INFLUENCE OF COMPOUNDING AND PROCESS VARIABLES ON QUALITY OF CONDOMS MADE FROM NATURAL RUBBER LATEX

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This is to certify that the thesis entitled **"Influence of compounding and process variables on quality of condoms made from natural rubber latex"** is an authentic record of the research work carried out by Smt. Jasmin Maret under my supervision for the award of the PhD degree of Cochin University of Science and Technology and further that no part thereof has been presented before for any other degree.

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DECLARATION

I, Jasmin Maret, do hereby declare that the thesis entitled **"Influence of compounding and process variables on quality of condoms made from natural rubber latex"** is a bonafide record of the research work done by me under the joint guidance of Dr.N.M.Mathew, Rubber Research Institute of India, Rubber Board, Kottayam and Prof(Dr.)D.Joseph Francis, Department of Polymer science and Rubber Technology, Cochin University of Science and Technology, Cochin, and that no part of this thesis has been submitted earlier for the award of any other degree or diploma or recognition.

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ABBREVIATIONS

A/O - Antioxidant

BV - Burst volume

BP - Burst pressure

DRC - Dry rubber content

E - Elongation

EB - Elongation at break

HA - High ammonia

HST - Heat stability time

JIS - Japanese Industrial Standard

KΩ - Kilo ohm

KOH - Potassium hydroxide

KPa - Kilo Pascal

LA - Low ammonia

LATZ - Low ammonia TMTD/ZnO preserved latex

MΩ - Mega ohm

MPa - Mega pascal

M500 - Modulus at 500% elongation

MST - Mechanical stability time

nBA - Normal butyl acrylate

NR - Natural rubber

NTP - Nocceller TP

phr - Parts per hundred rubber

PVA - Poly vinyl alcohol

rpm - Rotations per minute

RSS - Ribbed smoked sheet

RVNRL- Radiation vulcanised natural rubber latex

SP - Styrenated phenol

TA - Total alkalinity

TS - Tensile strength

TSC - Total solids content

VFA - Volatile fatty acid

ZHST - Zinc oxide heat stability time

ZMBT - Zinc mercaptobenzo thiazole

ZMST - Zinc oxide mechanical stability time

ZOV - Zinc oxide viscosity

ZST - Zinc oxide stability time

CHAPTER I

INTRODUCTION

Natural rubber is obtained from the latex of various plants. Latex is present in 12500 species belonging to 900 genera, predominantly distributed over twenty families. Latex of only about 2000 of these species contains rubber as a constituent. The rubber content in latex varies considerably in different species and in many species difficulties are involved in collecting latex.

Hevea brasiliensis is the most important species which supplies the natural rubber of commerce today. 99 percent of the world's natural rubber is produced by *Hevea brasiliensis* which belongs to the family Euphorbiaceae. Its yield and quality of rubber are superior to those of all other species. The plant is a sturdy perennial tree which attains a height of about 30 m. Latex is present in almost all parts of the plant but only the bark of the trunk is usually exploited. The tree has a straight trunk with light grey bark. Branches are usually developed in such a way as to form an open leafy crown. Latex vessels which contain white or yellowish white latex, exclusively occur in the phloem region.

Latex

Freshly tapped latex is a whitish fluid of density between 0.975 and 0.980 gm^{-1}, pH from 6.5 to 7.0 and surface free energy from 40 to 45 ergs cm^{-2}. Hevea latex is a hydrosol in which the dispersed particles are strongly protected by a complex film made of proteins, neutral lipid and phospholipid. Rubber is the principal water insoluble component of latex and it occurs as discrete particles. From a cytological point of view latex can be considered as a specialised form of cytoplasm. What flows out on tapping is the fluid fraction of this cytoplasm.

