Studies for Improving the Degradation Resistance of Natural Rubber Latex Vulcanizates with Special Reference to Heat and UV-Radiation

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Jaimon K. Kurian

Rubber Research Institute of India
Kottayam 686 009

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DECLARATION

I hereby declare that the work presented in this thesis is based on the original work done by me under the joint supervision of **Dr. N. R. Peethambaran** *and* **Dr. Baby Kuriakose** *at the Rubber Research Institute of India, Kottayam-686 009. No part of this thesis has been presented for any other degree or diploma from any other institution.*

Kottayam
1.10. 2002.

Jaimon K. Kurian

PHONE : 570127, 570168, 570187, 570201

GRAMS : RUBRBOARD
FAX : 0481-570303, 578317

रबड बोर्ड
(वाणिज्य मन्त्रालय, भारत सरकार)
THE RUBBER BOARD
(Ministry of Commerce, Government of India)
प्रशिक्षण और तकनीकी परामर्श विभाग
DEPARTMENT OF TRAINING & TECHNICAL CONSULTANCY
रबड प्रशिक्षण केन्द्र
RUBBER TRAINING CENTRE

कोट्टयम - केरल
KOTTAYAM - 686 009
KERALA STATE

Ref. No. ....

Date: 1.10.2002

CERTIFICATE

This is to certify that this thesis is a report of the original work carried out by **Sri. Jaimon K. Kurian** *under our joint supervision and guidance. No part of this thesis has been presented for any other degree or diploma from any other institution. He has passed the qualifying examination and has fulfilled the necessary requirements for the submission of the thesis.*

Dr. Baby Kuriakose
Joint Director (RT)

Dr. N. R. Peethambaran
Deputy Director (TRG)

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Jaimon K. Kurian

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CHAPTER I

INTRODUCTION

ABBREVIATIONS

A.O	Anti oxidant
CFC	Chloro fluoro carbon
Ci	Curie
Co-60	Cobalt-60
CV	Conventional vulcanization
DRC	Dry rubber content
E.B	Elongation at break
ENR	Epoxidised natural rubber
EV	Efficient vulcanization
HA	High ammonia
HALS	Hindered amine light stabiliser
IIR	Isobutylene isoprene rubber
IS	Indian standards
kGy	Kilo gray
KOH	Potassium hydroxide
LA-TZ	Low ammonia tetramethyl thiuram disulphide-zinc oxide
Mpa	Mega pascal
Mrad	Mega rad
MST	Mechanical stability time
n-BA	n-butyl acrylate
NBR	Acrylonitrile butadiene rubber
NR	Natural rubber
NRS	Non-rubber solids
phr	Parts per hundred parts rubber
PMMA-g-NR	Polymethyl methacrylate graft natural rubber
R-H	Rubber hydrocarbon
RVNRL	Radiation vulcanized natural rubber latex
SEM	Scanning electron microscope
Styrene-g-NR	Styrene graft natural rubber

SVNRL	Sulphur vulcanized natural rubber latex
TBq	Tera bequerel
TMTD	Tetra methyl thiuram disulphide
UTM	Universal testing machine
UV	Ultra violet
VFA	Volatile fatty acid
Vr	Volume fraction of rubber
XSBR	Carboxylated styrene butadiene rubber
ZDBC	Zinc dibutyl dithiocarbamate
ZDEC	Zinc diethyl dithiocarbamate
ZMBT	Zinc mercapto benzothiazole
ZnO	Zinc oxide

CHAPTER I

INTRODUCTION

Natural rubber latex has been known to the civilized world for the last few centuries. But the technology of rubber latex did not develop much until the early nineteenth century. Prior to that, the processing of rubber latex was a primitive handicraft and the products were only subjects of great curiosity. The two major defects with the products made at that time were stiffness in cold weather and tackiness in hot weather. The latter was overcome by the discovery of vulcanization. In 1839, Charles Goodyear and in 1843, Thomas Hancock independently discovered the process of vulcanization which brought about drastic changes in the properties of rubber products. The strength and elasticity of the products were increased greatly and it did not soften in hot weather. Even after this, the latex industry was not developed as the latex coagulated within a few hours of leaving the tree.

This problem was solved with the discovery of ammonia as a preservative for natural rubber latex by Johnson and Norris in 1853.[1] Commercial use of latex did not take place until concentrated latex was marketed in 1920.[2] A number of patents relating to latex products were taken during this period.[3] The two most notable products to emerge from this new industry were extruded thread and foam rubber. These products were markedly different from anything obtainable from dry rubber. By 1940, a substantial proportion of rubber thread used in clothing industry was made from natural rubber latex.[4] Also foam rubber seating found outlets in vehicles, public buildings and hospitals.[5]

The past twenty five years have witnessed considerable changes in the types of products made from natural rubber latex concentrates. Now natural rubber latex is predominantly employed in those applications where its supreme film forming ability and high wet gel strength are required. Dipped goods, latex thread, foam and adhesives are therefore likely to remain as its major outlets in the foreseeable future. But the observed changes in latex consumption have not been accompanied by corresponding changes in production technique.[6]

A severe problem faced by the latex industry is the loss of physical properties of latex products during their service life. All rubber like materials whether natural or synthetic, are subject to deterioration.[7,8] Some of the degradation factors are external to rubber and some of them internal. The man made protectants added during the processing of rubber are generally referred to as 'antioxidants'.

I.1 NATURAL RUBBER LATEX

Natural Rubber (NR) latex is mainly obtained from the bark of *Hevea brasiliensis* by the process of tapping. The freshly tapped latex is a whitish fluid of density between 0.975 and 0.980 gml^{-1}, pH from 6.5 to 7.0 and surface free energy from 40 to 45 $ergscm^{-2}$. The rubber content of latex varies between 25 and 40 per cent by weight and this variation is owing to factors such as type of tree, tapping intensity, soil conditions and the season. In addition to the rubber hydrocarbon, a large number of non-rubber constituents are also present in latex. The rubber hydrocarbon in latex is predominantly cis 1,4-polyisoprene and it occurs as molecular aggregates in the form of discrete particles, which are usually spherical with diameter ranging from about 0.02 to 3 microns.[9]

I.1.1 Composition of Latex

NR latex is a hydrosol in which the dispersed rubber particles are protected by a complex film containing proteins and phospholipids. Excluding rubber and water, the substances present are proteins, lipids, quebrachitol and inorganic salts. The total protein content is about 1-2 per cent of which 20 per cent is adsorbed on the surface of the rubber particles and the rest is dissolved or dispersed in the serum.[10] The lipids consist of fats, waxes, sterol esters and phospholipids and their total content is about 0.9 per cent. The total concentration of inorganic materials is about 0.5 per cent, the main constituents being salts of potassium, magnesium, copper, iron, sodium, calcium and phosphorous.[11]

I.1.2 Preservation and Concentration of Latex

As the latex comes out of the tree, it gets contaminated with microorganisms like bacteria and yeast. The microorganisms metabolise the non-rubber constituents of the latex and produce volatile fatty acids such as formic, acetic and propionic acids which lead to coagulation of latex.[12] Therefore preservatives are added to latex immediately after its collection.[13,14,15] Among the preservatives, ammonia is still used widely and it inhibits bacterial growth, acts as an alkaline buffer and raise the pH and neutralize free acid formed in latex. But ammonia has the disadvantage that it is pungent smelling and prolonged exposure to the gas can cause discomfort to workers. Some of the western countries have introduced legislation regarding the maximum permissible limit of ammonia in a factory atmosphere. Also high concentrations of ammonia lead to processing problems. Therefore attempts have been made to develop low-ammonia preservation systems.[16,17,18] A commonly used low ammonia system is LA-TZ, which consists of 0.2 per cent ammonia, 0.013 per cent TMTD, 0.013 per cent zinc oxide and 0.05 per cent lauric acid.[19,20]

Preserved field latex is unsuitable for most latex applications as its rubber content is low. For most product manufacture, a latex of 60 per cent rubber content is essential.[21] The important methods for the concentration of preserved field latex are (i) evaporation (ii) creaming (iii) centrifuging and (iv) electrodecantation. The first method involves the removal of water only and hence the particle size distribution remains unaffected. On the other hand the other three methods involve partial removal of non-rubber constituents and the particle size distribution of the concentrate differs from that of the initial latex as a proportion of smaller particles are eliminated in the serum. Among these only centrifuging and creaming are commercially used for the production of latex concentrates.[21]

I.1.3 Properties of Latex Concentrate and Effect of Ammoniation

NR latex concentrate is a highly specified material. The latex properties of significance are,[22] dry rubber content (DRC), non-rubber solids content (NRS), mechanical stability time (MST), volatile fatty acid number (VFA), potassium hydroxide number (KOH) and alkalinity. The significance of these properties has been discussed by Blackley[22] and Cockbain.[23] Latex concentrate is a non-Newtonian fluid and its viscosity decreases with increasing shear rate.[24] Natural rubber latex has a measurable electrical conductivity due to the salts dissolved in the aqueous phase and in most centrifuged latices it ranges from 3.0 to 5.0 ms at 25^0C.[25]

The non-rubber materials in the serum of the latex concentrate comprise of a variety of chemical species. In consequence to the addition of ammonia for preserving it, the proteins and lipid materials are believed to be hydrolysed slowly releasing fatty acids, which form soaps which are adsorbed on to the particle surface.[25] The adsorption of these soaps is thought to account for the spontaneous rise in mechanical stability when ammoniated latex concentrate is stored.[26.27] Eventhough a great deal is known about the composition of latex concentrate and its serum content, the relation between composition and properties is still vaguely understood. The real cause for batch to batch variation in processing behaviour is still largely unexplored. Recently it was pointed out that the amount or the nature of serum anions are not sufficient to explain the observed processibility variations and it seems that the answer may lie in variability at the particle serum interface.[6]

I.1.4 Latex Compound and its Processing

The conversion of NR latex into a product is accomplished in many ways and a stable colloidal system is maintained until it is converted into a solid product.[28] The different ingredients used in a latex compound are (i) surface active agents (ii) vulcanizing agents (iii) accelerators (iv) activators (v) antioxidants (vi) fillers and (vii) special additives. The water soluble materials are added as solutions, insoluble solids as dispersions and immiscible liquids as emulsions.[28] The particle size of the ingredients should be reduced to that of the rubber particles in latex for getting uniform distribution in the latex compounds.[29,30,31,32,33] Further the colloidal stability of the dispersions and emulsions should be comparable to that of the latex for maintaining the colloidal stability of the final mix.

I.1.4.a Surface active agents

Surface active agents are substances which can bring about marked modifications in the surface properties of aqueous media, even though they are present in small amounts (of the order of 1 per cent or less). This has great importance in latex technology and in this respect latex technology differs significantly from that of dry polymer or polymer solutions.[29] Stabilising agents, dispersing agents, emulsifiers, wetting agents, viscosity modifiers and protective colloids come under this group. They are classified as anionic, cationic, amphoteric and non-ionic types.[29] The dispersing agents prevent the dispersed particles from reaggregating and alkyl sulphonates are generally used for this. Emulsifying agents are soaps, usually oleates formed in situ. Wetting agents are used to reduce the interfacial tension between two surfaces. Proteins, alginates, polyvinyl alcohols and cellulose derivatives are used as protective agents and viscosity modifiers in the processing of latex compound.[29,34,35]

I.1.4.b Vulcanizing agents

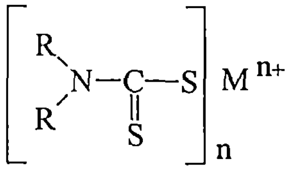
Sulphur is the most important vulcanizing agent for NR latex. Thiuram polysulphides along with thiourea are used as vulcanizing agents for heat resistant products.[36] Dunn[37] reported that butyl xanthogen disulphide in conjunction with a zinc dithiocarbamate may be used to vulcanize latex film in the absence of sulphur. It has also been reported that organic peroxides and hydroperoxides may be used to vulcanize latex films.[29]

I.1.4.c Accelerators

The important classes used in latex compounding are the metallic dialkyl dithiocarbamates.[29] The thiozoles and to a lesser extent thiurams are of importance as secondary accelerators in conjunction with dithiocarbamates.[29]

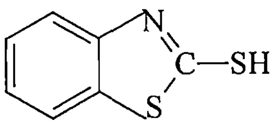
1) Dithiocarbamates

The salts of the dialkyl dithiocarbamic acid have the general structure as shown below.



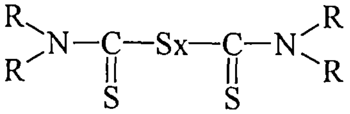
Although a considerable range of accelerators are available under this, zinc diethyldithiocarbamate (ZDEC) and zinc dibutyldithiocarbamate (ZDBC) are the most widely used. They are very active in latex mixes even in the absence of zinc oxide and activates thizole accelerators.[38]

2) Thiazoles



Thiazoles are insufficiently active to be used on their own for latex work, but they function as secondary accelerators for the dithiocarbamate, giving vulcanizate of high modulus.[39] The most common thiazole in latex compounding is the zinc salt of 2-mercapto benzothiazole (ZMBT). It is activated by thiurams and dithiocarbamates.[38]

3) Thiuram sulphides



As a class thiurams are insufficiently active to accelerate satisfactory vulcanization of latex. In combination with other accelerators, the most commonly used thiuram in latex compounding is tetramethylthiuram disulphide (TMTD).[29]

I.1.4.d Activators

Zinc oxide is used as an activator to the vulcanization process and its effect includes increase in the tensile strength and modulus of the vulcanizate. Zinc oxide causes destabilisation and thickening of ammonia preserved natural rubber latex due to the formation of zinc-ammine complexes. Hence only small amount of zinc oxide is included in latex formulations.

I.1.4.e Special additives

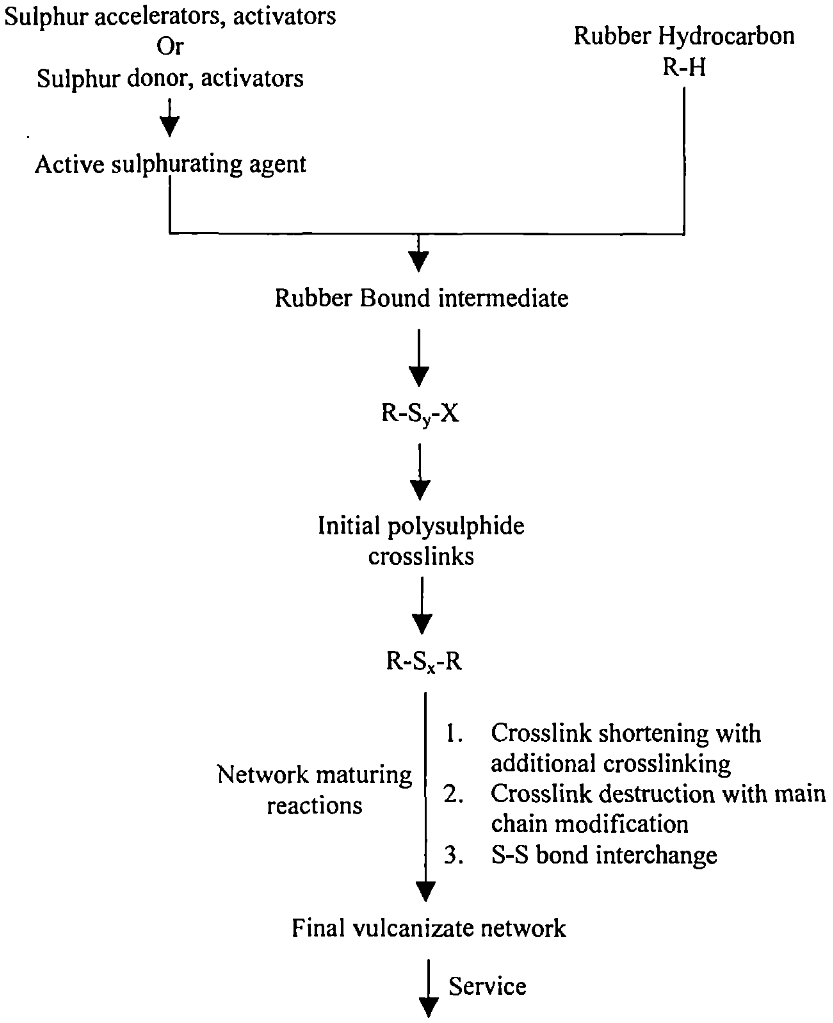
Depending on the nature of process or end use, ingredients like fillers, pigments, antioxidants, gelling agents, flame proofing agents, tackifiers, colours, etc. are added.[39,40]

I.2 VULCANIZATION

Vulcanization is the process by which the mainly viscous rubber is converted into elastic rubber through the crosslinking of the macromolecules at their reactive sites. It is an intermolecular reaction, which increases the retractive force and reduces the amount of permanent deformation remaining after removal of the deforming force. According to the theory of rubber elasticity the retractive force resulting from a deformation is proportional to the number of network supporting polymer chains per unit volume of elastomer.[41] Vulcanization usually produces network junctures by the insertion of chemical crosslinks between polymer chains. The crosslinks may be formed through chains of sulphur atoms, single sulphur atom or carbon- carbon bonds. The vulcanizate properties are not functions of cross link density only; they are affected by the type of crosslink, nature of polymer, type and amount of fillers, etc.[41,42] The most generally favoured and widely used vulcanization procedure even today is merely elaborations of the original method of heating rubber with sulphur discovered by Charles Goodyear (1839) and by Thomas Hancock in 1843.[43] The introduction of organic accelerators in the vulcanization of rubber which began more than 75 years ago led to revolutionary changes in the manufacturing of rubber products.[43] The accelerators enabled vulcanization time to be reduced. The proportion of sulphur required for optimum physical properties could be reduced, thus improving the resistance of rubber goods to ageing and preventing blooming of sulphur.[43]

I.2.1 Accelerated Sulphur Vulcanization

The overall course of accelerated sulphur vulcanization can be represented as follows.[44]



Scheme I.1

I.2.2 Vulcanizing Ingredients

The structural modifications of the main chain which can occur during the accelerated vulcanization process has already been studied in detail.[44] The function of accelerator combination is to increase the crosslinking efficiency and to minimise wastefully combined sulphur by decreasing (i) cyclic monosulphide formation, (ii) vicinal crosslinks, (iii) the length of sulphur chain 'S_x' in crosslinks.[45] Although the primary requirement of vulcanization is covalent crosslinking of the rubber chains, other modifications can occur concurrently at sites distant from the crosslinks. The accelerators have a great effect on physical, mechanical and service properties of the finished article.

I.2.3 Accelerators in Latex Compounding

The use of organic accelerators in latex compound is basically different from their use in dry rubber compounds.[46,47] Natural latex contains a lot of non-rubber materials which function as accelerators and activators. In addition to this, the vulcanization temperature for a latex compound is substantially lower than that for a dry rubber compound. In the manufacture of high quality products two or more accelerators are being used.[48] A combination of ZDEC or ZDBC with ZMBT is used for getting improved modulus.[29] and a combination of TMTD, thiourea and ZDEC is used as vulcanization system in heat resistant products.[49] But only a few systematic study involving the different accelerator combinations under conventional and efficient (low sulphur) vulcanization has been reported. According to Blokh,[50] the protection of a vulcanizate against ageing depends mainly on the nature of accelerators employed and only less on antioxidants.

I.2.4 Effect of Crosslink Structure on Properties

The properties mentioned above depend mainly on degree of crosslinking but they also depend to some extent on the way in which the vulcanizate is crosslinked.[51] This is owing to the fact that the free mobility of the chain segments depends on the structure of the crosslinks (C–C, C-S-C, $C–S_x–C$). A number of studies have been conducted in this line.[52,53,54] At a given degree of crosslinking the tensile strength is the highest in the vulcanizate with polysulphide bonds. The poorest tensile strength values are found in association with pure C-C crosslinks. The vulcanization system and vulcanizing conditions determine the structure of crosslinks and the extent to which the polymer chains are modified chemically during vulcanization.[55]

I.2.5 Vulcanizate Properties

a) Modulus

The force necessary to deform the material is often known as modulus, i.e. tensile stress at a given elongation. It is proportional to the number of crosslinks formed and hence to the degree of vulcanization or crosslinking.

b) Tensile strength and Elongation at break

Tensile strength, unlike modulus, does not rise continuously with the number of crosslinks. Therefore tensile strength is less suitable than modulus in showing whether or not the optimum degree of vulcanization has reached.[56] Tensile strength varies appreciably with vulcanization systems. This variation may be due to differences in the crystallinity-extension relationship. Elongation at break decreases with increasing degree of crosslinking.

c) Swelling

Crosslinked rubber does not dissolve but merely swells and the swelling decreases with increasing crosslinks. According to the Flory-Rehner equation [57] the increase in volume becomes less and less as the degree of crosslinking rises. A rapid method for determining degree of crosslinking has also been reported.[58]

I.3 FILLERS AND PIGMENTS

Inorganic fillers and pigments are added to latex compounds for various reasons, the principal of which are to stiffen the product obtained from the latex, to cheapen it, or to colour it. In the case of latex based surface coatings, the filler particles confer durability as well as rigidity upon the eventual paint film. The presence of significant levels of filler particles in a latex compound is also likely to affect the flow behaviour.[59]

There is an important difference between the behaviour of inorganic fillers in vulcanized rubbers derived from latices and those produced by the techniques of dry rubber technology. In the latter vulcanizates, some inorganic fillers, notably the fine particle carbon blacks, kaolinite clays and silicas, function as what are known as reinforcing agents but they do not reinforce rubber vulcanizates when they have been incorporated by latex compounding.[60,61] The failure of inorganic fillers to reinforce rubbers from the latex compound is a consequence of failure to achieve interaction at the molecular level between segments of the rubber macromolecules and the surface of the filler particle. In dry rubber technology, chemical interaction between rubber macromolecules and the surface of filler particle is promoted by rupture of those macromolecules under the influence of high shear stresses at the time of mastication, to produce free radicals at each new chain end. These free radicals interact with reactive sites on filler particles to form covalent chemical bonds.[62] For filled rubber vulcanizates produced by latex technique, there are several factors which are believed to militate against reinforcement by filler particles. The shear stresses which develop during mixing are very much less. In latex, the rubber macromolecules are present as separate particles, so that less interaction with filler and rubber molecules takes place. The rubber macromolecules present in latex are of higher molecular mass and lower molecular mobility. There has been considerable interest in the possibility of reinforcing vulcanized rubber produced by latex technique in connection with the manufacture of unsupported latex products.

The important non-black fillers used in latex compounding are clays, calcium carbonate, barium sulphate (barytes) and silica. It was reported that small addition of bentonite clay can increase the tensile strength and modulus of latex vulcanizates.[40] The various forms of calcium carbonate used in latex technology are ground and precipitated whitings, ground chalks and ground limestones. The most common types used are ground and precipitated whitings.[63] Barium sulphate or barytes is used in latex compounding where strong deposit is required. A disadvantage is its tendency to sediment rapidly because of its high specific gravity. White pigments are added to latex compounds either to impart whiteness to the final product or to provide a white background for pastel shades. Silica filler is of acidic in reaction so its use in latex compounds is limited. Both rutile and anatase type titanium dioxide are used as white pigments.[64.65]

I.4 PREVULCANIZATION

The most industrially important chemically modified latex is that commonly known as prevulcanized natural rubber latex. It is a curious property of natural rubber latex and also of certain other types of diene rubber latex, that it is possible to vulcanize the individual particles in the latex without destroying the colloidal character of the latex as a stable hydrophobic sol. The product is a colloidally stable latex, the dispersed polymer of which is crosslinked into networks of indefinite extent.[66] There are three principal ways in which natural rubber latex can be prevulcanized. They are (1) Sulphur prevulcanization using sulphur, organic accelerators and an inorganic vulcanization activator (2) Peroxide prevulcanization using organic peroxides and hydroperoxides (3) Radiation prevulcanization by exposing the latex to high energy radiation in the form of electromagnetic waves or electrons. Sulphur prevulcanization is made by heating the raw latex with accelerators, activator and sulphur at about 70^0C until the required degree of crosslinking is obtained. A lot of studies were conducted about factors affecting sulphur prevulanization.[67] Prevulcanization time can be reduced by elevating the temperature of prevulcanization. Maximum crosslinking can be obtained when prevulcanization is conducted at 80^0C for 2h.[67] At lower temperature the rate of reaction is slow.

Prevulcanized latex is suitable for products made by dipping because of the convenience of vulcanizing latex in bulk in relation to the trouble and expense of curing the equivalent amount of rubber in the form of thin deposits over innumerable formers. The latex does not require compounding and vulcanization by the product manufacturer. Better quality control can be achieved by the use of prevulcanized latex in product manufacture. But prevulcanized latex does not find application in latex foam manufacture mainly on account of its poor wet gel strength.

I.4.1 Radiation Prevulcanized Natural Rubber Latex (RVNRL)

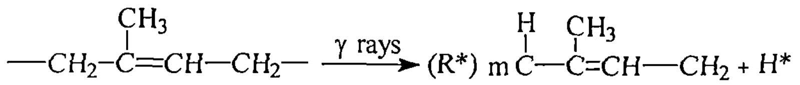
Natural rubber latex can be prevulcanized by exposing it to high energy electromagnetic radiation or electron beam.[68] The natural rubber latex products made using sulphur vulcanization are increasingly substituted now-a-days by radiation vulcanized natural rubber latex products. Certain accelerators at the time of curing, produce nitrosoamines which are extremely poisonous and cause hazard to health. In order to overcome nitrosoamine problem, radiation vulcanized NR latex (RVNRL) is used, in which vulcanization is effected without adding sulphur, accelerators etc. Radiation vulcanized natural rubber latex is very suitable for production of medical rubber goods which are coming in direct contact with human body like catheters etc.[69,70,71]

In natural rubber latex free radicals are generated both in the rubber particles and aqueous phase of the latex by interaction between the high energy radiation and water and other molecules. These radicals may then be absorbed into the rubber particles, and bring about crosslinking by hydrogen abstraction and subsequent combination of resultant polymeric free radicals, analogously to crosslinking by free radicals derived from decomposition of peroxides.[72]

Minoura and Asao have reported the effects of various organic chlorine compounds, at levels in the range 1-5 phr upon the prevulcanization of natural rubber latex by exposure to cobalt-60 γ-radiation.[73] The compounds used were carbon tetrachloride, chloroform and 1,2-dichloro ethane. Of the various monofunctional monomers investigated by Makuuchi et al, n-butyl acrylate and 2-ethyl hexyl acrylate were found to be effective for obtaining sufficient crosslink density.[74] Usually 5phr n- butyl acrylate is used as a radiation sensitiser and irradiation dose is 15-20 kGy for natural rubber latex. The radiation prevulcanized natural rubber latex products are having poor ageing characteristics. So in order to exploit the commercial possibilities of RVNRL, it should be made to meet the severe service conditions.

I.4.2 Mechanism of RVNRL Production

When polymeric substances absorb energy, two types of reactions follow depending on nature of polymeric chain. In straight chain polymers, these radiations mostly produce crosslinks. But branched chain polymers, specially those having tertiary carbon atoms, may be degraded by the absorbed radiation. Gamma rays are supposed to produce the following effect on rubber hydrocarbon chain.



$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- \xrightarrow{\gamma\ \text{rays}} (R^*)\ m\,\overset{H}{\overset{|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH-CH_2 + H^* \qquad I(1)$$

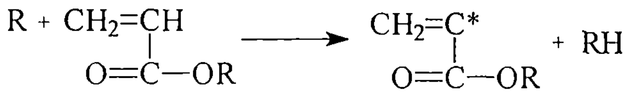
$$H^* + H^* \longrightarrow H_2\ \text{(Termination)} \qquad I(2)$$

$$R^* + R^* \longrightarrow \text{Crosslink} \qquad I(3)$$

$$H^* + \text{Polymer} \longrightarrow R^* + H_2 \qquad I(4)$$

$$R^* + \text{Polymer crosslinks} \longrightarrow \text{Crosslinks} + H^* \qquad I(5)$$

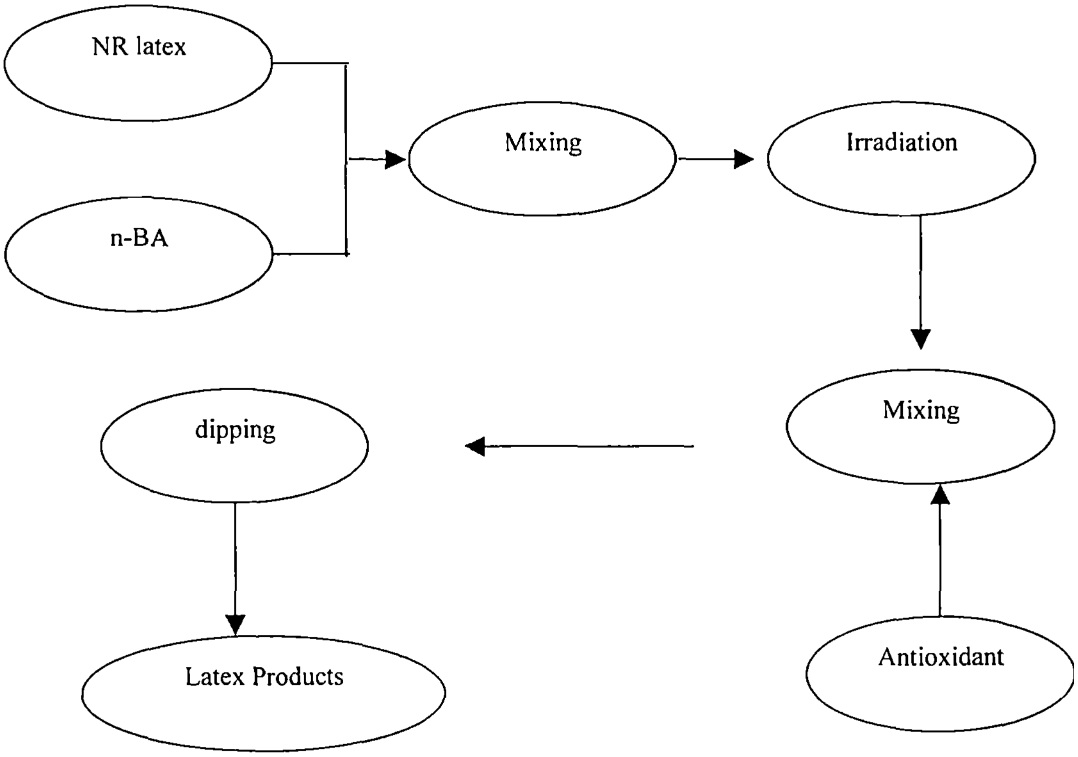
Different mechanisms are suggested for the action of sensitisers. Poly functional monomers are supposed to react through graft polymerisation. Monomers also get in the polymer chain during crosslinking. Chain transfer to the monomer is believed to be in following route.



$$R + \underset{O=C-OR}{\underset{|}{CH_2=CH}} \longrightarrow \underset{O=C-OR}{\underset{|}{CH_2=C^*}} + RH \qquad I(6)$$

The monomer radical can now propagate the reaction by hydrogen abstraction or through attaching to radicals.[75] The production of RVNRL involves the following steps.

