixing in the Haake Rheomix 600 allowed for a few minutes of mixing the rubber on its own before adding the initiator and curative systems. The antiozonant was always added last in order to minimise losses due to quick melting. Samples with higher amounts of antiozonants were given a few more seconds of mixing in order to attain a homogeneous mix.
7.3.2 Mixing of Nipol compounds:

As a liquid rubber, Nipol 1312 could not be mixed in either the Francis Shaw K1 Intermix or the Haake Rheomix 600 in case the compound adhered to the rotors and necessitated a complete dismantling of the machines in order to clean them. All Nipol 1312 compounds were mixed in two stages in which an electric stirrer and a Brabender Z-blade mixer were used. The mixing regime followed a general outline of compounding of liquid rubbers as set up below:

- Grinding of all powder ingredients in a mortar as a means of disagglomeration and to enhance dispersion during the mixing process;
- Division of the liquid rubber into two portions;
- Mixing one portion of the liquid rubber with all curing powders to make a paste;
- Dispersion of the paste produced into the second portion of liquid rubber by means of a mechanical stirrer;
- Addition of part of the carbon black into the rubber paste while stirring until the mass is difficult to mix, and
- Complete the mixing by shearing the mass in a Brabender Z-blade mixer for an hour and a half. The compound mix is left to mature for over twenty four hours before being used in the coating exercise.

Initial trial compounds of Nipol 1312 compounds with conventional levels of sulphur took very long periods to cure and this necessitated a change in the general curing system of the rubber. The ingredients involved in the initial trial compounds were based on blend compounds of Nipol and NBR and the appropriate amounts were calculated based on 100 phr of Nipol. Common ingredients between the natural rubber compounds and the Nipol compound were zinc oxide, stearic acid, carbon black and sulphur. In order to achieve shorter cure times, two main ingredients in the curing system had to be changed and these were tetramethylthiuram disulphide (TMTD), a secondary accelerator and sulphur the main crosslinking agent.
Figure 7.3- TMTD amount vs cure time

Using a simple screening variables method where a variable is individually changed while others are kept constant until the best effect is achieved, several levels of TMTD were tested for cure while sulphur and dibenzothiazole disulphide (MBTS) levels remained unchanged. (Figure 7.3) With accelerator levels in turn kept constant, several cure trials were carried out with varying sulphur levels and the best dose of sulphur for the compound was deduced. (Figure 7.4)
The final recipe used for all coatings using Nipol 1312 coating compound is given in Table 7.6.

Table 7.6 - Nipol 1312 coating compound formulation

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Amount (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nipol 1312</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>N550 Black</td>
<td>20</td>
</tr>
<tr>
<td>Accelerator$^a$</td>
<td>2</td>
</tr>
<tr>
<td>Accelerator$^b$</td>
<td>1</td>
</tr>
<tr>
<td>Sulphur</td>
<td>7$^1$</td>
</tr>
<tr>
<td>Plasticiser$^c$</td>
<td>30</td>
</tr>
</tbody>
</table>

$^1$ It should be noted that the amount of sulphur in this recipe remains relatively high but this level was maintained to ensure best cure results.
7.3.3 Moulding design and application.

Moulding is an operation of shaping and vulcanising a plastic rubber compound, by means of heat and pressure resulting in the production of an elastic product in a mould of appropriate form. Fundamentally, all moulding processes are similar but the ways of introducing the material into the mould cavity distinguishes one technique from another. The most commonly used commercial moulding processes are: injection moulding, compression moulding, transfer moulding, rotational moulding and reaction injection moulding. For this project, in-mould coating with compression moulding was chosen as the process method for all the required test pieces. This method was opted for because it requires simple moulds with a minimum of material and it is also simple to operate for experimental purposes.

A three cavity mould (Figure 7.5) designed to produce ASTM D1149/D518 standard test pieces of 150 x 25 x 2 mm for ozone testing was made and used for moulding all test pieces, coated and uncoated. The mould was made with these dimensions so that cutting of test pieces using a dumbbell cutter could be avoided especially for coated samples. For such coated specimens, cutting would expose the unprotected substrate to ozone resulting in erratic cracking often leading to complete test-piece rupture. Test pieces for tensile tests were moulded in a similar dumbbell mould which required no cutting after moulding.

a. Dibenzothiazole disulfide (MBTS), (DuPont)
b. Tetramethylthiuram disulphide (TMTD) Vulkacit Thiuram, (Bayer)
c. Dioctyl phthalate (DOP), (Monsanto)
Figure 7.5 - Diagram of three cavity mould for all test pieces.

Strips to be moulded were cut in the format of the cavity, weighed prior to compressing them in the mould. Unless otherwise stated, all mouldings were done at 160°C with natural rubber samples taking some ten minutes to cure. The pre-cure time for the coating material was set at five minutes after which the sample to be coated was placed into the mould cavity and left to reach an optimum cure as determined in a curemeter. Before placing these strips into the respective cavities, the mould was heated to a set temperature of 160°C. At this temperature, a small amount of Nipol
compound, enough to cover the cavity surface area, was evenly smeared onto the hot cavity surface. The compound proved easy to spread with a brush onto the cavities at this high temperature but still with no visible flow. Once smeared on the cavity surface, the compound gradually formed a stable film preventing any material movement. The Nipol coating was precured for five minutes before the natural rubber substrate was quickly introduced into the mould and pressing resumed for the duration of the cure period.

7.4 Testing

There are three areas of interest in testing namely, ozone testing which is the main thrust of the project in accessing the resistance of a produced coating to cracking in an environment with ozone, tensile testing which seeks to evaluate the effect of the coating on the physical properties of the substrate rubber and diffusion tests which assess the effect of a coating on the migration and loss of a chemical antiozonant.

7.4.1 Tensile testing:

The Hounsfield Tensile Machine model H500L was used for tensile property tests for the following three parameters; ultimate tensile strength (UTS), 300% modulus (M@300%) and elongation at break (E_b) for the base material. All test pieces for this exercise were moulded using a dumbbell mould to produce pieces 75 mm long x 3.2 mm wide and approximately 2 mm in thickness. Both coated and uncoated samples were tested for the above. The machine was normally set with a 500N load cell, a screen display of 800%, a test speed of 500 mm/min and set to record four modulus values of 100%, 200%, 300% and 400% extension. An average of twelve coated and twelve uncoated samples were tested.

7.4.2 Ozone testing:

All test pieces for this exercise were moulded using the three cavity mould in Figure 7.4. Two types of standard testing were conducted namely, static ozone testing and dynamic ozone testing. Both tests were conducted on coated and uncoated
samples and also on samples with and without an antiozonant system in them. While all static ozone tests were carried out at Metalastic-Dunlop in Leicester using a standard ozone chamber and method (ASTM D1149-91/D518-91) for rectangular pieces, dynamic tests were conducted at Goodyear Technical Centre in Luxembourg. Some samples were put under test with broken coating (deliberately cut) to expose the inner substrate to ozone. Test pieces for the latter testing were prepared by making 5 mm incisions with a sharp razor blade over the Nipol coating surface of standard moulded ozone pieces. (Figure 7.6) Test pieces were then extended with a 20\% extension prior to exposing them to ozone for 72 hours.

Machine setting and sample specifications for ozone test are given in Table 7.7 below.

Table 7.7 - Ozone test specifications.

<table>
<thead>
<tr>
<th>Ozone concentration</th>
<th>ppm</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temperature</td>
<td>°C</td>
<td>40</td>
</tr>
<tr>
<td>Conditioning of samples</td>
<td>hr</td>
<td>&gt; 24</td>
</tr>
<tr>
<td>Duration of Exposure</td>
<td>hr</td>
<td>72</td>
</tr>
<tr>
<td>Extension</td>
<td>%</td>
<td>20</td>
</tr>
<tr>
<td>Specimens</td>
<td>mm</td>
<td>150x25x2 thick</td>
</tr>
</tbody>
</table>
The ozone in the system is produced from irradiation of an air stream pumped over a mercury vapour lamp. (Figure 7.7) Ozonized oxygen or air may as required be diluted with normal air to attain the required ozone concentration. The ozonized air is fed from the source into the chamber via a heat exchanger to adjust its temperature to that required for the test and also brought to the specified relative humidity. When using a vapour lamp, the amount of ozone produced can be controlled by adjusting the voltage applied to the tube or the gas flow rate, or by shielding part of the tube exposed to the gas flow. It is important to ensure that after each occasion that the test chamber is opened for insertion or inspection of test pieces, the ozone concentration returns to the test concentration within 30 minutes.

Figure 7.7- Schematic diagram of ozone apparatus
Preparation of test pieces prior to mounting them on test frames involves applying Collodion Flexible coating onto all the edges and surfaces where clamping pieces are fixed. This physical protection is to ensure that ozone does not attack from all directions but only from the surfaces purposely marked and exposed for the duration of the test. All test pieces are mounted on test frames (Figure 7.8) and drawn to cause an extension of 20%. After mounting the specimens onto the frames, they are conditioned for a period of not less than twenty four hours at room temperature in an ozone free atmosphere.

The frames are then put into the chamber where they are kept rotating as the pieces are exposed to the controlled stream of ozone for the set test period. Recordings of
observations are made at set intervals of 24, 48 and 72 hours from the time the samples are placed into the chamber.

7.4.3 Flex testing
The flexing test was carried out as an indicator for cracking and/or delamination of the coating material. A standard ASTM D430-88 Method B was used in which the De Mattia Flexing Machine is applied. Test specimens for bend flexing were moulded using a standard mould of 150 mm x 25 mm x 6.35 mm with a central groove of radius 2.39 mm. Precise specimen thickness was recorded for each test piece. Two sets of 12 specimens were prepared for testing at different temperatures. Test samples were conditioned at the working temperatures for more than twelve hours prior to commencing the test. The first set of six coated and six uncoated samples were flex tested at 23°C while the other similar set was tested at 60°C in the test chamber. All test specimens were checked for cracks and delamination at intervals during which flexing cycles were also recorded.

7.5 Coating/antiozonant diffusion systems
This exercise on diffusion of an antiozonant through a coating was carried out to determine the loss of antiozonant through coated and uncoated samples. The ability of the coating to retain a diffusing antiozonant means that less of the antidegradant will be lost through blooming and thus ensure a longer life span for a rubber product. Compound formulations for diffusion studies are shown in Table 7.2 and all the compounds were mixed using the Haake Rheomix 600. Both coated and uncoated test pieces for diffusion studies were moulded using a 4 cm-square mould plaque to produce sheets with a thickness of about 1 mm as shown in the figure below.
Two test pieces were taken from each of the five compounds, weighed and then conditioned for twenty four hours at 40°C to allow for the even distribution of the antiozonant within each piece. After conditioning, the pieces were placed in an air circulating oven set at 60°C and their weight loss from blooming monitored for twelve days. The blooming antiozonant was removed by way of sticking and pressing Sellotape onto the surface of the piece and then gently stripping off the tape with the blooming material stuck on. The daily weight of each piece prior to the removal of the bloom was taken as the initial weight for each subsequent reading and was compared with the previous reading.

7.6 Alternative coating system - PVC

Work was also done using polyvinyl chloride (PVC) as an alternative coating material to Nipol 1312 for a natural rubber substrate. This exercise was also done to demonstrate that other polymer materials besides liquid elastomers, can be used for coating natural rubber without the need for solvents to achieve the required coating viscosity. As has been seen from the literature (references 37 and 38 in Chapter 2), PVC has for years been used in blends with NR and NBR to enhance the ozone resistance of these rubbers. For this project work, PVC was used in plastisol form as given in the following recipe.

Figure 7.9 - Schematic diagram of mould plaque
Table 7.8- PVC formulation:

<table>
<thead>
<tr>
<th>INGREDIENT</th>
<th>Amount(phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC resin MP7154</td>
<td>100</td>
</tr>
<tr>
<td>Plasticiser*</td>
<td>50</td>
</tr>
<tr>
<td>Stabilizer**</td>
<td>3</td>
</tr>
</tbody>
</table>

* Dioctyl phthalate (DOP), (Monsanto)

** Interstab M722-(Ba/Zn), (Akzo Chemicals Ltd. UK)

Due to the powdery nature of the PVC resin MP7154, a product of European Vinyl Corporation (UK) Limited, mixing was first carried out using a speed controlled food mixer and finalised in a Brabender Z-blade mixer to achieve a low viscosity plastisol. Samples were prepared and cured in two different ways:

- The first set of test pieces were prepared from previously cured natural rubber samples. The cured samples from the three cavity mould were conditioned overnight at 110°C after which they were dipped into a container with a PVC coating compound. The test pieces were slowly removed from the container allowing for a film of the coating compound to remain on the surface. The coating was then fused in an oven for five minutes at 170°C. (post-mould fusion)

- The second set of test pieces were prepared directly from the three cavity mould (Figure 7,4) by coating the mould cavities with the PVC coating compound. Natural rubber samples were then placed into the mould and curing done at 160°C for ten minutes (in-mould coating). Only a visual comparison of the test results and observations were made from both these tests.
CHAPTER 8.