Particulate composition of latex

The dominant particulate phase of freshly collected latex is the rubber hydrocarbon(1). Particles of this make up 30-45 percent of the whole volume and occur in size ranging from 0.02 - 3.00 µ with the majority in the region of 0.1µ. Rubber particles are usually spherical but sometimes oval or pear shaped(2). Next in abundance are the lutoid particles which are subcellular membrane bound bodies ranging in size from 2-5µ(3). They constitute 10 to 20 % of the volume. Lutoid serum present in lutoid particle is a destabilizer of rubber hydrocarbon. Another type of particle present is known as Frey-Wyssling particles which is spherical, larger in size than rubber and of yellow colour.

By centrifuging, latex may be divided into three main fractions, a white upper layer of rubber particles, a middle aqueous serum and the bottom fraction. The serum contains most of the soluble substances normally found in plant cells including aminoacids, proteins, carbohydrates, organic acids, inorganic salts and nucleotidic materials(4). The bottom fraction consists mainly of lutoid particles, mitochondria and other particulate components of normal plant cell having a density greater than that of serum.

Chemical composition of latex

Depending upon the physiological variation in flow, the composition of latex collected after tapping and that inside the vessels may vary. Excluding rubber and water, the substances present in fresh latex are mainly carbohydrates, proteins, lipids and inorganic salts(5). Numerous other components are also present in small quantities.

Carbohydrates

Quebrachitol(methyl inositol) is the most concentrated single component in the serum phase, constituting about 1 % of the whole latex. The concentration of sucrose, glucose and fructose in latex vary with planting materials, tapping system and stimulation.

Proteins

Total protein content of fresh latex is approximately 1% of which about 20% is adsorbed on rubber particles, and another 20% found in bottom fraction and the remainder in serum phase(5). Presence of protein bands was demonstrated in the serum of fresh latex(6). Bottom fraction of latex was found to contain 8 proteins. The isoelectric point of rubber particles in fresh latex varies from 4.0-4.6 and the variation has been ascribed to the presence of more than one protein on the rubber particle. The quantity of adsorbed proteins on rubber particles is a clonal characteristic(7). Proteins in latex function as stabilizers for the otherwise unstable hydrocarbon colloid.

Lipids

Lipids of fresh latex consists of fat, waxes, sterols, sterol esters and phospholipids(5).These compounds are all water soluble and are concentrated in the rubber phase with small quantities in the bottom fraction and Frey-Wyssling particles. There is clonal variation in the total lipid content in latex.

Other constituents

Nineteen aminoacids have been identified in latex. Total concentration of inorganic ions in fresh latex is 0.5%, the main ions being those of potassium, magnesium, copper, iron, sodium, calcium and phosphate. Low molecular weight thiols, which are of importance in the redox potential of their environment and enzymes normally present in the cytoplasm are also found in latex(5).

Tapping

Tapping is the process of controlled wounding of the bark to extract latex from the tree. The main principle of the present method of tapping is causing continuous excision of bark in a systematic manner. In this method, a sloping cut is made with a special knife and the same cut is regularly reopened by removing a thin shaving of bark at each tapping. This method takes into account the specific characteristics of the anatomy of bark and a skilled tapper can avoid injuring the cambium when this method is adopted.

Biochemical properties of latex

If fresh latex is allowed to stand for twelve hours it coagulates and forms a spongy mass of rubber. Cause of this coagulation is believed to be an enzyme called coagulase. The experimental basis for the belief in the existence of this substance is that the coagulation of latex occurs even in the presence of poisons which are supposed to kill bacteria only; but this coagulation does not occur if poisons which also affect enzymes are added to the latex. Oxidases and peroxidases are also found in latex. These enzymes catalyse the action of oxygen and peroxides on certain of its ingredients. Through their activity, acid coagulated rubber, when exposed to the air develops a greyish or purplish colour which is almost impossible to remove. This type of discoloration is prevented by the addition of sodium bisulphite to latex before coagulation.

At least twenty seven species of bacteria have been observed in latex, one of which is known to act specifically on sugars, whereas others act primarily on proteins.

The argument as to whether latex is naturally coagulated by the action of bacteria or by the action of the enzyme coagulase has not been definitely settled. It is known however, that sterile latex, that is, latex obtained from trees under sterile conditions and kept in sterilized containers can stand at least one month without coagulation.