1) Mixing NR latex with sensitiser, n-butyl acrylate
2) Irradiating with gamma rays



Scheme I.2 Procedure of RVNRL Production

I.5 MODIFIED NATURAL RUBBER LATICES

Natural rubber latex can be modified via chemical or radiation techniques to get latices of superior properties.[76] The important modifications of natural rubber in latex form other than prevulcanization are the following;

1. Epoxidation
2. Graft copolymerisation
3. Cis trans isomerisation
4. Cyclisation
5. Halogenation
6. Hydrohalogenation
7. Halogeno alkylation
8. Depolymerisation and oxidation of natural rubber in latex form
9. Modifications involving only the surface of the latex particle

Of these graft copolymerisation, epoxidation and surface chlorination of films are the most widely used modifications of natural rubber latex.

I.5.1 Graft Copolymerisation Reactions in Latices

A graft copolymer is a specialized type of block copolymer in which blocks of one monomer units are covalently bonded to main chain (backbone) polymer comprising exclusively units derived from the other monomer. The monomer units constituting the attached blocks are said to be grafted on to the main chain polymer. Many methods are available for the preparation of graft copolymers. In one of these, an olefinic monomer is polymerised by free radical mechanism within the latex of a polymer from another monomer. If the reaction conditions are favourable, much of the added monomer graft copolymerises on to the polymer molecules of latex particles.[77]

Free radical graft co-polymerisation reaction involving an olefinically unsaturated polymer such as natural rubber can occur by both the mechanisms. The polyisoprene chain of natural rubber is an example of a polymer which contains allylic (α-methylinic) hydrogen atoms susceptible to abstraction by interaction with free radicals, there by generating reactive sites from which copolymer grafts can propagate.[78] The reaction by which such sites are generated in polyisoprene by this means is as follows.

$$—CH_2{-}C(CH_3){=}CH—CH_2— + R^{\bullet} \longrightarrow —CH_2{-}C(CH_3){=}CH—\dot{C}H— + RH \qquad I(7) \qquad —+RH$$

Grafting can also occur by polymerisation through the olefinic double bonds of the polyisoprene chain as follows

$$—CH_2{-}C(CH_3){=}CH—CH_2— + R^{\bullet} \longrightarrow —CH_2{-}CR(CH_3){-}\dot{C}H—CH_2— \qquad I(8)$$

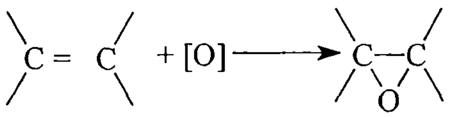
The indications are that, for natural rubber grafting tends to occur more readily by hydrogen abstraction than by copolymerisation.[79]

A combination of tert-butyl hydroperoxide and tetraethylene pentamine initiates rapid and smooth polymerisation of both methyl methacrylate and styrene in ammonia preserved natural rubber latex, the former monomer at normal ambient temperatures.

Cockbain, Pendle and Turner have shown that the graft copolymerisation of methyl methacrylate onto natural rubber in latex form can be initiated by irradiation with cobalt-60 γ- rays.[80] The resultant latices give coherent coagula when colloidally destabilized and dry down to continuous coherent films.

I.5.2 Epoxidation of Natural Rubber in Latex Form

The epoxidation of an olefinically unsaturated polymer involves the addition of one oxygen atom to a proportion of the carbon-carbon double bonds, thereby converting them to oxirane (epoxide) rings. [81,82]



I(9)

The effect of epoxidation is to increase the polarity of the polymer, and hence its glass transition temperature and its resistance to swelling in non polar organic liquids. The magnitude of these effects depends upon the extent to which the rubber has been epoxidised, i.e., upon the proportion of olefinic double bonds which have become converted to oxirane rings.

Currently this is in the range 25-50% mol/mol. It has been convenient to carry out the epoxidation reaction upon natural rubber in latex form, and then to separate the modified polymer for application as bulk rubber. The immediate product of the epoxidation reaction is a rather dilute latex. Difficulty has been encountered in concentrating this dilute latex.

For epoxidation of natural rubber in latex form, mixtures of hydrogen peroxide and a water soluble carboxylic acid are the preferred type of reagents. It is believed that the actual epoxidising reagent is the corresponding peroxy carboxylic acid formed in situ by interaction between the hydrogen peroxide and the carboxylic acid. Within this group of reagents, the most cost effective reagent has been found to be a mixture of formic acid and hydrogen peroxide.[83,84]

$$\mathrm{HCO.OH + H_2O_2 \rightleftharpoons HCO.OOH + H_2O} \qquad \mathrm{I(10)}$$

The oxygen which effects epoxidation of the polyisoprene is derived almost exclusively from decomposition of the peroxoformic acid back to formic acid. Thus formic acid effectively functions as a catalyst for epoxidation of the polymer by hydrogen peroxide.

Bulk epoxidised natural rubber can be vulcanized by heating with sulphur and conventional organic vulcanization accelerators, by heating with peroxides. and by heating with dibasic acids.

I.6 SYNTHETIC LATICES

For many years, the term synthetic latex has been understood to mean an aqueous dispersion of a polymer which is produced by the chemical reaction known as emulsion polymerisation. The immediate product of emulsion polymerisation is subjected to various after-treatments such as partial agglomeration, concentration and chemical modification to get synthetic latices of appreciable total solid content. Emulsion polymerisation produces polymer in the form of a stable lyophobic sol.[85]

Synthetic latices differ from natural latices in various aspects. Particle shape, size and size distribution of synthetic latices are different from natural latices. The particles in a synthetic latex are exactly spherical in shape while natural rubber latex particle have complex geometrical forms. The particles in synthetic latices are considerably smaller than those of are many in ammonia preserved natural rubber latex. The particle size distribution is usually narrow in synthetic latices, usually in the range 50-100nm while in natural rubber latex particles as large as 5µm is possible. Specific surface area of polymer-aqueous phase interface is high in the case of synthetic latices which are having smaller particles. The ratio of the hydrophilic colloid stabilizers to polymer in synthetic latices is higher than ammonia preserved natural rubber latex. Deposits from synthetic rubber latices usually have low wet-gel strength relative to those from natural rubber latex, especially if the deposits are hot. Synthetic latices dry down to give deposits which tend readily to absorb larger quantities of water again from aqueous media than do deposits from ammonia-preserved natural rubber latex. This characteristic is primarily a consequence of the high ratio of hydrophilic colloid stabilizer to polymer. Synthetic latices are remarkably resistant to mechanical colloidal destabilization under conditions of high speed stirring such as are employed in the conventional test for the mechanical stability of ammonia preserved natural rubber latex. But these synthetics latices are very sensitive to the destabilisative effects of mechanical pressure. The chemical composition of synthetic latices is relatively simple, and is in principle largely controllable by the producer. Synthetic latices are devoid of proteinaceous substances and other natural products found in natural rubber latex.[85]

I.6.1 Latices of Styrene-Butadiene Copolymers (SBR)

Styrene butadiene copolymer latices comprise a large family of general purpose synthetic latices which are industrially very important. They have found wide spread application in many areas which include replacement for natural rubber latex in the manufacture of latex foam rubber, carpet backing, textile applications and in paper coating applications, for the above two purposes usually functionalised (carboxylated) SBR latices are used.[86] SBR latices are also used as general purpose adhesives for paper and fibrous materials and also as rubber to textile bonding adhesives for tyre-cords etc. Usually styrene butadiene ratio in co-polymer latices is 30/70 m/m. They are produced by emulsion polymerisation technique. Styrene-butadiene rubber in latex form is used to produce four types of composite materials which are of importance in relation to the processing of the bulk rubber. They include the masterbatches of carbon blacks and oil extended SBR and styrene–butadiene copolymers of high styrene content.

I.6.2 Latices of Acrylonitrile–Butadiene Copolymers (NBR)

Acrylonitrile-butadiene latices are produced by the emulsion copolymerisation of acrylonitrile and butadiene.[87] Polymer repeats units derived from acrylonitrile are far more polar than are those derived from styrene. The principal effects of polarity of acrylonitrile units are the increase of Tg and associated changes are that adhesion to polar substrates is increased and the extent of equilibrium swelling of vulcanizates in hydrocarbon liquids is reduced. The NBR latex is available in low, medium or high acrylonitrile content.

I.7 LATEX BLENDS

Mixing of latices is the simplest method available for getting elastomer-elastomer blends. No expensive equipment is required and high temperatures are not needed.[88] Moreover, in a latex, polymers are present as suspended microspheres. Interactions of neighbouring spheres are prevented by suspending medium(soap).After thorough blending a mixture of two latices of different polymers contains a random suspension of dissimilar particles, each unaffected by the other. Coagulation too is random because the rate of flocculation is dependent entirely on the soap concentration and not on polymer characteristics. Thus much attention has been directed to its use in commercial manufacturing processes compared to solution and melt blending.[89] Currently natural rubber latex is supplemented by a wide range of synthetic latices produced by emulsion polymerisation. These include latices of SBR, NBR, CR, carboxylated SBR etc. Additionally graft polymers such as PMMA-g-NR, Styrene–g–NR and epoxidised NR latices are also there. Usually NR latex blends with the above mentioned synthetic or modified latices are employed for applications in which latex products need special properties.

I.8 LATEX PRODUCTS

The important applications of NR latex are in the manufacture of (a) dipped goods (b) latex foam (c) elastic thread and (d) adhesive.

I.8.1 Dipped Goods

A wide range of articles such as gloves, medical tubing, condoms, balloons, rubber band etc. are manufactured by dipping process. The process consists in the immersion of a former into a suitably compounded latex, followed by slow withdrawal in such a way as to leave a uniform deposit of latex on the former. The process is completed by drying, leaching and vulcanizing the deposits. The principal dipping methods are straight dipping, coacervant dipping and heat sensitised dipping. In straight dipping a deposit is formed by virtue of the viscosity of latex compound and of its tendency to wet out the former. This process is used for the manufacture of thin walled articles. In coacervant dipping, a coacervant is used to assist the formation of deposit and is the most common dipping method. Heat sensitised dipping produces the thickest deposit and the principle is to employ a heated former and a heat sensitive latex compound.

I.8.2 Latex Foam

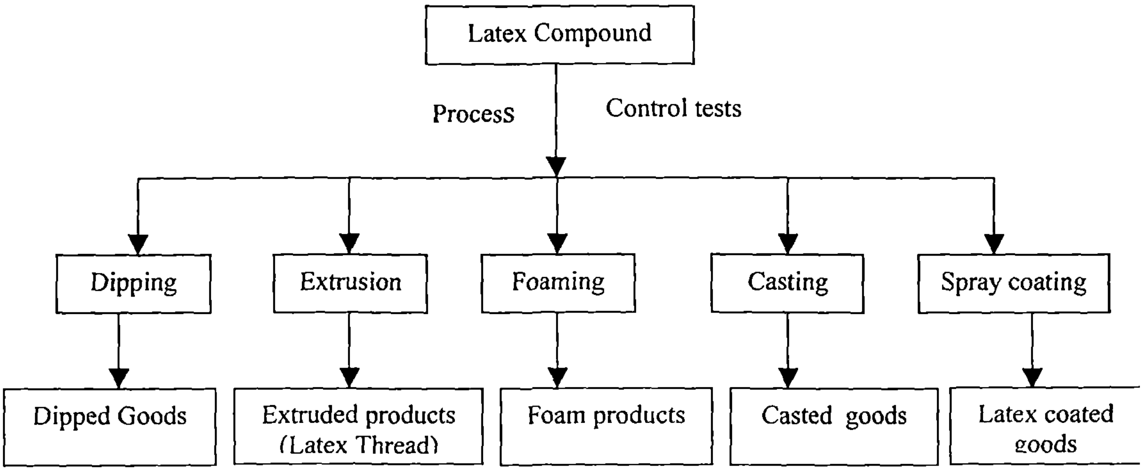
The basic steps involved in the production of latex foam rubber are (a) foaming of compounded latex (b) gelling of the foamed latex and (c) vulcanization of the foam rubber.[90] The important foam products are mattresses , pillows and cushions.

I.8.3 Elastic Thread

The essence of elastic thread production process is the extrusion of a latex compound through spinnerets into a coagulant solution.[91] The wet gelled filament is washed, dried and vulcanized. The latex thread is mainly used in the clothing industry.

I.8.4 Adhesives

NR latex is renowned for its high cohesive strength and intrinsic tack and is widely used in paper and textile combining. The performance of the adhesive is controlled by various additives apart from the polymer. Compounds based on NR are used for self sealing envelopes and for general applications like combining paper, cardboard and leather.



Scheme I.3 Manufacture of Latex Products

I.9 DEGRADATION

All rubber like materials whether natural or synthetic, are subject to degradation. Generally, the greater the amount of unsaturation in the polymer, the more susceptible it is to degradation.[8] Degradation of latex goods is caused by their exposure to

1. Heat
2. Humidity
3. Light
4. Oxygen
5. Ozone
6. Chemicals like detergents, strong acids, bases, oils etc
7. Pro-oxidant metal ions
8. Stress

Frequently the latex article is simultaneously subjected to several different types of exposure.

The compounder must be aware of the end use requirements of the product and the environmental conditions to which it will be subjected.[92] This knowledge will enable him to select for the compound the proper

1. Cure system: acceleration and crosslinking agent
2. Chemical type of latex or latex blends
3. Antidegradant or antidegradant blends

The following are symptoms of film degradation

1. Hardening or embrittlement
2. Softening
3. Tackiness
4. Oriented cracking
5. Non oriented cracking

6. Loss of tensile strength and tear strength
7. Loss of elasticity
8. Increase in permanent set

The exact symptoms of degradation which will be noted are dependent upon the elastomer compounded to produce the goods as well as the type of environmental exposure to which the goods have been subjected. Each symptom is indicative that oxidative film degradation has occurred.[93]

I.9.1 Mechanism of Degradation

The mechanism of polymer degradation is one of "autocatalytic free radical chain reaction". Free radicals are formed in the rubber by heat, light, oxygen etc. These free radicals then react either with oxygen or rubber to produce more free radicals and resulted into a degraded polymer chain.[94]

a) Initiation

$$RH \rightarrow R.+H. \qquad I(11)$$

b) Propagation

$$R. + O_2 \rightarrow ROO. \qquad I(12)$$

$$ROO. + RH \rightarrow ROOH + R. \qquad I(13)$$

$$ROOH \rightarrow RO. + OH. \qquad I(14)$$

$$RO. + RH \rightarrow ROH + R. \qquad I(15)$$

$$OH. + RH \rightarrow H_2O + R. \qquad I(16)$$

c) Termination

$2R. \rightarrow RR$ I(17)

$ROO. + R. \rightarrow$ ROOR (Inactive non radical products) I(18)

I.9.2 Thermo Oxidative Degradation

The main influence of temperature is of course on the rate of oxidation.[95] To a very rough approximation, the rate increases about 2.5 times for each 10^0C rise in temperature, and every one knows that a few days ageing in an oven is equivalent to a few years at normal temperature. Only 1-2% oxygen reacted is normally sufficient to deteriorate an elastomeric product severely. The reaction of oxygen with elastomers causes both chain scission and crosslinking. If chain scission dominates, the elastomer softens and eventually may become sticky with ageing, this is the usual behaviour of NR and IIR. Most elastomers, however harden and eventually embrittle during oxidation a consequence of crosslinking dominance.[96] Also stress hastens oxidation. For sulphur cured vulcanizates, the oxidation rate increases as sulphur content increases, it is believed that the allylic crosslink site is particularly susceptible to oxidation. One of the outcome of oxidation of rubber is scission (main chain rupture) of the rubber molecules which reduces their molecular weights and in consequence their physical properties.[97] The oxidation process requires contact between rubber and oxygen which normally can only occur at the surface of the product. The diffusion of oxygen in to the bulk of the rubber is a slow process, consequently, oxidation is confined to the surface of the thick articles. Latex products however, are usually quite thin and they tend to suffer much more from the effects of oxidation than many other rubber products, because the 'surface' represents a much higher proportion of the bulk.[98]

I.9.3 Photo Oxidative Degradation

Photo oxidative degradation will occur more readily in a rubber that contains double bonds.[99] The developments of a stiffened or crazed (i.e, dried mud-like) surface on light coloured products exposed to solar radiation is the result of photo oxidation. The same process causes stress relaxation in products held in tension. The greatest amount of light damage is done to rubber by ultraviolet light. Light promotes the action of oxygen at the surface of the rubber, producing a film of oxidised rubber having physical properties different from those of the original stock. This film then undergoes action by water vapour and heat to produce crazing and alligatoring.[100] The oxidised layer expands and contracts on heating and drying. Finally the oxidised layer washes away, leaving the filler exposed. The exposed filler can then be rubbed off, giving condition known as 'chalking'.

The energy of a photon of light is given by the relationship $E = h\nu$, where h is the Plank's constant and ν is the frequency of light. There are 6.02×10^{23} molecules in a mole. The energy associated with one mole of photons is called an einstein.[94] In a photo chemical reaction, quantum yield ϕ =No. of chain scissions/No. of photons absorbed. A quantum of light is absorbed by the polymer and this will raise certain bonds to an electronically excited state. The energy absorbed by the molecule will increase as the wavelength decreases and bond scission becomes possible when the wavelength energy corresponds to the energy of the bonds. For example the C–C bond has an energy of 83 kcal/mol equivalent to a wavelength of 342 nm. Ultraviolet light has a wavelength distribution of 100 nm (far UV) to 400 nm (near UV) while visible radiation covers wavelength from 400nm (violet) to 700nm (red), energy increases as shorter the wavelength.

Usually sulphur cured natural rubber disintegrates on exposure to light of approximately 400-600nm but doesn't form –C=O groups or –OH groups. Thus only the polysulphide bonds break down. Light of approximately 340-400nm decomposes the C-C, $C–S_x–C$ and C–S–S–C bonds with the formation of –C=O groups and –OH groups. In light of less than 340nm, crosslinking occurs and cracks are initiated.[101] The carbonyl compounds undergo photolytic cleavage mainly by Norrish type I or Norrish type II mechanism.

No radiation below 290 nm reaches the earth's surface and although most of the light in the near UV region of 300-400 nm is absorbed by the ozone layer in the upper atmosphere, sufficient harmful radiation still reaches the ground level to initiate polymer degradation.[102] The most dangerous part of UV-radiation is falling in the wavelength region 290-350 nm. During the early stages of degradation the surface can soften due to chain scission, but over a relatively short period hardens up considerably via extensive crosslinking. Normally photo oxidation is entirely restricted to surface and in light coloured rubber goods UV-radiation causes discolouration due to the production of chromophoric groups within the polymer matrix. So latex products being light coloured and very thin are extremely get affected by UV-radiation in outdoor applications, but not much systematic studies are reported in this filed.[103]

So latex goods must be protected against photo oxidative degradation by suitable type of compounding using different accelerators, with different chemical types of latices and also by adding special chemicals which destroy the action of singlet oxygen on latex products.

I.9.4 Protective Measures Against Degradation

a) Antioxidants

To prevent extensive deterioration of the polymer it is necessary to interrupt the chain reaction and stop the autocatalysis. It can be seen that we can accomplish this by either terminating free radicals or by decomposing the peroxides into harmless products. Actually antioxidants function by doing just this. Antioxidants are employed to slow down oxidation. It is widely accepted that there are two primary ways in which they function. Representatives of the first type called preventive antioxidants, react with hydroperoxides to form harmless nonradical products. In the process, the antioxidant is oxidised. Representatives of the second type, chain breaking antioxidants, destroy peroxy radical that otherwise would propagate. Chain breaking antioxidants are aromatic and contain labile protons, which are donated to peroxyradicals. This occurs readily because the resulting antioxidant radical is highly resonance stabilised. A small amount of antioxidant (1-2 phr) present at the start of oxidation can give a large amount of protection for rubber.

A simplified picture of antioxidant action is as follows, [94,95,104]

$$R. + AH \rightarrow RH + A. \qquad I(19)$$

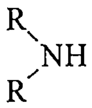
$$ROO. + AH \rightarrow ROOH + A. \qquad I(20)$$

$$RO. + AH \rightarrow ROH + A. \qquad I(21)$$

$$ROOH + AH \rightarrow \text{Harmless fragments} \qquad I(22)$$

The antioxidant free radical (A.) is incapable of propagating the chain reaction.

Practically all of the commercially important antioxidants fall into three classes.

1) Secondary amine bodies 
$\begin{array}{l} R\diagdown \\ \quad NH \\ R\diagup \end{array}$

2) Phenolic bodies $R(OH)_x$

3) Phosphites $(RO)_3P$

The amine antioxidants constitute the more important group commercially. They are strong protective agents but discolour and stain to various degrees. So they are less used in latex goods. The phenolics are less effective but are essentially non-discolouring and non-staining. Phosphites are very few in number.

Amines are of two types. (1) monoamines, the important ones in this category are phenyl naphthylamines and diphenylamines (2) Diamines. These are all derivatives of p-phenylene diamine.

Commercial phenolic antioxidants are generally alkyl derivatives of phenols and napthols. Styrenated phenols are used widely. The only representative of the alkylated phenol phosphite class used in rubber is Tris nonylated phenyl phosphite.

During service some elastomeric products get contacted with fluids, which can leach out antioxidant. Polymer-bound antioxidants have been employed to solve this problem.[104]

b) UV-Stabilisers

Light ageing in rubber can be retarded by (a) providing a physical screen against UV-radiation (b) by adding UV-absorbers and (c) inhibiting any subsequent oxidation by the use of antioxidants. Carbon black pigmented vulcanizates are highly resistant to photo oxidation since the filler is not only a light screen but is also a fairly powerful UV-absorber, by virtue of the energy level transition that can take place in its polynuclear aromatic structures. But their use in light coloured latex products is not possible. The titanium dioxide pigment is capable of reflecting the light radiation to a certain extent so they can be applied in latex products.

Considering the initiating steps detailed above the following possibilities can be taken into account for intervention in the photo oxidation process or for stabilisation of the polymer systems.[99,102]

1) Ultraviolet screening

The light falling on the surface of the polymer can be screened by non-transparent fillers (Screens) eg; carbon black, various pigments etc. However some of these can only be used in non-transparent pigmented polymer.

2) Ultraviolet absorption

Ultraviolet absorbers blended into the polymer can absorb actinic light which is harmful to the polymer. The absorbed excitation energy dissipated harmlessly, the stabilisers being reconverted to their original ground states.

3) Quenching

The excess excitation energy can be transferred to quenchers from the excited carbonyl or singlet oxygen followed by harmless dissipation.

4) Radical scavenging

Radicals formed during oxidation can react with radical scavengers to give non radical products.

5) Peroxide decomposers

Hydroperoxides causing degenerate chain branching can be decomposed by peroxide decomposers in a non-radical process.

6) Metal ion deactivators

Finally the complexing agents may deactivate catalyst residues. (These stabilisers are of no practical significance).

There are mainly three classes of UV-stabiliser chemicals used (1) substituted benzophenones (2) substituted benzotriazoles (3) Hindered amine light stabilisers (HALS). These stabilisers work in polymer matrix in one or two ways stated above. Their use in plastics is common but no systematic studies are seen about the use of these stabilisers in natural rubber latex vulcanizates. The sites of activation of thermal degradation and light degradation differ.[102]

Light degradation

$$-CO-O-C-C-C-C-O-C-C- \longrightarrow -CO^{\bullet} + -O^{\bullet}-C-C-C-C-O-C-C- \qquad I(23)$$

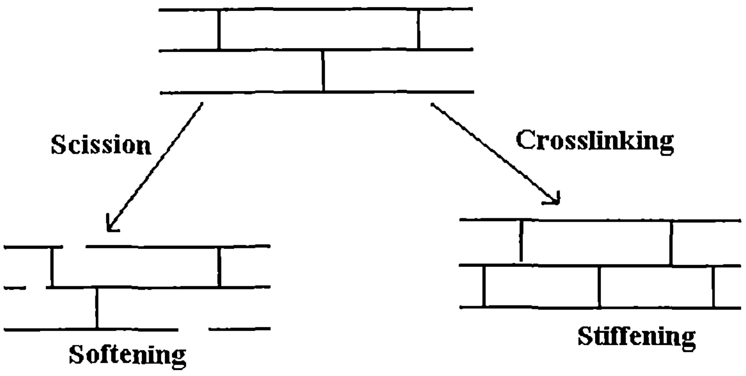
Thermal degradation

$$-CO-O-C-C-C-C-O-C-C- \longrightarrow -CO-O-C-C-C-\dot{C} + \dot{O}-C-C- \qquad I(24)$$

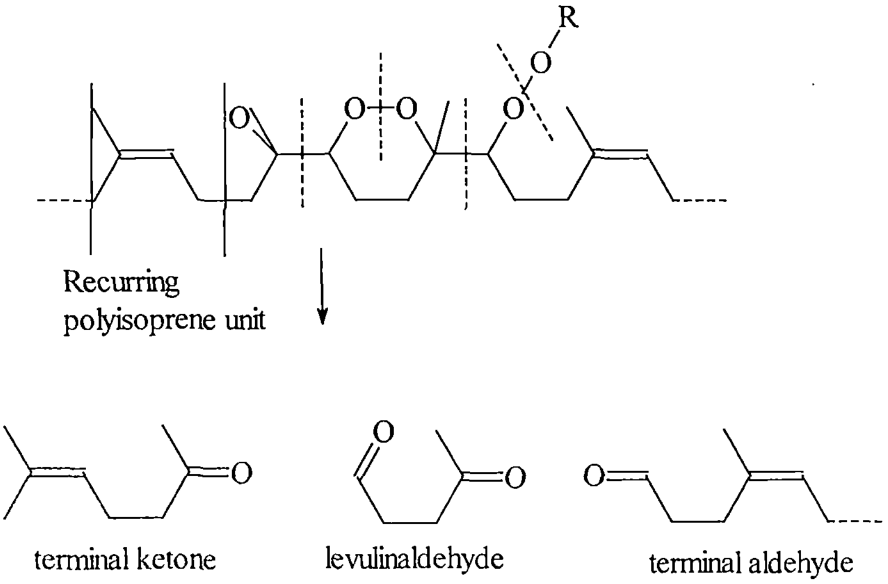
The variation is due to the high photo reactivity of the carbonyl group.

The various structural changes taking place during oxidative degradation are given in following schemes.