RESULTS AND DISCUSSION.

8.1 Introduction
This chapter brings together all the results from the practical work described in the preceding chapter. The results are interpreted in view of the initial objectives of this project which are:

- the formulation of a non-migrating antiozonant coating compound from an ozone resistant polymer material and
- to study the effectiveness of a combined antiozonant system in the protection of natural rubber against ozone.

Two main rubber compounds labelled (NR₀)- natural rubber compound(s) without antiozonant ingredients and (NRₐ₀)-natural rubber compound(s) with a specified antiozonant system, are used in this project. Results are also discussed for coated and uncoated samples from these compounds vis-à-vis physical and antiozonant properties like tensile strength, ozone resistance and diffusion characteristics. The layout of this chapter is to be as follows:

8.2 - Comment on practical work and methodology: This section gives a general overview on the equipment and the preparation of compounds used in this project.
8.3 - Comment on liquid nitrile rubber as a coating material. The estimation of compatibility of nitrile rubber with natural rubber through its solubility parameter is assessed in relation to other materials.
8.4 - Tensile properties: Under this section the effect of a coating on ultimate tensile strength of a test piece is discussed. The modulus and strength of the coating material is estimated.
8.5 - Ozone resistance under static deformation: Test pieces from compounds NR₀ and NRₐ₀ are exposed to ozone under static conditions and results evaluated. A brief
Sheets were cooled and kept in a flat position to maintain a form suitable for compression moulding. Carbon black was used as a filler to enhance the physical properties of the liquid nitrile rubber and also to improve the ultra violet degradation resistance of the compound. However, only 20 phr of the filler was added to the compound so that the low viscosity of the liquid rubber would be maintained.

Above all immediate needs was the task of selecting an appropriate vessel for mixing the compound as the Francis Shaw K1 Intermix was not suitable because of two major reasons namely:

- very small quantities of coating material were required and therefore the use of the 5.5 litre Intermix would have meant incurring losses in material;
- thorough cleaning of a machine the size of a Francis Shaw K1 Intermix would be impossible without dismantling the chamber to get rid of the sticky liquid rubber.

Preliminary mixing trials showed that it was necessary to grind all particulate ingredients in a mortar as a means of disagglomeration prior to mixing. This step proved necessary because the low viscosity of the liquid nitrile rubber generated inadequate stresses for disagglomeration during mixing. Powders were then added into the rubber by means of an electric stirrer after which the mixture was sheared in a Brabender Z-blade mixer for an hour and a half.

It should be noted that the ingredients for compounding of liquid nitrile rubber were selected to be compatible, to a large extent, with those used in the compounding of the natural rubber substrate to induce adhesion between the two rubbers. The common factor between the curing of liquid nitrile rubber and the curing of natural rubber is that both materials can be cured using the conventional sulphur curing system. While liquid nitrile rubber has been used as a plasticiser or softener at levels of 5-15 phr in rubber blend compounds without a great loss in physical properties, in the coating application however, the level reaches 100 phr and this requires the use of higher levels of sulphur to achieve sufficient crosslinking. The combined use of dibenzothiazole disulphide
(MBTS) as a primary accelerator with tetramethylthiuram disulphide (TMTD), which is a secondary accelerator, reduces the differences in cure times between the liquid rubber and natural rubber, making covulcanisation possible.

Once a satisfactory coating compound was produced, an appropriate coating technique had to be found to ensure that all test pieces had an acceptable finish for ozone testing. The final physical form of the coating compound determined, to a large extent, the coating methods i.e. either spraying or brushing. The option of spraying could not be used with such a sticky compound as produced from Nipol 1312 without the compound being dissolved in some solvent before the coating process. Brush coating was therefore opted for as the method of coating although the process of smearing and spreading the coating material onto mould cavities is far from optimum as a coating technique. There are three main problems encountered in the exercise and these are:

- uneven distribution of coating resulting in different film thickness throughout the substrate surface;
- air trapping in the film as a result of irregular brush movements. The air bubbles expand as the coating temperature increases to that of the mould forming defects all over the substrate surface. Obviously such test pieces become unsuitable for ozone tests.
- the time taken to evenly cover the cavity surface with a coating film is relatively long since repeated applications with more material is necessary to obtain consistency in the coating. Despite the fact that a long coating period affects both cure time and moulding temperature, it is easier to apply the coating on a hot mould surface since at higher temperatures the viscosity of the coating material is reduced and spreads well.

Following the satisfactory brush coating of the substrate surface, covulcanisation of the system can be undertaken through compression moulding under pressure. Achievement of covulcanisation between a protective coating compound and a natural rubber substrate is uniquely different from known blend systems. It must be noted from the onset that the two components in this study were individually compounded each with its suitable vulcanising agents and only sulphur as a common factor. (Table 8.1)
Table 8.1- Cure Ingredients for NR/Nipol system

<table>
<thead>
<tr>
<th>Cure Ingredients</th>
<th>NR (phr)</th>
<th>Nipol (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerator^1</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>Accelerator*</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Accelerator^2</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.5</td>
<td>7.0</td>
</tr>
</tbody>
</table>

* N-cyclohexyl-2-benzothiazole sulfenamide (CBS), (Goodrich Chemical)
^1 Dibenzothiazole disulfide (MBTS), (DuPont)
^2 Tetramethylthiuram disulfide (TMTD), (Bayer)

High pressure exerted on the rubber during compression moulding ensured intimate physical contact across the coating-substrate interface. At high temperatures the coating compound flows into the irregular cavities of the substrate and, in turn, the substrate also flows to fill the mould area. It is at this point, according to diffusion studies on blend materials by Tinker[1], that the curatives from both phases are expected to preferentially diffuse to either of the elastomers depending on their solubility and in that process, cova
culcanisation takes place at the interface.

8.3 Comment on liquid nitrile rubber as coating material

Liquid nitrile rubber (Nipol 1312) was initially developed to be used as a polymeric plasticiser or softener, for other nitrile rubbers, in quantities ranging from 5 to 15 parts. [2] As such, every Nipol liquid rubber grade is compatible in all ratios with solid nitrile rubbers and fairly compatible too with antiozonants used with the respective solid rubbers. For all nitrile rubbers, i.e. both solid and liquid, an increase in acrylonitrile content increases the cohesive energy density (CED) and consequently increases also the solubility parameter (δ ) of the rubber. [3] Such an increase equally affects and changes the solubility
characteristics of the rubber in solvents of various polarity i.e. with differing solubility parameters.

CED is defined as a measure of strength of secondary bonds which, in conjunction with covalent bonds, hold together polymer segments and is expressed as:

$$CED = \frac{\Delta Ev}{V_1} \quad (8.1)$$

where $\Delta Ev$ is the molar energy of vapourisation and $V_1$ is the molar volume of the liquid.

The solubility parameter ($\delta$) is an indicator of compatibility or incompatibility between a polymer and a solvent or additive. It is well known that systems with similar or close solubility parameters tend to be mutually compatible while those with diverse solubility parameters are normally incompatible. The relationship between CED and $\delta$ is given by

$$\delta = \sqrt{CED} = \left(\frac{\Delta Ev}{V_1}\right)^{\frac{1}{2}} \quad (8.2)$$
The compatibility of additives is determined through thermodynamic considerations of the heat of mixing ($\Delta H^m$) and the relationship between the difference in solubility parameters and the associated heat of mixing as expressed by Hilderbrand\cite{5} in the following equation for non-polar components.

$$\Delta H^m = \Phi_1 \Phi_2 V (\delta_1 - \delta_2)^2$$  \hspace{1cm} (8.3)

where $\Phi_1, \Phi_2$ are molar volume fractions with subscripts 1 and 2 referring to the polymer and additive respectively and $V$ is the total volume of the mixture.

$\Delta H^m$ turns out to be very small for mixtures with similar solubility parameters and that indicates a degree of compatibility between the components.

For polymers however, the enthalpy of vaporisation cannot be used to calculate their solubility parameters. The $\delta$ of a polymer is normally reached at by finding a solvent which will produce maximum swelling of its network and thereby indicating maximum compatibility. The value of the $\delta$ of the solvent is then assigned to the polymer.

A good estimate of the solubility parameters of most polymers can also be made using series of group molar attraction constants suggested by Small and Hoy.\cite{6}

When using these constants, the solubility parameter is expressed as follows:

$$\delta = \left( \frac{\sum F}{M_o} \right) \rho$$ \hspace{1cm} (8.4)

where $\sum F$ is the sum of the various molar attraction constants, $M_o$ is the molar mass of the polymer repeat unit and $\rho$ is the density of the polymer.
Table: 8.2 - Group contributions to F

<table>
<thead>
<tr>
<th>Group</th>
<th>Small</th>
<th>Hoj</th>
<th>Group</th>
<th>Small</th>
<th>Hoj</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH₃</td>
<td>438</td>
<td>303.4</td>
<td>cyclopentyl</td>
<td>-</td>
<td>1295.1</td>
</tr>
<tr>
<td>-CH₂</td>
<td>272</td>
<td>269.0</td>
<td>cyclohexyl</td>
<td>-</td>
<td>1473.3</td>
</tr>
<tr>
<td>H</td>
<td>1</td>
<td>176.0</td>
<td>phenyl</td>
<td>1304</td>
<td>1398.4</td>
</tr>
<tr>
<td>-Cl</td>
<td>552</td>
<td>419.6</td>
<td>p-phenylene</td>
<td>1346</td>
<td>1442.2</td>
</tr>
<tr>
<td>-F</td>
<td>(250)</td>
<td>84.5</td>
<td>-F</td>
<td>(250)</td>
<td>84.5</td>
</tr>
<tr>
<td>-Br</td>
<td>696</td>
<td>527.7</td>
<td>-Br</td>
<td>696</td>
<td>527.7</td>
</tr>
<tr>
<td>-I</td>
<td>870</td>
<td>-</td>
<td>-I</td>
<td>870</td>
<td>-</td>
</tr>
<tr>
<td>-CN</td>
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<td>-CN</td>
<td>839</td>
<td>725.5</td>
</tr>
<tr>
<td>-CH₃</td>
<td>272</td>
<td>269.0</td>
<td>-CH₃</td>
<td>272</td>
<td>269.0</td>
</tr>
<tr>
<td>-OH</td>
<td>143</td>
<td>233.3</td>
<td>-OH</td>
<td>143</td>
<td>233.3</td>
</tr>
<tr>
<td>-CO</td>
<td>563</td>
<td>538.1</td>
<td>-CO</td>
<td>563</td>
<td>538.1</td>
</tr>
<tr>
<td>-COOH</td>
<td>-</td>
<td>-</td>
<td>-COOH</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-CH(CH₃)</td>
<td>495</td>
<td>(479.4)</td>
<td>-CH(CH₃)</td>
<td>495</td>
<td>(479.4)</td>
</tr>
<tr>
<td>-C(CH₃)₃</td>
<td>686</td>
<td>(672.3)</td>
<td>-C(CH₃)₃</td>
<td>686</td>
<td>(672.3)</td>
</tr>
<tr>
<td>H</td>
<td>454</td>
<td>497.4</td>
<td>H</td>
<td>454</td>
<td>497.4</td>
</tr>
<tr>
<td>C=C</td>
<td>454</td>
<td>497.4</td>
<td>C=C</td>
<td>454</td>
<td>497.4</td>
</tr>
<tr>
<td>C≡C</td>
<td>266</td>
<td>421.5</td>
<td>C≡C</td>
<td>266</td>
<td>421.5</td>
</tr>
<tr>
<td>-CH=CH</td>
<td>(704)</td>
<td>(724.9)</td>
<td>-CH=CH</td>
<td>(704)</td>
<td>(724.9)</td>
</tr>
</tbody>
</table>

In the case of Nipol 1312 with ANC% of 28, M_w=107 and ρ = 0.96g/cm³, using the Hoy attraction constants yields the following results:

δ_{NBR} = (2209.9)×0.96/107

= 19.83 (J/cm³) ½

Using the same method, the average solubility parameters of some classical antiozonants and natural rubber were calculated.
Table 8.3 - Solubility parameters

<table>
<thead>
<tr>
<th>Material</th>
<th>S (J/cm³)^1/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPPD</td>
<td>17.49</td>
</tr>
<tr>
<td>DPPD*</td>
<td>19.90</td>
</tr>
<tr>
<td>6PPD*</td>
<td>19.89</td>
</tr>
<tr>
<td>Flectol H*</td>
<td>18.90</td>
</tr>
<tr>
<td>NBR_Nipol</td>
<td>19.83</td>
</tr>
<tr>
<td>NR</td>
<td>17.64</td>
</tr>
</tbody>
</table>

* See Appendix A: Glossary

The resultant solubility parameters of these antiozonants indicate that all others are likely to be compatible with Nipol with the exception of IPPD which has a solubility parameter closest to that of natural rubber. However, none of these antiozonants are known to react with Nipol spontaneously but IPPD has been used as an antiozonant for nitrile rubbers for a long time. It can also be said from Table 8.3 that natural rubber and nitrile liquid rubber are not easily compatible because the difference between their solubility parameters is big. This can be supported by the fact that the two rubbers are of different polarities with natural rubber being non-polar and nitrile rubber being polar.