The electrical charge on latex particles

According to generally accepted theories, one of the main causes of the stability of colloidal suspensions is an electrical charge assumed to be situated on the surface of each particle. In as much as particles of like charge repel each other this force prevents the aggregation of two or more particles and so tends to stabilize the colloidal suspension. It is not understood, how the latex particles become charged. One possible explanation is that the protein adsorbed on the rubber hydrocarbon is joined to the latter by means of only a few groups of the large protein molecule. The other groups are still free to act as they would in an ordinary protein solution. It is known that many proteins can ionize both as acids and as bases to a slight extent, much in the same manner as do amino acids. The kind and extent of this ionization depends on the hydrogen ion concentration of the solution. If this is true, in a highly basic solution the protein molecule while adsorbed on the rubber hydrocarbon, can act as an acid, losing hydrogen ions to the solution. These in turn combine with the hydroxyl ions already present to form neutral water, while the negatively charged protein anions remain adsorbed on the hydrocarbon particle. In this way the particle acquires a negative charge.

According to another theory, soap adsorbed on the rubber hydrocarbon ionizes and brings about the electrical charge. But this theory failed to explain all the facts related to isoelectric point etc.

Non-newtonian behaviour of latex

Latex concentrate is a non-newtonian fluid and its viscosity decreases with increasing shear rate(8).

Conductivity of latex

Natural rubber latex has a measurable electrical conductivity due to the salts dissolved in the aqueous phase and in most centrifuged latices it range from 3.0 to 5.0 ms at 25°C(9).

Collection and processing of latex

Seventy to eighty percent of the crop harvested from rubber plantations is in the form of latex. Latex in the latex vessels of rubber tree is sterile, but as it comes out, it gets contaminated by bacteria and yeast from tapping knife, tapping panel, spout and collection cups. Field latex after routine collection, contains 10,000-10,00,000 bacteria and 10-100 yeast per ml(10). These organisms proliferate at the expense of the non-rubber constituents of latex, producing organic acids capable of coagulating latex. Increase in bacterial population to about a billion cells per ml is sufficient to cause premature coagulation (pre-coagulation). When precoagulation occurs in latex, processing it into high quality product is difficult. For preventing precoagulation several anticoagulants are used. Sodium sulphite, ammonia and formalin are popular anticoagulants.

Formalin is not generally used in latices which are to be used in the production of pale latex crepe or concentrated latex. In the case of PLC it may create discolouration while in the case of concentrated latex, it may react with ammonia which is used as a preservative for concentrated latices.

Preserved field latex

Natural rubber latex is a negatively charged colloidal dispersion of rubber particles in an aqueous serum. Because of the proliferation of microorganisms, organic acids are produced and these decrease the stability of latex and eventually coagulate it. Hence if latex is to be kept for longer periods, bacterial activity should be suppressed. This is accomplished by the addition of preservatives.

Various chemicals are used as preservatives among which ammonia is of prime importance. Other chemicals used along with ammonia are known as secondary preservatives.

Ammonia as preservative

In plantations ammonia at a concentration of 0.7-1.0% by weight of latex is added for preservation. This treatment preserves latex and maintains it in a stable colloidal condition almost indefinitely. Also during storage, the higher fatty acid esters present in latex get hydrolysed into ammonium soaps which improve the mechanical stability of latex.

Ammonia is effective as a bactericide at concentrations above 0.35 percent. Being an alkali, it imparts an alkaline reaction to latex, thereby enhancing the magnitude of negative charge on the particles and the zeta potential at the rubber-serum interface, thus improving the stability. Some metal ions which tend to coagulate latex are inactivated by ammonia by forming insoluble compounds or complexes with them. Ammonia raises the pH value of latex to about 10.

The advantage of this as has been mentioned is that the optimum range of activity of most putrefactive actions is at a considerably lower pH value and so ammonia prevent the putrefactive action and coagulation. It is cheap and non-toxic in small concentrations. Also it is volatile and therefore evaporates from the rubber when the latex films are dried. However, the odour of ammonia is a disadvantage for some applications of latex.