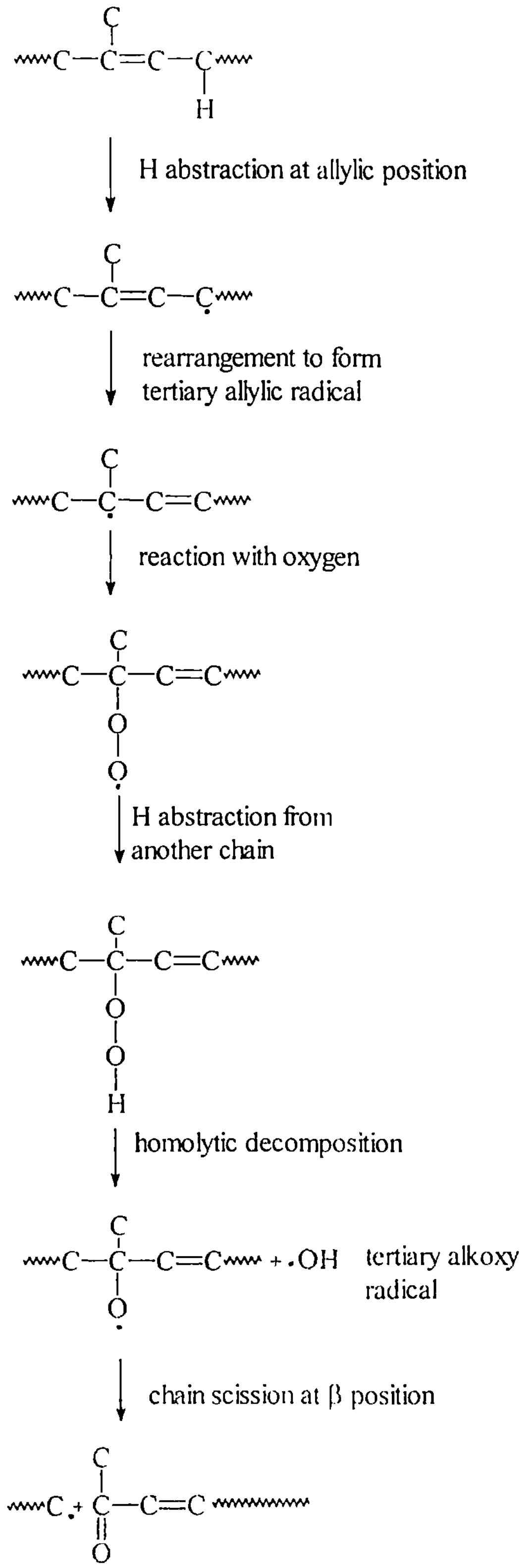
Scheme I.4 Network changes and their effects on properties



Scheme I.5 One mechanism of oxidative chain scission



Scheme 1.6 Mechanism of oxidative degradation in NR



Carbonyl groups, hydroperoxides and peroxides formed during oxidation are readily detected by Infrared spectroscopy[105].

I.10 SCOPE OF THE PRESENT WORK

It is a matter of great importance to ensure adequate service life for competitive marketing of natural rubber latex products. All rubber like materials, whether natural or synthetic are subject to deterioration, generally the greater the amount of unsaturation in the polymer, the more susceptible it is to degradation. Most often the deterioration is seen as a loss of physical properties-usually strength or as a deterioration in the appearance of the product. Latex products are usually quite thin and they tend to suffer much more oxidative degradation because the 'surface' represents a much higher proportion of the bulk.

During their service life, many of the latex products are exposed to various environmental and external degradation agencies like light, heat, oxygen, chemicals etc. Natural rubber latex thread is exposed to sunlight and heat during routine washing, drying and ironing of the clothes. Meteorological and other type of balloons are exposed to solar radiation and heat during their service life. The various medical latex products like gloves, catheters etc. are now-a-days sterilized widely using ultraviolet radiation. Latex surface coating industry is very much in need to develop better photo oxidative degradation resistance for their products. We cannot change the external factors affecting degradation of latex products but can improve their degradation resistance by changing the internal factors, which give optimum service properties. Only very few systematic work is seen on the various aspects which will give better photo oxidative and thermo oxidative degradation resistance to the latex products.

According to Blokh, the protection of a vulcanizate against ageing depends mainly on the nature of accelerators employed and only less on antioxidants.[50] An understanding of the effect of various ultra accelerator combinations in natural rubber latex thread with conventional and efficient vulcanization systems against photo oxidative degradation as well as thermal degradation and against their combined action may lead to manufacture of natural rubber latex thread with better service properties. Also the effect of the major three class of antioxidants viz., phenolic, amine and phosphite type in NR latex thread against photo and thermal degradation is very important. But hardly any report is available in this line.

Inorganic non-black fillers and pigments are commonly added into latex thread in order to cheapen and stiffen the product or to colour it. These fillers and pigments have some reflectance properties. The effect of these fillers and pigments in natural latex thread against photo degradation and heat is very much critical for better service life of thread. But very little published information is available on the subject.

There are very limited information available on the various aspects of technological properties of blends of natural rubber latex with modified NR and synthetic rubber latices. Normally natural rubber latex is blended with modified rubbers and synthetic polymers in order to modify its technological properties. Rare studies have been reported on the effect of blending natural rubber latex with modified natural rubber latices like grafted and epoxidised latices and synthetic rubber latices against UV-radiation and heat.

As far as the latex goods industry is concerned, prevulcanized latex is a convenient form of material for bulk production. Now-a-days radiation prevulcanized natural rubber latex (RVNRL) is widely used for the production of medical goods since it is free from toxic nitrosoamines. Only few reports are available on the degradation aspects of RVNRL films with various antioxidant combinations and fillers cum pigments against light and heat ageing. Since the RVNRL does not contain sulphur, accelerators or zinc oxide, it is of high importance to study the degradation of RVNRL goods.

Because of the presence of chloro flouro carbons and other gases, now-a-days, 'green house effect' is an internationally discussed problem. Due to this effect, global warming takes place, CFC also destroys the 'ozone umbrella' in the earth's outer atmosphere which actually absorbs the harmful range of UV- radiation in solar spectrum. Now this 'ozone umbrella' holes cause excess UV-radiations which are dangerous to all materials to reach on the earth's surface. So in the future, it is very critical for the rubber industry to develop products with good photo oxidative and thermo oxidative degradation resistance for their existence. In plastics, UV-stabiliser class of chemicals are used widely, but no reports are seen on the use of UV-stabilisers and their combinations with different existing antioxidants in natural rubber latex products.

In the light of the above, detailed investigations have been taken up to study the role of the following aspects on the degradation resistance against UV-light and heat ageing of latex films/vulcanizates.

- Effect of accelerator combinations and antioxidants
- Effect of non-black fillers and pigments
- Effect of blends of natural rubber latex with modified and synthetic rubber latices
- Effect of antioxidant combinations and various non-black fillers and pigments in radiation prevulcanized natural rubber latex (RVNRL)
- Effect of UV-stabilisers and their combination with various antioxidants.

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CHAPTER II

EXPERIMENTAL TECHNIQUES

The materials used and the experimental procedures adopted in the present investigations are described in this chapter.

II.1 MATERIALS

II.1.1 Centrifuged Natural Rubber Latex

High ammonia type 60 per cent centrifuged latex conforming to the specifications of the Bureau of Indian Standards: BIS 5430-1981 obtained from the Pilot Latex Processing Centre of Rubber Board was used in this study. The properties of the latex estimated by us are as follows.

Sl. No.	Parameters	Values
1	Dry rubber content, % by mass	60.00
2	Non-rubber solids, % by mass	1.50
3	Coagulam content, % by mass	0.03
4	Sludge content, % by mass	0.007
5	Alkalinity as ammonia, % by mass	0.75
6	KOH number	0.65
7	Mechanical stability time, seconds	1075
8	Volatile fatty acid number	0.04
9	Copper content, ppm on total solids	3
10	Manganese content, ppm on total solids	2

II.1.2 Modified Natural Rubber Latices

II.1.2.a Epoxidised natural rubber latex (ENR)

High ammonia type centrifuged NR latex (deammoniated to 0.3% ammonia) was used. Formic acid (98%), hydrogen peroxide (30%), formalin (40%), sodium bicarbonate, and methanol were of laboratory reagent grade. Spectroscopically pure toluene was used for IR studies. The non-ionic stabiliser used was Vulcastab VL, the active ingredient of which is an ethylene oxide condensate, supplied by ICI (India) Ltd. The reaction recipe used is given below.[1]

1) Reaction Recipe

Reagents	Concentration
Rubber Hydrocarbon	2.94 moles of isoprene units dm^{-3}
Formic acid	0.955 moles dm^{-3}
Hydrogen peroxide	3.75 moles dm^{-3}
Non ionic stabiliser	3 phr

2) Preparation of epoxidised natural rubber (ENR) latex

100ml of NR latex was taken in a three necked RB flask equipped with a stirrer, thermometer and a condenser. The latex was stabilised by adding 11ml of Vulcastab VL (20% W/V). It was placed in a constant temperature bath. The ammonia in the latex was neutralised by adding quantitative amounts of formalin. The latex was diluted with water and the required amount of formic acid was added followed by hydrogen peroxide and the DRC was adjusted at 20%. The temperature of bath was maintained at 40 ± 0.1^0C. The reaction was allowed to continue for 24 hours. At the end of the reaction, the acid was neutralised with saturated sodium bicarbonate solution and then with ammonia solution. The latex was used for further blending studies by keeping it in a closed container. The ENR latex obtained was of 50 mole% epoxy content and known as ENR-50.

II.1.2.b Graft co-polymers of natural rubber latex

1) Radiation induced graft copolymerisation of methylmethacrylate in natural rubber latex

a) Materials

High ammonia preserved centrifuged natural rubber latex conforming to BIS 5430-1981 was used for grafting reactions. Methyl methacrylate was freed from inhibitor by washing first with 10% solution of sodium hydroxide and then with distilled water and finally dried over anhydrous sodium sulphate.

b) Graft Copolymerisation

A gamma chamber model 5000 supplied by the Bhabha Atomic Research Centre, Mumbai was used as the source for γ-radiation. The dose rate was 0.1 Mrad./h.

A 50% emulsion of methyl methacrylate was prepared by mixing monomer under stirring with equal weight of water containing vulcastab VL as the emulsifying agent. It was then mixed with high ammonia preserved centrifuged latex in the ratio of 1:1 by dry weight. The mixture was then subjected to a total irradiation dose of 0.5 Mrad.[2] The percentage yield of the product which was a mixture of graft copolymer, free poly methyl methacrylate and unreacted rubber was determined, after FTIR characterisation. The obtained methyl methacrylate grafted NR latex known as MGNR 50 was kept in sealed containers for blending studies after making the ammonia concentration to 0.7%.

c) Recipe for 50% MMA emulsion preparation

Ingredients	Parts by (Wt)
Methyl Methacrylate (Washed)	100
Water	95
Vulcastab VL (20%)	5

II.1.2.b 2) Radiation induced graft copolymerisation of styrene in natural rubber latex

a) Materials

High ammonia preserved centrifuged natural rubber latex conforming to BIS-5430, 1981 was used. Styrene was washed first with 10% sodium hydroxide solution to free it from inhibitor and then with distilled water.

b) Graft Copolymerisation

A gamma chamber model 5000 supplied by the Bhabha atomic research centre, Mumbai was used as the radiation source. The dose rate was 0.1 Mrad/h. Centrifuged latex (preserved with 0.7% ammonia) and styrene as 50% emulsion were mixed in the ratio 1:1. The latex mixture was then irradiated to a total dose of 0.75 Mrad.[3] The percentage yield of the product which was a mixture of graft copolymer, free polystyrene, and free NR was determined, after FTIR characterisation. The obtained styrene grafted NR latex (SGNR-50) was kept in closed container after making the ammonia concentration to 0.7% for further blending studies.

c) Recipe for 50% Styrene emulsion

Ingredients	Parts by (Wt)
Styrene (Washed)	100
Water	85
Vulcastab VL (20%)	15

II.1.2.c Preparation of radiation prevulcanized natural rubber latex: (RVNRL)

A gamma chamber model 5000 supplied by the Bhabha Atomic Research Centre, Mumbai, was used as the radiation source. High ammonia preserved centrifuged natural rubber latex stabilised with a solution of KOH (0.2phr) was used for radiation vulcanization. The radiation sensitiser n-butyl acrylate (n-BA), 5phr was added to the stabilised NR latex while stirring. Stirring was continued for 1h and the mixture was then irradiated with gamma rays from the C_0-60 source at a total dose of 1.5 Mrad. The irradiation was conducted at a constant dose rate of 0.1Mrad/h at room temperature[4]. The radiation prevulcanized natural rubber latex (RVNRL) thus obtained was kept at room temperature tightly covered to prevent any loss of volatile materials such as ammonia.

1) Recipe for radiation prevulcanized NR latex (preparation)

Ingredients	Weight (gms.)
60% centrifuged NR latex	167
10% KOH solution	2
n-butyl acrylate (n-BA)	5

Total dose 1.5 Mrad at a dose rate of 0.1 Mrad/h

The specifications of Gamma chamber 5000 is given below.

Gamma chamber 5000 is a compact self shielded Cobalt-60 gamma irradiator providing an irradiation volume of 5000c.c. The materials for irradiation is placed in an irradiation chamber located in the vertical drawer inside the lead flask. The drawer can be moved up and down with the help of a system of motorised drive which enables precise positioning of the irradiation chamber at the centre of the radiation field.

The photograph showing the instrument is given in Figure II.1.

2) Specifications

Minimum Co-60 source capacity : 444 TBq (12,000 Ci)

Dose rate at maximum capacity : 9kGy/h (0.9 Mrad/h) at the centre of sample chamber

Dose rate uniformity : +25% or better radially

-25% or better axially

Irradiation volume : 5000 c.c. approx

Size of sample chamber : 17.5 c.m (dia) x 21.0 cm (ht)

Shielding material : Lead and stainless steel

Weight of the units : 5000 Kg approx.

Size of the unit : 125c.m (l) x 106.5c.m.(w) x 150cm (ht)

Timer range : 6 seconds onwards

II.1.3 SYNTHETIC LATICES

a) Carboxylated styrene butadiene rubber (XSBR) latex
Total Solid Content (TSC) = 50%
Carboxyl content = 3%, Grade Powerene PLX-802
Source – Apar Ltd, Gujarat, India

b) Acrylonitrile-butadine rubber (NBR) latex
Total solid content (TSC) = 41%
Acrylonitrile content = 28%. Grade Perbunan N 2890
Source- Bayer AG, W. Germany

II.2 RUBBER CHEMICALS

II.2.1 Accelerators

The accelerators used in this study were obtained from M/S Indian Explosives Limited (IEL), Culcutta. A short description of the important accelerators used given below:

a) Zinc diethyl dithiocarbamate (ZDEC)

This ultra accelerator is a cream white powder of density 1.47 g/cm^3, m.p 175^{0}C; soluble in carbon disulphide, benzene and chloroform and is non-toxic. It ensures rapid low temperature vulcanization in the presence of a small amount of sulphur and is active in latex mixes even in the absence of zinc oxide.

b) Zinc salt of 2-mercapto benzothiazole (ZMBT)

A light yellow powder, density 1.63 g/cm^3, m.p 145^{0}C, non-toxic, soluble in benzene, ethanol and chloroform. It is a slow accelerator and it can not be used alone in latex work.

c) Tetramethyl thiuram disulphide (TMTD)

A white powder, density 1.29g/cm^3, m.p 165^{0}C, soluble in chloroform, benzene and hot alcohol and is an ultra accelerator.

d) Zinc dibutyl dithiocarbamate (ZDBC)

This ultra accelerator is a white yellow powder of density 1.26g/cm^3, m.p 104^{0}C, Zinc content 15%, soluble in chloroform, it is more active than zinc diethyl dithiocarbamate accelerator in latex mixes and providing higher modulus for vulcanizates.

II.2.2 Fillers and Pigments

Anatase form of titanium dioxide (TiO_2) was obtained from M/S Travancore Titanium Products, Trivandrum, precipitated calcium carbonate, china clay and barium sulphate (barytes) used in this study were of commercial grade obtained locally.

II.2.3 Antioxidants

a) Antioxidant SP

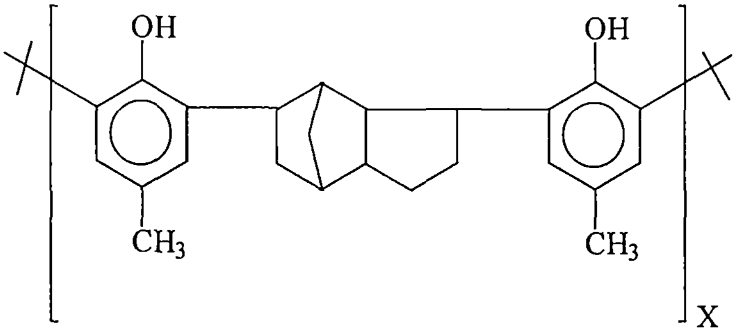
This is styrenated phenol and was obtained from M/S Indian Explosives Limited, Calcutta.

b) Wingstay-L

This is chemically butylated reaction product of p-cresol and cyclopentadiene. It is a cream coloured powder of density 1.1g/cm^3, melting range 100°C minimum. It is a non-staining substituted phenolic type antioxidant widely used in latex for high temperature protection.

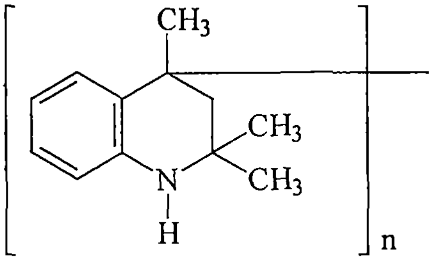
Manufactured by Vanderbilt rubber chemical company. CT, USA in the trade name Vanox L.

The structure is given below



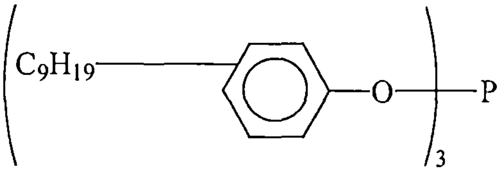
c) Antioxidant HS

This is chemically 1,2-dihydro 2,2,4-trimethyl quinoline. It is obtained as brown solid flakes of density 1.08g/cm^3 with m.p 90^{0}C. It is a staining type amine antioxidant. It is insoluble in water but soluble in benzene. The structure is given as



d) Crystol EPR 3400

Molecular Weight = 689. It is chemically Tris (nonyl phenyl) phosphite. It is a non-staining phosphite type antioxidant. It is a colourless viscous liquid used widely in SBR formulations. The structure is given as,



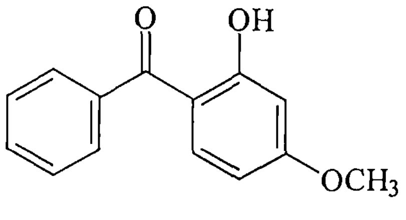
II.2.4 UV-stabilisers

The Lowilite class of UV-stabilisers used in this study were obtained from M/S Great Lakes Chemicals, W. Lafayatte, IN, USA.

a) Lowilite 20

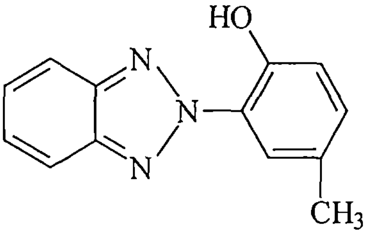
It is a benzophenone class UV-stabiliser. It is chemically 2-hydroxy, 4-methoxy benzophenone. It is a creamy powder of molecule weight 228, m.p 62^{0}C, TGA (at 214^{0}C, 50% mass loss), insoluble in water but soluble in acetone and ethyl acetate.

The structure is



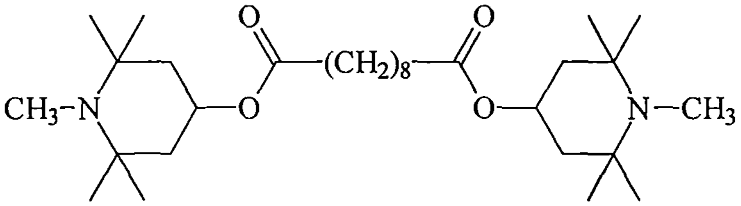
b) Lowilite 55

It is a benzotriazole class UV-stabiliser and is chemically 2-(2^1-hydroxy-5^1-methyl phenyl) benzotriazole. It is a creamy powder of molecular weight 225, m.p 128^{0}C, TGA (at 213^{0}C, 50% mass loss), insoluble in water but sparingly soluble in acetone and ethyl acetate. The structure is



c) Lowilite 76

It is a hindered amine class light stabiliser (HALS). It is chemically Bis (1,2,2,6,6 penta methyl-4-piperidinyl) sebacate. It is an amber liquid of molecular weight 509, m.p 31°C, TGA (at 323^{0}C, 50% mass loss), insoluble in water, acetone and ethyl acetate. The structure is



The first two were added as aqueous dispersions while third one was made into emulsion with oleic acid and ammonia and administered into latex compound.

II.2.5 Other Chemicals

Thiourea, oleic acid, zinc oxide (ρ=5.5) and elemental sulphur (ρ=2.05) were of commercial grade.

II.2.6 Special Chemicals

Propane-2-thiol and piperidine were of analytical grade and were obtained from Fluke A.G West Germany. n-butyl acrylate was obtained from IPCL Chennai.

II.2.7 Solvents

Benzene, toluene, n-heptane, petroleum ether were of analytical grade.

II.2.8 Surface Active Agents

a) Dispersol F

It is sodium salt of a sulphonic acid manufactured by M/S Indian Explosives Limited, Culcutta. It was used as a dispersing agent in the preparation of dispersion of solid ingredients.

b) Potassium laurate

It is an anionic soap, soluble in water and is used as a stabilising agent in latex. This was prepared from chemically pure lauric acid and potassium hydroxide.

II.3 LATEX COMPOUNDING

II.3.1 Preparation of Dispersions

The solid ingredients were added into latex as dispersions. The materials were made to dispersion in water by grinding action and the dispersing agents prevent the dispersed particles from reaggregating. The quantity of dispersing agent to be used for preparing dispersions depends on the nature of materials to be dispersed. For very fine particle size ingredients like zinc oxide, the quantity of dispersing agent required is about 1 per cent by weight where as for materials like sulphur, 2 to 2.5 per cent is required. There are different types of grinding equipments like ball mill, ultrasonic mill and attrition mill. In the present study a ball mill was used for making the dispersions of the ingredients.

A ball mill consists of a cylindrical container in which the slurry is placed together with a charge of balls. When the mill is working the container rotates and the balls are carried round with the container a short way and then cascade. It is this process of cascading which causes the particles of slurry to be comminuted. The efficiency of ball mill depends on speed of rotation of the container, size and material of the ball, viscosity of the slurry, period of ball milling etc.

Formulations of the dispersions used in this study are given below.

a) **Sulphur dispersion (50%)**

Sulphur : 100
Dispersol F : 3
Deionised water : 97
Ball milled for 72 hours

b) **ZDEC Dispersion (50%)**

ZDEC : 100
Dispersol F : 2
Deionised water : 98
Ball milled for 48 hours

c) **ZMBT dispersion (50 %)**

ZMBT : 100
Dispersol F : 2
KOH : Trace
Deionised water : 98
Ball milled for 24 hours

d) **ZDBC dispersion (50%)**

ZDBC : 100
Dispersol F : 2
Deionised water : 98
Ball milled for 48 hours

e) **TMTD dispersion (50%)**

TMTD : 100
Dispersol F : 2
10% ammonium caseinate : 5
Deionised water : 93
Ball milled for 48 hours

f) ZnO dispersion (50%)

ZnO : 100
Dispersol F : 1
Deionised water : 99
Ball milled for 48 hours

g) Titanium dioxide dispersion (33%)

TiO_2 : 100
Dispersol F : 2
Deionised water : 198
Ball milled for 48 hours

h) Precipitated calcium carbonate dispersion (50%)

Precipitated calcium carbonate : 100
Dispersol F : 2
Deionised water : 98
Ball milled for 24 hours

i) China clay dispersion (50%)

China clay : 100
Dispersol F : 2
KOH : Trace
Deionised water : 98
Ball milled for 24 hours

j) Barium sulphate (Barytes) dispersion(50%)

Barium sulphate : 100
Dispersol F : 2
Deionised water : 98
Ball milled for 24 hours

k) Wingstay-L dispersion (50%)

Wingstay-L : 100
Dispersol F : 2
Deionised water : 98
Ball milled for 24 hours

l) Antioxidant HS dispersion (50%)

Antioxidant HS : 100
Dispersol F : 2
Deionised water : 98
Ball milled for 24 hours

m) Lowilite 20 dispersion (50%)

Lowilite 20 : 100
Dispersol F : 2
Deionised water : 98
Ball milled for 24 hours

n) Lowilite 55 dispersion (50%)

Lowilite 55 : 100
Dispersol F : 2
Deionised water : 98
Ball milled for 24 hours

II.3.2 Preparation of Emulsions

The liquid antioxidant SP and Crystol EPR 3400 are immiscible with water and added into latex compound as emulsions. The following recipe was used for preparing emulsions:

a) Antioxidant SP emulsion (50%)

Part A

Antioxidant SP : 100
Oleic acid : 3

Part B

Liquor ammonia : 3
Deionised water : 94

Part A was warmed and added to B in small quantities under high speed stirring.

b) Crystol EPR 3400 emulsion (50%)

Part A

Crystol EPR 3400 : 100
Oleic acid : 3

Part B

Liquor ammonia : 3
Deionised water : 94

Part A was warmed and added to B in small quantities under high speed stirring.

c) Lowilite 76 emulsion (50%)

Part A

Lowilite 76 : 100
Oleic acid : 3

Part B

Liquor ammonia : 3
Deionised water : 94

Part A was warmed and added to B in small quantities under high speed stirring.

II.3.3 De ammoniation of Latex

As High Ammonia type concentrated latex was used, it was de-ammoniated to 0.3 per cent by stirring in a laboratory type de-ammoniation tank for 3 hours. The high ammonia content in latex will create problems in its conversion to solid products or in the stability of the latex compound in the presence of zinc oxide. The concentration of ammonia in latex was estimated as per BIS 3708-Part I 1966.

II.3.4 Compounding

The mixing of the ingredients was done as per the order given in the compound formulations given in the respective chapters. The stabilisers were first added as solutions, followed by the other ingredients.[5] Mixing was done in a glass vessel and stirring for homogenisation was done using a laboratory stirrer at 10-20 rpm. It was occasionally stirred during storage in order to prevent settling of the ingredients.

II.3.5 Maturation

The latex compound was matured at ambient temperature for 24 hours. This was done with the following objectives.[5]

a) To equilibrate the added surface active agents and those naturally present between the aqueous and interfacial phases.

b) To remove the air bubbles introduced in the compounds while compounding.

c) To dissolve the vulcanizing agents in the aqueous phase and make them migrate into rubber particles which can offer better technological properties.

d) To obtain a certain degree of prevulcanization to the latex.

e) To allow time for the reaction of ammoniated latex with zinc oxide for getting uniform physico chemical properties.

II.4 PREPARATION OF TEST SAMPLES

II.4.1 Latex Film

Latex films were cast on glass cells using the latex compounds as described by Flint and Naunton.[6] Cellophane adhesive tapes were stuck to the edges of the glass plates to form the cells. The size of the glass cells was 6"x6" and about 10-15 ml of the latex compound was poured and distributed so that a film of thickness 0.3-1 mm was obtained upon drying. The glass cells with the latex compound were placed on leveled table and dried overnight at ambient temperature.

II.4.2 Latex Thread

Latex thread was prepared by extruding the latex compounds through a glass capillary tube into an acid bath (20 per cent formic acid). As the latex filaments passed through the bath, acid diffused into the centre of the thread and total gelation occurred. The thread was then washed, dried and vulcanized. The diameter of the latex thread was controlled by adjusting the following factors.

a) Hydrostatic pressure on the latex compound in the capillaries.

b) The internal diameter of the capillaries.

c) The rubber content and viscosity of the latex compound.

d) The rate at which the transfer rollers remove the thread from the acid bath.

A schematic diagram of the latex thread plant used in this experiment is given in Figure II.2. The plant consisted of a header tank, constant pressure head device, coagulant bath, washing bath, drying chamber and the talc dusting system. Constancy of the extrusion pressure was ensured by feeding the nozzles through a manifold which was connected to the constant pressure head. The level of this head may be altered within limits if desired.

The compounded latex after maturation was stored in the header tank. From the header tank the latex passed to a manifold extruding head which distributed the compound to the capillaries through flexible tubes. Glass nozzles of 0.6mm diameter were used and immersed in a bath of 20 per cent formic acid. The length of the acid bath was 10 feet. The coagulated thread was transferred to the washing bath of 6 feet length containing water at 70^0C. After washing the thread entered the air drying oven of 12 feet length set at 100^0C, where it was dried. Talc powder was then applied over the thread to remove tackiness and the thread was wound on wooden frames. The drying was completed at ambient temperature.

II.5 VULCANIZATION OF TEST SAMPLES

II.5.1 Latex Films

Dried latex film was used for preparation of vulcanized dumbbell samples. Latex films under conventional vulcanization system were cured for 60 minutes in boiling water while those in efficient vulcanization system were cured for 90 minutes.

II.5.2 Vulcanization of Latex Threads

The threads were vulcanized in boiling water. The threads with conventional vulcanizing system (CV) were vulcanized for 60 minutes and threads with efficient vulcanizing system (EV) were vulcanized for 90 minutes.

II.6 DEGRADATION STUDIES

The latex films prepared using different accelerator combinations and various fillers were cut into dumbbells conforming to ASTM D-412 after proper vulcanization. The dumbbell film samples and thread samples were UV-irradiated for different durations and also heat aged at 100^0C for 22 hours. These were then used for chemical and physical testing.

II.6.1 Heat Ageing

Heat ageing studies were conducted in an air circulating multicellular hot air oven (TEMPO). The ageing was conducted at 100^{0}C for 22 hours.

II.6.2 UV-Irradiation Chamber

It is a metallic chamber of 86 x 30 x 58 cm dimensions. The UV-light sources are fitted at the top and bottom parts of the chamber in a face to face manner. A plain glass sheet of area 2580cm^2 is fitted inside the middle of the chamber and it holds the samples for irradiation. Both the surfaces of the latex test specimens were simultaneously exposed to UV- radiation for fixed durations. The chamber has holes at the base, so that air can freely pass through the chamber. The UV-source was two 15W capacity fluorescent tubes. It was reported that fluorescent UV-sources are most effective for exposure studies.[7,8,9]

The photograph showing the instrument is given in Figure II.3.