8.4 Tensile properties

Tensile tests carried out in this project were done to evaluate the effect of the nitrile rubber coating on the basic physical properties of the substrate natural rubber. The experimental data is also used to estimate the tensile properties of the coating material. According to the results in the table above, both the addition of an antiozonant system and the application of the coating caused a decrease in modulus and strength of the samples. Values in all measured parameters of uncoated NR test pieces are consistent with a natural rubber compound with low modulus and high elongation. Coated samples recorded lower values in parameters measured. (Figure 8.2) Values in all
measured parameters of uncoated NR$_{A_0}$ samples are also higher than their coated counterparts of the same compound. (Figure 8.3)

Table 8.4 - Tensile test results

<table>
<thead>
<tr>
<th>TEST PARAMETERS</th>
<th>NR$_{o}$</th>
<th>NR$_{A_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>uncoated</td>
<td>coated</td>
</tr>
<tr>
<td>300% Modulus (MPa)</td>
<td>17.1</td>
<td>13.6</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>454</td>
<td>434</td>
</tr>
<tr>
<td>Ultimate Tensile strength (MPa)</td>
<td>27.8</td>
<td>24.2</td>
</tr>
</tbody>
</table>

* natural rubber compound without antiozonant ingredients
** natural rubber compound with an antiozonant system

Ultimate tensile strength values of both coated and uncoated NR$_o$ and NR$_{A_0}$ test pieces show that there is a reduction in tensile strength following the addition of an antiozonant system in the compounds. It is however, interesting to note that the average ultimate tensile strength of a coated NR$_o$ compound compares well with the tensile strength of the uncoated NR$_{A_0}$ compound. By comparing the ultimate tensile strength (UTS) of coated and uncoated samples in both compounds, the percentage loss (% loss) in tensile strength can be calculated from the following formula:

$$\%\text{loss} = \frac{UTS_{\text{uncoated}} - UTS_{\text{coated}}}{UTS_{\text{uncoated}}} \times 100$$  \hspace{1cm} (8.5)

In the case of the NR$_o$ compound, the average percentage loss in tensile strength resulting from coating is calculated to be about 13 % and for the NR$_{A_0}$ compound the loss is at 22 %. The effect of the coating in reducing the strength of the substrate sample is examined in the section that follows
It can be noted that the difference in tensile strength between uncoated NR_o and NR_A0 samples is 3.1 MPa which translates to 11%. This loss can be attributed to the introduction of the antiozonant system in the latter compound. The loss of tensile strength in the NR_A0 compound can be attributed to the antiozonant system because the added microcrystalline antiozonant wax also acts as a process aid and as such reduces the bonding effect between the polymer chains.\textsuperscript{[7]} The higher the loading of the wax in the presence of fatty acid activators like stearic acid, the more likely its effect as a lubricant on physical properties are perceptible. It cannot be ascertained however, whether this loss is due to an independent effect of the antiozonant system or to its combined effect with other ingredients in the formulation.

If the total loss in tensile strength for the NR_o compound is taken as additive i.e. involving loss to antiozonant system and loss to coating material then the following calculation can be made:
Total % loss = loss_{Ao} + loss_{Co} \quad (8.6)

where  \( \text{loss}_{Ao} \) is loss to antiozonant system and
\( \text{loss}_{Co} \) is loss to coating

Using the above formula, the different losses can be calculated from UTS results as follows:

\[
\text{loss}_{Ao} = \frac{(NR_o-NR_{Ao})}{NR_o} \times 100 = 11\%
\]
\[
\text{loss}_{Co} = \frac{(NR_o-NR_{Co})}{NR_o} \times 100 + \frac{(NR_o^{\text{c}}-NR_{o^{\text{c}}})}{NR_o^{\text{c}}} \times 100 = 24\%
\]

where  \( NR_o \) is the uncoated substrate sample
\( NR_o^{\text{c}} \) is the coated substrate sample

The total percentage loss in UTS can also be calculated from the difference in values between uncoated  \( NR_o \) samples and the coated  \( NR_{Ao} \) samples which results in 30.5% loss. From the calculations above, the sum of \( \text{loss}_{Ao} \) and \( \text{loss}_{Co} \) is 3.5 % more than the 30.5 % total loss. When equation (8.5) is applied for \( NR_{Ao} \) compounds, the average loss in tensile strength between the coated and uncoated samples stands at 22%, higher than the 13% in  \( NR_o \) compound. Taking into account the initial 11% loss to the antiozonant system, the total percentage loss can be taken as 33%.

This outcome shows that the effect of the coating and the antiozonant on tensile strength of the test pieces is not additive although the differences are within the range of experimental error. It should be noted however that the effect of coating on \( NR_{Ao} \) samples is greater than in \( NR_o \) samples and further work is necessary to determine the exact relationship of all parameters involved in total percentage loss. It can also be said that the high losses in UTS due to coating are a result of the small total thickness of the sample. In practical applications where coating thicknesses of the order of 0.5mm
would form a small part of the total product thickness, the losses of UTS would be minimised.

![Graph](image)

**Figure 8.3** - Tensile strength results for NR$_{A_0}$ compounds

### 8.4.1 Estimation of modulus of coating material.

From both coated and uncoated samples, the parameters modulus and tensile strength can be estimated and the total effect of the coating on the test sample can be assessed. It is evident from the results that the coating film on the substrate reduces the specific modulus values and subsequently the ultimate tensile strength of the material. The mechanism of reduction of these parameters is clearly based on the differences in deformation behaviour between the two materials.

If it were to be assumed that the arrangement between the coating film and the substrate is like an idealised lamellae arrangement in composite formation, then the force acting on the test piece ($F_T$) in an identified direction, can be taken as a sum of the forces acting on both the coating film and the substrate. (Figure 8.4)

$$F_T = F_s + F_c$$  (8.7)
where \( F_s \) is the force acting on the substrate and
\( F_c \) is the force acting on the coating material.

\[
\begin{align*}
F_s & \text{ the force acting on the substrate} \\
F_c & \text{ the force acting on the coating material}
\end{align*}
\]

Figure 8.4-Dimensions of a coated tensile test piece.

Measurements of a typical test piece are shown in table 8.5 below.

Table 8.5-Test piece measurements.

<table>
<thead>
<tr>
<th>( l_s ) (mm)</th>
<th>( w ) (mm)</th>
<th>( h ) (mm)</th>
<th>( x ) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>3.1</td>
<td>2.2</td>
<td>0.46</td>
</tr>
</tbody>
</table>

The stress in the substrate can be obtained directly from a tensile test on an uncoated specimen leaving the stress in the coating as the only unknown quantity. This stress can be determined by substitution into Equation 8.8.

\[
F_T = \sigma_s A_s + \sigma_c A_c \quad (8.8)
\]
where $\sigma_s$ is the stress in the substrate

$\sigma_c$ is the stress in the coating

$A_s$ is area of the substrate and

$A_c$ is area of coating

From Figure 8.3, the area of the coating and that of the substrate can be expressed as:

$$A_c = 2(h + w)x \quad (8.9)$$

$$A_s = (w-2x)(h-2x) \quad (8.10)$$

where $w$ is the width of the test piece

$h$ is the height of the test piece, and

$x$ is the thickness of the test piece

By using a Griffin Linear Vernier Microscope, the average thickness of coating applied on the substrate was found to be 0.46mm. Using this coating thickness, $A_c$ and $A_s$ can be calculated and values used in estimation of the modulus for the coated specimen.

From equations 8.8, 8.9 and 8.10, the expression for stress in the coating can be given as follows:

$$\sigma_c = F_T - 2\sigma_s \frac{(w-2x)(h-2x)}{2(h+w)x} \quad (8.11)$$

where $\sigma_s$ is taken directly from the tensile test on an uncoated specimen.

If the force $F_T$ is a product of the stress of coated specimen and the total coated surface area (i.e. area of substrate and area of coating), $F_T = \sigma_T(A_T)$, then the values of $\sigma_c$ can be calculated from experimental data through $\sigma_s$ values. The stress/elongation results of the substrate and coating materials calculated for NR$_s$ samples are shown in Figure 8.5.
Figure 8.5-Stress vs elongation for NR, substrate and coating material.

It can be seen from Figure 8.5 that the modulus of the coating is lower than that of the substrate and the differences become bigger at higher extensions. This indicates that the coating does not adversely affect the tensile properties of the substrate which remain with high elongation at break and low modulus. The coating should therefore perform well in conjunction with the substrate particularly because for practical applications the level of strain normally required in service is lower than the performance result in Figure 8.5.

8.5 Ozone Resistance Under Static Deformation

According to Veith\(^8\), static ozone cracking can be observed when a “stationary” rubber specimen or product unprotected by an antiozonant is exposed to a flow of ozone. The severity of ozone cracking is invariably dependent upon the strain under which the specimen is subjected during the exposure period. In another study Lake and Lindley\(^9\) showed that the rate of growth of a cut due to ozone under static conditions is zero when the tearing energy of the cut is less than the critical tearing energy. The
rate of growth of a cut, \( \frac{dc}{dt} (\text{cm/s}) \), becomes a function of ozone concentration and the vulcanizate once the tearing energy is equal or more than the critical tearing energy. (Equation 8.12)

\[
\frac{dc}{dt} = \alpha q
\]

(8.12)

where \( \alpha \) is a constant dependent on the vulcanizate and

\( q \) is the ozone concentration.

Static ozone tests carried out in this project were conducted under standard ASTM D1149-81/D518-91 methods with samples under 20 % strain. The results of the tests are shown in Table 8.6.

Table 8.6 Results of ozone exposure tests under static conditions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Test number</th>
<th>Status</th>
<th>Results after 72 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR_o</td>
<td>1</td>
<td>not coated</td>
<td>cracks</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>coated</td>
<td>no cracks</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>coated/cut</td>
<td>cracks</td>
</tr>
<tr>
<td>NR_ko</td>
<td>1</td>
<td>not coated</td>
<td>no cracks</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>coated</td>
<td>no cracks</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>coated/cut</td>
<td>no cracks</td>
</tr>
</tbody>
</table>

All test pieces with a complete coating on their surfaces withstood the 72 h ozone exposure test while uncoated samples from NR_o compound cracked within a few hours of starting the test. The cracking of these samples was indeed expected, since no protective ingredients were incorporated into the compound on mixing. (Figure 8.6). Cracks formed on the surfaces of the pieces were long and extended deep into the bulk of the rubber and both the top and the bottom faces of the test pieces were affected. In all test pieces the general pattern of cracks was the same i.e. cuts in the exposed area
at 90° to the applied deformation and yet the distribution of cracks on the surface was not even in most pieces as shown in the photograph in Figure 8.7.

Figure 8.6- Ozone cracks (magnified 20X) on samples from uncoated NR₆ sample after 72 hours of static testing.

Two main possibilities arise as cause for this uneven distribution of cracks and these can be explained as:

- rubber components have naturally occurring flaws which, when the applied strain is raised to certain levels form stress raisers which initiate the cracking process in the rubber.\(^ {10,11}\) With the magnitude of these stress concentrations being different at different parts of the rubber matrix, the distribution of cracks is also bound to be irregular.

- if the general 20% extension of the test piece is not evenly achieved over the area to be exposed to ozone due to the localised pinning of the sample, the less extended parts are likely to have few and deep cracks while the more extended parts have many small cracks. Lake\(^ {12}\) has shown that above the critical tearing energy of a test
piece, the crack density increases with increasing strain while the dimensions of individual cracks decrease with increasing strain.

Figure 8.7- Uneven distribution of ozone cracks(magnified 20X) in uncoated NRo samples after 72 hours static testing.

All coated NRo and NRao test pieces did not crack under static ozone testing. (Figure 8.8) This lack of cracking can be attributed to the presence of the coating on the surface of the substrate. The inherent ozone resistant nature of the coating was able to prevent the ozone from penetrating into the double bond structure of the natural rubber substrate. It can also be said that the critical tearing energy on the surface of the coating remained higher than any other energy resulting from stress concentrations in flaws within the test pieces. As a result of the high critical energy, no cracks were initiated on the surface of the substrate under static conditions. Studies have shown that N-isopropyl N-phenyl-p-phenylenediamine (IPPD) does not bloom at levels less than 2 phr in natural rubber unless assisted by an effective wax addition to the rubber compound of between 1.5 to 2 parts.
Figure 8.8—Crack free surface typical of coated NR₀ and NRₐ₀ samples after 72 hours of static testing.