Low-ammonia preservative system

The presence of high concentration of ammonia presents problems in some manufacturing processes. Apart from handling difficulties, the high concentration of ammonia aggravates the inherent tendency of some serum constituents to get hydrolysed and decomposed into a variety of compounds including simple salts and soaps. This results in a progressive loss of zinc oxide stability of latex which is a property of importance in industrial applications. Because of these disadvantages of ammonia, use of chemicals like tetrahydronaphthalene, alkyl mercury chlorides, arsenious oxide, acetaldehyde, nitrophenols and other organic nitrocompounds morpholine and formaldehyde as secondary preservatives has been reviewed(11). Use of sodium pentachlorophenate as secondary preservative along with 0.2% of ammonia has also been reported(12). Ammonium pentachloro phenate zinc dialkyldithiocarbamate, aminophenols,EDTA, and boric acid have also been used as preservatives(13). Use of 8-hydroxyquinoline and its various halogen and metal derivatives as secondary preservatives in low ammonium natural rubber latex concentrates has also been described(14). Evaluation of miscellaneous vulcanization accelerators as secondary preservatives was also carried out(15). Zinc oxide which is known to be a good enzyme poison, has been tried for the inhibition of volatile acid formation in field latex(16). RRII has introduced monomethylamine as an effective preservative for natural rubber latex concentrate(17).

Preparation of preserved field latex

Latex from the field is sieved and bulked and ammonia bubbled through it so as to get a concentration of 0.7-1.0 percent on volume of latex. It is then kept undisturbed for about 15-20 min to allow separation of sedimentable impurities and reaction products. It is then transferred to drums; sealed and marketed.

If secondary preservatives are also used the concentration of ammonia can be suitably reduced after considering the period to which it is preserved.

Concentration of latex

Natural rubber latex can be concentrated by removing substantial quantity of serum from field latex thus making latex richer in rubber content. Reasons for latex concentration are economy in transportation, preference for high DRC by the consuming industry, better uniformity in quality and higher degree of purity. Evaporation, creaming, centrifuging and electrodecantation are the four main processes used for concentration of latex. Evaporation method involves the removal of water only. Hence the ratio of nonrubber constituents to rubber remains unaffected by this process. The particle size distribution also is unaffected. On the other hand the other three processes involve the partial removal of non rubber constituents and smaller rubber particles. Because of this the range of particle size is reduced and a higher degree of purity is obtained.

Preserved latex concentrates are available in three major types. They are high ammonia, medium ammonia and low ammonia types.

Latex compounding

Uncompounded, unvulcanized rubber is not suitable for use in most rubber products. The quality and durability of modern rubber goods have been made possible only by the practical science of rubber compounding and vulcanizing.

The manufacture of latex goods consists essentially of three steps. 1) Compounding of latex with definite ingredients. 2) Processing or working with the unvulcanized mixtures to form the article to be vulcanized. 3) Actual vulcanisation.

The success of the whole process depends on the suitability of the properties of the original compounds prepared.

Major compounding ingredients are vulcanising agents, accelerators, antioxidants, fillers and pigments, surface active agents, viscosity modifiers and protective colloids and other special ingredients.

Vulcanizing agents

Sulphur is the common vulcanizing agent for natural latex. Thiuram and xanthogen polysulphides are used in some cases. It has been claimed that organic peroxides and hydroperoxides may be used to vulcanize natural rubber latex deposits giving products of a high order of translucency. Recently high energy radiations have been in use for vulcanisation of latex.

Accelerators

Of the wide variety of vulcanisation accelerators available, it is only those of the highest activity which are of importance for the technology of rubber latices. The most important classes are the metallic and amine dialkyldithiocarbamates. The thiazoles and to a lesser extent the thiurams are of importance as secondary accelerators to be used in conjunction with dithiocarbamates. The metal xanthates also find limited application.