II.7 PHYSICAL TESTS

II.7.1 Mechanical Stability Time (MST)

The mechanical stability of latex means the ability of latex to withstand the colloidal destabilisative effects of mechanical origin such as shearing and agitation. 80gm latex (compounded) of 55% total solid content, after reaching 35^{0}C temperature was subjected to mechanical agitation in a KLAXON (UK) MST tester at 14000rpm. The time elapses before gross colloidal destabilisation appearance was denoted as MST in seconds.

II.7.2 Viscosity of Latex Compounds

Many methods are used for this. Brookfield (LVT model) is a technical viscometer and is used for determining the viscosity of latex compound. It consists of a rotating member which is usually a cylinder driven by a synchronous motor through a beryllium-copper torque spring. The viscous drag on cylinder causes an angular deflection of the torque spring which is proportional to the viscosity of the fluid in which the disc is rotating. The torque and therefore the viscosity is indicated by means of the pointer and scale. A range of speed of the discs and cylinders are available so that a wide range of viscosity may be covered. Natural rubber latex is non-Newtonian fluid and its viscosity decreases with increasing shear rate. In the present study the viscosity of the latices was measured at ambient temperature at 60 rpm (using spindle No.2).

II.7.3 Modulus, Tensile Strength and Elongation at Break

At least three specimens per sample were tested for each property and the mean values reported.

In the present work these tests were carried out using an Instron Universal Testing Machine (UTM) model D 4411. The machine consisted of load frame and an electronic control unit. Load measuring device is a load cell fixed at the top of the load frame. Below the load cell is a moving platform driven by continuously variable speed motor. Grips suitable for dumb bell specimens are fixed on to the load cell and moving platform. During testing the specimen is subjected to stretching at constant speed. Force and elongation are continuously monitored by the electronic unit. As soon as the test specimen breaks test results are displayed in the electronic unit.

All the tests were carried out at ambient temperature (30^0C). Specimens were cut from the cast vulcanized films. The thickness was measured by bench thickness gauge. The moving cross head was adjusted by operating the switch. The velocity of the moving cross head was adjusted to be 500mm/min.

The specimen was elongated and the values corresponding to ultimate tensile strength, elongation and modulus were obtained.

II.8 CHEMICAL TESTS

II.8.1 pH

The pH of rubber latices was measured with a glass electrode and saturated calomel cell after standardising the pH metre.

II.8.2 Determination of Swell Index and Volume Fraction of Rubber

Samples of approximately 1cm diameter, 0.25cm thickness and 0.3g weight were punched from the central portion of the vulcanized latex film and allowed to swell in thiophane free benzene containing 0.5 per cent phenyl β naphthylamine at 35^0C in a thermostatically controlled water bath. Swollen samples taken after 48 hours were blotted with filter paper and weighed quickly in a stoppered weighing bottle. For natural rubber vulcanizates, the 36h was found to be sufficient for attaining equilibrium. Samples were dried in an oven for 24h at 70^0C, and then in vacuum and finally weighed after allowing them to cool in a desiccator. Duplicate readings were taken for each sample. Swell index was the weight of benzene absorbed per gram of sample. The volume fraction of rubber "Vr" was calculated by the method reported by Ellis and Welding,[10] which takes into account the correction of swelling increment with duration of immersion after the equilibrium is attained.

$$\mathrm{Vr} = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}} \qquad \mathrm{II(1)}$$

Where T is the weight of test specimen, D its deswollen weight, F, the weight fraction of insoluble components, and A_0 is the weight of the absorbed solvent, corrected for the swelling increment ρ_r and ρ_s are the densities of rubber and solvent respectively.

ρ_r(NR) = 0.92

ρ_s(benzene) = 0.875

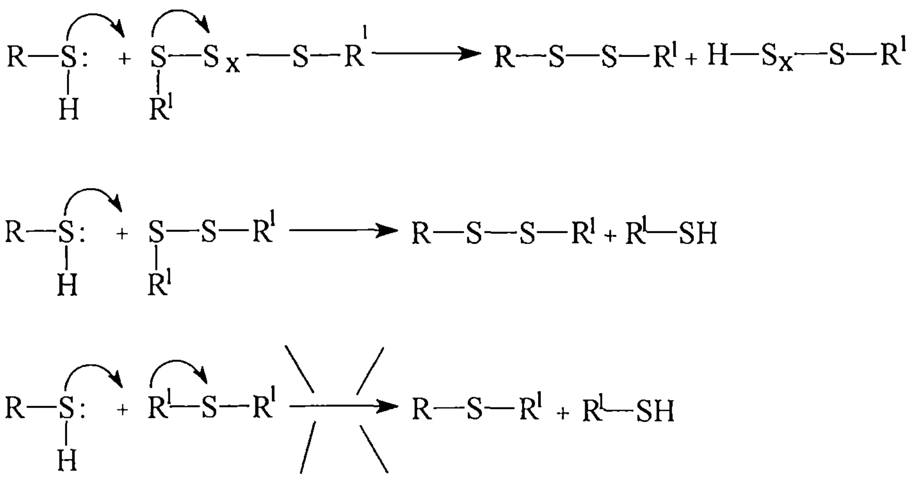
From the collected data, the value of A_0 was calculated. The value of "Vr" can be taken as a measure of crosslink density.

II.8.3 Ammonia-modified Swelling

The samples of the vulcanized latex films containing different filler contents were swollen for 48h in flat dishes containing benzene in ammonia atmosphere.[11] For this the samples were put in a desiccator the bottom of which contained liquor ammonia. After swelling in ammonia atmosphere the samples were thoroughly washed with benzene and dried in a vacuum desiccator at room temperature (30^0C) and tested for Vr by swelling in benzene. The difference in chemical crosslink density as obtained by swelling in benzene of the original vulcanizate and the same after ammonia treatment gives a measure of rubber-filler attachment or coupling bond. In this, the ammonia permeates the benzene solvent and preferentially cleaves the rubber-filler attachment.

II.8.4 Determination of Concentration of Different Types of Crosslinks

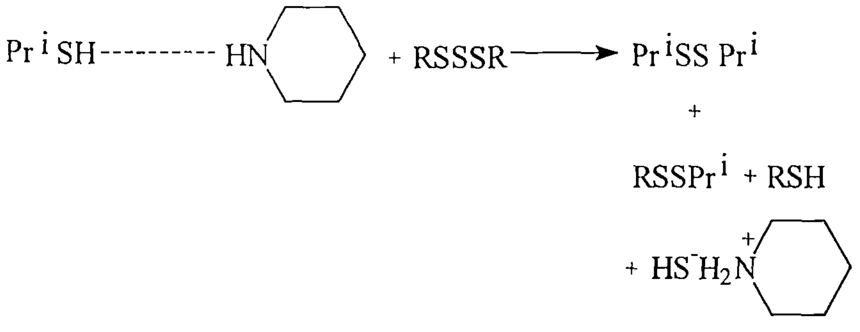
The concentration of polysulphidic crosslinks (-Sx-) was estimated from the determination of chemical crosslinks of the vulcanizate before and after treatment with thiolamine. Treatment of the vulcanizate with propane-2-thiol (0.4m) and piperidine (0.4m) in n-heptane at room temperature for 2h cleaves the polysulphidic crosslinks in the network. The experimental method used is as described in detail by Campbell.[12,13] Action of propane 2-thiol is based on nucleophilic displacement reactions by alkane thiols on sulphur atoms of polysulphides to cleave the sulphur bonds as shown below. They depend on the relative rates of the two displacement reactions and high resistance of the carbon-sulphur linkage in monosulphides to such nucleophilic displacement.



Scheme II.1

II.8.5 Treatment with Propane-2-thiol

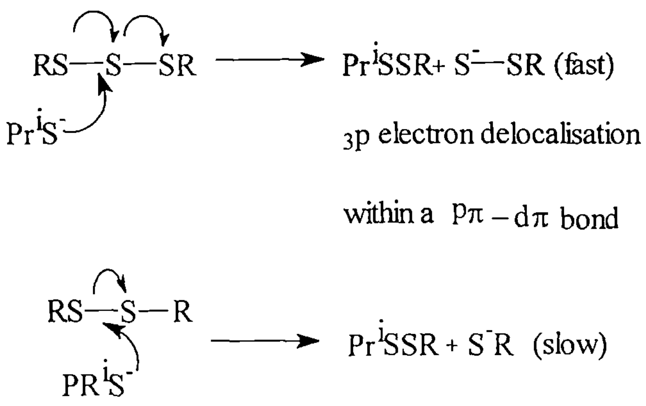
The samples (1mm thick and 0.3g weight) were placed in a cylindrical tube 30cm long and 3cm in diameter, clamped horizontally and purged with nitrogen. The specimens were well covered with 100ml of the thiol-amine reagent (prepared by dissolving in n-heptane, and making upto one litre with further pure heptane).[14] The gas tap was closed to maintain the nitrogen blanket in the tube. The solution was agitated occasionally during the two hour period. After renewing the stream of nitrogen through the apparatus the reagent was run off and replaced by 100ml of petroleum ether (b.P 40-60^{0}C) and the apparatus was agitated occasionally during one hour. This cold extraction was repeated with fresh petroleum ether every hour until four such extractions were made under nitrogen. The specimens were then removed and dried overnight in vacuum to constant weight. Then the chemical crosslink density, was measured by equilibrium swelling method as described earlier. When the sample thickness was more than 1mm, the specimens were swollen in n-heptane overnight at room temperature under nitrogen and sufficient propane-2-thiol and piperidine were added to give concentrations of 0.4m for each reagent in the final solution. The cleavage reaction in the presence of propane-2-thiol, piperidine and n-heptane is exemplified for trisulphide in the following equation.



where Pr^i = isopropyl

Scheme II.2

The thiol-amine combination gives an associate possibly piperidinium propane-2-thiolate in ion pair, in which the sulphur atom has enhanced nucleophilic properties[15] which is capable of cleaving organic trisulphides and higher polysulphides within 30 minutes at 20^0C, while reacting with corresponding disulphides at about one thousandth of this rate. The favoured polysulphide cleavage is due to delocalisation of the displaced 6-electron pair of RSS^- shown in following equation.



Scheme II.3

Pr^iS^- is used to represent the nucleophilic thiol-amine associate.

The difference in the Vr values of the sample before and after thiol-amine chemical probe gives the polysulphidic crosslink content in the vulcanizate.

II.8.6 Determination of Sol Content

The extent of chain scission in a vulcanizate was estimated by determining its sol content. The estimation was done by the method described by Bristow[16] in which the samples were extracted with cold acetone in the dark for 8 to 10 days, the acetone being replenished four times during this period. This samples were then dried to constant weight in vacuum at room temperature. Weighed samples were extracted with cold benzene in the dark for 8 to 10 days, the benzene being replenished four times during this period. After benzene extraction, the samples were dried to constant weight in vacuo. The sol content is the weight loss during benzene extraction.

II.9 CHARACTERISATION

Infrared studies were carried out using SHIMADZU 8101M (JAPAN) FTIR spectrometer. The graft co polymer purified by solvent extraction was used in each case for taking the IR spectrum. The copolymer was dissolved in toluene and cast into a film on a sodium chloride cell and the IR spectrum was taken in the frequency range of 4000-400 cm^{-1}. Epoxidised NR also was dissolved in spectroscopically pure toluene and absorption spectra was recorded.

II.10 MORPHOLOGICAL STUDIES

II.10.1 Optical Microscope

Test samples of gum latex vulcanizates of NR which were unexposed and exposed to UV-radiation were examined for morphological changes. Photomicrographs were taken on Leica Wild M8 Zoom stereo Microscope and wild MPS 46/52 photoautomate using Kodak max 400 films.

II.10.2 Scanning Electron Microscope

The surface of the unexposed and UV-exposed cast latex film with and without UV stabiliser was sputter coated with gold and photomicrographs were taken using a JEOL JSM-5600 LV model scanning electron microscope.

II.11 DISCOLOURATION

The colour changes of the UV exposed and unexposed samples were photographed using Kodak max 400 films.

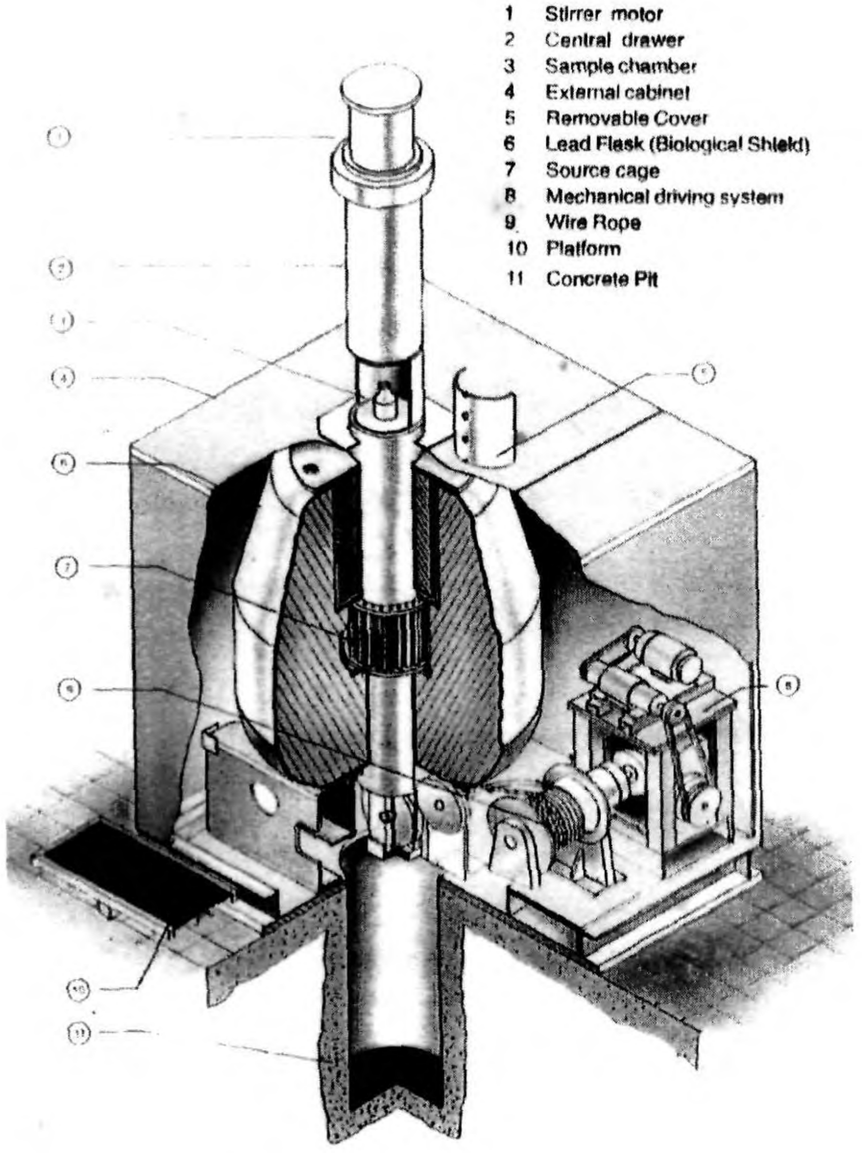


Figure II.1 Gamma Chamber 5000

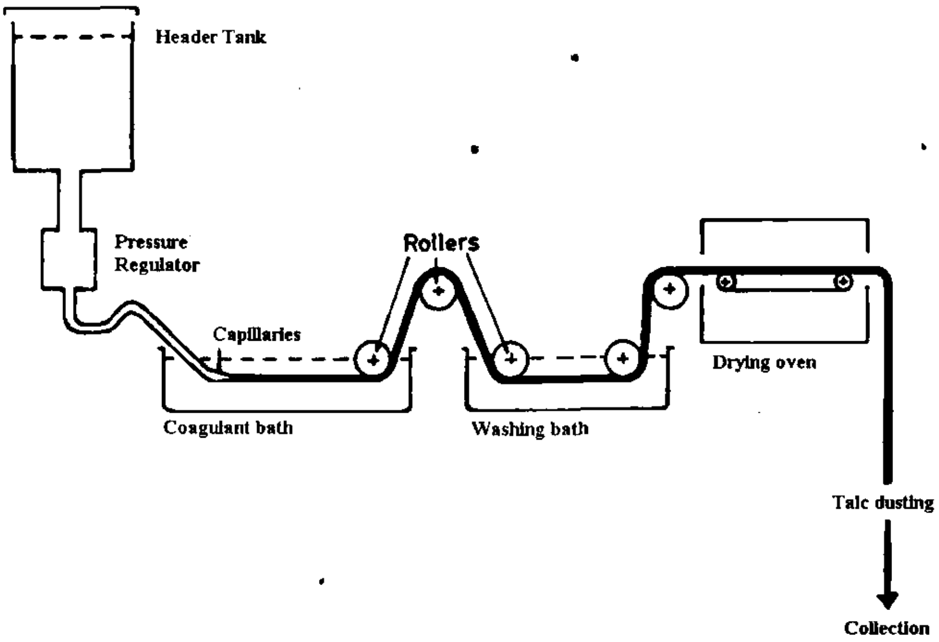


Figure II.2 Schematic diagram of latex thread plant

Fig. II.3: UV-Irradiation chamber

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CHAPTER III

STUDIES ON DEGRADATION RESISTANCE OF LATEX THREAD UNDER UV- RADIATION

PART I. Effect of Vulcanization Systems and Antioxidants on Discolouration and Degradation of Latex Thread Under UV-Radiation

PART II. Effect of Non-Black Fillers and Pigments on the Physical Properties and Degradation Resistance of Latex Thread Exposed to UV-Radiation

PART -I

Effect of Vulcanization Systems and Antioxidants on Discolouration and Degradation of Latex Thread Under UV-Radiation

The result of this experiment was published in Journal of Applied Polymer Science. 78 (2000) 304-310.

Properties of natural rubber (NR) latex thread mainly depend on the vulcanization system and antioxidant used in its production. The properties of the thread set out in quality standards include modulus, tensile strength, elongation at break and resistance to degradation.[1] The modulus of the thread is very critical for its application in textiles.[2] The above properties of the thread are to a great extent controlled by the vulcanization system which can be conventional type using elemental sulphur (CV system) or a system involving sulphur donor accelerator (EV system).[3,4] In order to improve the technical properties of the thread, different accelerator combinations are used and vulcanizates containing binary accelerator systems are reported to give superior physical properties.[5-7]

NR latex thread is more vulnerable to degradation than other latex products owing to its low bulk and large surface area. Degradation of the thread is caused by heat, light, oxygen, ozone, detergents, etc. The effect of heat and oxygen on the degradation aspects of the thread has already been investigated in detail.[8] But little study is seen reported on the effect of light on degradation of threads. It is reported that the UV-radiation in sunlight is causing discolouration and degradation of rubber products.[9,10]

In the present work, the results of a systematic study on the effect of accelerator combinations and antioxidants, on UV-degradation of NR latex threads with conventional and efficient vulcanization systems are presented.

Centrifuged (60%) high ammonia type NR latex conforming to BIS 5430-1981 was used for this study. Latex compounds were prepared according to the formulations given in *Table III.Ia* and the compounding ingredients used were of commercial grade. The latex was first stabilized by adding solutions of potassium hydroxide and potassium laurate. The other compounding ingredients were added as dispersions/emulsions. The compounds were then matured at 30°C for 96 h and sieved through 100 mesh sieve. Each compound was then run on a pilot plant for thread manufacture through a glass capillary of 0.6 mm diameter, using 20% formic acid as the coagulant. The thread was then washed in hot water at 70°C, dried in a hot chamber at 90°C, wound on wooden frames and vulcanized in boiling water. The threads with the conventional cure systems were vulcanized for 60 min and those with the efficient cure systems for 90 min and finally dried in an air oven at 60°C. Cast latex films of thickness 1 mm were also prepared from each latex compound. The films were then vulcanized in boiling water and dried as in the case of latex thread samples.

Portions of the thread and the film samples were then exposed to UV-radiation from a UV-source (Philips-TLD 30 W-Holland) for 24, 48 and 96 h. The effect of UV-light on colour and tensile properties of the thread was then examined. The colour was graded visually and the tensile properties of the thread determined according to ASTM D412 using an Instron D-4411 universal testing machine. The thread and the film samples after 24 h exposure to UV-radiation, were also subjected to heat ageing at 100°C for 22 h and its effect on colour and tensile properties was determined. The film samples were tested for measuring the changes in crosslink density by the method suggested by Ellis and Welding.[11] The results are given in *Tables III.2a, III.2b, III.3 and III.4.*

In order to assess the effect of antioxidants on the degradation of thread samples under UV-radiation, two typical mixes, CV_1 and EV_1 were selected. Latex compounds containing each of the antioxidants Wingstay L (Reaction product of butylated p-cresol and dicyclopentadiene) Crystol EPR 3400 (Tris-nonylated phenyl phosphite), Antioxidant SP (Styrenated phenol) and Antioxidant HS (Polymerized 1,2-dihydro 2,2,4-trimethyl quinoline) were prepared as per the formulations given in *Table III.1b.* The thread samples were then prepared as described above and subjected to UV-radiation for 24, 48 and 96 h. The colour and tensile properties were then examined as described earlier. The results are given in *Table III.5.* The photographs showing the discolouration of the aged thread samples are given in Figures III.1 and III.2.

III.1 RESULTS AND DISCUSSION

The properties of latex thread samples having different accelerator combinations before and after exposure to UV-radiation are given in *Tables III.2a and III.2b.* It is observed that there is no discolouration for all the thread samples before exposure to UV light. It is also evident that the modulus of the thread produced using ZDBC + ZMBT and ZDBC + ZDEC combinations is higher than that of ZDEC + ZMBT combination in the conventional system. In the case of efficient system also TMTD + ZDBC combination is better than TMTD + ZDEC combination for getting higher modulus for the threads. This is attributed to the higher activity of ZDBC in crosslink formation as reported earlier.[2] The values of swell index which is a measure of crosslink density values of the cast latex film samples given in *Table III.4* also support this. It is also observed that the sample containing ZDEC + ZMBT combination in the CV system turned to light yellowish than the thread sample containing TMTD + ZDEC combination on UV-irradiation. The thread with the other accelerator combinations retained almost their original colour. It is also observed that all the thread sample turned to little opaque on UV-exposure and this may be due to surface oxidation.

During UV-irradiation chain scission may occur as a result of the following reactions.[10,12]

$$\text{Polymer} \xrightarrow{h\nu} R^{\cdot}$$

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot}$$

$$RO_2^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$$

$$2RO_2^{\cdot} \longrightarrow \text{Non-radical products}$$

Scheme III.1

The importance of hydroperoxide in the photo-oxidation process is well established and the photo oxidation rate is proportional to the initial hydroperoxide concentration.[13] The protective action of a chemical against UV light depends on several factors such as enhanced catalytic activity for hydroperoxide decomposition, UV absorption and deactivation of the absorbed light, better light stability and increased solubility of the chemical in the polymer. In the region of 290-350 nm which is the critical region of sun's spectrum responsible for sensitization of photo oxidation, ZDEC is reported to absorb much less light. In addition to this ZDBC has a better solubility in NR due to its higher alkyl chain length compared to ZDEC. The action of ZMBT as a catalyst for decomposition of hydroperoxide is very much dependent on the molar ratio of the hydroperoxide to ZMBT.[14] At lower ratios, ZMBT is reported to have a pro-oxidant effect. Hence the higher degradation effect of ZDEC + ZMBT combination over that of

ZDBC + ZMBT can be attributed to the combined effect of lower solubility of ZDEC in NR, its lower level of UV-absorption, deactivation of the absorbed light and the higher pro-oxidant activity of ZMBT under UV-irradiation.[14] Furthermore CV_1 system is little more yellowish than EV_1 system after UV exposure and this may be due to the high sulphur content in the former system which can produce more coloured species with other organic ions or groups. ZDBC is capable of incorporating more sulphur into the crosslinks so that less discolouration and higher modulus for the thread is obtained.

The effect of UV-irradiation for longer periods on the physical properties of the thread is depicted in *Tables III.2 a and III.2 b.* It can be seen that UV-light is causing considerable deterioration on the tensile strength of the thread. Among the different accelerator combinations ZDBC + ZDEC combination is found to be better in retaining the tensile properties on long term UV-irradiation. In the case of EV system, TMTD + ZDBC is better than TMTD + ZDEC in retaining the tensile properties. The thread samples with ZDEC + ZMBT combination showed the maximum deterioration in the CV system. The combined effect of UV-light and heat given in *Table III.3* also indicated that samples containing ZDEC + ZMBT underwent more degradation than the other systems.

The test results of the threads with various antioxidants in the CV_1 and EV_1 compounds are given in *Table III.5.* The results show that antioxidant (SP + HS) combination have imparted discolouration of the thread under UV-radiation. But Crystol EPR 3400, which is a phosphite-type antioxidant, reduced the discolouration to a considerable level. This can also be attributed to the similar action as described in the case of ZDBC in reducing the radical formation. But as an antioxidant it was found less powerful at the dosage used in the formulation. Wingstay L is found to be giving better protection to the thread under long term UV-irradiation than the (SP + HS) system, and the effect of antioxidant is found to be more pronounced in the CV system.

In conclusion, it is observed that the effect of accelerator combinations on discolouration and degradation of latex threads under UV-radiation depends on the type of accelerators. ZDBC + ZDEC and ZDBC + ZMBT combinations are found to be better in giving better colour and degradation resistance to the thread than ZDEC + ZMBT combination under CV system. Similarly under EV system, TMTD + ZDBC is better than TMTD + ZDEC combination. It is also observed that antioxidants Wingstay L and (SP + HS) combinations are more effective in retaining the physical properties of the thread than Crystol EPR 3400 under long term UV-irradiation and the phosphite type antioxidant Crystol EPR 3400 is better in reducing the discolouration under UV-radiation.