Such a combination of wax and chemical antiozonant is known to produce a synergistic effect which provides the best chemical protection for rubber currently available for both static and dynamic conditions. Compound NRₐ₀ was made with a combination of 2 phr of wax and 1 phr IPPD and all test pieces from the compound withstood ozone exposure tests without cracking. (Figure 8.9)
Figure 8.9-Crack free surface of uncoated NR₀ sample after 72 hours of static testing.

All coated/cut NR₀ samples cracked on exposure to ozone for the duration of the test. (Figure 8.10)

Figure 8.10-Ozone cracks(magnified 20X) on samples from coated/cut NR₀ samples after 72 hours static testing
The result in Figure 8.10 was as expected because the incisions allowed ozone to diffuse at the surface of the rubber and attack the natural rubber substrate. Although only three incisions were made on the sample surface, cracks appeared all over the surface indicating that the ozone was able to diffuse freely through the bulk of the rubber despite the coating. Coated/cut samples from the NR_{Ao} compound showed no sign of cracking even in the vicinity of the 5 mm incisions. (Figure 8.11)

Figure 8.11-Crack free surface of coated/cut NR_{Ao} sample after 72 hours static testing

The result in Figure 8.11 can be explained by the fact that besides the protective coating on the surface of the pieces, the compound contains an antiozonant system of IPPD and a microcrystalline wax.

8.6 Ozone resistance under dynamic deformation.
Dynamic ozone cracking can be viewed as cracking caused by ozone to rubber specimens under cyclical strain changes. Following the work done by Braden and Gent on the growth of a single cut in a test piece under static conditions, Lake and Lindley expressed the rate of growth of a cut due to ozone under dynamic conditions, dc/dn (mm/Mc), by using the following relation:
\[ \frac{dc}{dn} = (F/f) \frac{dc}{dt} = (F/f) \alpha q \]  

(8.13)

where \( n \) is the number of cycles

\( F \) is a time fraction of each cycle for which the test piece is strained,

\( f \) is the frequency of cycling and

\( t \) is time

It is known that both ozone cracking under static conditions and dynamic ozone cracking require a certain amount of critical tearing energy in order for a cut to start and develop.\(^{[14]}\) Above the critical tearing energy, crack growth under dynamic conditions is time dependent and the rate of crack growth is independent of the strain imposed on the rubber.\(^{[13]}\) The opposite is true for ozone cracking under constant load. In a normal service environment an unprotected rubber product is more likely to experience early cracking under dynamic conditions than when used under static conditions since the critical tearing energy under dynamic conditions is lower than \( 10^5 \text{ N/mm} \) whereas the critical tearing energy under static conditions is above \( 10^4 \text{ N/mm} \).\(^{[9]}\)

The main objective of the dynamic tests recorded in this project was to determine if the material used as protective coating would provide the natural rubber substrate with protection from dynamic ozone cracking, without undergoing fatigue cracking or delamination. Tests were conducted either under continuous dynamic ozone exposure or under intermittent dynamic ozone exposure conditions. Other testing conditions followed are given in Table 8.7. It can be noted that the dynamic testing conditions above are almost similar to standard (ASTM) D518-91 static ozone cracking specifications which require a test temperature of 40°C and an extension of 20% for the test piece.
Table 8.7-Dynamic testing conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extension (%)</td>
<td>25</td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>40</td>
</tr>
<tr>
<td>Test temperature (^C)</td>
<td>38</td>
</tr>
<tr>
<td>Frequency (Hz)</td>
<td>0.5</td>
</tr>
<tr>
<td>Ozone concentration (pphm)</td>
<td>50</td>
</tr>
<tr>
<td>Test duration (h)</td>
<td>12</td>
</tr>
<tr>
<td>Dynamic cycle (min)</td>
<td>20</td>
</tr>
<tr>
<td>Intermittent interval (min)</td>
<td>100</td>
</tr>
</tbody>
</table>

Results of the dynamic tests are summarised in Table 8.6 below followed by an analysis.

Table 8.8-Results of dynamic tests

<table>
<thead>
<tr>
<th>Compound</th>
<th>Status</th>
<th>Continuous dynamic test</th>
<th>Intermittent dynamic test</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR_o</td>
<td>uncoated</td>
<td>cracks-long and deep</td>
<td>cracks-numerous, hairline,</td>
</tr>
<tr>
<td>NR_o</td>
<td>coated</td>
<td>cracks-long and deep, No delamination</td>
<td>cracks-in clusters, deep, No delamination</td>
</tr>
<tr>
<td>NR_a</td>
<td>uncoated</td>
<td>cracks-small, all over,</td>
<td>cracks-isolated, hairline,</td>
</tr>
<tr>
<td>NR_a</td>
<td>coated</td>
<td>cracks-in clusters, deep, No delamination</td>
<td>No cracks No delamination</td>
</tr>
</tbody>
</table>

Although waxes provide excellent protection against ozone attack under static conditions, it is known that they do not provide rubber with protection against ozone under dynamic conditions.\textsuperscript{15} A study by Lederer et al.\textsuperscript{16} concluded that under dynamic test conditions, antiozonant waxes reduce both fatigue life and dynamic ozone resistance while low levels of chemical antiozonants (ca.1phr) are also ineffective against dynamic ozone cracking.
This study by will be referred to in the following results analysis, bearing in mind that the levels of wax and chemical antiozonant in the NR$_{A0}$ compound used in the current study were 2 phr and 1.5 phr respectively.

Results from dynamic tests show, as expected, that unprotected natural rubber cracks, both under continuous dynamic ozone test conditions and under intermittent dynamic ozone exposure. (Figures 8.12 and 8.13)

Figure 8.12-Ozone cracks (magnified 20X) on uncoated NR$_o$ sample after 12 hours continuous dynamic testing viewed at 25% extension.

Under strain in static and dynamic conditions, the surface of unprotected rubber easily allows the access of ozone to the surface of the rubber where the exposed double bond structure is attacked by the ozone, resulting in the formation of surface cracks. Lake$^{[12]}$ has shown that an increase in strain for test pieces under static conditions results in increase in the density of cracks. While cracks produced under continuous dynamic ozone testing are clear and appear to go deep into the test piece, cracks produced under intermittent dynamic testing are clustered with increased density but less clear dimensions. (Figure 8.13)
Figure 8.13-Ozone cracks (magnified 20X) on uncoated NR₀ sample after 12 hours of intermittent dynamic testing viewed at 25 % extension.

The increase in density of cracks is an indication that cracks are growing from smaller natural flaws as a result of reduced critical tearing energy. As more and more cracks are produced, the dimensions of individual cracks in the plane of the major surface decrease due to interference between adjacent cracks.⁹¹ Cracks produced under continuous dynamic testing are similar to those produced under static testing conditions despite the fact that test pieces were tested under slightly different strains. (see Figures 8.6 and 8.7) However, a study by Lake and Lindley¹⁷ has shown that under both static and dynamic ozone test conditions, ozone is solely responsible for the cracking since the rate of ozone crack growth ($r_o$) is independent of strain, (see equation 8.12). Coated test pieces from NR₀ samples cracked during both continuous dynamic and intermittent dynamic ozone testing, (Figures 8.14 and 8.15). From Figure 8.14, it can be seen that cracks produced during continuous dynamic ozone testing are more evenly spread on the sample surface than those produced under intermittent dynamic testing.
Figure 8.14-Ozone cracks (magnified 20X) on coated NR$_s$ sample after 12 hours continuous dynamic testing viewed at 25 % extension.

It can be noted that when the same coating material was used on test pieces for static ozone testing, no cracks appeared for the duration of the test suggesting that the coating has a high level of critical tearing energy under static conditions. In dynamic ozone testing however, the continuous stretching and relaxing of the rubber surface will cause a decrease in both critical tearing energy and ozone resistance resulting in the formation of surface cracks.

Cracks due to intermittent dynamic ozone exposure on coated NR$_s$ samples appear in irregular clusters with patches of crack free coating on the surface. (Figure 8.15) These crack free patches can be taken as areas with higher critical tearing energy resulting from uneven stresses due to flaws on the surface of the rubber.
The density of cracks is much less than in continuous dynamic testing. This difference in crack density can be explained if it is assumed that with every cycle, a specific number of cracks is produced for both continuous and intermittent testing as the test pieces are under equal stress. While the number of cracks continue to rise in continuous cracking, there are no additional cracks during the interval in intermittent testing because of the static protection of the antiozonant system. After a 12 hour testing period, the density of cracks for the continuous dynamic test piece will be more than those in intermittent test pieces. Another reason for the difference in crack density might be the effect of the coating in preventing crack formation during the interval of intermittent testing. During this interval, no new cracks are formed since the coating has also proved effective under static conditions.

It is however, interesting to note that where cracks are present in intermittent dynamic tested samples, the areas around the cracks appear to be “raised” above their adjacent crack free patches. These cracks seem to have “bubbled up” from nuclei beneath the surface and cut their way upwards into the coating and downwards deep into the substrate. This phenomenon suggests that either the critical tearing energy of the interface...
is lower than the critical tearing energy of the coating surface or delamination of the coating from the substrate has occurred after crack formation.

By measuring the stress sensitivity of several rubber gums, Salomon and Bloois\textsuperscript{18} were able to classify rubber materials according to their sensitivity to ozone. Comparing natural rubber and nitrile butadiene rubber, the study showed that natural rubber was more sensitive to ozone and this resulted in ozone cracks on a natural rubber surface being initiated at very low values of stored elastic energy compared with nitrile rubber. This study can provide a starting point to the explanation of the cracking mode observed above.

Dynamic test results for uncoated NRAo test pieces show the effects of combining a wax and a chemical antiozonant to improve the ozone protection of a product. Pictures of cracks from both continuous dynamic ozone testing and intermittent dynamic exposure tests of uncoated NR\textsubscript{Ao} samples are shown in Figures 8.16 and 8.17. As can be seen from the pictures, a high density of cracks was produced during continuous dynamic testing while test pieces exposed to intermittent dynamic testing had a limited distribution of hairline cracks. A very large proportion of the surfaces of intermittent dynamic ozone tested samples had no cracks.

With reference to work done by Lederer et al. (quoted above), waxes are ineffective under dynamic conditions and only help to increase localised stresses resulting in loss of ozone resistance. The presence of only 1 phr of IPPD does little to improve ozone resistance either because there is no synergism between wax and IPPD (or any other PPD) under dynamic conditions. From Figures 8.12 and 8.16 it can be seen that under continuous dynamic conditions there can be as much cracking in the NRA as in the NR\textsubscript{Ao} uncoated samples. However, an increase of IPPD of between 2 and 4 phr was shown to improve the level of ozone resistance under these conditions.\textsuperscript{16}
Figure 8.16-Ozone cracks (magnified 20X) on uncoated NR_{Ao} sample after 12 hours continuous dynamic testing viewed at 25 % extension.

Figure 8.17 shows that the level of ozone resistance during intermittent dynamic testing is much more improved for uncoated NR_{Ao} samples than in uncoated NR_{o} in Figure 8.13.

Figure 8.17-Ozone cracks (magnified 20X) on uncoated NR_{Ao} sample after 12 hours intermittent dynamic testing viewed at 25 % extension.
Although the same levels of both wax and chemical antiozonant used for samples tested under dynamic ozone exposure were applied for static ozone tests without cracks appearing, these levels prove inadequate for dynamic tests. Under intermittent dynamic testing, waxes have been shown to provide protection against ozone cracking during the static interval while chemical antiozonants provide the necessary protection during the dynamic cycle. Such synergism between waxes and chemical antiozonants has been reported by researchers like Lederer and Dimauro.

Coated NR$_{ae}$ test samples produced interesting results for both continuous dynamic ozone testing and intermittent dynamic ozone exposure. The pattern of crack distribution from continuous dynamic testing Figure 8.18 is similar to that of cracks produced on coated NR$_e$ samples as seen in Figure 8.14 despite the fewer cracks in the former picture. In fact, the phenomenon of cracks emanating from beneath the coating surface as described for cracks in Figure 8.14 is more pronounced in Figure 8.18 below.

Figure 8.18-Ozone cracks (magnified 20X) on coated NR$_{ae}$ sample after 12 hours continuous dynamic testing viewed at 25% extension.
It is likely that the observed "raised areas" around the cracks are an indication of delamination at the interface of the coating and the substrate. The pattern of crack formation seems to indicate that the cracks start at the surface of the coating and proceed to the interface, where a form of delamination occurs forcing the areas around the crack opening to be raised. The fact that there are no raised regions on the crack free surface suggests that the cracks are not initiated from beneath the coating. It can be assumed that the cracks will continue from the interface into the substrate depending on the magnitude of energies reached by the dynamic testing. In this picture the crack free patches with protective coating still intact are much bigger than those observed in Figure 8.14.