Antioxidants

Substances which when added to rubber in small proportions retard atmospheric oxidation or the effects of oxidation of rubber have been commonly referred to as antioxidants. It is not always the practice to incorporate antioxidants into rubber latex compounds since the ageing characteristics of polymers in latex form are intrinsically good. Also the polymer has not been subjected to degradation by mastication or to high temperatures during processing. Account must also be taken to the fact that natural rubber latex and many synthetic latices contain substances which function as polymer antioxidants. But it was practically found useful to incorporate an antioxidant into high quality latex products of high rubber content. The common antioxidants used in latex work are amine derivatives and phenolic derivatives. Amine type antioxidants are generally powerful against the effects of heat, light and trace metals; but they tend to cause discoloration of rubber during ageing. Phenolic derivatives are generally not very effective as antioxidants, but they have the advantage of not causing discoloration.

Fillers and pigments

Inorganic and organic substances are used as fillers.

Inorganic fillers and pigments may be added to a latex inorder to cheapen and stiffen the product or to colour it. It must be emphasized that no effects analogous to the reinforcement of dry rubbers by certain inorganic fillers are applicable in latex compounds. Carbon black and fine particle kaolinite clays do not enhance the tensile strength and tear strength of vulcanised latex deposits as they do for products made from dry rubber. This difficulty is associated with the absence of a mastication step in the case of latex products. Carbon black is used as a black pigment in latex products.

Titanium dioxide is the most effective white pigment. Clay, calcium carbonates etc are also used as fillers in latex to cheapen and to increase the stiffness of the product.

Organic fillers such as high styrene resins and resorcinol-formaldehyde resins are also used for latex work.

Surface active agents

Surface active agents are substances which bring about marked modifications in the surface properties of aqueous media. For majority of surface active materials the principal effect is a lowering of the surface free energy against air and the interfacial free energy against immiscible organic liquids. Substances which have this effect are of great importance in the technology of latex and it is in this respect that latex technology differs most significantly from that of dry polymers and polymer solutions.

Surface active agents are classified as wetting agents, dispersing agents, dispersion stabilisers, emulsifiers, foam promoters, foam stabilisers etc in one classification and in another they are grouped as anionic, cationic, amphoteric and non-ionogenic types.

Viscosity modifiers and protective colloids

Almost all substances considered in this section are hydrocolloids which are soluble in water to give viscous solutions and display the properties of a typical lipophilic colloid system. Their application in latex technology is maintained as modifiers of bulk flow behaviour. The whole relationship between shear rate and applied stress for the system may be radically modified by their inclusion. These substances also function as dispersion and emulsion stabilisers, and in this respect they are often referred to as protective colloids. Whilst they are added to disperse systems in order to enhance the colloid stability, it is important to realise that it is not possible to separate the effects upon stability. For this reason there is a considerable overlap of function between these substances and some of the surface active substances. In addition to their properties as viscosity modifiers and protective colloids, many of these substances possess the ancillary function of being able to accelerate the creaming and sedimentation of dispersions and latices.

Plant hydrocolloids such as alginates, gum arabic, gum tragacanth, gum karaya, locust bean gum, irish moss extract, protein based substances such as casein, glue, gelatin, haemoglobin and chemicals such as polyvinyl alcohol, cellulose derivatives, poly acrylates and methacrylates, carboxylate copolymers, and colloidal clays all come under the group of viscosity modifiers and protective colloids.

Other compounding ingredients

Other special compounding ingredients are also used where latices are compounded for specific applications.

For example mineral oil and nonvolatile esters are used as polymer softeners and plasticisers. Certain waxes and petroleum jellies are used in latex compounding for obtaining certain specific surface effects. Tackifying resins find considerable application in latex adhesives. Antifoaming and antiwebbing agents are important for dipped articles. Corrosion inhibitors, preservatives and fungicides are important in connection with the formulation of latex paints.