Table III.1a Formulation of latex compounds (Accelerator combinations)

Formulations	**CV system**			**EV system**	
	CV_1	CV_2	CV_3	EV_1	EV_2
60% Centrifuged NR latex	167	167	167	167	167
10% Potassium hydroxide solution	2	2	2	2	2
10% Potassium laurate solution	0.5	0.5	0.5	0.5	0.5
50% Sulphur dispersion	3.6	3.6	3.6	0.6	0.6
50% Zinc diethyl dithiocarbamate dispersion (ZDEC)	2.0	-	2.0	1.0	-
50% Zinc di-butyl dithiocarbamate dispersion (ZDBC)	-	2.0	1.0	-	1.0
50% Zinc 2-mercabtobenzothiazole dispersion (ZMBT)	1.0	1.0	-	-	-
50% Tetramethyl thiuram disulfide dispersion (TMTD)	-	-	-	4.0	4.0
20% Thiourea solution	-	-	-	3.5	3.5
50% Zinc oxide dispersion	1.0	1.0	1.0	1.0	1.0

Table III.1b Formulation of latex compounds (Antioxidants)

Formulations	CV system			EV system		
	CV_{1a}	CV_{1b}	CV_{1c}	EV_{1a}	EV_{1b}	EV_{1c}
60% Centrifuged NR latex	167	167	167	167	167	167
10% Potassium hydroxide solution	2	2	2	2	2	2
10% Potassium laurate solution	0.5	0.5	0.5	0.5	0.5	0.5
50% Sulphur dispersion	3.6	3.6	3.6	0.6	0.6	0.6
50% Zinc diethyl dithiocarbamate dispersion (ZDEC)	2.0	2.0	2.0	1.0	1.0	1.0
50% Zinc 2-mercabtobenzothiazole dispersion (ZMBT)	1.0	1.0	1.0	-	-	-
50% Tetramethyl thiuram disulphide dispersion (TMTD)	-	-	-	4.0	4.0	4.0
20% Thiourea solution	-	-	-	3.5	3.5	3.5
50% Zinc oxide dispersion	1.0	1.0	1.0	1.0	1.0	1.0
50% Wingstay L dispersion	2	-	-	2	-	-
50% Crystol EPR 3400 emulsion	-	2	-	-	2	-
50% Antioxidant SP emulsion	-	-	1	-	-	1
50% Antioxidant HS dispersion	-	-	1	-	-	1

Table III.2a Appearance and physical properties of latex thread before and after UV exposure

Formulations		CV_1 UV irradiation time (h)				CV_2 UV irradiation time (h)				CV_3 UV irradiation time (h)			
	Properties	**0**	**24**	**48**	**96**	**0**	**24**	**48**	**96**	**0**	**24**	**48**	**96**
1.	Discolouration	Nil	Light yellow	Light yellow	Light yellow	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
2.	Physical properties:												
	Modulus (300%) (MPa)	1.6	1.57	1.54	1.1	2.3	2.2	2.2	1.90	2.1	2.2	2.1	2.0
	Tensile strength (MPa)	23	20	17	8.75	22	17	16	13.1	21	18	16	15
	Elongation at break (%)	1560	1500	1454	1192	1300	1280	1223	1039	1310	1250	1240	1091

Table III.2b Appearance and physical properties of latex thread before and after UV exposure

Formulations		EV_1				EV_2			
		UV irradiation time (h)				UV irradiation time (h)			
	Properties	**0**	**24**	**48**	**96**	**0**	**24**	**48**	**96**
1.	Discolouration	Nil	Slight yellow	Slight yellow	Slight yellow	Nil	Nil	Nil	Nil
2.	Physical properties:								
	Modulus (300%) (MPa)	1.2	1.25	1.06	1.04	1.6	1.44	1.2	1.1
	Tensile strength (MPa)	20	19	15	12	19	19	18	15
	Elongation at break (%)	1590	1580	1550	1285	1550	1500	1403	1330

Table III.3 Appearance and physical properties of latex thread after 24 h UV irradiation and heat ageing

Formulations	Discolouration	24 h UV exposed and aged at 100°C/22 h		
		Physical properties		
		Modulus, 300% (MPa)	Tensile strength (MPa)	Elongation at break (%)
CV_1	Yellow	1.0	6	1200
CV_2	Yellow	2.0	12.5	1250
CV_3	Yellow	1.95	12	1200
EV_1	Yellow	1.25	9.5	1500
EV_2	Yellow	1.3	13	1400

Table III.4. Changes in crosslink density after 24 h UV irradiation and ageing at 100°C/22 h

Formulations	Swell index (Weight in grams of benzene absorbed per gram of the sample)		
	Before UV irradiation	After 24 h UV irradiation	After 24 h UV irradiation and ageing at 100°C/22 h
CV_1	3.9	3.9	4.4
CV_2	3.8	3.6	3.8
CV_3	3.9	3.8	3.9
EV_1	4.7	4.6	5
EV_2	4.8	4.6	4.8

Table III.5Appearance and physical properties of the thread with different antioxidants before and after UV irradiation

Formulations		CV$_1$				EV$_1$			
		UV irradiation time (h)				UV irradiation time (h)			
Properties	**Antioxidant**	**0**	**24**	**48**	**96**	**0**	**24**	**48**	**96**
Discolouration	Wingstay L	Nil	Light yellow	Light yellow	Light yellow	Nil	Slight yellow	Slight yellow	Slight yellow
Physical properties:									
Modulus (300%) (MPa)		1.58	1.57	1.20	1.05	1.25	1.40	1.15	1.0
Tensile strength (MPa)		23	21	19.5	17.4	19	15	12	10
Elongation at break (%)		1610	1556	1461	1447	1620	1580	1571	1454
Discolouration	Crystol EPR 3400	Nil	Slight yellow	Slight yellow	Slight yellow	Nil	Nil	Nil	Nil
Physical properties:									
Modulus (300%) (MPa)		1.20	1.30	1.14	1.06	1.28	1.0	0.9	0.4
Tensile strength (MPa)		20	14	12.5	8.0	20	11	8.0	3
Elongation at break (%)		1700	1680	1648	1558	1640	1630	1513	1011
Discolouration	(SP+HS) Combination	Light yellow	Yellow	Yellow	Yellow	Slight yellow	Yellow	Yellow	Yellow
Physical properties:									
Modulus (300%) (MPa)		1.50	1.54	1.5	1.35	1.25	1.32	1.30	1.2
Tensile strength (MPa)		22	20	18.7	14.1	19	18	11	9
Elongation at break (%)		1650	1670	1499	1551	1630	1500	1450	1425

Discolouration index: Yellow > light yellow > slight yellow

Fig. III.1. Photograph showing the discoulouration of 96 h UV-exposed thread samples

(a) Threads containing ZDBC + ZMBT accelerator combination (CV_2)
(b) Threads containing ZDEC + ZMBT accelerator combination (CV_1)

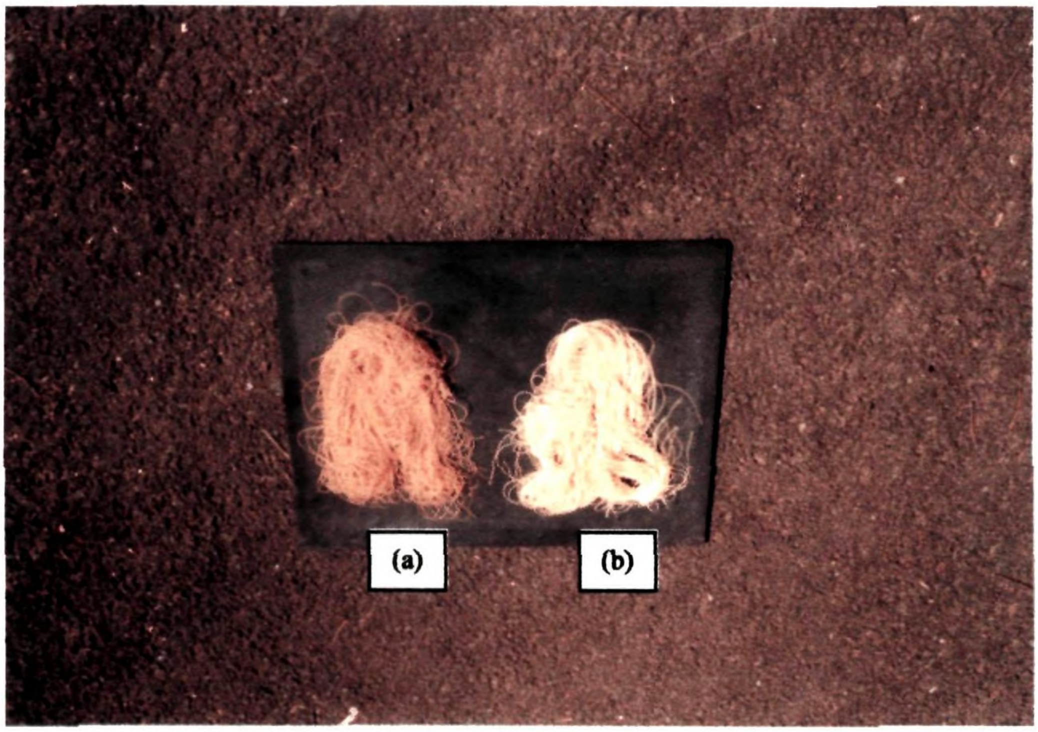

Fig. III.2. Photograph showing the discolouration of unaged and $100^0C/22h$ heat aged thread samples

(a) Aged thread sample containing ZDEC + ZMBT accelerator combination (CV_1)

(b) Unaged thread sample containing ZDEC + ZMBT accelerator combination (CV_1)

PART II

Effect of Non-Black Fillers and Pigments on the Physical Properties and Degradation Resistance of Latex Thread Exposed to UV-Radiation

The result of this experiment was published in Indian Journal of Natural Rubber Research. 14 (2) (2001) 102-105.

Among the physical properties of latex thread, the most important parameters are the modulus and tensile strength. A lot of studies have been reported on the effects of vulcanization systems and accelerator combinations on the above properties.[15,16,17] Due to its large surface area, the thread is more vulnerable to degradation which is caused mainly by detergents, heat, light and oxygen. UV-light causes both degradation and discolouration.[18,19] Studies have also been reported on the effects of various antioxidants for retarding the degradation.[20] Generally certain non-black fillers are added at low dosages (below 10 phr) along with titanium dioxide in latex thread compounds for getting better modulus and colour respectively. But no systematic study is reported on the effects of common non-black fillers and pigments on the physical properties of latex threads.

In dry rubber compounding, fillers generally act as reinforcing agents, but in latex they weaken the rubber film rather than improving its strength, due to the poor rubber-filler interactions.[21,22] But it has also been reported that china clay at low dosages can improve the physical properties of latex vulcanizates.[23]

The present work reports on the effect of titanium dioxide (pigment) and fillers like china clay, precipitated calcium carbonate and barium sulphate (barytes) along with titanium dioxide on the physical properties of latex thread, with special reference to its degradation under UV-radiation.

Centrifuged high ammonia type natural rubber latex conforming to BIS 5430-1981 was used in this study. Latex thread compounds were prepared as per the formulations given in Tables III.6a and III.6b. The compounding ingredients were added as fine dispersions/solutions. The compounds were matured at 30°C for 96 h and sieved through 100 mesh sieve cloth. Each compound was then run on a pilot plant for thread manufacture through a glass capillary of 0.75 mm diameter using 20% formic acid as the coagulant. The threads were then dried at 70°C for 1 h and vulcanized in boiling water. The threads with conventional cure system were vulcanized for 60 min and those with efficient vulcanization system were cured for 90 min. Cast latex film using each latex compound was also prepared and it was also vulcanized to the same extent as that of the thread sample.

A portion of thread sample was tested for its tensile properties as per ASTM D412 using Instron D4411 universal testing machine. Another portion of thread sample and the film sample were then exposed to UV-radiation from a UV-source (Philips-TLD 30W, Holland) for 24,48 and 96 h. The tensile properties of the thread samples after the exposure were then determined. The thread samples were also subjected to heat ageing at 100°C for 22 h in a multicellular ageing oven and then determined their tensile properties. The results are given in Tables III.7 to III.10.

The extent of rubber-filler attachment in the filled vulcanizates were assessed by ammonia modified swelling studies[24] as described in section II.8.3 of Chapter II. The results of the changes in V_r values after ammonia modified swelling and 96 h UV irradiation are given in Table III.11. The photograph given in Figure III.3 shows thread samples with and without TiO_2 pigment.

III.2 RESULTS AND DISCUSSION

The tensile properties of latex thread samples containing fillers and titanium dioxide pigment having conventional and efficient vulcanization systems, before and after exposure to UV-light are given in Tables III.7 and III.8. It can be seen that the latex compounds with titanium dioxide alone are giving no marked improvement in the modulus and tensile strength. But all the thread samples having the combination of the filler and the pigment showed higher modulus and tensile strength. This may be due to the effect of better rubber-filler interaction.[25,26] The difference in V_r values (Vro–Vra) given in Table III.11 support this. For the samples C, D and E the V_r values reduced more after ammonia modified swelling indicating higher rubber–filler interaction. When the thread samples are exposed to UV light the tensile properties decreased in all cases. In the conventional vulcanization system thread sample containing precipitated calcium carbonate filler and titanium dioxide pigment gave better resistance to UV-light whereas in efficient vulcanization system all the fillers behaved almost similarly. This can be attributed to the high sulphur content in the CV system which can contribute to more crosslink formation on rearrangement.

During the photo-oxidative ageing of natural rubber, the rubber hydrocarbon produces free radicals, by absorbing energy from UV-radiation falling in the region of 290-350 nm.[27] Water which is capable of hydrolysis and the acidic nature of some fillers also cause the breakage of rubber hydrocarbon chain network under UV-light and heat. The precipitated calcium carbonate is alkaline which is showing better values than the others like clay and barytes. The white pigment TiO_2, which is having good reflectance properties[28] against light when used alone or with other fillers, is not able to give satisfactory protection to NR latex products like thread. The chain breakage of NR hydrocarbon during photo oxidative ageing results in poor properties of the exposed thread samples. The filled thread samples having an efficient vulcanization also showed a decreasing trend in properties after exposure to UV-light for 96 h. The changes in V_r values given in Table III.11 of the cast latex film samples after photo oxidative ageing support this. Here also the mechanism of degradation reaction is the same as in the above case.

The properties of the unfilled and filled thread samples before and after heat ageing at 100°C for 22 h are given in Tables III.9 and III.10. The properties, mainly the tensile strength values, are decreased to a higher extent for those samples having conventional vulcanization system when the thread samples are heat aged. Here also the thread samples filled with precipitated $CaCO_3$ along with TiO_2 pigment showed better values compared to other samples filled with TiO_2, clay, barytes, etc. This shows the higher activity of precipitated $CaCO_3$ in NR latex products than other fillers due to its higher alkaline behaviour, which is harmless to rubber hydrocarbon. When the NR latex thread is exposed to UV-light and heat, the hydrocarbon gets oxidised to hydroperoxides in presence of atmospheric oxygen. The hydroperoxides are further decomposed into oxide and a new free radical is formed.[27,29,30,31] Thus the scission of rubber hydrocarbon molecules reduces the properties of the thread samples. The metal components existing in the rubber and filler favour electron transfer and accelerates the production of free radicals which in turn accelerate oxidation.[32,33] It is also known that active sites like hydroxyl groups, coordinatively unsaturated metal atoms, free radicals present on the surface of any filler etc. are capable of chemical interaction with the polymer.[34] At excited energy conditions like photo irradiation, water molecules co-ordinatively bonded to the filler or pigment surface may participate in hydrolysis and acidolysis of polymers possessing unsaturated bonds.

Based on the above discussion, we can attribute the degradative effects of UV-irradiation on the properties of the filled NR latex thread sample to the combined action of acidic nature of fillers, water, metal ion present in the filler and due to the high energy radiation. In this experiment we have also noticed that in the case of heat ageing efficient vulcanized products exhibited very good performance in retaining the physical properties than the conventionally vulcanized products. But in the case of photo irradiation, the trend is same but the difference in the properties after long term UV-exposure is narrow compared to the results shown in heat ageing between CV and EV systems.

From the investigations, it can be concluded that china clay, precipitated calcium carbonate and barytes at low dosages along with titanium dioxide can impart better modulus and tensile strength to thread samples both under the conventional and efficient vulcanization systems due to better rubber-filler interaction. The titanium dioxide pigment has no marked effect in retaining the physical properties under photooxidative ageing. Precipitated calcium carbonate and titanium dioxide combination is found better in retaining the physical properties of the thread in conventional vulcanization system against photo-oxidative ageing.

Table III.6a. Formulations for latex compounds (CV system)

Formulations	A	B	C	D	E
60% Centrifuged HA latex	167.0	167.0	167.0	167.0	167.0
10% Potassium hydroxide solution	2.0	2.0	2.0	2.0	2.0
50% Sulphur dispersion	3.6	3.6	3.6	3.6	3.6
50% ZDEC* dispersion	2.0	2.0	2.0	2.0	2.0
50% ZMBT* dispersion	1.0	1.0	1.0	1.0	1.0
50% Zinc oxide dispersion	1.0	1.0	1.0	1.0	1.0
33% Titanium dioxide dispersion	-	22.5	7.5	7.5	7.5
50% China clay dispersion	-	-	10.0	-	-
50% Precipitated $CaCO_3$ dispersion	-	-	-	10.0	-
50% Barytes dispersion	-	-	-	-	10.0

*ZDEC – zinc diethyl dithiocarbamate, ZMBT – zinc 2-mercaptobenzothiazole

Table III.6b Formulations for latex compounds (EV system)

Formulations	F	G	H	I	J
60% Centrifuged HA latex	167.0	167.0	167.0	167.0	167.0
10% Potassium hydroxide solution	2.0	2.0	2.0	2.0	2.0
50% Sulphur dispersion	0.5	0.5	0.5	0.5	0.5
50% ZDEC dispersion	1.0	1.0	1.0	1.0	1.0
50% TMTD* dispersion	4.0	4.0	4.0	4.0	4.0
50% Zinc oxide dispersion	1.0	1.0	1.0	1.0	1.0
20% Thiourea solution	3.5	3.5	3.5	3.5	3.5
33% Titanium dioxide dispersion	-	22.5	7.5	7.5	7.5
50% China clay dispersion	-	-	10.0	-	-
50% Precipitated $CaCO_3$ dispersion	-	-	-	10.0	-
50% Barytes dispersion	-	-	-	-	10.0

*TMTD – tetramethyl thiuram disulphide

Table III.7 Tensile properties of the latex thread before and after UV irradiation (CV system)

Formulations	Modulus 300% (MPa)				Tensile strength (MPa)			
	Un-exposed	UV-exposure time (h)			Un-exposed	UV-exposure time (h)		
		24	48	96		24	48	96
A	1.26	1.40	1.40	1.20	21	15	13	9
B	1.30	1.10	1.10	1.00	23	14	9	4
C	1.50	1.50	1.50	1.10	26	20	14	4
D	1.60	1.70	1.60	1.60	26	22	20	11
E	1.50	1.80	1.40	1.40	26	22	14	4

Table III.8 Tensile properties of the latex thread before and after UV irradiation (EV system)

Formu-lations	Modulus 300% (MPa)				Tensile strength (MPa)			
	Un-exposed	UV-exposure time (h)			Un-exposed	UV-exposure time (h)		
		24	48	96		24	48	96
F	1.20	1.00	0.85	0.80	18	12	10	8
G	1.25	1.10	0.86	0.75	22	14	9	7
H	1.50	1.43	1.10	0.95	25	19	14	8
I	1.40	1.20	1.12	0.84	24	17	13	8
J	1.40	1.40	0.86	0.81	24	18	14	8

Table III.9 Tensile properties of latex thread after 22 h heat aged at 100°C (CV system)

Formulations	Modulus 300% (MPa)		Tensile strength (MPa)	
	Original	Heat aged at 100°C for 22 h	Original	Heat aged at 100°C for 22 h
A	1.26	0.73	21	5.0
B	1.30	1.08	23	4.5
C	1.50	1.00	26	3.0
D	1.60	1.56	26	8.0
E	1.50	1.10	26	3.5

Table III.10 Tensile properties of latex thread after 22 h heat aged at 100°C (EV system)

Formulations	Modulus 300% (MPa)		Tensile strength (MPa)	
	Original	Heat aged at 100°C for 22 h	Original	Heat aged at 100°C for 22 h
F	1.20	1.50	18	16.0
G	1.25	1.60	22	14.5
H	1.50	1.30	25	8.0
I	1.40	1.80	24	16.0
J	1.40	1.30	24	10.0

Table III.11 Changes in V_r values after ammonia modified swelling and UV irradiation

Formulations	V_r original (Vr_o)	V_r after ammonia modified (Vr_a)	Difference in V_r values (Vr_o-Vr_a)	V_r values after 96 h UV irradiation
A	0.1860	0.1823	0.0037	0.1768
B	0.1873	0.1794	0.0079	0.1712
C	0.1911	0.1757	0.0154	0.1693
D	0.1919	0.1722	0.0197	0.1800
E	0.1894	0.1722	0.0172	0.1709
F	0.1626	0.1617	0.0009	0.1544
G	0.1723	0.1591	0.0132	0.1582
H	0.1879	0.1652	0.0227	0.1716
I	0.1811	0.1685	0.0126	0.1668
J	0.1791	0.1687	0.0104	0.1641

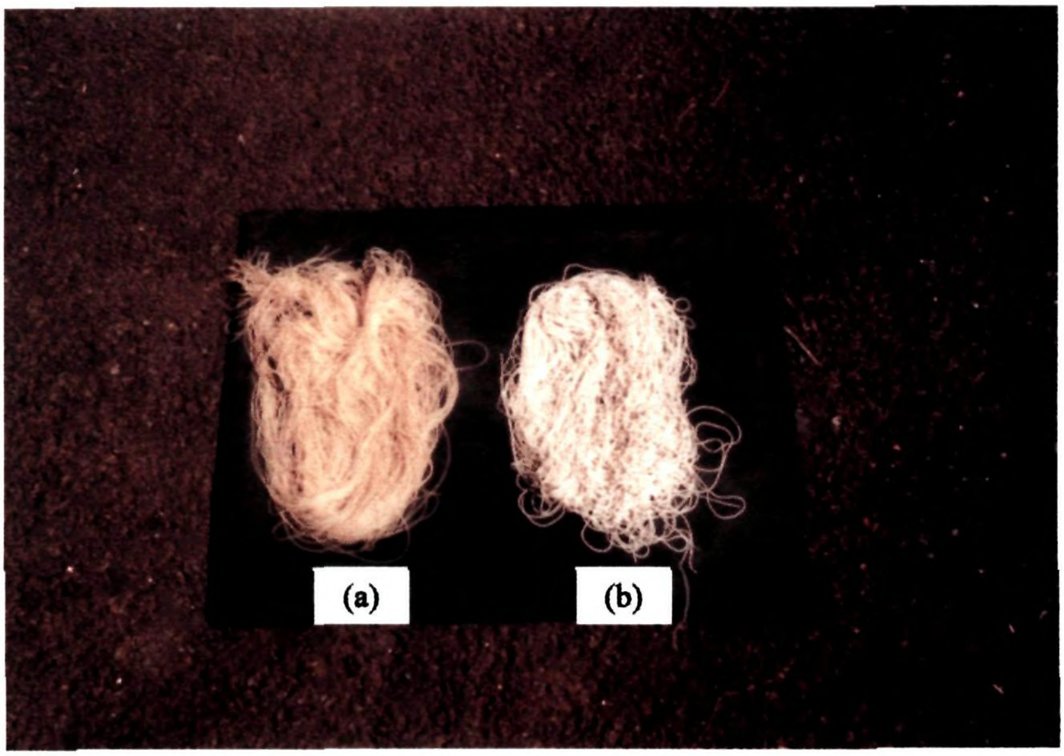

Fig. III.3. Photograph showing the appearance of threads with and without TiO_2 pigment

(a) without TiO_2 pigment

(b) with TiO_2 pigment

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CHAPTER IV

STUDIES ON BLENDS OF NATURAL RUBBER LATEX WITH MODIFIED NATURAL RUBBER AND SYNTHETIC RUBBER LATICES WITH SPECIAL REFERENCE TO DEGRADATION UNDER UV-RADIATION

Normally natural rubber (NR) is blended with modified rubbers and synthetic polymers in order to modify its technological properties[1,2] A lot of studies are reported on the blending of rubber at the dry stage.[3-5] The blending of polymers at the latex stage is much convenient than the blending at the dry stage. The latex stage blending offers the possibility of finer scale dispersion of the components in the blends.[6,7] Some studies have been reported on the blends of natural rubber latex with synthetic rubber latices.[8-10] Iino and coworkers[11] compared properties of latex and mill mixed blends of carboxylated styrene butadiene rubber (XSBR) and vinyl pyridine styrene butadiene rubber (PSBR). Latex blending was found to be better than mill mixing for achieving interactions between these acidic and basic rubbers. A few studies are also reported on the blending of natural rubber latex with modified rubber latices.[12-14] Cockbain et al.[15] studied the film forming properties of graft copolymer latices of methyl methacrylate and natural rubber prepared using gamma radiation. Blending of two or more polymers can also enhance degradation resistance. But only a few studies have been reported on the effect of blending natural rubber latex with modified NR latex and synthetic latices to achieve resistance against various degrading agencies.[16] This chapter of the thesis contains the results of the studies on blends of 60% centrifuged natural rubber (NR) latex with modified natural rubber latices such as methyl methacrylate grafted natural rubber latex (PMMA-g-NR), styrene grafted natural rubber latex (styrene-g-NR) and epoxidised natural rubber latex (ENR) and various synthetic rubber latices like carboxylated styrene butadiene rubber latex (XSBR), acrylonitrile butadiene rubber latex (NBR) with reference to the degradation resistance of the blended vulcanizates against UV-light and heat.

Centrifuged high ammonia type 60% natural rubber latex conforming to BIS 5430-1981 was used in this study. Styrene grafted natural rubber (styrene-g-NR) having 50% total styrene content was prepared by mixing styrene emulsion with centrifuged natural rubber latex and irradiating the blend using γ radiation.[17] Similarly methyl methacrylate grafted natural rubber latex (PMMA-g-NR) having 50% methyl methacrylate (MMA) content was also prepared.[18] Epoxidised natural rubber latex having 50 mole% epoxidation level and 20% total solid content (ENR-50) was prepared in the laboratory by *in situ* epoxidation of natural rubber latex using performic acid formed by the reaction between hydrogen peroxide and formic acid.[19]

Infrared characterisation studies were carried out on the modified NR samples and given in Figure IV.1. The graft copolymer purified by solvent extraction was used in each case for taking the IR spectrum. The graft copolymer, pure NR and ENR were dissolved in toluene and cast into a film on a sodium chloride cell. Then the FTIR spectrum was taken in the frequency range of 4000-400 cm^{-1}.

Synthetic rubber latices like carboxylated styrene butadiene rubber latex (XSBR) having 50% total solid content was obtained from Apar Ltd., Gujarat, India. Acrylonitrile butadiene rubber latex (NBR), having total solid content 41% was obtained from Bayer AG, West Germany.

The other compounding ingredients were of commercial grade obtained locally.

Latex blends were prepared as per the formulations given in Table IV.1. The NR latex was first stabilised using 10% KOH solution and 10% potassium laurate solution. Then different modified NR and synthetic rubber latices were blended with NR latex in dry weight ratio of 25:75 (NR = 75 parts). The other compounding ingredients were added as fine dispersions. The blended compounds were matured at 30°C overnight and sieved through a 100 mesh sieve cloth. The compounds were then cast into films having a thickness of 0.3 mm on glass plates. The cast films were then dried at 70°C and vulcanized in boiling water for optimum cure.

The dumbbell test pieces cut from each sample were tested for their tensile properties as per ASTM D412 using Instron D4411 universal testing machine. Another set of dumbbell pieces were exposed to UV-radiation from a UV-source (Philips TLD-30W-Holland) for 24, 48 and 96 h. The tensile properties of the dumbbell pieces after exposure to UV-light were then determined. The dumbbell test pieces were also subjected to heat ageing at 100°C for 22 h in a multicellular ageing oven and tensile properties were determined. The combined effect of UV-light and heat was also measured by testing tensile properties of the dumbbell pieces after 24 h UV irradiation and ageing at 100°C for 22 h. The results obtained are given in Tables IV.2 to IV.4.

IV.1 RESULTS AND DISCUSSION

Characterisation of the Modified Rubbers by Infrared Studies

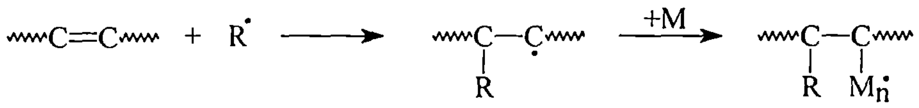
Fig.IV.1a shows the FTIR spectrum of NR. The absorption peak obtained at 837 cm^{-1} corresponds to C-H stretching of C=CH in NR. Also the peaks at 887,1375and 1456 cm^{-1} were due to the aliphatic C-H stretching in NR.

Fig IV.1b shows the characteristic FTIR spectrum of 50 mol% ENR. Epoxidation leads to oxirane ring absorption at 870 cm^{-1}. Ring opened products lead to additional absorptions at 1051 cm^{-1} due to furan ring and 1713 cm^{-1} due to carboxyl group of formate ester and a broad band at 3600-3200 cm^{-1}due to hydroxyl groups associated with the furan ring block or the diols. The other characteristic absorption peaks of NR are also obtained.

Figure IV.1c indicates the FTIR spectrum of styrene-g-NR, (after removing free NR and free polystyrene). Peaks at 2870 and 3026cm^{-1} corresponds to aromatic C-H stretching in polystyrene. Peaks at 1601 and 1541 cm^{-1} corresponds to C=C stretching of aromatic ring of polystyrene. A strong peak at 698 cm^{-1} stands for the mono substituted benzene ring along with characteristic absorptions of NR.

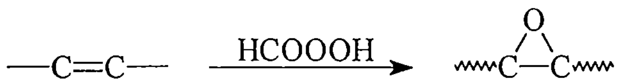
Figure IV.1d gives the absorption peaks for PMMA-g-NR. (After removing free NR and free PMMA). The FTIR spectrum of graft copolymer shows intense absorption at 1736 cm^{-1} which represents the =C=0 stretching in methyl methacrylate. The peak at 1377cm^{-1} represents the C-H stretching in methyl methacrylate along with other characteristic absorption of NR.