Coated NR_{Ao} test pieces did not crack when tested through intermittent dynamic exposure to ozone and there is also no evidence of delamination on the surface. (Figure 8.19)

Figure 8.19- Uncracked coated NR_{Ao} sample (magnified 20X) after 12 hours intermittent dynamic testing.

During intermittent ozone exposure the combination of wax and chemical antiozonant produces a synergistic effect which enhances ozone resistance (Figures 8.17) while the
presence of a coating alone also increases ozone resistance. (Figure 8.15) The result in Figure 8.19 therefore shows that the combination of an antiozonant complex and a coating results in a protective system with improved ozone resistance under intermittent dynamic testing. It is proposed here that such a system provides a "double synergistic" effect in which the coating doubles up with the wax to give static protection during intermittent pauses and enhances the chemical antiozonant in providing resistance to ozone under dynamic cycles. The ability of the wax to provide static ozone protection will depend, to a large extent, on the solubility of the wax in the coating material, the rate of wax bloom and the length of the interval during intermittent dynamic testing. Further work with different antiozonants will be necessary to clarify some of the suggestions above.

8.7 Mechanism of ozone protection by coating layer.

Research work\(^{(20-22)}\) over the years has established that classical chemical antiozonants protect by migrating from the product matrix to the surface, where an impermeable film is subsequently formed as a result of the reaction between the antiozonant and the surface ozone. (Chapter 2) The use of a coating as a protective antiozonant provides a different mechanism since the film on the substrate is "non-migratory."

![Diagram of coating mechanism](image)

Figure 8.20- Mechanism of ozone protection.

The mechanism of protection in this case is a direct result of the basic ozone resistance of the material used as a coating i.e. the liquid nitrile butadiene rubber. According to a research by Ossefort\(^{(23)}\), general nitrile rubber becomes ozone resistant only when
properly compounded and the final resistance depends on many independent factors like curing system, fillers and/or other ageing inhibitors. Different grades of nitrile rubbers show varying degrees of ozone resistance depending on the molecular weight of the polymer and compounding ingredients. The analysis of cracking and protection can therefore follow from the scheme given in Figure 8.20. Although the structure of NBR indicates the presence of a double bond system which is prone to ozone attack, the number of double bonds in the coating is determined by the curing system used. Non-sulphur curing systems are known to respond more satisfactorily to the inhibition against ozone cracking than sulphur based systems. For best results in ozone resistance, compounding techniques used should result in low unsaturation in the coating. The presence of -CN groups in the matrix of the coating material is a further guard against ozone attack as the polar characteristics of this group makes the reaction with ozone more difficult.\textsuperscript{[24,25]}

As long as the coating on the surface of the substrate remains undamaged, protection against ozone will be provided. If however, during application the coating is damaged and through dynamic cycling the critical tearing energy is reduced, when ozone gets into the underlying rubber cracking will result. Such cracking will continue throughout the bulk of the rubber for as long as new surfaces with double bond structures are uncovered by the ozone. The major advantage of this coating is that it does not require constant replenishment as is the case with the classical antiozonants.

8.8 Flexing properties
The main objective of carrying out the De Mattia test was to determine whether the nitrile rubber coating on a natural rubber substrate would delaminate through flexing. The bend flexing test was carried out using the standard ASTM 430-88 method. Twelve coated samples were tested, six at 23°C and the other six at 60°C flexing at 300± 10 flexes per minute. Results of the test are shown in the Table 8.9 below.
**Table 8.9- Flexing test results**

<table>
<thead>
<tr>
<th>Test</th>
<th>Sample Number</th>
<th>Temp. (°C)</th>
<th>Uncoated NR.</th>
<th>Coated NR.</th>
<th>Total Test Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>No. of cycles to failure**</td>
<td>No. of cycles to failure**</td>
<td>(min)</td>
</tr>
<tr>
<td>23</td>
<td>1</td>
<td>N</td>
<td>damaged</td>
<td></td>
<td>270</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>O</td>
<td>10500</td>
<td>270</td>
<td>81000</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td>15994</td>
<td>270</td>
<td>81000</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>C</td>
<td>18284</td>
<td>270</td>
<td>81000</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>R</td>
<td>21310</td>
<td>270</td>
<td>81000</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>A</td>
<td>18608</td>
<td>270</td>
<td>81000</td>
</tr>
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<td>1</td>
<td>C</td>
<td>12428</td>
<td>270</td>
<td>81000</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>K</td>
<td>9147</td>
<td>270</td>
<td>81000</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>I</td>
<td>4500</td>
<td>270</td>
<td>81000</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>N</td>
<td>8036</td>
<td>270</td>
<td>81000</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>G</td>
<td>11750</td>
<td>270</td>
<td>81000</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>S</td>
<td>11457</td>
<td>270</td>
<td>81000</td>
</tr>
</tbody>
</table>

* 1 minute = 300± 10 cycles

** failure refers to delamination.

When a rubber vulcanizate is flexed, both fatigue and ozone cracking can occur\(^{[26]}\) and according to Gent\(^{[27]}\) fatigue can be defined as the gradual weakening of rubber specimens and their eventual fracture brought about by repeated deformations at strains much lower than the breaking strain. No such cracking from fatigue was observed on the specimens subjected to de Mattia testing at short flexing times but more than half the total number of test pieces showed signs of delamination after the duration of the test. All failed test pieces showed localised delamination i.e. the
delamination did not cover the whole surface area with a coating but appeared on different parts of the coating as small pin-head nuclei. These were observed as delamination through a microscope. (Figure 8.21) Areas with delamination grew bigger with increase in number of flexes.

![Figure 8.21-Coating delamination (magnification 25 X) after 3hr flexing on de Mattia machine.](image)

No cracking of the rubber was observed throughout the test for both coated and control samples. Three samples tested at 23°C failed while four failed at 60°C. Samples tested at room temperature took much longer time to show signs of delamination while those tested at 60°C indicated failure much earlier. In both cases the delamination was a result of flexing and the magnitude of strains generated through flexing. The measure of extension ($\varepsilon$) for a standard De Mattia test piece can be calculated from the following expression:

$$\varepsilon = \frac{l_f - l_e}{l_e} \times 100$$  \hspace{1cm} (8.14)
where \( l_d \) is directly measured length of test piece when folded backwards with the A side flat on the B side. (see Figure 8.22)

\( l_0 \) is the initial diameter of the groove which equals to 2r.

![Diagram of De Mattia test piece with labels A and B and radius r = 2.40 mm]

Figure 8.22- Standard De Mattia test piece for flexing.

Measurements from test pieces used gave an average \( l_d \) of 12.0 mm and with that value, the average extension during De Mattia testing was estimated to be 61 %. Under static ozone testing conditions, a strain extension of 20 % was used for all test pieces and cracks were observed on unprotected specimens. (see Figures 8.6 and 8.7) Cracks were also produced on unprotected test pieces under dynamic continuous ozone testing where an extension of 25 % was used. (Figures 8.12 and 8.13) In the absence of ozone during the De Mattia testing, no cracks appeared at the estimated strain extension of 61 % which resulted in delamination of the coating.

8.8.1 Analysis of delamination

Delamination as observed in the outlined test is a physical process which implies failure in adhesion at the interface of the nitrile rubber coating and the natural rubber substrate. Possible causes of delamination are given below:

- poor compatibility between the materials;
- different rates of vulcanisation resulting in early or late cures of one of the materials - yielding generally poor covulcanisation;
- poor adhesive properties of one or both materials;
• poor wetting (contact) between the surfaces;
• the presence of an oil or lubricant between the surfaces, and
• weak link in hybrid interface.

The delamination observed in this study is likely to be a result of different rates of vulcanisation coupled with poor compatibility between the materials.

Figure 8.23-Cure characteristic of natural rubber and NBR-Nipol using a conventional sulphur cure system at 160°C. (cure test experiments)

Besides the low compatibility of materials, as shown by the difference in solubility parameters (section 8.3), the conventional sulphur curing system\(^ {28} \) is known to result in faster cures for NR than it does for NBR. (Figure 8.23) In order to reduce cure times for the Nipol compound, the doses of sulphur and TMTD were determined by using a screening variables method. (see Figures 7.3 and 7.4) Final levels for the accelerator and the curing agent were taken to give an average cure time of 10 minutes for the natural rubber substrate. Despite the achievement of shorter cure times through the suggested changes to the cure system, similar cure rates between natural rubber and coating were not attained as seen from Figure 8.23.
8.9 Diffusion studies

The main objective of the diffusion exercise was to determine if the nitrile butadiene rubber coating could inhibit the migration and loss of a chemical antiozonant system based in a natural rubber substrate. Two sets of five specimens, one set coated and the other uncoated, were prepared from specific compounds, (see Table 7.2). Test pieces were conditioned at 40°C for twenty four hours prior to placing them in an air circulating oven set at 60°C where the blooming of the antiozonant took place. The weight loss of each specimen measured to an accuracy of ± 0.001g was monitored for the duration of the two week test period.

![Graph showing weight loss over time for uncoated samples with different antiozonant content](image)

**Figure 8.24** - Weight loss in uncoated samples with lower antiozonant content

Substantial differences in weight loss between coated and uncoated test pieces were recorded with uncoated samples yielding higher losses. The general pattern of weight loss reflected well the amount of antiozonant incorporated in each sample. The lower the amount of antiozonant in the compound, the shorter the time required for the sample weight to stabilise. (Figure 8.24) Both figures (8.24) and (8.25) give a very clear contrast between the weight losses in samples with lower...
concentrations of the antiozonant. All in all, coated samples lost very small amounts of antiozonant and reached shorter equilibrium times.

![Coated samples graph](image)

**Figure 8.25**-Weight loss in coated test samples with lower antiozonant content

For both coated and uncoated samples, control specimens were first to stabilise in weight with the coated test pieces taking only two days to achieve that status while the uncoated pieces took three days longer. The difference between weight loss recorded for the coated control sample and that of the uncoated control sample is very conspicuous. While the total loss from the coated control sample was 0.001g, the total loss from the uncoated control sample was 0.017g. This is a clear indication that the coating material reduces the amount of antiozonant diffusing to the surface of the moulding. In like manner, losses from both coated and uncoated samples with 2 phr of antiozonant were also indicative of the fact that the coating allowed less antiozonant to pass to the surface. Studies\(^3\) have shown that in natural rubber, IPPD blooms at doses above 2.5 parts while in typical synthetic rubbers (depending on the molecular structure of the particular rubber) the same antiozonant has to be above 4 parts to be able to bloom. Consequently, no blooming of the antiozonant was observed on the test pieces with 2 phr and lower amounts of antiozonant, even after a week into the test. The other reason for lack of blooming in the sample with 2 parts of antiozonant might be temperature based.
The test temperature of 60°C can be considered high enough to allow for a reasonable degree of solubility of the antiozonant, whose melt temperature is about 73°C. Both coated and uncoated samples with 10 and 15 phr of antiozonant lost a considerable amount of weight within the first five days of the test. (Figures 8.26 and 8.27) These samples with higher content of antiozonant took even longer times to stabilise in weight. The blooming antiozonant was observed in all cases and removed as outlined in Section 7.4.3. Weight losses in all coated samples were evidently lower than those recorded for uncoated sample equivalents.