Preparation of solutions, dispersions and emulsions for latex compounding

Compounding ingredients are added to latices as aqueous solutions, dispersions or emulsions according as they are water soluble liquids. Direct addition of dry fillers to certain latex foam compounds and the direct addition of ester type plasticisers to polyvinyl acetate latices are the notable exceptions.

The particle size or droplet size, stability and pH of the dispersions or emulsions should be comparable to that of the latex to which it is to be added.

Preparation of solution is important because certain compounding ingredients such as water soluble accelerators, hydrocolloids etc may not be very soluble in water and their solubility will be temperature dependent. Sometimes there will be a tendency for some water soluble accelerators to undergo hydrolysis and this may lead to development of turbidity and sediment. Thus the accelerating activity may get reduced. Casein is very sparingly soluble in water. But it is readily soluble in dilute acids and alkalies. Alkaline solutions of casein can be used in latex compounding whereas acid solutions of casein have little application in latex technology.

Preparation of dispersions

For the preparation of dispersions of solid compounding ingredients, a coarse slurry of the powder is prepared with water, which contains small amounts of dispersing agent and stabiliser. This will be ground in a suitable mill to produce a dispersion of small particle size comparable to that of latex to which it is to be added.

Colloid mills are those which merely break down aggregates of fine particles but do not effect any reduction of ultimate particle size.

Ball or pebble mills, ultrasonic mills and attrition mills are those which do effect a reduction of ultimate particle size as well as dispersing any agglomerates which may be present.

Ball and pebble mills consist essentially of cylindrical containers in which the slurry is placed together with a charge of balls or pebbles. Presence of air space is necessary for satisfactory grinding. The mill is operated by causing the cylindrical container to revolve slowly about its longitudinal axis, which is horizontal. When the mill is working properly, the balls are carried round with the container a short way and then allowed to cascade. It is this process of cascading which causes the particles of the slurry to be comminuted. The container must not be rotated too quickly. Otherwise the balls tend to centrifuge to the sides of the container and fail to cascade. Ball mills are lined with steel and have steel balls.

Pebble mills have ceramic linings and use grinding media such as flint pebbles or porcelain balls. Pebble mills are somewhat lighter than ball mills, and are of lower capacity than a ball mill of similar size and consume less power.

Of the various parameters which affect the efficiency of a ball or pebble mill, the more important are mill speed, size of balls, distribution of ball sizes, ball material, charge volumes of balls and slurry, mill diameter and viscosity of slurry.

It is the emulsions of the oil in water type which are of interest in latex technology. The general procedure for preparing such emulsions is first to make a coarse suspension of oil droplets in water and then subject this to a retiring process which may involve intense shearing and impact. Mainly there are two techniques available for the preparation of coarse emulsions and rather different types of formulation are appropriate to each. The first technique is the obvious one of dissolving the dispersing aids, stabilisers, thickeners etc in water and then adding the oil under high speed stirring. The second technique and more effective is often referred to as the soap-in-situ method. Here a soap is used as the principal dispersion aid. The fatty acid component of the soap is dissolved in the oil and the alkali component dissolved in water together with any stabilisers and thickeners required. The oil phase is then poured into the aqueous phase with rapid stirring, whereupon emulsification takes place spontaneously. The method derives its effectiveness from the fact that soap forms spontaneously wherever a new oil water interface is created, until of course, either the fatty acid or the alkali becomes exhausted. The overall ratio of alkali to acid determines the equilibrium pH of the emulsion. Normally it is desired that the emulsion should be mildly alkaline. A few of the currently available phenolic type antioxidants are liquids and have to be emulsified before addition to latex. Being polar in nature they are quite readily emulsified.

Waxes and petroleum jellies are most conveniently dispersed by melting them and then emulsifying in hot water. It has also been found possible to disperse some of the solid resinous antioxidants by melting them with an equal weight of an oil and then emulsifying the mixture in hot water.

In some cases it may be preferable to add the aqueous phase to the oil phase with stirring so as to produce initially a water-in-oil emulsion. This will subsequently undergo an inversion of phase as more aqueous phase is added.