Table IV.2 shows the tensile strength, modulus and elongation at break values of the vulcanizates of NR/modified NR latex blends. The tensile strength increases on blending grafted NR latices like PMMA-g-NR and styrene-g-NR with NR latex. The NR/styrene-g-NR latex blend has higher tensile strength than NR/PMMA-g-NR latex blend. The modulus values also increase on blending these grafted latices with NR latex. But the modulus improvement is higher for NR/PMMA-g-NR latex blend. These variations can be mainly attributed to the bulkiness or bigger size of styrene-g-NR latex particles than PMMA-g-NR latex particles. These both grafted latices act like reinforcing fillers.[20] They form rigid spheres which occupy the NR latex particle interstitial voids so that increased tensile strength, modulus (300% and 500%) and decreased elongation at break are obtained. The structure of graft copolymers is given under.



$$\sim\!C{=}C\!\sim \; + \; R^{\bullet} \longrightarrow \sim\!\underset{R}{\underset{|}{C}}{-}\overset{\bullet}{C}\!\sim \xrightarrow{+M} \sim\!\underset{R}{\underset{|}{C}}{-}\underset{M_n^{\bullet}}{\underset{|}{C}}\!\sim \qquad IV(1)$$

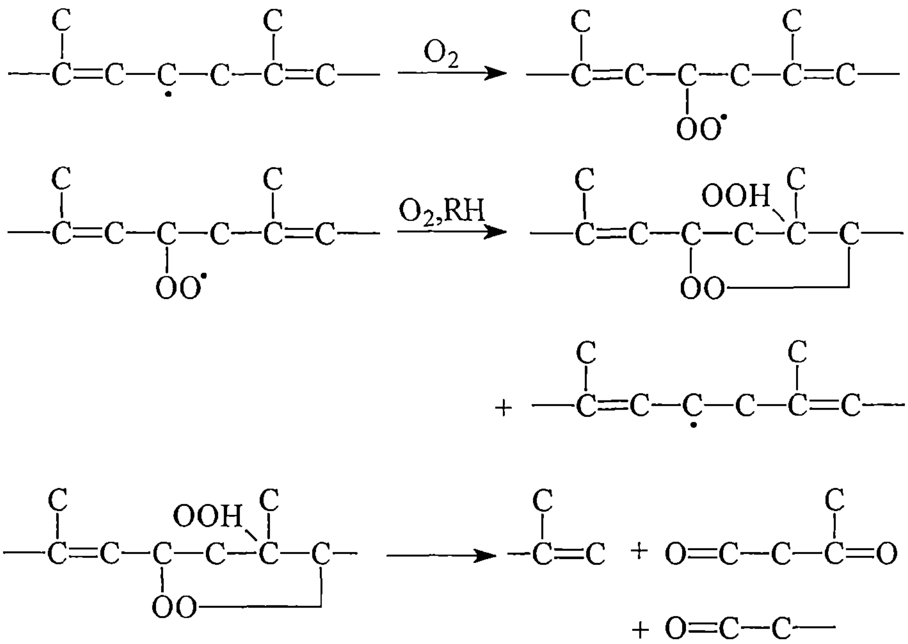
In Table IV.2 when we examine the technological properties of NR/epoxidised natural rubber (ENR) latex blend, no increase in tensile strength is observed. But the modulus (at 300% and 500% elongation) values are showing considerable increment compared to those of NR latex vulcanizates. This shows better crosslink formation in NR/ENR latex blends. From Table IV.2, it is clear that the elongation at break (%) is also lower for NR/ENR latex blend than the NR sample. Even though ENR latex is having polar functional groups it can have better interaction with the natural rubber hydrocarbon (cis-1,4-polyisoprene) chains compared with other polar latices of nitrile and carboxylated SBR.[21] This may also account for the enhanced technological properties of the NR/ENR latex blend. The structure of ENR is given below.[21]



$$—C{=}C— \xrightarrow{HCOOOH} \sim\!C\overset{O}{—}C\!\sim$$

IV(2)

When *the resistance to photo oxidative ageing of natural rubber* latex vulcanizates is considered, it is clear from Table IV.2 that the tensile properties are getting considerably decreased after 96 h UV-light exposure. This is due to the chain breakage caused in NR hydrocarbon by the high energy UV-radiation. Free radicals are produced in rubber on interaction with UV-radiation. These free radicals abstract H-atom from polyisoprene chains, thereby producing more free radical sites at the chain. These alkyl free radicals react with oxygen in atmospheric air to produce hydroperoxides. These free radical chain reaction continues until the entire rubber get degraded.[22] The mechanism of oxidative degradation in unsaturated polymers is shown under.



Scheme IV.1

The tensile properties of the NR/modified NR blends after UV-exposure are given in Table IV.2. After long term UV-irradiation all the technological properties are showing a decreasing trend. Between the two grafted NR latex blends, NR/styrene-g-NR latex blend shows good tensile properties after long term (96 h) UV-irradiation than NR/PMMA-g-NR latex blends. It has been reported earlier that in methyl methacrylate grafted natural rubber latex, phase separation occurs readily.[20] So the film formed from the blends of NR and PMMA-g-NR latex is not coherent or uniform. The retention of tensile properties after 96 h UV-irradiation for the NR/styrene-g-NR blends is quite better than that of NR/PMMA-g-NR blends. There is less tendency of phase separation in styrene-g-NR vulcanizates than PMMA-g-NR ones. The film formed from styrene-g-NR is more uniform and coherent than the methyl methacrylate grafted NR latex.[20] Also there is the possibility of electron rearrangement in styrene ring of polystyrene part grafted to polyisoprene chain. Electron delocalisation is far easy in styrene ring at excited energy states. This type of resonance stabilised electron delocalisation as in aromatic ring systems is not possible in methyl methacrylate part attached to NR.[23] So this may be the reason for better performance of NR/styrene-g-NR blends under high energy UV-radiation. The styrene part which is having higher molecular weight than methyl methacrylate molecule, requires more energy to produce styrene radicals. This is also a favourable factor for NR/styrene-g-NR blends against photo oxidative ageing.

From Table IV.2 it is observed that NR/ENR blend shows the best retention of tensile properties after long term UV-exposure among the NR/modified NR blends. In epoxidised natural rubber (ENR-50) used here, about half of the unsaturated positions are converted to oxirane ring systems (epoxide groups).[24] This reduced the available sites of free radical attack. Also epoxidised natural rubber shows better resistance to air permeability[25] which avoids the inner NR hydrocarbon chains to come in contact with oxygen during UV-exposure. This may also contribute for the better resistance to chain breakage in these blends. ENR does not prevent the strain induced crystallisation behaviour of NR, so that no decrease in tensile properties on blending is expected.

Table IV.3 illustrates the tensile properties of the NR/synthetic rubber blends. The synthetic rubbers used for blending are carboxylated SBR (XSBR) and acrylonitrile-butadiene rubber (NBR) latex. The tensile strength values are decreased by blending with these synthetic rubbers. These synthetic rubbers lack strain induced crystallisation. So their tensile strength is lower than that of NR.[26,27] The same factor might have caused the reduction in tensile properties of the blends. The modulus values of the NR/XSBR blend is higher than that of the NR sample. This may be attributed to the higher stiffness of the XSBR film.

From Table IV.3, it is observed that after long term UV-irradiation the tensile properties of both the NR/SR blends are drastically decreased. Between the two, NR/NBR latex blend showed better retention in tensile properties than NR/XSBR latex blend. This shows the higher activity of acrylonitrile part which has the chromophoric –C≡N group to absorb high energy UV-radiation and dissipate it as heat energy. The –C≡N group gives better polarity compared to XSBR.[28] From this experiment it is proved that NR/XSBR blend has poor resistance to photooxidative ageing than NR/NBR blend.

Table IV.4 gives the tensile properties of different NR/modified NR and NR/synthetic rubber blends after heat ageing at 100°C for 22 h. It also illustrates the combined effect on tensile properties after 24 h UV-irradiation and heat ageing at 100°C for 22 h. From the results it is clear that among the grafted latex blends with NR, styrene-g-NR and NR latex blend shows better properties after heat ageing than PMMA-g-NR latex blend with natural rubber latex. This follows the same pattern as in the case of light ageing. The modulus values are also drastically reduced after combined light and heat ageing.

The NR/ENR blend showed the maximum retention of tensile strength after heat ageing at 100°C for 22 h. This also supports the higher resistance to chain breakage of NR/ENR blends under thermo oxidative conditions. But when the combined effect of UV-light and heat ageing is considered, NR/ENR blend has undergone more degradation giving lower tensile properties.

Between the two NR/synthetic rubber blends, the blend of NR/XSBR showed the better properties after thermal ageing than NR/NBR blend. Both of these NR/SR blends showed drastic reduction in tensile properties after thermal ageing. There is only slight difference between these two after combined ageing under UV-light and heat indicating that thermal ageing is more severe than the photooxidative UV-light ageing.

From these results it is clear that natural rubber latex blends with modified natural rubber latices show high modulus and high tensile strength with good ageing resistance. The NR latex blend with synthetic rubber latex showed inferior tensile properties and more prone to degradation under UV-light and heat.

From the investigations it can be concluded that the effect of blending of latices on physical properties and degradation of latex film under UV-light and heat depends on the type of modified/synthetic rubber latex used. The blends of NR latex with modified NR latices (grafted and epoxidised) gives better physical properties and resistance to degradation under UV-light and heat. Styrene-g-NR and PMMA-g-NR latex blends with NR latex showed better improvement in physical properties than NR/ENR latex blend. But blend of ENR latex with NR shows the maximum resistance to UV-light and heat degradation among the modified latex blends except when the combined effect of UV-light and heat was considered. The synthetic rubber latices such as XSBR and NBR latex are not showing enhancement in properties. These NR/synthetic rubber latex blends are less powerful than NR/modified NR latex blends to offer resistance to deterioration under UV-light and heat. NBR latex blends with NR latex is better than NR/XSBR latex blend when long term exposure to UV-radiation is considered.

Table IV.1 Formulation for latex compounds

Formulations	B_1	B_2	B_3	B_4	B_5	B_6
60% Centrifuged NR latex	167	125.25	125.25	125.25	125.25	125.25
50% PMMA-g-NR latex	-	50	-	-	-	-
50% Styrene-g-NR latex	-	-	50	-	-	-
20% Epoxidised NR (ENR-50) latex	-	-	-	125	-	-
50% Carboxylated SBR latex	-	-	-	-	50	-
41% Acrylonitrile butadiene rubber latex	-	-	-	-	-	61
10% KOH solution	3	3	3	3	3	3
10% Potassium laurate solution	0.5	0.5	0.5	0.5	0.5	0.5
50% sulphur dispersion	3.6	3.6	3.6	3.6	3.6	3.6
50% ZDEC dispersion	2	2	2	2	2	2
50% ZMBT dispersion	1	1	1	1	1	1
50% ZnO dispersion	1	1	1	1	1	1

Table IV.2. Effect of UV-irradiation on the physical properties of blends of NR and modified NR latex (vulcanizates)

Formulation	B_1				B_2				B_3				B_4			
UV-exposure time (h)	0	24	48	96	0	24	48	96	0	24	48	96	0	24	48	96
Modulus (300%) (MPa)	2.19	2.29	2.15	2.05	3.6	3.5	2.9	1.9	2.90	2.8	2.8	2.7	2.7	2.4	2.3	2.2
Modulus (500%) (MPa)	3.96	4.37	4.06	3.95	9.7	9.4	7.5	4.6	7.2	7.1	7.0	6.2	6.7	5.2	5.5	5.0
Tensile strength (MPa)	28.90	28	27.5	14.1	37.6	36.0	27.4	11.5	39.6	31.9	24.1	17.8	28.5	24.4	23	22.4
Elongation at break (%)	944	924	922	757	861	853	844	732	871	849	776	747	774	769	756	773

Table IV.3 Effect of UV-irradiation on the physical properties of NR latex blends with synthetic latex (vulcanizates)

Formulation	B_5				B_6			
UV-exposure time (h)	0	24	48	96	0	24	48	96
Modulus (300%) (MPa)	3.18	3.06	3.09	2.3	2.09	2.42	2.25	2.57
Modulus (500%) (MPa)	7.47	7.05	7.1	5.1	5.45	5.00	5.03	5.06
Tensile strength (MPa)	25.6	23.1	12.9	6.64	23.4	23.0	22.2	15.0
Elongation at break (%)	804	791	634	550	933	873	803	718

Table IV.4 Effects of heat ageing on the physical properties of latex vulcanizates (Blends)

Properties	B_1			B_2			B_3			B_4			B_5			B_6		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
Modulus (300%) (MPa)	2.19	1.1	1.0	3.6	1.74	1.16	2.9	1.6	1.4	2.7	1.2	0.94	3.18	1.8	1.5	2.09	1.6	1.4
Modulus (500%) (MPa)	3.96	2.0	2.0	9.7	4.1	2.6	7.2	3.2	3.0	6.7	2.5	-	7.47	3.9	2.8	5.45	2.7	-
Tensile strength (MPa)	28.90	4.2	2.6	37.6	5.0	3.1	39.6	11.5	4.2	28.5	13.1	1.3	25.6	5.9	2.5	23.4	3.8	3.0
Elongation at break (%)	944	724	540	861	547	509	871	867	604	774	663	363	804	563	428	933	464	370

(a) Original; (b) Heat aged at 100°C for 22 h; (c) 24 h UV-light exposed and heat aged at 100°C for 22 h

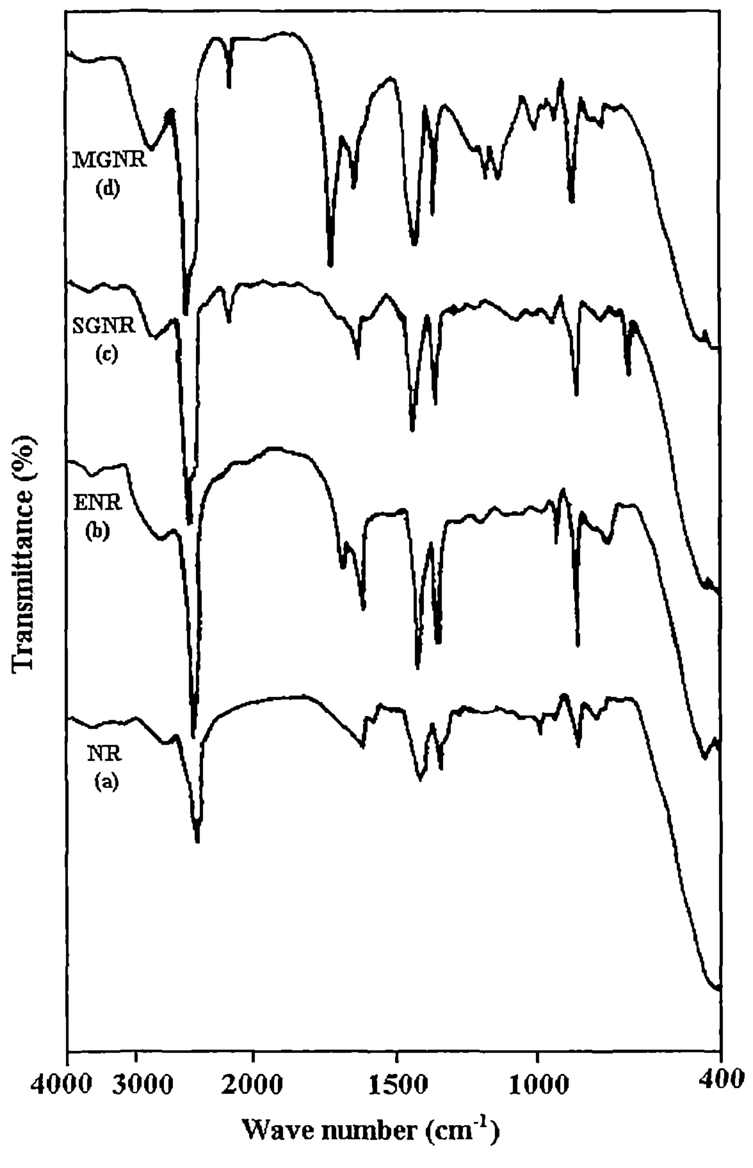


Figure IV.1 FTIR Spectrum of NR and modified NR

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CHAPTER V

STUDIES ON DEGRADATION RESISTANCE OF RADIATION VULCANIZED NATURAL RUBBER LATEX FILMS

PART I. Effect of Antioxidants and their Combinations on the Physical Properties of Radiation Vulcanized Natural Rubber Latex Films Under UV-Radiation

PART II. Effect of Non-Black Fillers and Pigments on the Physical Properties of Radiation Vulcanized Natural Rubber Latex Films Under UV-Radiation

PART I

Effect of Antioxidants and their Combinations on the Physical Properties of Radiation Vulcanized Natural Rubber Latex Films Under UV-Radiation

The natural rubber latex products made using sulphur vulcanization are increasingly substituted now-a-days by radiation vulcanized natural rubber latex (RVNRL) products. The sulphur and accelerators at the time of curing produces nitrosoamines which are extremely poisonous and causes hazard to health.[1-3] Inorder to reduce nitrosoamine level radiation vulcanized natural rubber latex is used in which vulcanization is effected using high energy γ-radiation. Radiation vulcanized natural rubber latex (RVNRL) products have been shown to have the following advantages over conventional sulphur vulcanized natural rubber latex (SVNRL) products. The absence of carcinogenic nitrosoamines, low cytotoxicity, transparency and softness. These properties are mainly due to the absence of residual sulphur, zinc oxide and dithiocarbamates that occur in conventional SVNRL. The RVNRL products are now widely used for making dipped goods like gloves, balloons, catheters etc. The need to protect latex films from degradation is very crucial. Films obtained from radiation vulcanized natural rubber latex (RVNRL) had poor ageing characteristics especially after it has been subjected to leaching.[4,5] This may be due to the elution of naturally occurring antioxidants during the leaching process. Recently much progress has been made to improve the physical and mechanical properties of RVNRL, especially the tensile strength, through proper selection of latex, use of new sensitisers and improved formulations etc[6].

Unfortunately little work had been done to improve poor ageing characteristics of RVNRL obtained in those studies.

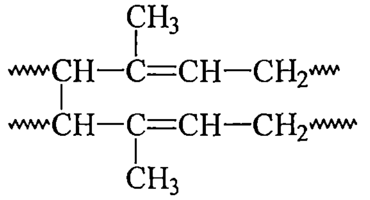
This chapter contains the results of the investigation on some antioxidants and their combinations with the objective to improve the degradation resistance of RVNRL against UV-light and heat.

Specially stabilized 60% centrifuged high ammonia type natural rubber latex conforming to BIS 5430-1981 was used for the preparation of radiation prevulcanized natural rubber latex (RVNRL). The radiation sensitiser, n-butyl acrylate (n-BA), 5 phr, was added to the stabilised NR latex while stirring. Stirring was continued for 1hour and the mixture was then irradiated with Co-60 γ radiation at a total dose of 1.5 Mrad. The irradiation was conducted at a constant does rate of 0.1 Mrad/h at room temperature. After irradiation the latex was kept at room temperature, tightly covered, to prevent loss of volatile materials such as ammonia.

Latex compounds were prepared according to the formulations given in Table V.1 and the antioxidants used in these experiments were Crystol EPR 3400, Wingstay-L and antioxidant HS which were of commercial grade. They were added as dispersions or emulsions. The antioxidants were added into the radiation vulcanized latex at concentrations up to 2 phr and stirred for 1h to ensure that they mixed well. Test samples were prepared by casting the latex on glass cells and dried at 70^0C in a hot air oven until the films became clear. The films were then subjected to leaching in water at 70^0C for 15 minutes and dried at 70^0C until the films became clear again. The experimental dumbbell test pieces were cut from each film sample and exposed to UV-radiation from a UV-source (PHILIPS TLD 30w-HOLLAND). The exposure was continued for durations 24, 48 and 96h. The film test pieces were also heat aged at 100^0C for 22h. The combined effect of UV-light and heat were investigated by heat ageing the samples at 100^0C for 22h after 24h UV-irradiation. Then the tensile properties of the test pieces were determined using an Instron D 4411 universal testing machine. The results are given in Tables V.2 to V.4. The swell index values of the unaged and aged film samples were measured as described in section II.8.2 of Chapter II and given in Table V.5.

V.1 RESULTS AND DISCUSSION

The tensile properties of the RVNRL films are comparable to that of sulphur vulcanized natural rubber latex (SVNRL) film as obtained from Table V.2 (see Table VI.5 of Chapter VI also). RVNRL films are less cytotoxic than sulphur vulcanized NR latex films. So it is clear that RVNRL can be used similar to SVNR latex for product manufacture. In Table V.2, when we examine the UV-light ageing properties of RVNRL films, it is clear that RVNRL films have considerable resistance to photo oxidative ageing. After 96h UV-light exposure, the tensile strength, modulus and elongation at break shows good retention when compared to original values. The structure of RVNRL can be represented as.[6]



Scheme V.1

In this structure carbon-carbon (C-C) single covalent bonds are formed at allylic position to the double bonds in adjacent rubber hydrocarbon chains. When RVNRL films are exposed to UV-radiation, at initial stages, due to the presence of some trapped free radicals and the residual grafted sensitizer poly n-BA some crosslinking takes place, but on prolonged exposure, chain scission reactions outweigh crosslinking reactions. From Table V.2, it is seen that even after long term UV-exposure RVNRL films show very small decrease in tensile strength, indicating the good light stability of C-C crosslinks.

In Table V.2 the tensile properties of RVNRL films with 2 phr of various antioxidants before and after exposure to UV-radiation are given. The results indicate that even in the absence of any antioxidant, there is not much drop in tensile properties and the RVNRL film exhibits good retention of tensile properties against photo oxidative ageing. The phosphite type antioxidant Crystol EPR 3400 and phenolic type antioxidant Wingstay L and their combination provide good light stability to RVNRL.

Table V.3, contains the tensile strength, modulus (at 300% and 500%) and elongation at break (%) values of RVNRL films with three combinations of antioxidants. All these combinations especially, Crystol EPR 3400 + antioxidant HS and Wingstay -L + antioxidant HS in RVNRL films give good retention of tensile properties after long term UV-irradiation. Antioxidant HS which is an amine type antioxidant (a staining type antioxidant), with Crystol EPR 3400 (compound R_5) gave maximum tensile strength values for RVNRL films after long term UV-irradiation. This may due to a synergistic effect of phosphite type and amine type antioxidant against UV light. The swell index values of the UV-exposed RVNRL film samples given in Table V.5 are not showing considerable difference from those of original ones, indicating the good photo oxidative ageing resistance of RVNRL films.

The physical properties given in Table V.4, indicate that RVNRL films without added antioxidants show very poor properties after heat ageing at 100^{0}C for 22h. It is reported earlier that the poor ageing properties of RVNRL films may be due to the loss of natural antioxidants during leaching and also due to the absence of dithiocarbamate accelerators, which are also powerful antioxidants. From Table V.4, it is clear that all the antioxidants and their combinations showed better retention of tensile properties of RVNRL films after heat ageing. Among the various antioxidants the substituted phenolic type antioxidant Wingstay-L has shown the maximum tensile strength (compound R_3) after heat ageing. The combination of antioxidants Wingstay-L + Crystol EPR 3400 (compound R_4) has shown the least retention in tensile properties on heat ageing of RVNRL films. This may be due to the absence of any synergetic effect in this antioxidant combination. Modulus and elongation at break percentage are also retained well in the presence of antioxidants on ageing. The higher swell index value given in Table V.5 indicates that chain breakage is more in the case of RVNRL films without any antioxidant, after heat ageing.

The degradation process in rubber products when exposed to UV-light, heat etc. follows an oxidative free radical chain reaction mechanism, so that extensive chain scission occurs and lowering of physical properties of rubber vulcanizate resulted.[7]

The antioxidant if present in rubber matrix, check this degradation by either combining with these free radicals or decomposing the hydroperoxide radicals to harmless products.

Thus the above results indicate the necessity of suitable antioxidants or their combinations in RVNRL products for thermal oxidation stability.

From Table V.4, again we can observe that the tensile properties of the RVNRL films without any antioxidants were very much badly decreased after 24h UV-irradiation and heat ageing at 100^{0}C for 22h. This indicates RVNRL products without any antioxidant are not suitable for any outdoor application. The antioxidant Wingstay-L again showed maximum tensile strength (compound R_3) after combined light and heat ageing. The other antioxidants Crystol EPR 3400, and the combinations Crystol EPR 3400 + Wingstay L, Wingstay L+ antioxidant HS, and Crystol EPR 3400 + Wingstay L + antioxidant HS have shown good performance. But the combination Crystol EPR 3400 + antioxidant HS (compound R_5) has been badly affected after combined UV-light and heat ageing. Tensile strength has decreased drastically. This may be due to the fact that, in certain combinations, one antioxidant may hinder the reaction of other one because of the peculiar and very dissimilar chemical nature of individual antioxidants. Thus from the above experiments again the necessity for selection of suitable antioxidants either singly or in certain of their combinations in RVNRL products for getting good service life was made clear.

From the investigations it can be concluded that radiation prevulcanized natural rubber latex films are possessing comparable tensile properties as that of sulphur vulcanizates of NR latex. The photo oxidative ageing properties of RVNRL films without any antioxidant is better than that of gum sulphur vulcanizates, but heat ageing and combined UV-light and heat ageing properties of RVNRL films are very much lower. So inorder to get good heat ageing properties, antioxidants are necessary in RVNRL products. The antioxidants Wingstay-L and Crystol EPR 3400 are very good in retaining the tensile properties of aged RVNRL films. The antioxidants exhibited good action when they are used singly, than in certain of their combinations.

Table V.1. Formulations of latex compounds

Formulations	R_1	R_2	R_3	R_4	R_5	R_6	R_7
60% RVNR latex	167	167	167	167	167	167	167
50% Crystol EPR 3400 emulsion	-	4	-	2	3	-	2
50% Wingstay-L dispersion	-	-	4	2	-	3	1
50% Antioxidant HS dispersion	-	-	-	-	1	1	1

Table V.2. Tensile properties of the RVNRL films before and after UV exposure

Formulations	R_1				R_2				R_3				R_4			
UV-irradiation time(h)	0	24	48	96	0	24	48	96	0	24	48	96	0	24	48	96
Modulus (300%) (MPa)	1.48	1.49	1.49	1.51	1.12	1.14	1.18	1.18	1.28	1.29	1.3	1.29	1.46	1.38	1.40	1.40
Modulus (500%) (MPa)	2.4	2.34	2.41	2.40	1.72	1.74	1.76	1.77	2.1	2.0	2.2	2.16	2.7	2.5	2.5	2.6
Tensile strength (MPa)	26.1	26.0	25.8	25.1	25.5	25.4	25.1	25.0	26.1	25.8	25.6	25.5	25.8	25.4	25.1	25
Elongation at break (E.B) (%)	1150	1129	1115	1107	1170	1160	1145	1128	1155	1135	1124	1107	1065	1056	1049	1014

Table V.3. Tensile properties of the RVNRL films before and after UV exposure

Formulations	R_5				R_6				R_7			
UV-irradiation time (h)	0	24	48	96	0	24	48	96	0	24	48	96
Modulus (300%) (MPa)	1.41	1.50	1.44	1.43	1.33	1.31	1.34	1.30	1.31	1.30	1.26	1.29
Modulus (500%) (MPa)	2.5	2.6	2.7	2.5	2.5	2.52	2.61	2.60	2.2	2.2	2.1	1.95
Tensile strength (MPa)	28.2	27.6	27.1	26.8	26.2	25.7	25.1	25	25.4	25.2	25.1	24.9
Elongation at break (EB) (%)	1094	1077	1045	1040	1091	1081	1050	1043	1101	1079	1058	1026

Table V.4. Tensile properties of the RVNRL films after UV irradiation and heat ageing

Formulations	R_1			R_2			R_3			R_4			R_5			R_6			R_7		
Properties	**(a)**	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**
M_{300} (MPa)	1.48	1.06	0.79	1.12	1.12	1.14	1.28	1.2	1.2	1.46	1.1	1.06	1.41	1.3	1.06	1.33	1.21	1.2	1.31	1.2	1.1
M_{500} (MPa)	2.4	1.79	1.4	1.72	1.71	1.74	2.1	2	1.9	2.7	1.9	1.8	2.5	2.3	1.9	2.5	1.95	1.9	2.2	2.0	2.0
T.S (MPa)	26.1	10.2	2.9	25.3	23	21.0	26.1	25	24.5	25.8	15.3	14.6	28.2	23.8	7.8	26.2	21.7	20.2	25.4	23.3	18.4
EB(%)	1150	957	661	1170	1150	1140	1155	1130	1120	1065	1050	1030	1094	1049	830	1091	1080	1020	1101	1060	1000

(a) = original, (b) = 100^0C/22h, heat aged, (c) = 24h UV exposed and heat aged at 100^0C/22h.

Table V.5. Swell Index values of RVNRL film samples (weight in gms. of benzene absorbed per gram of sample after 48 h swelling)

Formulations	Swell Index (original)	Swell Index (96h UV-exposed)	Swell Index (100^0C/22h heat aged)
R_1	5.1	5.1	6.5
R_2	5.6	5.5	5.8
R_3	5.3	5.25	5.6
R_4	5.1	5.2	6
R_5	5	5.0	5.6
R_6	5.1	5.0	5.7
R_7	5.2	5.3	5.5

PART II

Effect of Non-Black Fillers and Pigments on the Physical Properties of Radiation Vulcanized Natural Rubber Latex Films Under UV-Radiation

Radiation vulcanized natural rubber latex (RVNRL) products have been shown to have the following advantages over conventional sulphur vulcanized natural rubber latex (SVNRL) products. The absence of carcinogenic nitrosoamines, low cytotoxicity, low emission of sulphur dioxide on combustion, softness and transparency.[8,9,10] Radiation prevulcanized natural rubber latex is now widely used for making many dipped goods especially in medical field. These products have to withstand many severe conditions during their service life. Inorganic fillers and pigments are added to latex compounds inorder to stiffen the products, to cheapen it or to colour it. In dry rubber compounding, fillers generally act as reinforcing agents, but in latex compounding not much reinforcement is obtained by incorporating the filler.[11] Much studies have been done about the effect of fillers in sulphur vulcanized natural rubber latex products.[12] Lamm and Lamm[13] claimed that if the latex compounded with fillers is exposed to Cobalt-60 γ-rays, some degree of reinforcement can be obtained, but very little information is available about the effect of common pigments and fillers in radiation prevulcanized natural rubber latex products. The present work reports on the effect of titanium dioxide (pigment) and fillers like china clay and precipitated calcium carbonate on the physical properties of radiation prevulcanized natural rubber latex films with special reference to degradation under UV-radiation and heat.