Figure 8.26-Weight loss in uncoated test samples with higher antiozonant content

Based on weight losses incurred in both control samples i.e. coated and uncoated samples with no added antiozonant, the total losses for each specimen can be viewed as additive. Taking into account the fact that all control samples had no added antiozonant in them, the total weight loss in these samples can be attributed to loss of other volatile constituents. Assuming these volatile losses also occur in samples with 2, 5, 10 and 15 phr of antiozonant, the actual antiozonant loss in each case can be given as the difference between the total weight loss for the sample and the loss from the respective control sample. If the total loss from the control sample of an uncoated specimen is 0.017g and the total loss from a specimen from the same set with 5 phr of antiozonant is 0.020g, then the actual amount of
antiozonant lost can be taken as the difference between the loss incurred by the specimen with 5phr and that incurred by the control sample i.e. 0.003g. The procedure described above can be expressed in the following relations:

$$\text{Total weight loss} = \text{loss}_{\text{Ao}} + \text{loss}_{\text{Vol}}$$  \hspace{1cm} (8.15)

where loss$_{\text{Ao}}$ is antiozonant loss and 
loss$_{\text{Vol}}$ is loss of other volatile constituent = loss in control sample

**Table 8.10** Additive weight loss for uncoated and coated samples.

<table>
<thead>
<tr>
<th>Initial amount (phr)</th>
<th>Uncoated samples</th>
<th>Coated samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total loss (g)</td>
<td>A$_e$ loss (g)</td>
</tr>
<tr>
<td>0</td>
<td>0.017</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.018</td>
<td>0.001</td>
</tr>
<tr>
<td>5</td>
<td>0.020</td>
<td>0.003</td>
</tr>
<tr>
<td>10</td>
<td>0.022</td>
<td>0.005</td>
</tr>
<tr>
<td>15</td>
<td>0.024</td>
<td>0.007</td>
</tr>
</tbody>
</table>

The daily average weight loss for each of the five coated samples was about 0.3 mg and this small amount was a clear indication that little blooming took place across the coated surfaces. In fact, of all the coated samples, only specimens with 10 and 15 phr of antiozonant showed a fair amount of bloom for the first few days, after which all weights stabilised. Undoubtedly the presence of a protective coating on the natural rubber substrate reduced the amount of antiozonant loss. Since all test samples were subjected to the same temperature conditions, it can be observed that the high temperature of 60°C does not prevent the coating material from acting as an effective barrier of the antiozonant. Although the test temperature did not hinder the coating material from acting as a barrier, the solubility of the antiozonant in each of the elastomeric materials at that temperature also affects the amount that can diffuse to the surface.
Figure 8.27- Weight loss in coated samples with higher antiozonant content.

Data in Table 8.10 can be used to plot both the total weight loss and the antiozonant weight loss against the initial amount of antiozonant in each compound as shown in Figures 8.28 and 8.29. It is clear from Figure 8.28 that the average weight loss for the uncoated samples during the two weeks of testing was above that reached by coated samples. While the control coated sample lost a total of 0.001 g, the control uncoated one lost 0.017 g. This means that the coating prevented over 94% of material being lost through blooming. For all the other higher antiozonant concentrations, the scale of loss restriction from the coating remains above 80%.
Figure 8.28-Total weight loss in two weeks.

Figure 8.29 also shows a clear proportionality between the amount of antiozonant in the initial compound and the total amount lost through blooming.

Figure 8.29-Antiozonant loss in two weeks.

In Figure 8.29, both coated and uncoated samples with 2 phr of antiozonant lost an equal amount of 0.001 g throughout the duration of the test. This is a fair result since no blooming of antiozonant was expected from both samples with such a low concentration of the antiozonant, as indicated in the literature.\textsuperscript{[3]} If the antiozonant
IPPD only blooms effectively at levels above 2 phr and assuming an initial antiozonant level of 4 phr is used, then the service life of the antiozonant can be estimated for both coated and uncoated samples. (Figure 8.30) It can be seen from Figure 8.30 that it takes about 13 days for the amount of antiozonant to drop to the 2 phr level in the uncoated sample while it takes about 18 days to reach the same level in the coated sample. This means that the coating has the ability to prolong the service life of a product.

![Figure 8.30- Estimation of antiozonant service life at 60\(^\circ\)C](image)

It should be noted that the antiozonant service life estimated above is based on a service temperature of 60\(^\circ\)C. In waxes, such a temperature would affect both the diffusion coefficient of the wax and its protection ability since bloom development of the wax and its effectiveness depend on its melt temperature.\(^{[15]}\) It has been established in many investigations that the temperature dependence of the coefficient of diffusion can be formulated in good approximation by an Arrhenius type expression.\(^{[29-31]}\)

\[
D = D_0 e^{E_d / RT} \quad \text{or} \quad D = (1/6\nu d^2) \exp(E_d/RT)
\]

(8.16)

where \(D\) is the diffusion coefficient of the diffusing substance.
$D_0$ is the frequency factor based on the mean vibration frequency of the rubber material ($\nu$) and the square of the free path of the diffusing molecule in a unit diffusion step ($d^2$) and

$E_a$ is the activation energy of diffusion

Braden\cite{32} has however, shown that most chemical antiozonants have very low diffusion coefficients which do not control their protective ability. The service life of such antiozonants depends more on the stability of their reaction products with ozone on the surface than on the service temperature. Studies have shown that reaction products of antiozonants and surface ozone are insoluble in rubber\cite{33} even at elevated temperatures. As long as the reaction products are unaffected by high temperature, the probability of the service life of an antiozonant used at 60°C being as long as that of an antiozonant used at 25°C will remain high. If however, the antiozonant is used in conjunction with a wax to enhance static properties, the service life of the antiozonant system is affected by changes in temperature.\cite{15}

With increase in the initial concentration to 10 phr and 15 phr respectively, the percentage of material retained by the presence of the coating rises to 40% and then falls to 29%. Despite this low percentage at 15 phr which is likely to be a result of raw data error, the percentage of retained antiozonant remains proportional to its initial concentration at all levels as seen in Figure 8.29. This implies that the effectiveness of a coating in deterring the loss of an antiozonant is not dependent on the initial amount of the antiozonant in the compound.

The work outlined above can be discussed in view of studies done by Lederer et al.\cite{34} and Nah et al.\cite{35} which involves general diffusion processes. As such, the data for antiozonant loss, surface area of the test pieces and time allowed for the blooming exercise can be plotted to show proportionality between loss and the square root of time. (Figures 8.31 & 8.32)
In the initial stages of both traces, the antiozonant loss is closely proportional to $t^{1/2}$ as expressed in equation (8.15) which indicates a diffusion controlled process. In Figure 8.31, it is clear that the diffusion process continues in uncoated samples well after the process seems to have stopped in the coated samples. This is demonstrated by the further losses in weight following in uncoated samples while losses in coated samples tend to plateau. It is however unlikely that the diffusion in coated samples summarily ceases at this stage but rather the rate becomes much slower. Based on data in Table 8.10 and Figure 8.31, diffusion in coated and uncoated test pieces reaches equilibrium at different levels of antiozonant loss. While in uncoated specimens the diffusion stops after about 11 days with 75% of the total antiozonant loss, in coated specimens the diffusion stops after 7 days with 48% of the total antiozonant loss.

Figure 8.31- Diffusion traces of coated and uncoated samples
Figure 8.32- Diffusion traces of coated and uncoated samples.

Figure (8.32) also shows the same picture in which the diffusion process for samples with 15 phr of antiozonant continues for much longer in uncoated samples as it does in coated ones. Due to the original higher level of antiozonant in this compound, the diffusion process in coated samples from the 15 phr specimens tend to proceed for much longer than is the case in Figure 8.31 where the initial antiozonant level is lower. After 12 days of testing, the diffusion process stopped with 85% of the antiozonant lost from the uncoated test piece. In the coated test piece the diffusion lasted for 10 days resulting in 71% of the antiozonant loss. The levels of antiozonant loss recorded from the samples with 10 and 15 phr of antiozonant indicate that the initial antiozonant level is a determining factor for the duration of the diffusion process. However, the measure of bloomed material does not only depend on the quantity of antiozonant in the system but also on the ability of the antiozonant molecules to migrate through the rubber matrix and the coating material. This would explain why more antiozonant is lost in uncoated samples than in coated ones. The rate of diffusion in the same system also depends on the compatibility of the antiozonant in the rubber at the set operational temperature. On comparing the two sets of traces, it is easy to see that the diffusion in uncoated samples went on for much longer than it occurred in the coated specimens.
It is fair to say that the presence of a coating on the surface of the substrate reduced the mobility of the antiozonant molecules. Only samples with higher levels of antiozonant in both coated and uncoated specimens have been used to illustrate the diffusion process because it is mainly in these that the phenomenon is more pronounced. In the final analysis, the diffusion studies undertaken demonstrate well that the degree of compatibility between the applied coating material and antiozonant IPPD is less than the compatibility of the latter with natural rubber. (see Table 8.3) This means that the nitrile rubber protective coating on a natural rubber substrate is well suited to slow down the process of blooming by an antiozonant and in that sense is able to retain the needed antidegradant in the matrix of the material for much longer periods. In an atmosphere with ozone therefore, a rubber vulcanizate with a protective coating and an incorporated antiozonant stands a better chance to resist cracking for much longer than one without a surface coating.

8.9.1 Estimation of Diffusion Coefficient

In an earlier chapter on Diffusion in Elastomers the diffusion coefficient was defined as a proportionality constant that gives information of the nature of the transport process and the interaction of the molecules involved. Many ways of determining this parameter have been explored by different researchers and the accuracy of each method depends entirely on the nature of the diffusion process involved and the ease with which the acquired data is used. Following the diffusion experiments carried out, an attempt to calculate the diffusion coefficient can be made using the following expression which relates well with Figures 8.28 and 8.29:

\[
D = \frac{(m^2\pi)}{(4tc^2)}
\]  

(8.17)

where \( m \) is the total amount of diffusing substance

\( t \) is the time taken to complete the diffusion process (seconds)

\( c_\infty \) is the final concentration of the diffusing substance.
Using the additive method of determination of antiozonant loss discussed in Section 8.7, the final amount of diffused material can be calculated and used to estimate the respective diffusion coefficients as shown in Table 8.11.

Table 8.11- Calculated diffusion coefficients for coated and uncoated samples

<table>
<thead>
<tr>
<th>Initial level (phr)</th>
<th>( m ) (mg)</th>
<th>( c_0 ) (mg/cm²)</th>
<th>( D ) (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>uncoated</td>
<td>coated</td>
<td>uncoated</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
<td>2</td>
<td>0.063</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>3</td>
<td>0.188</td>
</tr>
<tr>
<td>10</td>
<td>22</td>
<td>4</td>
<td>0.313</td>
</tr>
<tr>
<td>15</td>
<td>24</td>
<td>6</td>
<td>0.438</td>
</tr>
</tbody>
</table>

Results in Table 8.11 show the strong dependence of the diffusion coefficient on the concentration of the antiozonant. In general, uncoated samples have higher diffusion coefficients because the amount of diffusing substance, which is a determining factor in the equation, is higher in these samples than in coated ones. In both coated and uncoated samples, the diffusion coefficients increase with decrease in the final concentration of the diffusing substance. At levels of 5, 10 and 15 phr, the diffusion coefficient gradually falls indicating that the rate of diffusion as a function of initial concentration is also decaying. For practical service purposes therefore, levels of antiozonant between 2 and 5 phr will be considered adequate while taking into account the losses to be incurred through weathering, flexing and general handling.

8.9.2 Mechanism of reduction in antiozonant loss by nitrile rubber coating.

The question of compatibility between natural rubber and a protective coating in the current project is regarded as a pivotal one since the migration of an antiozonant can be traced from the matrix of the substrate, through the substrate-coating interface to the surface of the coating material. The mechanism of antiozonant loss through a coating material can therefore be illustrated as shown in Figure 8.30 below.
Theoretical calculations of the solubility parameters of both natural and nitrile rubbers (Table 8.3) indicate that the two materials are not easily compatible one with the other while the solubility parameter of the antiozonant IPPD is placed closer to that of natural rubber. This means that in practical terms the antiozonant is more compatible with natural rubber than it is with nitrile rubber. In essence this also means that at a set test temperature, the antiozonant will be more likely to remain in solution in the natural rubber than to pass into the nitrile rubber coating. In an uncoated test piece, the antiozonant migrates from the bulk of the substrate to the surface where it accumulates and maintains an equilibrium with the remainder of the material in the substrate. As the antiozonant on the surface is depleted through reactions with oxygen or ozone or in some cases being physically removed, more diffuses to the surface to replenish the loss. Due to the combined effect of the non-polar nature of natural rubber and the high melting temperature of IPPD, the diffusion by the antiozonant to the surface is made easier and the rate is also faster. In the coated test pieces however, the polar nature of the nitrile butadiene rubber coating inhibits diffusion. A higher amount of antiozonant will therefore accumulate at the interface before a smaller amount manages to pass the
barrier to the surface. As a result of this mechanism, the nitrile rubber coating is able to retard the rate of migration of the antiozonant through to its surface, reduce the total amount of loss at the surface and therefore prolong the life span of a product in respect to ozone resistance.

8.10 PVC coating results and method assessment.
The coating exercise carried out with polyvinyl chloride (PVC) showed that it is possible to coat a rubber substrate through both post-mould coating and in-mould coating processes. Although test pieces from both cure systems were not subjected to specific adhesion tests, it was observed that interfacial adhesion of post-mould cured samples was poorer than the adhesion of in-mould cured samples. While the coating on oven fused test pieces formed a smooth skin on the substrate surface, the coating on in-mould cured samples had a rough surface appearance due to the compression applied during fusion. The smooth skin coating on oven fused samples was easily detachable from the substrate surface but the coating on in-mould cured samples adhered firmly on the substrate surface. This difference in adhesion observed between oven-fused and compression cured samples emphasises the importance of pressure during the curing process. Unless the coating with PVC is meant as a decorative finish for products that do not experience dynamic changes during service, curing in a fusion oven without pressure exerted on the samples can not be recommended for products that require functional adhesion at the interface.