Vulcanisation

Vulcanisation or cure is an irreversible chemical process during which the ability of an elastomer to flow is reduced and its elastic properties enhanced(18).

Vulcanisation of rubber with sulphur in the presence of low levels of organic accelerators, referred to as conventional vulcanisation, proceeds through a complex series of consecutive and often competing reactions. These involve the initial formation of a complex between the organic accelerator and zinc salts, followed by reaction of this complex with elemental sulphur to form a polysulphidic reactive species. This reacts with the rubber molecules to give polysulphidic crosslinks. This sequence of reactions is further complicated by the thermal instability of the crosslinks formed. Much of the complex chemistry of the reactions was explained by the painstaking work of Moore and his coworkers during the sixties(19). 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(20). Vulcanisation, by chemically crosslinking the long, flexible rubber chains to form a three dimensional network, converts the rubber from a plastic substance of very low strength and breaking elongation into a resilient highly elastic material of considerable strength. Changes in accelerator sulphur ratio cause marked changes in vulcanizate structure which are in turn reflected in changes in physical properties and ageing behaviour(21,22)

The nature and type of vulcanizing agent accelerator systems and activators decide the type of crosslinks formed and thereby determine the physical properties of the elastomer. Zinc oxide is the usual activator used in latex compounding. It has two effects on the reactions of sulphur with olefins. It increases the rate and it changes the product distributions. There is general agreement that zinc oxide promoted reactions proceed by ionic reaction paths(23,24). Zinc dialkyl dithiocarbomate accelerated vulcanisation reactions, which are among the fastest known, are considered to proceed by polar reaction sequences. Differences of opinion exist as to whether the crucial intermediates are ionic molecular fragments or polarised molecules(25).

All chemicals of the vulcanizing system used for the processing of the latex facilitate the fabrication of the product, regulate the rate of vulcanization, effect vulcanization, affect vulcanizing properties and improve the quality and stability of the product in service.

Stability of latex

A stable latex can be defined as one in which no aggregation of the particles occurs under the conditions of test. In all commercial latices, particle aggregation is prevented or retarded by an adsorbed film of one or more surface active compounds surrounding the polymer particles. The latex stabilizers also influence the wet gel strength of latex films.

Stability of latex is of greatest practical importance whenever latex is handled. There are mainly two types of stability problems which are of significance during product manufacture. Mechanical stability and chemical stability. During concentration, pumping, transportation and in compounding and processing, mechanical forces are applied, and the possibility of destabilization exists. The measurement and control of mechanical stability is therefore of considerable importance to both producers and consumers of latex.

A number of published papers have discussed certain aspects of the mechanical stability of natural latex and its compounds. Madge (26,27) examined the effect of soaps on mechanical stability of latex.

Added fatty acid soaps are well known to be capable of increasing the MST of natural latex, and it has been shown previously(28) that the optimum carbon chain length for a saturated fatty acid soap is in the region of 10-12. The increase in MST obtained by addition of soaps depends not only on the soap chain length but also on the VFA of latex(29).

Chemical stability is affected whenever an external chemical substance is added to latex. Chemical coaservation function mainly by reducing the zeta potential which is associated with the electrical double layer surrounding the latex particle. Direct chemical coaservants of a carboxylate stabilised anionic latex can be classified in five groups. They are strong acids, metallic ions, water-miscible organic solvents, polymer miscible organic solvents and cationic surface active substances.

Coalesced or flocculated state is one of lower free energy a the dispersed state and in this respect all latices are thermodynamically unstable.

Ageing

Ageing may be defined as an unwanted deterioration in the physical properties of a polymer due to the action of heat, radiation, oxygen, ozone, or mechanical work either separately or in combination. Degradation and crosslinking of elastomers during storage or service both cause ageing. Reduction in molecular weight of the polymer main chain or reduction in crosslink density from scission of the main chain results in reduction of modulus and tensile strength. Stabilisation against thermal oxidation has been reviewed recently in considerable detail by Shelton(30).