Specially stabilised centrifuged high ammonia NR latex conforming to BIS 5430-1981 was radiation vulcanized by gamma rays from Co-60 source at a dose rate of 0.1 Mrad/h and total dose of 1.5 Mrad. 5 phr of n-butyl acrylate was added to the latex as a sensitiser. The titanium dioxide pigment (33%) and the fillers china clay (50%) and precipitated calcium carbonate (50%) were prepared as dispersions in water. These pigments and fillers were added into latex at 10 phr concentration as per formulation given in Table V.6 and stirred well to ensure that they mixed well. Test samples were prepared by casting the latex on glass plates. The film samples were then leached in hot water (70^0C) for 15 minutes and dried in hot air oven at 70^0C. Then dumbbell pieces cut from each set of film samples were tested for their tensile properties as per ASTM D412 using Instron D4411 universal testing machine. Another set of dumbbell pieces were exposed to UV-radiation from a UV-source (Philips TLD-30W-Holland) for 24,48 and 96h. The tensile properties of the dumbbell pieces after exposure to UV-light were then determined. The dumbbell test pieces were also subjected to heat ageing at 100^0C for 22 h in a multicellular ageing oven and tensile properties were determined. The combined effect of UV-light and heat was also measured by testing tensile properties of the dumbbell pieces after 24h UV-irradiation and ageing at 100^0C for 22h. The results obtained are given in Tables V.7 and V.8. To assess the extent of rubber-filler attachment in the filled vulcanizates, rubber-filler bonds were cleaved chemically by swelling the vulcanizate samples for 48h in flat dishes containing benzene in ammonia atmosphere. The result of changes in swell index values after ammonia modified swelling are given in Table V.9.

V.2 RESULTS AND DISCUSSION

The tensile properties of the unfilled and filled RVNRL film samples are given in Table V.7. The tensile strength of the RVNRL film samples are getting decreased on loading with titanium dioxide pigment and fillers china clay and precipitated calcium carbonate. The maximum decrease in tensile strength is observed on loading with titanium dioxide pigment. This indicated the poor rubber-filler interaction in filled RVNRL film samples. The swell index values of the filled RVNRL film samples after ammonia modified swelling given in Table V.9 support this. There is no considerable difference in swell index values after swelling over ammonia atmosphere. Unlike in dry rubber technology, the RVNR latex is not subjected to high shear forces after loading with fillers, so that less intimate contact between rubber particles and filler particles expected.[4] The coupling bonds produced between rubber and filler particles are negligible, so that on loading with fillers no reinforcement for radiation prevulcanized NR latex film samples are produced.

Again from Table V.7, it is clear that the tensile properties of unfilled RVNRL film samples are not much decreased after long term UV-irradiation. This indicates the better photo oxidative ageing resistance of virgin RVNRL film. In the case of filled RVNRL films, precipitated calcium carbonate filler gives the best retention of tensile strength after photo oxidative ageing. At initial stages, the modulus values increases but on prolonged exposure modulus and elongation at break (%) values are decreasing.

The effect of heat ageing on various unfilled and filled RVNRL film samples are given in Table V.8. It shows the very poor heat ageing properties of the unfilled RVNRL film samples. Some melting of RVNRL film samples are observed at high temperatures. On loading with titanium dioxide pigment and china clay good retention of tensile strength, modulus and elongation at break are obtained for RVNRL films after thermo oxidative ageing. This may be due to a shielding effect of these fillers by covering the inner NR hydrocarbon chains in RVNRL films against thermo oxidation. Precipitated calcium carbonate filled RVNRL films show very poor tensile properties after heat ageing. From Table V.8, the combined effect of UV-irradiation and heat aging on

RVNRL films are obtained. Again unfilled RVNRL films are showing poor tensile properties. Titanium dioxide and clay both giving good retention of tensile properties to RVNRL films after combined photo oxidative and thermo oxidative ageing. The precipitated calcium carbonate filler imparted a pro-oxidant effect in RVNRL films after combined UV-light and heat ageing, so that maximum decrease in tensile properties is observed. This may be due to the presence of some components in commercial grade precipitated calcium carbonate which favour the thermo oxidative process in RVNRL but not sensed by UV-radiation.

From the above investigations, it can be concluded that the radiation prevulcanized natural rubber latex (RVNRL) films loaded with titanium dioxide pigment, china clay and precipitated calcium carbonate fillers did not show any reinforcement effect of the fillers, due to poor rubber-filler interaction. The virgin, unfilled RVNRL films made using n-BA as sensitiser has shown better retention of tensile properties after long term UV-irradiation, but showed very poor physical properties after thermo oxidative ageing. The RVNRL films filled with titanium dioxide pigment and the filler china clay have shown significant retention of physical properties after thermo oxidative ageing, while the precipitated calcium carbonate filler loaded RVNRL films produced maximum deterioration of tensile properties after thermo oxidative ageing.

Table V.6. Formulations of latex compounds

Formulations	RF_1	RF_2	RF_3	RF_4
60% RVNR latex	167	167	167	167
33% Titanium dioxide dispersion	-	30	-	-
50% clay dispersion	-	-	20	-
50% precipitated calcium carbonate dispersion	-	-	-	20

Table V.7. Tensile properties of the RVNRL films before and after UV exposure

Properties	RF$_1$				RF$_2$				RF$_3$				RF$_4$			
UV-irradiation time (h)	0	24	48	96	0	24	48	96	0	24	48	96	0	24	48	96
M 300 (Mpa)	1.33	1.28	1.23	1.22	1.28	1.23	1.21	1.08	1.4	1.6	1.6	1.55	1.4	1.5	1.5	1.4
M 500 (Mpa)	2.9	2.4	2.2	2.1	2.5	2.0	1.8	1.5	3	3.2	3.4	3.3	2.8	2.8	2.7	2.6
T.S (MPa)	25.15	23.01	23.0	22.04	20	19.1	18.9	16.7	23.8	22.4	22.1	21	23.5	22.8	22.6	22.1
E.B (%)	1049	1039	1014	989	1020	1019	1008	1006	1081	1049	1013	994	1081	1046	1040	1035

Table V.8. Tensile properties of the RVNRL films after UV irradiation and heat ageing

Properties	RF$_1$			RF$_2$			RF$_3$			RF$_4$		
	(a)	(b)	(c)	(a)	(b	(c)	(a)	(b)	(c)	(a)	(b)	(c)
M 300 (MPa)	1.33	0.86	0.85	1.28	1.05	0.97	1.4	1.2	1.1	1.4	0.7	0.6
M500 (MPa)	2.9	1.4	1.4	2.5	1.95	1.7	2.8	2.2	2.1	2.8	1.05	1.03
T.S (MPa)	25.15	7.3	7.1	20	15.5	14	23.8	15.2	15	23.5	6	3.5
E.B (%)	1049	987	964	1020	1006	986	1089	998	987	1081	875	815

(a) = original, (b) = 100^{0}C/22h, heat aged, (c) = 24h UV exposed and heat aged at 100^{0}C/22h.

Table V.9. Swell Index values before and after NH_3 modification (Benzene in gms. absorbed per gram of sample)

Formulations	Swell Index (original)	Swell Index (After ammonia modification)
RF_1	5.12	5.09
RF_2	5.04	5.05
RF_3	4.9	5.1
RF_4	5.14	5.17

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CHAPTER VI

STUDIES ON THE EFFECT OF UV-STABILISERS IN NATURAL RUBBER LATEX VULCANIZATES

PART I. Effect of UV-Stabilisers on the Physical Properties of Natural Rubber Latex Vulcanizates

PART II. Effect of Combinations of UV-Stabiliser and Antioxidants on the Physical Properties of Natural Rubber Latex Vulcanizates

PART I

Effect of UV-Stabilisers on the Physical Properties of Natural Rubber Latex Vulcanizates

NR latex products are extensively used in out door applications. The important products from NR latex are various dipped goods like gloves, balloons, foam products, thread, adhesives, coatings etc. During their service life they have to meet several severe environmental conditions. The important degradative agencies on NR latex products are heat, light, oxygen, ozone, humidity, stress, γ-radiation, metals etc.[1] The NR latex products are UV-sterilised extensively in medical applications. Also UV-radiation in sunlight is causing much deterioration to the physical properties of natural rubber latex vulcanizates viz., tensile strength, modulus, elongation at break (%) etc. when they are in out-door applications. Much studies were done in the field of heat degradation of NR latex products and their various protection mechanism.[2-5] But no significant studies are done in the field of UV-stabilisation of NR latex products.

The NR latex vulcanizates can be given resistance to photo oxidative degradation by various techniques. The choice of suitable vulcanization system and accelerators, inclusion of various non black light absorbing and reflecting fillers, compounding with more photo resistable modified or synthetic polymers and applying special purpose UV-stabilisers[6] are some of such techniques. There are different types of UV-stabilisers like substituted benzophenones, benzotriazoles and hindered amine light stabilisers[7] (HALS). Their stabilisation mechanism and effectiveness in various polymers are different.[8] This work presents, the effect of above mentioned major three classes of UV-stabilisers on the physical properties of natural rubber latex vulcanizates and their mechanism of protection in these systems, under UV-radiation and heat.

Centrifuged high ammonia type 60% natural rubber latex conforming to BIS 5430-1981 was used in this study. The major three classes of UV-stabilisers viz., Lowilite 20 (2-hydroxy-4-methoxy benzophenone), Lowilite 55 [2-(2'-hydroxy-5' methyl phenyl)benzotriazole] and Lowilite 76 [Bis (1,2,2,6,6 pentamethyl-4-piperidinyl) sebacate] were used in this study. The structure and physical properties of these chemicals obtained from Great Lakes Chemicals, USA are given in Table VI.1. The first two of these chemicals were added as fine dispersions while the third one is a liquid which was added as 50% emulsion. The other compounding ingredients were of commercial grade and obtained locally.

Latex vulcanizates were prepared according to the formulations given in Table VI.2. The latex was first stabilised by adding potassium hydroxide and potassium laurate solutions. The other compounding ingredients were added as dispersions or emulsions. The compounds were then matured at 30^0C for overnight and sieved through a 100 mesh sieve. Then at 55% TSC, the Brook field viscosity was measured at 60 rpm using spindle no.2 in a Brookfield viscometer. Then the pH and MST (mechanical stability time) were measured. The results obtained are given in Tables VI.3 and VI.4, which indicates the raw processing characteristics of latex.

The compounds were then cast into films having a thickness of 0.3 mm on glass plates. The cast films were then dried at 70^0C and vulcanized in boiling water. The films with conventional cure system were vulcanized for 60 minutes and those with efficient cure systems were vulcanized for 90 min., and they were finally dried in an air oven at 60^0C.

The dumbbell test pieces taken from each sample were then exposed to UV-radiation from a UV-source (NEC FL 15 BL-30W-JAPAN) for 6, 12 and 24h. The effect of UV-light on the colour and tensile properties of the dumbbell pieces were then examined. The colour was graded visually and the tensile properties of the vulcanizates were determined according to ASTM D412-98 using an Instron D-4411 universal testing machine. The dumbbell tests pieces were also subjected to heat ageing at 100^0C for 22h in a multicellular ageing oven and colour and tensile properties were determined. The combined effect of UV-light and heat was also measured by testing tensile properties of the dumbbell pieces after 12h UV-irradiation and ageing at 100^0C for 22h. The results are given in Tables VI.5 to VI.8.

The film samples were tested for measuring the changes in crosslink density by the method described in section II.8.2 of Chapter II. The results are given in Table VI.9. The morphological characteristics of these films with and without UV-stabilisers before and after UV-irradiation were examined using optical microscope (Leica Wild) and Scanning Electron Microscope (JEOL) and given in Figures VI.1 to VI.3.

VI.1 RESULTS AND DISCUSSION

The latex stage quality parameters viz., pH, MST and viscosity of the compounded NR latex with and without UV-stabilisers after 24h maturation are given in Tables VI.3 and VI.4. The values are not showing any detrimental effects on latex with the addition of these UV-stabilisers. This indicated that these three classes of UV-stabilisers or UV-protectants can be applied in NR latex formulations without any harmful effect on processing safety and physical stability of vulcanizates.

Table VI.5 gives the tensile values viz., tensile strength, modulus, elongation at break and colour properties of the gum vulcanizates and after addition of UV-stabilisers in conventional cure system before and after exposure to UV-radiation for 6,12 and 24h. The values indicate that the tensile strength, modulus and E.B decreased considerably after 24h UV-irradiation for gum vulcanizates. Better retention of tensile properties were shown after UV-exposure when these UV-stabilisers are added.

Among the various UV-stabilisers, Lowilite 55, which is a benzotriazole class UV-stabiliser gave maximum retention of tensile properties after UV-light ageing in these conventional vulcanizates compared to Lowilite 20 and Lowilite 76.

Table VI.6 gives the values of the tensile strength, modulus, E.B of different vulcanizates in the efficient vulcanizing system with and without addition of UV-stabilisers before and after exposure to UV-radiation. The tensile values viz., tensile strength, modulus (at 300% and 500%), elongation at break (%) etc. decreased to very low values after 24h exposure to UV-radiation of the gum efficient vulcanizates. When we examine the tensile properties of the different efficient vulcanizates with UV-stabiliser, all of them have shown very good retention of tensile properties after prolonged UV-exposure. This indicated the effectiveness or better activity of UV-protectants in NR latex vulcanizates against UV-radiation. Among the various class of stabilisers tried in EV system Lowilite 55 again has shown maximum retention of tensile properties when compared to Lowilite 20 and Lowilite 76. The colour when graded visually showed no predominant yellowing on exposure after addition of these stabilisers.

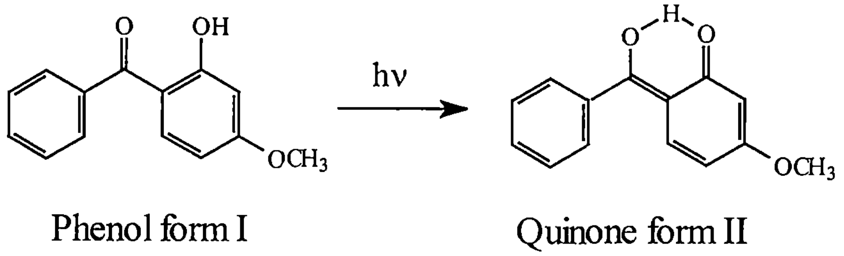
Thus the above results indicate the resistance action of *UV-stabilisers in NR latex vulcanizates against photo oxidative* degradation. Mainly NR latex vulcanizates get degraded by a chain free radical reaction mechanism under UV-radiation. These high energy UV-radiation produce alkyl free radicals in rubber matrix which react with excited state singlet oxygen from the surrounding atmosphere to produce alkyl peroxy radicals which abstract H-atom from some other polyisoprene chains in rubber matrix to produce hydroperoxides and new free radical sites on neighbourhood chains. Thus chain scission occurs eventually and entire polymer get degraded.

In order to resist this type of photo oxidative degradation, either of the following 4 methods should be adopted.

1) To absorb the incident UV-radiation and to shield or screen the polymer matrix from reacting with these high energy radiation.
2) To quench the excited free radicals produced to some what lower energetic state so that reaction is not feasible.
3) To decompose the hydroperoxides to harmless products.
4) To scavenge the free radicals formed and change them into an inert form.

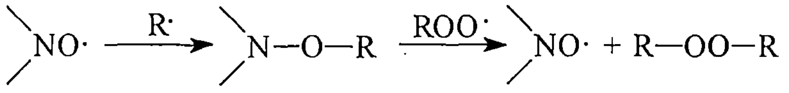
The three class of UV-stabilisers are acting in either one or two of the above 4 methods. The Lowilite 20 which is a substituted benzophenone type

UV-stabiliser, acts in two different ways. They absorb the UV-radiations in the range 290-350 nm which is the most dangerous part of sun's UV-spectrum. This is done by forming H-bonded intermediate structure in the excited stage.[7] On de-excitation they dissipate the excess energy into heat energy and return to ground stage having no H-bonding.



VI(1)

Also substituted benzophenones are good excited free radical quenchers. They convert the high energy radicals to low energy radicals by interacting with them through the tautomeric conversions. But in this experiment even though they are giving good UV-stabilisation, Lowilite 55 is better than this compound. Lowilite 55 is a substituted benzotriazole which acts mainly as a UV-absorber, they are having less radical scavenging and quenching action. But yet they have given good retention of tensile properties in NR latex vulcanizates under UV-radiation. The Lowilite 76 is having no action in their original form. These are hindered amine light stabilisers (HALS). They actually form nitroxyl radicals on interaction with free radicals in the rubber matrix under UV-radiation, which can react with alkyl and peroxy free radicals and make them inert. Nitroxyl radicals are also able to absorb UV-radiations.



VI(2)

Also HALS are expected to form charge transfer complexes with macroperoxy radicals and on dissociation of these complexes, harmless products are given out.[8]

$$\mathrm{POO\cdot} + \mathrm{HALS} \rightleftharpoons [\mathrm{POO\cdot}\text{-----}\mathrm{HALS}]$$

$$[\mathrm{POO\cdot}\text{—}\mathrm{HALS}] + \mathrm{POO\cdot} \rightleftharpoons [(\mathrm{POO\cdot}\text{—}\mathrm{HALS})\text{---}\mathrm{PO}_2^{\cdot}]$$

eg. POOP + O_2 etc.

Scheme VI.1

Thus from Table VI.5 and VI.6 Lowilite 76 (HALS Type) is also proved to be a good UV-protector in NR latex compound in both conventional (high sulphur) and efficient (low sulphur) curing systems but less powerful when compared to Lowilite 55. The higher swell index values of the gum latex vulcanizates after UV-exposure given in Table VI.9 indicate the high extent of chain scission occurred in these samples in the absence of UV-stabilisers.

Table VI.7 shows the tensile properties of the conventional vulcanizates after heat ageing at 100^0C for 22h in a multicellular air oven. The tensile properties are extremely decreased after heat ageing of the gum vulcanizates and those with UV-stabilisers. From the results it is clear that vulcanizates with UV-stabilisers are showing less tensile strength than gum vulcanizates. But their modulus values are higher than that of gum vulcanizates, after heat ageing. This indicates that at high temperatures they are less active. But when the combined effect is considered after 12h UV-exposure and 100^0C/22h heat ageing the tensile strength values of the vulcanizates with UV-stabilisers are better than the gum vulcanizates. This once again indicate the resistance power of these chemicals against the photo oxidative initiation of chain scission of NR latex vulcanizates.

Table VI.8 gives the tensile values of the efficient vulcanizates after heat ageing at 100^0C for 22h in a multicellular air oven. The values of tensile strength, modulus etc. are retained better than those of conventional vulcanizates after heat ageing. Those with UV-stabilisers in this case also give no improvement in tensile properties after thermo oxidative ageing. But when the combined effect of UV-exposure and heat ageing is considered these gum vulcanizates were melted away, while those with UV-stabilisers were not melted away, even though tensile values are very much decreased. Among the vulcanizates with different UV-stabilisers, those with Lowilite 55, retained better properties after light and heat ageing. This indicated once again the higher activity of Lowilite 55 in NR latex vulcanizates. Thus above results indicated that UV-stabilisers used in this study are effective for giving adequate protection to NR latex vulcanizates in both vulcanization systems against photo oxidative degradation, but they are not effective against thermo oxidative degradation of vulcanizates.

The swell index values given in Table VI.9 support the above findings for the vulcanizates. It is also clear that from Table VI.7 and VI.8, that the vulcanizates were all undergone discolouration (yellowing) after heat ageing and combined UV-light and heat ageing.

The optical and SEM micrographs given in Figures VI.1, VI.2 and VI.3 shows the cracks in the gum conventional vulcanizates after UV-exposure. The SEM micrographs of vulcanizates with Lowilite 55 showed no cracks after long term UV-irradiation.

In conclusion, we observed that the natural rubber latex vulcanizates get degraded extremely and their physical properties correspondingly get reduced after UV-irradiation in conventional and efficient cure systems without any UV-stabilisers. All the three classes of UV-stabilisers used in this experiment , Lowilite 20, Lowilite 55 and Lowilite 76 excellently retained the physical properties of the NR latex vulcanizates after UV-irradiation, in both CV and EV systems. Among the various stabilisers, Lowilite 55 which is a substituted benzotriazole class stabiliser showed the maximum retention of tensile properties.

The processing properties of latex also retained very well after addition of these UV-stabilisers. No discolouration of films observed after prolonged UV-exposure. The three UV-stabilisers used in this study are not able to give satisfactory protection to latex vulcanizates against thermo oxidative ageing in both CV and EV systems. But when the combined effect of photo oxidation and thermo oxidative degradation is considered, then the films which contained the UV-stabilisers retained the physical properties better than the gum vulcanizates in both CV and EV systems; even though the level of protection obtained was inferior.

Table VI.1. Structure and physical properties of important UV-Stabilisers

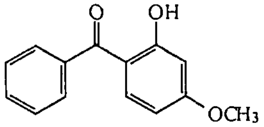
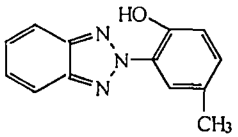
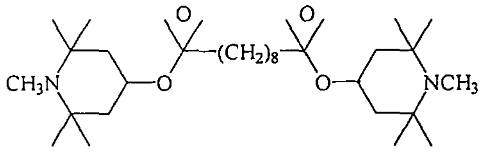
Sl. No.	Chemical name and structure	Appearance	Mol:Wt.	M.P. Range	TGA(^{0}C, % mass loss)		Solubility (g/100 g solvent at 25^{0}C)
1.	2-Hydroxy-4-Methoxy benzophenone (Lowilite 20) 	Powder	228	62-65^{0}C	116	5%	Water < 0.1
					179	10%	n-Hexane 3.5
					214	50%	Methanol 2.7
							Acetone 65
							Ethylacetate 75
2.	2-(2'-hydroxy-5'-methylphenyl)benzotriazole (Lowilite 55) 	Powder	225	128-132^{0}C	164	5%	Water < 0.1
					175	10%	n-Hexane 0.8
					213	50%	Methanol 0.2
							Acetone 3
							Ethylacetate 3.5
3.	Bis(1,2,2,6,6 Pentamethyl-4-piperidinyl) Sebacate 	Amber Liquid	509	31-33^{0}C	257	5%	Water < 0.001
					279	10%	n-Hexane m
					323	50%	Methanol m
							Acetone m
							Ethylacetate m

Table VI.2. Formulations of latex compounds

Formulations	CV System				EV System			
	CU_1	CU_2	CU_3	CU_4	EU_1	EU_2	EU_3	EU_4
60 % Centrifuged NR latex	167	167	167	167	167	167	167	167
10% Potassium hydroxide soln.	2	2	2	2	2	2	2	2
10% Potassium laurate soln.	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
50% Sulphur dispersion	3.6	3.6	3.6	3.6	0.5	0.5	0.5	0.5
50% ZDEC dispersion	2	2	2	2	1	1	1	1
50% ZMBT dispersion	1	1	1	1	-	-	-	-
50% TMTD dispersion	-	-	-	-	4	4	4	4
20% Thiourea soln.	-	-	-	-	3.5	3.5	3.5	3.5
50% Zinc oxide dispersion	1	1	1	1	1	1	1	1
50% Lowilite 20 dispersion	-	2	-	-	-	2	-	-
50% Lowilite 55 dispersion	-	-	2	-	-	-	2	-
50% Lowilite 76 emulsion	-	-	-	2	-	-	-	2

Table VI.3. Physico-chemical characteristics of latex compounds (CV system)

Properties	CU_1	CU_2	CU_3	CU_4
pH	11.2	11.1	11.1	11.1
Mechanical stability time MST (Sec) (55% TSC)	960	950	950	970
Brookfield Viscosity (cps) (55% TSC) 60 rpm, spindle No.2	28	28	28	27

Table VI.4. Physico-chemical characteristics of latex compounds (EV system)

Properties	EU_1	EU_2	EU_3	EU_4
pH	10.7	10.6	10.6	10.6
Mechanical stability time MST(Sec) (55% TSC)	1080	1060	1060	1070
Brookfield Viscosity (cps) (55% TSC) 60 rpm, spindle No.2	27	27	27	27

Table VI.5 Appearance and physical properties of latex films before and after UV-exposure

Formulation		CU_1				CU_2				CU_3				CU_4			
UV-irradiation time (h)		0	6	12	24	0	6	12	24	0	6	12	24	0	6	12	24
Tensile strength (MPa)		29.5	30	25	11	26	26	24	22	34	32.5	32	32	31	30	29	18
Modulus (MPa)	M_{300}	1.47	1.56	1.63	1.13	1.92	1.98	2.2	1.8	1.76	1.79	1.93	2.1	1.87	1.89	1.86	1.86
	M_{500}	2.35	2.58	2.76	1.74	3.4	3.56	3.8	3.46	2.9	3	3.41	3.60	3.2	3.32	3.46	3.57
E.B (%)		1110	1050	1025	815	955	908	882	870	1076	1020	1010	1004	997	957	931	829
Discolouration		Nil				Nil				Nil				Nil			

Table VI.6 Appearance and physical properties of latex films before and after UV-exposure

Formulations		EU_1				EU_2				EU_3				EU_4			
UV-irradiation time (h)		0	6	12	24	0	6	12	24	0	6	12	24	0	6	12	24
Tensile strength (MPa)		24.1	16.3	12.4	6	25	25	24.3	22	25.7	25.5	24.5	24.1	25.5	23.2	16	15.5
Modulus (MPa)	M_{300}	1.18	0.95	0.92	0.48	1.21	1.18	1.18	1.0	1.24	1.13	1.07	1.05	1.20	1.08	1.04	0.88
	M_{500}	1.72	1.45	1.32	0.75	1.76	1.43	1.38	1.32	1.90	1.60	1.53	1.39	1.74	1.51	1.46	1.2
Elongation at break (E.B) (%)		1160	1088	1083	1068	1180	1200	1168	1154	1164	1148	1159	1145	1220	1168	1140	1100
Discolouration		Nil				Nil				Nil				Nil			

Table VI.7. Appearance and physical properties of latex films before and after heat ageing

Formulations		CU$_1$			CU$_2$			CU$_3$			CU$_4$		
Properties		(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
Tensile Strength (MPa)		29.5	12.8	1.6	26	7.7	1.8	34	7.8	3.2	31	8.2	1.9
Modulus (MPa)	M$_{300}$	1.47	0.80	0.51	1.92	1.28	0.74	1.76	1.16	0.90	1.87	0.98	0.73
	M$_{500}$	2.35	1.40	0.76	3.4	2.2	1.25	2.9	1.92	1.43	3.2	1.6	1.16
Elongation at break (E.B) (%)		1110	1100	853	955	876	641	1076	906	780	997	990	698
Discolouration			Yellow			Yellow			Yellow			Yellow	

(a) = original, (b) = 100^{0}C/22h, heat aged, (c) = 24h UV exposed and heat aged at 100^{0}C/22h.