The achievement of good results with a post-moulding technique depends to a large extent on the flow properties of the coating compound, the gelation and fusion characteristics of the resin used and equally on the adhesion forces created at the interface of the substrate and the coating material. These parameters are best controlled by strict selection of a plasticiser which dissolves the PVC and lowers the glass transition temperature of the resin resulting in an increase in melt flow. If during a curing process the coating material undergoes thermal degradation, a visible change of colour occurs as the coloured polyene sequences are produced by the dehydrochlorination process. The elimination of hydrochloric acid in this process catalyses the degradation which continues until the temperature is lowered.
The temperature of the substrate prior to coating is crucial in creating conditions conducive for mechanical adhesion. The mechanical penetration of the coating material into the underlying layer of the substrate surface leads to improved adhesion at the interface during the fusion of the resin. As particles interlock at the interface, the degree of adhesion is enhanced further with the cooling of the materials.

8.11 Reliability of results

The discussions and conclusions given at the end of this project are based on the data and results obtained through practical work and analysis carried out. The reliability of these results therefore depends on:

- equipment used in practical work
- methods used for the analysis of results
- the general repeatability of the results and
- the reproducibility of the results.

It could be mentioned that both repeatability and reproducibility are parameters that show the scatter or spread of test results over a given period of time. While repeatability refers to the consistency in the spread of results obtained by one individual, reproducibility refers to the consistency in the spread of results obtained on an identical sample by several people or laboratories. Little can be said therefore on the latter concept regarding the current results although it is hoped that the results are also reproducible. Although two different mixing systems were used for compounding the substrate material and the coating compound respectively, the regimes and specifications within each mixing system were observed for every batch mixed. Such controls resulted in the achievement of repeatable results. Despite the fact that no strict shelf-life control of natural rubber compounds was done, different batch mixes retained high levels of tensile strength values during the period of study.
Results from the Hounsfield Tensile Machine showed low standard deviation values for the lot of samples tested. (Appendix C, Table C.1) The mean tensile strength and elongation of the natural rubber used is equally representative of the general values of these parameters for the same rubber.

Ozone test results were consistent and relevant across the whole range of samples tested. Although it was not possible to obtain a quantitative measure of repeatability, the systematic changes in ozone cracking between the samples give a high level of confidence in the results. All natural rubber substrates coated with the protective material survived the 72 h ozone exposure test much the same as natural rubber substrates compounded with a complex of wax and a chemical antiozonant but with no coating.

Results from diffusion studies are equally reliable since they compare well with analyses by van Amerongen\[31\] and Lederer et al.\[34\] for the determination of the diffusion coefficient and the work by Nah et al.\[35\] and Braden\[32\] to show the proportional relationship between the amount of material diffused and the square root of time. The method of bloom removal using adhesive tape also worked well, as the results of weight loss for individual test pieces indicated a steady decline. Further more, the differences in diffusion between coated and uncoated substrates clearly demonstrate the established fact that the antiozonant used in the study is more soluble in natural rubber than it is in nitrile butadiene rubber.

8.12 General Discussion.

The fact that nitrile butadiene rubber(Nipol grade) has potential as an ozone resistant coating material suggests that other rubbers can also be possible candidates for coating applications. For an elastomer to be used as an ozone resistant coating, the following requirements should be fulfilled:

- inherent ozone resistance;
- resistance to damage, abrasion and fatigue cracking;
- strong bonding with substrate material;
- low modulus and large elongation at break;
• inhibition of antiozonant loss from substrate;
• minimum interference with the deformation behaviour of the product, and
• easy application through routine product manufacturing methods.

Little information was found in literature concerning the bonding of rubber to rubber materials in the manner described in this project i.e. bonding through covulcanisation of the elastomers concerned. Through work done by Gent[39] on bonding of polybutadiene to glass with silane coupling agents, it can be said that the development of chemical bonding at the interface of two elastomeric materials results in an increase in the strength of adhesion between the two. The degree of chemical bonding is determined by the reactivity of the respective elastomers in the presence of the different curing systems used.

Results of diffusion studies in the current project show that a good ozone resistant coating should also be an inhibitor for chemical antiozonants. Because of the possibility of damage to the coating during service applications, it is proposed that the coating be used in conjunction with a chemical antiozonant compounded in the natural rubber. In the event of the coating being damaged the incorporated chemical antiozonant will continue to provide the product with the necessary protection from ozone. This approach to ozone protection is likely to raise the cost of the protection but the longer service life of the product can be expected to justify the increase in safety critical products.

It has been ascertained by this study that compounded Nipol 1312 adheres onto a natural rubber substrate through vulcanisation and while the film is undamaged on the surface, it acts as an effective antiozonant. The ingredients involved in the formulation of the compound used and outlined in Section 7.3.2 all play a vital role in achieving the useful properties of the coating material. The combination of zinc oxide and stearic acid works in much the same way in this compound as it does in a natural rubber compound i.e. as an activator. Activators in rubber compounds increase the effectiveness of the accelerators and where mercaptobenzothiazole(MBT) or its derivatives are used as accelerators, activators are able to improve the properties of the
respective compounds. It is not a coincidence therefore that both zinc oxide and stearic acid were found necessary as ingredients in compounds for both the substrate and the coating material.

Two types of accelerators are used in this coating compound namely dibenzothiazole disulphide (MBTS), a primary accelerator and tetramethylthiuram disulphide (TMTD), a secondary accelerator. The role of the latter accelerator, which is normally a fast curing-accelerator, is to activate the primary accelerator in cases where the synthetic rubber used is generally slow curing than natural rubber. This is a very necessary combination for the nitrile butadiene rubber grade used here as coating material in view of the recommendation in the producer’s technical notes which states "...at higher levels of the liquid rubber, additional sulphur or accelerator is necessary. Generally 0.5 parts of additional sulphur per 10 parts of liquid rubber is satisfactory to result in a cure."[2]

In this project however both the addition of sulphur (a curing agent) and an accelerator are found to be necessary and their respective amounts are worked out as outlined in the section referred to above. Due to the very high levels of liquid rubber required for the compound formulation, the amount of sulphur in the recipe remains high at 7 phr which amount achieves cure within a reasonable time of 15 minutes. Undoubtedly this is the grey area of the present formulation which can possibly be improved either by increasing the amounts of the accelerators while reducing the sulphur content or by using an alternative combination of diphenyl guanadine (DPG) and an MBTS-sulphur system.

A plasticiser was also considered necessary for the Nipol compound and dioctyl phthalate (DOP) taken as suitable for the purpose. As a plasticiser, DOP promotes the coalescence of the coating particles by dissolving the nitrile rubber resin and subsequently decreasing the melt viscosity of the coating. With the material freely flowing, the use of a brush for applying the coating is made much easier. Without a plasticiser, the mobility of the compound is very restricted even at higher temperatures. Too much plasticiser however, tends to have a negative effect on the curing process as
the vulcanizates come out with a "greasy" surface and in an undercured state. Even without the few improvements possible for this final compound, some of the merits and demerits of the formulated coating material can be summarised as below.

**Merits**

- Viscosity is easy to manipulate (without use of solvents) to suit coating requirements.
- Chemical bonding through vulcanisation ensures good adhesion between substrate and adhesive(coating).
- The coating functions as a **NON-MIGRATORY** antiozonant.
- Provides both static and dynamic protection.
- Good surface coating ensures total surface protection.
- Non-staining and inextractable coating
- If a chemical antiozonant is incorporated into the substrate compound prior to coating, the Nipol film is able to retard the amount of antiozonant bloom.
- Other than ozone resistance, Nipol 1312 imparts oil resistance properties to products.

**Demerits**

- Unvulcanised Nipol 1312 is sticky and difficult to compound. Coating applications are not easier.
- Nipol 1312 requires very high levels of sulphur to cure.

While at high temperatures the viscosity of Nipol is fairly well reduced, the spreading of the material onto the surface of the substrate is not always uniform. Judging by the results of the ozone tests carried out, it is evident that a coating of Nipol 1312 on a natural rubber substrate is able to protect natural rubber from ozone attack for a specified period of exposure. This fact in itself allows for a conclusion to be drawn that the ozone attack on the substrate is prevented by a **non-migrating antiozonant system**. It is logical to conclude that the non-migration of the system is achieved by the adhesion between the substrate and the coating material through vulcanisation since no adhesive was incorporated between the surfaces prior to
moulding. The mechanism of protection by this non-migrating system is easier to speculate since the coating material used is by nature inherently ozone resistant. Naturally therefore, as long as the coating remains on the rubber surface no attack by ozone is envisaged. In the likely event of the coating breaking through dynamic applications or any other form of damage, the future of the natural rubber substrate becomes very uncertain in an atmosphere with ozone. In cases where the substrate compound has no chemical antiozonant protection against ozone except from the coating, it is only rational to assume that the rubber is most likely to crack if the ozone by-passes the coating. This fact is one of the major shortfalls of this antiozonant system.
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CHAPTER 9

CONCLUSION AND RECOMMENDATIONS.

9.1 Conclusion

The following conclusions can be drawn from the work that has been done in this project:

1. A coating compound from nitrile butadiene rubber was formulated.

Nitrile butadiene rubber has been used before as a coating material for research purposes but not in the form it was used in this project. Previous coating applications with this rubber involved dissolving the material into a combination of solvents to achieve the required viscosity. In this project, a grade of low molecular weight nitrile butadiene rubber which required no use of solvents was used in the compound formulation. This grade of nitrile rubber normally used as a plasticiser for other nitrile rubbers has not been used before for coating purposes. Advantage was taken of the flow properties of this material at higher temperatures through which the classical method of applying the coating by brushing was achieved.

2. A film coating from the compound was able to protect a natural rubber substrate from ozone attack.

Following all the ozone tests carried out with the formulated coating compound, it was clear that the presence of the coating material on the substrate surface gave protection against ozone attack. Taking into account that one of the major properties of the coating material was its ozone resistance, the protection given to the natural rubber comes as no surprise. Ordinary high molecular weight nitrile butadiene rubber is only of medium resistance to ozone attack and once dissolved in some solvents, its ozone obstruction is weakened even further. The use of a low molecular weight nitrile rubber with good ozone resistance properties and the fact that no solvents were used to reduce the viscosity of the coating material, resulted in sound protection of the substrate from ozone attack.
3. A non-migrating antiozonant system was produced.
It is a fact that all antiozonants currently in use in the rubber industry are of a migratory nature mentioned in the foregoing literature review. Essentially this means that all these antiozonants operate through a mechanism which demands that the materials migrate from the matrix of the rubber (substrate) to the surface where such protection as against ozone attack is required. In the absence of such bulk movement of the antiozonant material, no protection can be guaranteed. With the success of this coating material, a non-migratory antiozonant, permanently on the surface of the substrate has been achieved. Such an antiozonant does not require periodic replenishment as do waxes and chemical antiozonants. This coating antiozonant system also alleviates the bulk of the disadvantages of conventional antiozonants like discolouration (staining), leaching out, limited protection and others.

Following all the diffusion exercises carried out, it can be concluded that the protective coating material retards the rate of loss of antiozonant while it also controls the amount of antiozonant lost by allowing only small amount to migrate to the surface at any given time. This is achieved due to the polarity of the coating material which results in a low solubility of the antiozonant. With the solubility of the antiozonant being higher in natural rubber than in nitrile butadiene rubber, the coating material acts as a barrier which prevents excessive loss of antiozonant from the bulk of the substrate to the surface while giving the rubber the necessary protection against ozone.

9.2 Recommendations
The project outlined in this thesis provides the basis for possible further research in the field of coating antiozonant systems. Based on this work, future work can be proposed in the following areas:
• Alternative curing system;
Although the curing system used in the current project is effective, the amount of sulphur used remained a concern. In this regard, an alternative cure system can be sought in order to cut down on both the cure time and the final cost of the coating compound.

• Mechanism of coating protection;
It is important to establish the mechanism of coating protection through a study of the surface reactions of the coating with ozone and also research on the effect of reaction products on ozone protection. The mechanism behind the protective coating as a non-migratory antiozonant system can be looked at from the inherent antiozonant nature of the coating material but the actual mode of ozone prevention needs to be studied.

• Coating measurements;
Ozone tests carried out in the current project gave the assurance that a coating film is produced on a rubber substrate through covalcanisation. However, the thickness of the film was not adequately established. A follow-up study can therefore access the effect of film thickness together with uniformity of the coating in order to determine the most appropriate technique of coating application. Such a study would also lead to specifications on effective coating thickness and therefore guard against excessive use of material when only small quantities are essential.

• Comparison of antiozonant systems;
The exercise of comparing coating antiozonant system with conventional antiozonant is a necessary conclusion if the new coating system is to find a place in industry. The main area of comparison can be the effectiveness of the systems over certain test periods and different environmental conditions. Such a study can lead to future projections in antiozonant research.
APPENDICES

Appendix A
Glossary

List of Abbreviations Used.

BMC - Bulk moulding compound
BPI - Dimethyl-3,5-di-t-butyl-4-hydroxybenzenepropanamido isophthalate
BR - Butyl rubber
CBS - N-cyclohexyl-2-benzothiazole sulfenamide
CR - Chloroprene rubber
CR-WRT - Chloroprene rubber-mercaptan modified
DENA - N,N'-diethyl-p-nitrosoaniline
DMC - Dough moulding compound
DMBPDP - N,1,3-dimethylbutyl-N'-diphenyl-p-phenylenediamine
DPG - Diphenyl guanadine
DPPD - N,N'-diphenyl-p-phenylenediamine
EPDM - Ethylene propylene diene terpolymer
EPM - Ethylene propylene copolymer
IPPD - N-Isopropyl-N'-phenyl-p-phenylenediamine
MBT - Mercaptobenzothiazole
MBTS - Dibenzothiazole disulphide
NBR - Nitrile butadiene rubber
NR - Natural rubber
NRPRA - Natural Rubber Producers' Research Association
phr - parts per hundred parts of rubber (resin)
PPDA - p-phenylenediamine
PRI - plasticity retention index
PVC - Polyvinylchloride
SMC - Sheet moulding compound
SMR - Standard Malaysian Rubber
SMR-LV - Standard Malaysian Rubber-low viscosity
TMTD - Tetramethylthiuram disulphide
TMTM - Tetramethylthiuram monosulphide
Appendix B

Effect of TMTD on Nipol cure

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Effect of sulphur on Nipol cure

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Appendix C
TENSILE Test to DIN 53 504 Hounsfield Test Equipment Ltd.

Test Report Modulus and Tensile Test (MPa)

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Mean

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Std. Dev.

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Appendix D

Tensile results on antiozonant free compounds

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Tensile results on compounds with antiozonant system

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Strain/stress measurements for substrate and coating

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<td>1.446</td>
<td>1.445</td>
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</table>
Cumulative daily weight loss on uncoated pieces

Table D. 5

<table>
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<th>Time (days)</th>
<th>0 phr</th>
<th>2 phr</th>
<th>5 phr</th>
<th>10 phr</th>
<th>15 phr</th>
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<tbody>
<tr>
<td>1</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
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<td>0.004</td>
<td>0.007</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>3</td>
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<td>0.006</td>
<td>0.011</td>
<td>0.008</td>
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<td>0.018</td>
<td>0.020</td>
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<td>0.023</td>
</tr>
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<td>0.018</td>
<td>0.020</td>
<td>0.022</td>
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</table>

Actual daily weight loss on coated pieces in (g).

Table D. 6

<table>
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<th>Time (days)</th>
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<th>2phr</th>
<th>5phr</th>
<th>10phr</th>
<th>15phr</th>
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<td>1.478</td>
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<td>1.478</td>
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<td>1.478</td>
<td>1.476</td>
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</tr>
<tr>
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<td>1.482</td>
<td>1.478</td>
<td>1.476</td>
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</tbody>
</table>
Total weight loss on uncoated and coated samples
Table D. 7

<table>
<thead>
<tr>
<th>IPPD (phr)</th>
<th>Uncoated loss (g)</th>
<th>Coated loss (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.017</td>
<td>0.001</td>
</tr>
<tr>
<td>2</td>
<td>0.018</td>
<td>0.002</td>
</tr>
<tr>
<td>5</td>
<td>0.020</td>
<td>0.003</td>
</tr>
<tr>
<td>10</td>
<td>0.022</td>
<td>0.004</td>
</tr>
<tr>
<td>15</td>
<td>0.024</td>
<td>0.006</td>
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</tbody>
</table>

Antiozonant loss on uncoated and coated samples
Table D. 8

<table>
<thead>
<tr>
<th>IPPD (phr)</th>
<th>Uncoated loss (g)</th>
<th>Coated loss (g)</th>
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</thead>
<tbody>
<tr>
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<td>0</td>
<td>0</td>
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<tr>
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<td>0.001</td>
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<tr>
<td>5</td>
<td>0.003</td>
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<tr>
<td>15</td>
<td>0.007</td>
<td>0.005</td>
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Cure characteristics of Natural rubber and Nipol with a conventional sulphur
cure system:

Table D. 9

<table>
<thead>
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<th>% cure</th>
<th>Cure time (NR)</th>
<th>Cure time (NBR)</th>
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<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>195</td>
</tr>
<tr>
<td>10</td>
<td>140</td>
<td>360</td>
</tr>
<tr>
<td>20</td>
<td>200</td>
<td>520</td>
</tr>
<tr>
<td>30</td>
<td>250</td>
<td>650</td>
</tr>
<tr>
<td>40</td>
<td>280</td>
<td>800</td>
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<td>400</td>
<td>1200</td>
</tr>
<tr>
<td>90</td>
<td>476</td>
<td>1420</td>
</tr>
<tr>
<td>95</td>
<td>520</td>
<td>1635</td>
</tr>
<tr>
<td>100</td>
<td>568</td>
<td>1800</td>
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Estimation of antiozonant service life at 60°C:
Table D. 10

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Uncoated level (phr)</th>
<th>Coated level (phr)</th>
<th>Minimum level (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>4</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>3.714</td>
<td>3.908</td>
<td>2</td>
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<tr>
<td>2</td>
<td>3.571</td>
<td>3.816</td>
<td>2</td>
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<tr>
<td>3</td>
<td>3.428</td>
<td>3.724</td>
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</tr>
<tr>
<td>4</td>
<td>3.285</td>
<td>3.632</td>
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<tr>
<td>5</td>
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<td>9</td>
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<td>2.141</td>
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<td>1.712</td>
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<td>1.210</td>
<td>1.884</td>
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Appendix : E

Antidegradants;
The following list of commercial antidegradants is not exhaustive of what is currently available in the market but a selection of most commonly used materials appearing under a wide range of names by different suppliers.

Antioxidants/Antiozonants:

1. p-Phenylenediamines

E. 1 N-Isopropyl-N'-phenyl-p-phenylenediamine (IPPD) strongly discolouring

<table>
<thead>
<tr>
<th>Trade names</th>
<th>Suppliers</th>
<th>Trade names</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antgene 3C</td>
<td>Sumitomo</td>
<td>Permanax IPPD</td>
<td>Akzo</td>
</tr>
<tr>
<td>Eastozone 34</td>
<td>Eman Chemicals</td>
<td>Santoflex IP</td>
<td>Monsanto</td>
</tr>
<tr>
<td>Flexoxzone 3C</td>
<td>Uniroyal</td>
<td>Vulkanox 4010 NA</td>
<td>Bayer</td>
</tr>
</tbody>
</table>

E. 2 N-1,4-dimethylphenyl-N'-phenyl-p-phenylenediamine (7PPD)

| Flexzone 11 L | Uniroyal       | Vulkanox 4050 | Bayer |
| Santoflex 14  | Monsanto       |               |       |

E. 3 N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine (6PPD) strongly discolouring

<table>
<thead>
<tr>
<th>Trade names</th>
<th>Suppliers</th>
<th>Trade names</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
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<td>Sumitomo</td>
<td>Permanax 6PPD</td>
<td>Akzo</td>
</tr>
<tr>
<td>Antozite 67</td>
<td>Vanderbilt</td>
<td>UOP 588</td>
<td>Universal Oil</td>
</tr>
<tr>
<td>Anto 3E</td>
<td>Pennwalt</td>
<td>Santoflex 13</td>
<td>Monsanto</td>
</tr>
<tr>
<td>Flexzone 7-F</td>
<td>Uniroyal</td>
<td>Vulkanox 4020</td>
<td>Bayer</td>
</tr>
</tbody>
</table>
E. 4  \( \text{N,N'-Diphenyl-p-phenylenediamine (DPPD)} \) strongly discolouring.

<table>
<thead>
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<th>Trade names</th>
<th>Supplier</th>
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</thead>
<tbody>
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<td>Vanderbilt</td>
<td>DPPD</td>
<td>Monsanto</td>
</tr>
<tr>
<td>Altofane DIP</td>
<td>Ugie Kuhlmann</td>
<td>Good Rite AO3152</td>
<td>BFGoodrich</td>
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<tr>
<td>Antioxidant DPPD</td>
<td>Anchor</td>
<td>J-Z-F</td>
<td>Uniroyal</td>
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<tr>
<td>Ekaland DPPD</td>
<td>Landaise</td>
<td>Permanax DPPD</td>
<td>Akzo</td>
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</table>

2. Phenylamine Antioxidants

E.5  Octylated diphenyl amine (ODPA) strongly discolouring.

<table>
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<th>Trade names</th>
<th>Suppliers</th>
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</thead>
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<tr>
<td>Agerite Gel</td>
<td>Vanderbilt</td>
<td>Lowinox ODE</td>
<td>Lowi</td>
</tr>
<tr>
<td>Agerite stalite S</td>
<td>Vanderbilt</td>
<td>Oxtamine</td>
<td>Uniroyal</td>
</tr>
<tr>
<td>Anox NS</td>
<td>Bozzetto</td>
<td>Pennox ODP</td>
<td>Pennwalt</td>
</tr>
<tr>
<td>Cyanox 8</td>
<td>Anchor</td>
<td>Permanax OD</td>
<td>Akzo</td>
</tr>
<tr>
<td>Flectol ODP</td>
<td>Monsanto</td>
<td>Vanox 12</td>
<td>Vanderbilt</td>
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<tr>
<td>Good Rite AO</td>
<td>BFGoodrich</td>
<td>Vulkanox OCD</td>
<td>Bayer</td>
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</table>

E.6  Acetone-diphenylamine condensation products (ADPA) strongly discolouring

<table>
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<th>Trade names</th>
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<td>Uniroyal</td>
<td>Good Rite 3146</td>
<td>BFGoodrich</td>
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<tr>
<td>BLE</td>
<td>Uniroyal</td>
<td>Naugard</td>
<td>Uniroyal</td>
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<tr>
<td>Flexamin</td>
<td>Uniroyal</td>
<td>Agerite Superflex</td>
<td>Vanderbilt</td>
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3. Dihydroquinoline derivatives

E. 7 2,2,4-Trimethyl-1,2-dihydroquinoline (polymerized) (TMQ) discolouring

<table>
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<th>Trade names</th>
<th>Suppliers</th>
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</thead>
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<td>BFGoodrich</td>
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<td>Bozzetto</td>
<td>Naugard Q</td>
<td>Uniroyal</td>
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<tr>
<td>Antigene RD</td>
<td>Sumitomo</td>
<td>Pennox HR</td>
<td>Pennwalt</td>
</tr>
<tr>
<td>Cyanox</td>
<td>Anchor</td>
<td>Permanax TQ</td>
<td>Akzo</td>
</tr>
<tr>
<td>Flectol H</td>
<td>Monsanto</td>
<td>Ralox TMQ</td>
<td>Raschig</td>
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</table>

4. Bisphenol Derivatives

E. 8 2,2'-Methylene-bis-(4-methyl-6-tert-butyl-phenol) (BPH) non-discolouring

<table>
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<tr>
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<th>Suppliers</th>
<th>Trade names</th>
<th>Suppliers</th>
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<td>Sumitomo</td>
<td>Naruxol 15</td>
<td>Uniroyal</td>
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<tr>
<td>Antioxidant 2246</td>
<td>Anchor</td>
<td>Ralox 2246</td>
<td>Raschig</td>
</tr>
<tr>
<td>Bisoxol D</td>
<td>CDF-Chimie</td>
<td>Santowhite PC</td>
<td>Monsanto</td>
</tr>
<tr>
<td>Cyanox 2246</td>
<td>Cyanamid</td>
<td>Vanox 2246</td>
<td>Vanderbilt</td>
</tr>
<tr>
<td>Lowinox 22 M 46</td>
<td>Lowi</td>
<td>Vulkacit BKF</td>
<td>Bayer</td>
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</table>

E. 9. Antiozonant Waxes

<table>
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<td>Schutz</td>
<td>Ökerin</td>
<td>Astor</td>
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<td>Schutz</td>
<td>Ozokerit</td>
<td>Kemi</td>
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<td>Controzon types</td>
<td>DOG</td>
<td>Paraffin</td>
<td>Malmsten</td>
</tr>
<tr>
<td>Heliozone</td>
<td>Du Pont</td>
<td>Protektor G</td>
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<td>Lunacera</td>
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<td>Sunolite</td>
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<td>BP</td>
<td>Sunproof</td>
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<td>Brk-Werk</td>
<td>Vanwax</td>
<td>Vanderbilt</td>
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