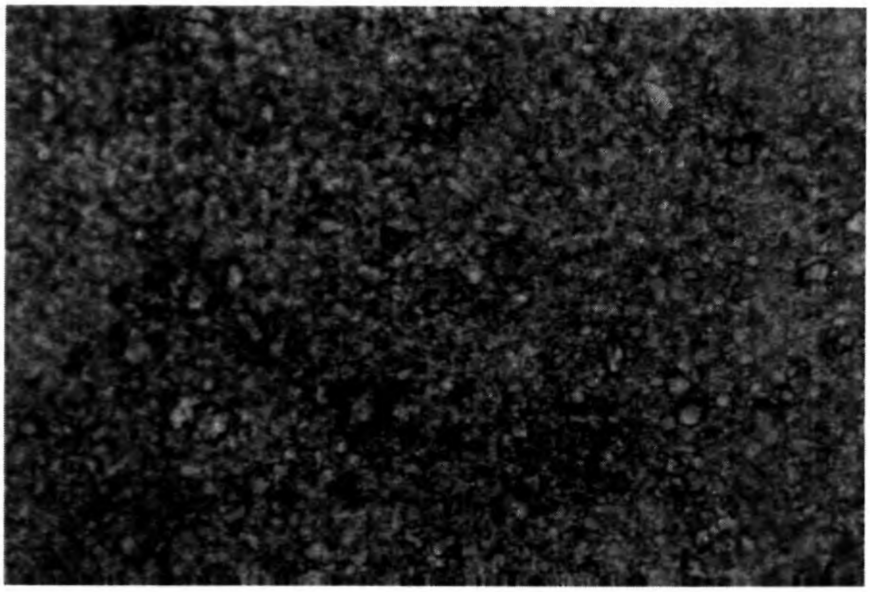
Table VI.8. Appearance and physical properties of latex films before and after heat ageing

Formulations		EU$_1$			EU$_2$			EU$_3$			EU$_4$		
Properties		**(a)**	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**
Tensile strength (MPa)		24.1	16.0	Melted	25	16.8	4	25.7	17	5	25.5	15.3	2.0
Modulus (MPa)	M$_{300}$	1.18	0.95	-	1.21	0.96	0.42	1.24	0.98	0.44	1.20	0.78	0.38
	M$_{500}$	1.72	1.15	-	1.76	1.21	0.65	1.90	1.24	0.68	1.74	1.12	0.45
Elongation at break (E.B) (%)		1160	1156	-	1180	1200	1170	1164	1161	1156	1220	1195	1104
Discolouration			Yellow			Yellow			Yellow			Yellow	

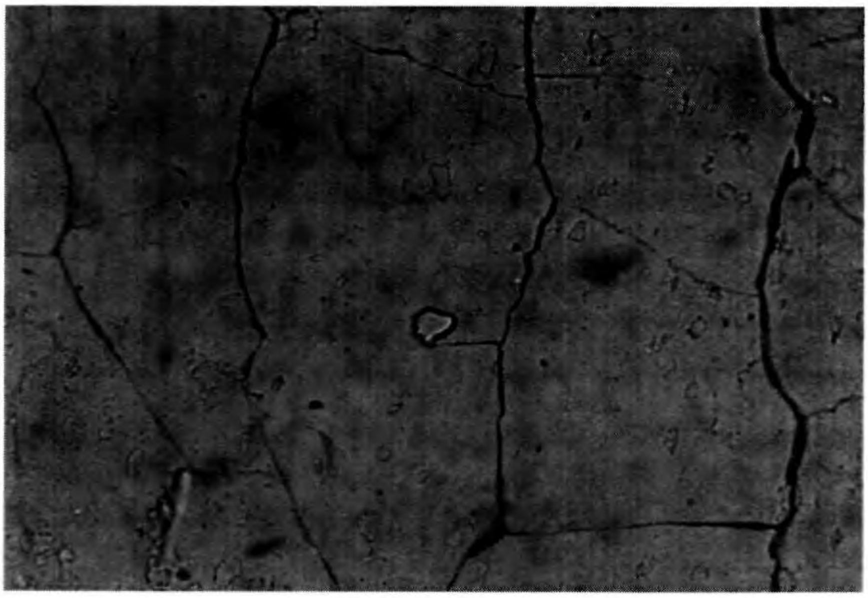
(a) = original, (b) = 100^{0}C/22h, heat aged, (c) = 24h UV exposed and heat aged at 100^{0}C/22h

Table VI.9. Swell Index values of cast films in benzene after 48h swelling (wt. of benzene in gms. absorbed per gm. sample)

Formulation	Sample	Original	After 24 h UV-exposure	After 100^0C/22 h heat ageing
CV	(CU_1)	3.97	6	6.8
	(CU_2)	4.23	4.24	6.9
	(CU_3)	4.30	4.33	6.9
	(CU_4)	4.12	5.12	7.2
EV	(EU_1)	5.53	9.6	7.9
	(EU_2)	5.34	5.36	8.4
	(EU_3)	5.48	5.5	8.0
	(EU_4)	5.45	6.0	9.0



(a)

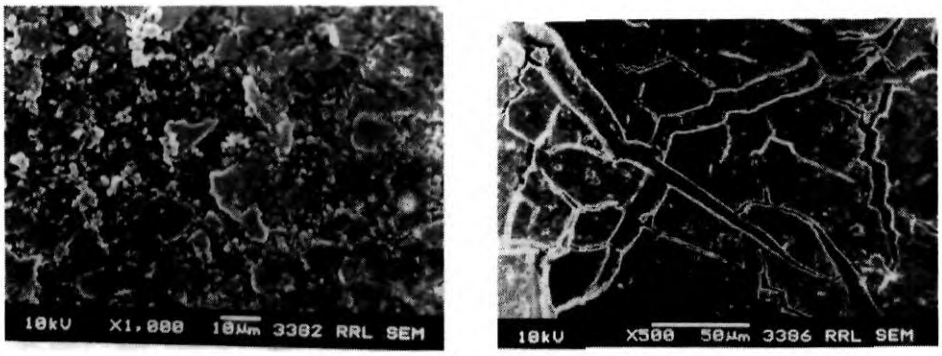


(b)

Fig. VI.1 Optical micrograph of gum NR latex film before and after 96 h UV-exposure (250 x)

(a) unexposed

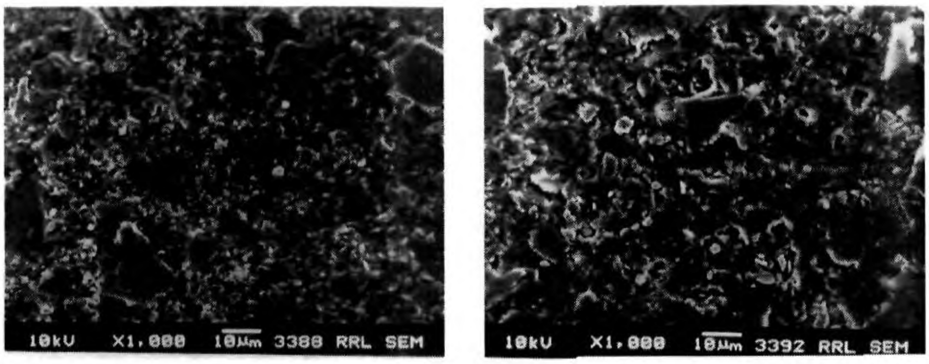
(b) 96 h exposed



(a) (b)

Fig. VI. 2 Scanning electron micrograph of gum NR latex films before and after 96 h UV-exposure

(a) unexposed (b) 96 h exposed



(a) (b)

Fig. VI. 3 Scanning electron micrograph of NR latex films containing the UV-stabiliser Lowilite 55 before and after 96 h UV-exposure

(a) unexposed (b) 96 h exposed

PART II

Effect of Combinations of UV-Stabiliser and Antioxidants on the Physical Properties of Natural Rubber Latex Vulcanizates

When the Natural Rubber (NR) latex products are used in outdoor applications, they have to resist both UV-light and heat degradation. This is very much true in the case of latex surface coatings, latex paints and other latex products used in environment.[9,10,11] From the work described in the previous chapters it is clear that no UV-stabilisers are satisfactory antioxidants and no antioxidants are perfect UV-stabilisers. It was also found from the previous part of this work that Lowilite 55, which is a substituted benzotriazole class UV-stabiliser provided the best photo oxidative ageing resistance to the sulphur vulcanizates of NR latex. Also we have early proved that phenolic and combination of phenolic and amine type antioxidants are better than phosphite type antioxidant to give adequate protection to NR latex sulphur vulcanizates against thermo oxidative degradation.[12] So in this experiment we have tried two combinations of a UV-stabiliser and antioxidants in both conventional vulcanization (CV) system and efficient vulcanization (EV) system of NR latex.

The physical properties of the vulcanizates of the following combination of UV-stabiliser and antioxidants are presented in this work.

I. Lowilite 55 2-(2'-hydroxy-5'-methylphenyl) benzotriazole

\+

Wingstay-L (reaction product of butylated p-cresol and dicyclopentadiene)

II Lowilite 55

+

Antioxidant SP(Styrenated phenol)

+

Antioxidant HS (polymerised 1,2-dihydro 2,2,4-trimethyl quinoline)

Centrifuged high ammonia type 60% natural rubber latex conforming to BIS 5430-1981 was used in this study. Latex compounds containing the combinations of the UV-stabiliser Lowilite 55 and antioxidants Wingstay-L, antioxidant SP and antioxidant HS were prepared according to the formulation given in Table VI.10. The other compounding ingredients were of commercial grade obtained locally. The latex was first stabilised by adding potassium hydroxide and potassium laurate solutions. The other compounding ingredients were added as dispersions or emulsions. The compounds were then matured at 30^0C for overnight and sieved through a 100 mesh sieve.

The latex compounds were then cast into thin films on glass plates. The cast latex films were then dried at 70^0C and vulcanized in boiling water. The films with conventional cure system were vulcanized for 60 minutes and those with efficient cure systems were vulcanized for 90 minutes, and then the films were finally dried in an air oven at 60^0C.

The dumbbell test pieces taken from each sample were then exposed to UV-radiation from a UV-source (NEC-FL 15BL-30W-JAPAN) for 6,12 and 24h. The effect of UV-light on tensile properties of the dumbbell pieces was then determined according to ASTM D 412-98 using an Instron D-4411 universal testing machine. The dumbbell test pieces were also subjected to heat ageing at 100^0C for 22h, in a multicellular ageing oven and tensile properties were determined. The combined effect of UV-light and heat was also measured by testing tensile properties of the dumbbell pieces after 12h UV-irradiation and ageing at 100^0C for 22h. The results are given in Tables VI.11 to VI.14. The film samples were tested for measuring the changes in crosslink density by the method described in section II.8.2 of Chapter II. The results are given in Table VI.15. The extent of chain scission was measured by noting the changes in sol content(%) and polysulphidic crosslink(%). The sol content(%) was determined as per procedure given by Bristow[13] and polysulphidic crosslink(%) by the method suggested by Campbell.[14] The results are given in Table VI.16 and VI.17.

VI.2 RESULTS AND DISCUSSION

The tensile properties of the conventional vulcanizates from NR latex before and after UV-irradiation are given in Table VI.11. The values indicate that the tensile properties viz. tensile strength, modulus and elongation at break of the gum vulcanizates without any UV-stabiliser and antioxidants decrease drastically after long term UV-irradiation. This proves the very poor photo oxidative ageing resistance of the conventional sulphur vulcanizates from NR latex. It is clear from Table VI.11, that all the tensile properties are retained almost fully after long term UV-irradiation of the conventional vulcanizates containing UV-stabiliser and antioxidants. Both the combinations Lowilite 55 + Wingstay L and Lowilite 55 + Antioxidant (SP + HS) retained the physical properties almost equally after long term UV-irradiation.

It is clear from Table VI.12 that the physical properties viz., tensile strength, modulus and E.B of the efficient NR latex vulcanizates without any UV-stabiliser and antioxidant were lowered very much after long term UV-irradiation. Both the samples containing the combinations Lowilite 55 + Antioxidant wingstay-L and Lowilite 55 + Antioxidant (SP + HS) have excellently retained the tensile properties after long term UV-irradiation. From the above results it is proved that the substituted phenolic type and amine type antioxidants used in this experiment do not hinder the protective action of UV-stabilisers present in both type of latex vulcanizates against photo oxidative degradation.

The effect of heat ageing and combined UV-light and heat ageing of the conventional vulcanizates are given in Table VI.13. The tensile properties especially tensile strength of the gum vulcanizates without any UV-stabiliser and antioxidant decreases to a very lower value after heat ageing. After combined UV-light and heat ageing, the tensile strength of the gum vulcanizate is negligible. This indicated the severity of chain scission that has occurred in the conventional vulcanizates because of photo oxidative and thermo oxidative degradation. Again from Table VI.13 it is seen that both the vulcanizates containing the UV-stabiliser and antioxidant retained the tensile properties to a very good extent compared to gum vulcanizate after heat ageing and combined UV-light and heat ageing. The combination, Lowilite 55 + Antioxidant Wingstay-L performed better than sample containing Lowilite 55 + Antioxidant (SP + HS) in conventional vulcanizate against combined photo oxidative and thermo oxidative ageing.

From Table VI.14, it is clear that the efficient vulcanizates without any UV-stabiliser and antioxidant retained the tensile strength, modulus and E. B to a good extent on heat ageing. But these vulcanizates, when subjected to combined UV-light and heat ageing, melted away indicating the very poor resistance of efficient vulcanizates of NR latex against combined photo oxidative and thermo oxidative degradation. Both the samples with UV-stabiliser and antioxidant excellently retained the tensile properties of the efficient vulcanizates compared to gum vulcanizates after heat ageing and combined UV-light and heat ageing. Both the combinations Lowilite 55 + Wingstay L and Lowilite 55 + Antioxidant (SP + HS) almost equally retained the physical properties after UV-exposure and heat ageing.

It was proved earlier from the investigations on plastics that both the photo oxidative and thermo oxidative degradation mechanisms follow the same free radical reaction path.[15,16] The only difference is in the initiation of the reaction. In photo oxidative degradation, the chromophores present in elastomer or polymer matrix absorb UV-light in the region 290-350 nm to produce excited chromophores which on reaction with the rubber hydrocarbon chains, produce alkyl free radicals; but in thermo oxidative degradation initiation is caused by some impurities in the polymer at high temperature. Eventually the alkyl radicals form peroxide radicals and hydroperoxides by reaction with atmospheric oxygen. This is an irreversible reaction and as a result extensive chain scission happens, marked by loss of physical properties, reduction in molecular weight, surface tackiness or embrittlement and discolouration. Thus the polymer has to come to an end of its service life.

Thus from the above and previous experiments, it is made clear that, for NR latex products meant for using in outdoor applications, durability and good service properties can be imparted by not only including a UV-stabiliser alone but a suitable combination of a UV-stabiliser and antioxidant in compounding recipe.

The results given in Table VI.15 support the above finding that in the samples containing a UV-stabiliser and antioxidant, crosslink breakage is lower after ageing as indicated by the lower swell index value of the samples C_1 and C_2 compared to C_0 and those of E_1 and E_2 compared to E_0.

The changes in the sol content percentage and poly sulphidic crosslink percentage given in Tables VI.16 and VI.17 indicate the extent of crosslink scission and chain scission occurred as a consequence of photo oxidative and thermo oxidative degradation.

In the light of the above findings, it can be concluded that natural rubber latex vulcanizates in both CV and EV systems undergo damage on photo oxidative and thermo oxidative degradation. By using a suitable combination of UV-stabiliser and antioxidant both the photo oxidative and thermo oxidative degradation resistance of NR latex vulcanizates can be excellently improved. The antioxidants used in this experiment viz., Wingstay-L and Antioxidant (SP + HS) combination did not hinder the UV-stabilising action of Lowilite 55 in both CV and EV systems. Both the antioxidants Wigstay-L, which is a substituted phenolic antioxidant, and a combination of phenolic and amine type antioxidant i.e., antioxidant

(SP + HS) combination along with the benzotriazole class UV-stabiliser, Lowilite 55 performed almost equally to impart resistance for both CV and EV vulcanizates of NR latex against UV-light and heat.

Table VI.10. Formulations of latex compounds

Formulations	C_0	C_1	C_2	E_0	E_1	E_2
60 % Centrifuged NR latex	167	167	167	167	167	167
10% Potassium hydroxide soln.	2	2	2	2	2	2
10% Potassium laurate soln.	0.5	0.5	0.5	0.5	0.5	0.5
50% Sulphur dispersion	3.6	3.6	3.6	0.5	0.5	0.5
50% ZDEC dispersion	2	2	2	1	1	1
50% ZMBT dispersion	1	1	1	-	-	-
50% TMTD dispersion	-	-	-	4	4	4
20% Thiourea soln.	-	-	-	3.5	3.5	3.5
50% Zinc oxide dispersion	1	1	1	1	1	1
50% Lowilite 55 dispersion	-	2	2	-	2	2
50% Wingstay- L dispersion	-	2	-	-	2	-
50% Styrenated phenol (sp) emulsion	-	-	1	-	-	1
50% antioxidant HS dispersion	-	-	1	-	-	1

Table VI.11. Tensile properties of latex films before and after UV-exposure

Formulations		C_0				C_1				C_2			
UV-exposure time (h)		0	6	12	24	0	6	12	24	0	6	12	24
Tensile strength (MPa)		29.5	30	25	11	29.2	28.9	28.7	27.9	29.1	29.0	28.5	27.7
Modulus (MPa)	M300	1.47	1.56	1.63	1.13	1.80	1.90	1.65	1.58	1.77	1.81	1.63	1.48
	M500	2.35	2.58	2.76	1.74	3.24	3.38	2.94	2.63	3.11	3.37	2.81	2.37
Elongation at Break (%)		1110	1050	1025	815	1020	1000	1010	990	1025	985	990	960

Table VI.12. Tensile properties of latex films before and after UV-exposure

Formulations		E_0				E_1				E_2			
UV-irradiation time (h)		0	6	12	24	0	6	12	24	0	6	12	24
Tensile strength(MPa)		*24.1*	*16.3*	*12.4*	*6*	*25.2*	*25.3*	*24.8*	*24.6*	*25.5*	*26*	*25.1*	*24.8*
Modulus (MPa)	M_{300}	1.18	0.95	0.92	0.48	1.22	1.08	1.02	0.96	1.27	1.13	1.05	0.88
	M_{500}	1.72	1.45	1.32	0.75	1.94	1.83	1.53	1.38	1.98	1.94	1.50	1.31
Elongation at break (%)		1160	1088	1083	1068	1282	1188	1160	1090	1260	1220	1080	1050

Table VI.13. Tensile properties of latex films before and after UV-exposure and heat ageing

Formulation		C_0			C_1			C_2		
Properties		**(a)**	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**	**(a)**	**(b)**	**(c)**
Tensile strength (MPa)		29.5	12.8	1.6	29.2	21	18.6	29.1	21.5	15
Modulus (MPa)	M_{300}	1.47	0.80	0.51	1.80	1.49	1.33	1.77	1.32	0.94
	M_{500}	2.35	1.40	0.76	3.24	2.89	2.24	3.11	2.39	1.67
Elongation at Break (%)		1110	1100	853	1020	986	960	1025	1010	985

(a)= Original, (b)=100^{0}C/22h heat aged, (c)=12h UV-exposed and100^{0}C/22h heat aged

Table VI.14. Tensile properties of latex films before and after UV-exposure and heat ageing

Formulation		E_0			E_1			E_2		
		(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
Tensile strength (MPa)		24.1	16.0	melted	25.2	19.7	16.3	25.5	20	16.0
Modulus (MPa)	M_{300}	1.18	0.95	-	1.22	0.82	0.70	1.27	0.83	0.54
	M_{500}	1.72	1.15	-	1.94	1.29	1.05	1.98	1.08	0.90
Elongation at Break (%)		1160	1156	-	1282	1190	1172	1260	1141	1046

(a)=Original,(b)=100^0C/22h heat aged,(c)=12h UV-exposed and 100^0C 22h heat aged.

Table VI.15. Swell index values of unaged and aged latex films(benzene in gms. absorbed per gram of sample)

Sample	Original	24h UV-exposed	100^0C/ 22h heat aged
C_0	3.97	6	6.8
C_1	4.19	4.24	4.52
C_2	4.20	4.29	4.91
E_0	5.53	9.6	7.9
E_1	5.41	5.65	6.49
E_2	5.42	5.80	6.56

Table VI.16. Changes in sol content (%)

Formulations	24h UV-exposed	Heat aged at 100^0C for 22h
C0	1.71	1.66
C1	0.62	1
C2	0.67	0.98
E0	2.54	1.91
E1	1.74	1.82
E2	1.68	1.79

Table VI.17. Changes in polysulphidic crosslink (%)

Formulations	Original	12h UV-exposed and100^{0}C/22h heat aged.
C0	42	14
C1	46	34
C2	45	32
E0	8	Melted
E1	10	6
E2	10	5

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CHAPTER VII

SUMMARY AND CONCLUSIONS

Systematic investigations for improving the degradation resistance of natural rubber latex products and vulcanizates against photo oxidative and thermo oxidative degradation have been carried out. A typical latex product viz. latex thread which has low bulk and large surface area has been chosen for the studies on the effect of vulcanization systems and antioxidants against UV-light and heat degradation. The parameters studied include the tensile properties, changes in crosslink density, and colour of the threads with various combinations of accelerators and antioxidants under UV-light and heat.

Generally certain nonblack fillers are added at low dosages along with a white pigment to latex thread compounds for getting better modulus and colour respectively. The effect of some fillers with pigment on the physical properties of latex threads having various vulcanization systems, with special reference to its degradation under UV-radiation and heat was evaluated. The extent of rubber-filler interaction has also been studied.

Normally dry natural rubber is blended with modified rubbers and synthetic polymers in order to improve its inherent poor heat ageing resistance. The photo oxidative and thermo oxidative degradation resistance of various blended vulcanizates of natural rubber latex with modified natural rubber latices and synthetic rubber latices were investigated.

Natural rubber latex products made using sulphur vulcanization are increasingly substituted now-a-days by radiation vulcanized natural rubber latex (RVNRL) products. The RVNRL products are free from toxic nitrosoamines, which cause hazard to health. RVNRL dipped goods are now widely used. The resistance to degradation of RVNRL films against UV-light and heat was investigated. The effects of different combinations of antioxidants and various non-black fillers and pigments on the physical properties of RVNRL films were also studied.

There are various class of UV-stabilisers. They are widely used in plastics. The natural rubber latex products are extensively used in day-to-day applications. The effect of various UV-stabilisers in NR latex vulcanizates has been investigated. The physical properties, processing characteristics, changes in crosslink density, colour etc. were investigated after addition of these chemicals. Effects of combinations of UV-stabilisers with antioxidants in NR latex vulcanizates were also investigated.

The effect of accelerator combinations and antioxidants on UV-radiation degradation of natural rubber latex thread with a conventional and efficient vulcanization system was presented in Chapter III. Zinc diethyl dithiocarbamate (ZDEC), Zinc dibutyl dithiocarbamate (ZDBC), Zinc mercapto benzothiazole (ZMBT) and tetramethyl thiuram disulphide (TMTD) were used as accelerators. The antioxidants used were reaction product of butylated p-cresol and dicyclopentadiene (Wingstay–L), Tris–nonylated phenyl phosphite (Crystol EPR 3400), styrenated phenol (SP) and polymerised 1,2–dihydro 2,2,4–trimethyl quinoline (HS). The thread samples were exposed to UV-radiation and heat aged and the appearance and physical properties of thread were examined. The results indicated that the threads having ZDBC + ZDEC and ZDBC + ZMBT combinations as accelerators are more resistant to UV–radiation and heat ageing than the thread having the ZDEC + ZMBT combination under CV system. Similarly, under the EV system the TMTD + ZDBC was found to be better than the TMTD+ZDEC combination. It is observed that the antioxidants Wingstay–L and (SP + HS) combination are more effective in retaining the physical properties of the thread than Crystol EPR 3400 under long term UV–irradiation and heat ageing in both CV and EV systems. The phosphite type antioxidant Crystol EPR 3400 was found to be better in reducing the discolouration under UV–radiation. The accelerator combinations containing ZDBC + ZDEC and ZDBC + ZMBT showed no discolouration after UV–exposure as evident from the photographs of the thread samples.

The second part of this Chapter described the effect of titanium dioxide pigment and its combination with fillers such as china clay, precipitated calcium carbonate and barium sulphate at low dosage (7.5 phr) on the physical properties and degradation resistance of latex thread prepared using conventional and efficient vulcanization systems. The fillers china clay, precipitated calcium carbonate and barytes at low dosages along with titanium dioxide pigment imparted better modulus, tensile strength and colour to thread samples both in the conventional and efficient vulcanization systems. This is due to the better rubber- filler interaction as indicated by the changes in Vr values after ammonia modified swelling. The titanium dioxide pigment alone has no marked effect in retaining the physical properties under photo oxidative ageing. Precipitated calcium carbonate and titanium dioxide combination was found to be better in retaining the physical properties of the thread in conventional vulcanization system against photo oxidative and thermo oxidative ageing. All the combinations of fillers and pigment in the threads under EV system showed comparable performance against UV-light.

The fourth Chapter contained the results of the studies on the effect of blending of natural rubber(NR) latex with modified NR and synthetic rubber latices on the technological properties with special reference to degradation by UV-light. The blending was done at a constant dry rubber weight ratio of 25:75 consisting of 75 phr. natural rubber. The type of modified/synthetic rubber latex has an influence on the tensile properties and degradation resistance of the blends. The blends of NR latex with modified NR latices (grafted and epoxidised) gave better physical properties and resistance to degradation under UV-light and heat. Styrene-grafted-NR and PMMA- grafted-NR latex blends with NR latex showed better tensile strength, modulus and elongation at break than NR/ENR latex blend. Blends of epoxidised NR latex (ENR) with NR latex showed good resistance to UV-light and heat degradation among the modified latex blends except when the combined effect of UV-light and heat was considered. The synthetic rubber latices did not show enhancement in tensile strength, but the modulus of the latex blend with NR latex increased when carboxylated SBR and Acrylonitrile butadiene rubber (NBR) latex were used. These NR/Synthetic rubber latex blends were less powerful than NR/modified NR latex blend to offer resistance to deterioration under UV-light and heat. NBR latex blends with NR latex was better in retaining the tensile strength than NR/XSBR latex blend after long term exposure to UV-radiation.

The effect of three class of antioxidants (viz., phenolic, phosphite and amine type) and their combinations on the physical properties of radiation vulcanized natural rubber latex (RVNRL) films under

UV-radiation has been described in Chapter V. From the investigations it was made clear that radiation prevulcanized natural rubber latex films using n-BA as sensitiser are possessing similar tensile strength as that of sulphur vulcanizates of NR latex. But modulus is lower for RVNRL films with good elongation at break. The photo oxidative ageing properties of virgin RVNRL film (without any antioxidants) was better than that of gum sulphur vulcanizates of NR latex. The thermo oxidative ageing and combined UV-light and heat ageing properties of virgin RVNRL films were very much poor. So inorder to get good heat ageing properties, antioxidants were found to be necessary in RVNRL products. The substituted phenolic type antioxidant, Wingstay-L and the phosphite type antioxidant Crystol EPR 3400 were found to be very good in retaining the tensile strength, modulus and elongation at break of heat aged RVNRL films. The antioxidants exhibited good action when they were used singly than in some of their combinations.

The results given in second part of Chapter V revealed the influence of nonblack fillers like china clay and precipitated calcium carbonate and titanium dioxide pigment on the physical properties of RVNRL films under photo oxidative and thermo oxidative ageing. The RVNRL films loaded with titanium dioxide pigment and the fillers china clay and precipitated calcium carbonate did not show any reinforcement in tensile strength or modulus. This is due to the poor rubber-filler interaction. The virgin unfilled RVNRL films using n-BA as sensitiser showed better retention of tensile properties after long term UV-irradiation, but they had very poor heat ageing properties. The RVNRL containing titanium dioxide pigment and the filler china clay showed better retention of tensile strength, modulus and elongation at break after thermo oxidative ageing and combined UV-light and heat ageing. The precipitated calcium carbonate filler loaded RVNRL films were more prone to degradation under thermo oxidative ageing, as indicated by the drastic drop in tensile properties.

Performance of special class UV-stabilisers on the physical properties of natural rubber latex vulcanizates was described in Chapter VI. The physical properties of NR latex vulcanizates severely get degraded after UV-irradiation in conventional and efficient vulcanization systems, without any UV-stabilisers. All the three class of UV-stabilisers used in this experiment i.e., Lowilite 20 (a substituted benzophenone class), Lowilite 55 (a substituted benzotriazole class) and Lowilite 76 (hindered amine light stabiliser) excellently retained the tensile strength, modulus and elongation at break of the NR latex vulcanizates in both CV and EV system after long term UV-irradiation. Among the various stabilisers, Lowilite 55 which is a substituted benzotriazole class stabiliser showed the maximum retention of tensile strength, modulus and elongation at break. The processing properties of latex viz., pH, MST, Brookfield viscosity etc. were not adversely affected with the addition of these UV-stabilisers. No discolouration of films were noted. These three UV-stabilisers alone were not found to be satisfactory in giving protection to NR latex vulcanizates against thermo oxidative ageing in both CV and EV systems. When combined UV-light and heat ageing was considered, NR latex vulcanizates with these UV-stabilisers retained the tensile properties better and that did not contain the stabilisers, but the values were inferior. The photographs also revealed that the films with UV-stabilisers did not develop any cracks after long term UV-irradiation.

The second part of this Chapter contained the results showing with the influence of combination of UV-stabilisers and antioxidants on the technological properties of NR latex vulcanizates. The NR latex vulcanizates in both CV and EV systems undergo marked changes in photo oxidative and thermo oxidative ageing. The result indicated that by using a suitable combination of UV-stabilisers and antioxidants both the photo oxidative and thermo oxidative degradation resistance of NR latex vulcanizates can be excellently improved. The antioxidants used in this experiment ie. Wingstay-L (phenolic type) and (SP+HS) combination (ie, phenolic + amine type) did not hinder the UV-stabilising action of lowilite 55 (benzotriazole class) in both CV and EV systems. The antioxidants viz., Wingstay-L and (SP+HS) combination with Lowilite 55 retained the tensile strength, modulus and elongation at break to an almost comparable level in both CV and EV systems of NR latex vulcanizates under UV-light and heat. The changes in crosslink density of the vulcanizates before and after exposure to UV- light and heat support this. Also the polysulphidic crosslink (%) and sol content (%) indicated the extent of chain scission occurred after photo oxidative and thermo oxidative degradation.

LIST OF PUBLICATIONS

1. Jaimon K. Kurian, N.R. Peethambaran, K. C. Mary and Baby Kuriakose. "Effect of vulcanization systems and antioxidants on discoloration and degradation of natural rubber latex thread under UV-radiation".

   Journal of Applied Polymer Science, 78 (2000) 304.

2. Jaimon K.Kurian, K.C Mary, N.R. Peethambaran and Baby Kuriakose, "Effect of non-black fillers and pigments on the physical properties and degradation resistance of natural rubber latex thread exposed to UV-radiation". Indian Journal of Natural Rubber Research, 14 (2): (2001) 102.

3. Jaimon K.Kurian, N.R. Peethambaran, K.C. Mary and Baby Kuriakose. "Studies on blends of natural rubber latex with modified natural rubber and synthetic rubber latices with special reference to degradation under UV-radiation". (Communicated).

4. Jaimon K.Kurian, K.C. Mary, Baby Kuriakose and N.R. Peethambaran, "Effect of some antioxidants, non-black fillers and pigments on degradation resistance of radiation vulcanized natural rubber latex films under UV-radiation". (Submitted).

5. Jaimon K.Kurian, K.C Mary, Baby Kuriakose and. N.R. Peethambaran "Effect of UV-stabilisers on the Physical properties of Natural rubber latex vulcanizates". (Submitted).

6. Jaimon K.Kurian, N.R. Peethambaran, K.C Mary and Baby Kuriakose, "Effect of combinations of UV-stabiliser and antioxidants on degradation resistance of natural rubber latex vulcanizates". (Submitted)