Antioxidants must be added to the polymers to protect the raw polymer during both finishing and storage. They must also be present in service. An extensive list of stabilisers for raw polymers antioxidants suitable for use in vulcanizates, together with their properties has been given in a review by Ambelong et al(31).

Ageing is easily recognised when a material has become unfit for service. It is more difficult to define it quantitatively and particularly during the initial stage where it is not evident superficially by obvious changes.

Accelerated ageing

A few attempts have been made to approach natural conditions of ageing by making several harmful agents act at the same time. But the complexity of multiple actions made it an unsuitable method of test. Accelerated ageing by heat has been considered for a long time but to Geer(32) is due the credit for having established a rational technique and for having developed it to a practical point.

Modified latices

Prevulcanized latex

It has been known for many years that the addition of sulphur, zinc oxide and accelerator to natural rubber latex caused crosslinking of rubber within the individual latex particles. When such crosslinking is slight and the latex product is post cured by conventional means, the precure step is often referred to as a maturing process. When the precure is considerable the latex is classed as a prevulcanized latex, although additional crosslinking normally occurs during drying of the finished article. Such latices are widely employed in the dipping and casting industries, where their use eliminates a compounding and post vulcanizing operation.

Prevulcanized latex is usually prepared by heating the latex with sulphur, zinc oxide and ultra accelerator for about 2 hours at 70°C. Dispersions of the vulcanizing ingredients should be of a particle size small enough to prevent rapid settling but large enough to enable unreacted sulphur and accelerator and zinc oxide to be removed by centrifuging after completion of vulcanization. This can be achieved by passing aqueous suspensions of the ingredients through a colloid mill. The accelerator used are normally of the dithiocarbamate type. The zinc oxide and ammonia content of the latex are important since ammonium salts formed during the vulcanisation have a destabilising influence on the latex which can be offset however, by the addition of suitable stabilisers. Nevertheless, low proportions of zinc oxide(eg.0.5%) are preferred. The combined sulphur content of commercially vulcanised latex is about 1.0%. Changes in the physical characteristics of latex take place for several days after vulcanisation and centrifuging but are almost complete after a weeks storage.

Dried films of properly prevulcanized natural latex are comparable in tensile strength and modulus with post vulcanized films prepared with the same vulcanising ingredients(33). One of the advantages claimed for pre vulcanised latex is that effective control of ultimate physical properties can be exercised before articles are actually manufactured from it. Disadvantages are that the wet gel strength of latex is not so high as that of unvulcanised latex and that the resistance of prevulcanised latex articles to hydrocarbon solvents is often inferior to that of post vulcanised latex product(34).

Although sulphur, zinc oxide and accelerator are normally used to prevulcanize latex, effective prevulcanisation can also be obtained by the use of dicumyl peroxide albeit at high temperatures. Dried film from such latex have a high clarity and good ageing characteristics. Alpha or Beta irradiation of natural rubber latex can produce a similar prevulcanisation to that obtained with dicumyl peroxide.

Radiation vulcanisation

The interaction of electromagnetic radiation with organic substrates is of widespread interest and has broad commercial applications. The use of electromagnetic radiation to alter the physical and chemical nature of a material is termed radiation curing.

The progress accomplished in radiation curing of natural rubber latex has resulted in the development of a promising new material radiation vulcanised natural rubber latex RVNRL(35,36,37).

Radiation vulcanized latex

The procedure for the preparation of radiation vulcanized natural rubber latex(38) consists of three main steps.

They are
1. Mixing of NR latex with sensitizer.
2. Irradiating with gamma rays or electron beams.
3. Adding antioxidants.

The resulting radiation vulcanised latex can be used for the manufacture of latex products by the conventional dipping process. The properties of RVNR latex depend on the quality of NR latex, amount of sensitiser and kind of antioxidant(39). Though the RVNRL has been investigated for a long time, the technique has not been used in industries. The high cost for irradiation for vulcanisation and low quality of products from the RVNR latex were believed to be the main reasons for the lack of interest from the industry.

Recent research in this field shows that radiation vulcanised NR latex have certain special advantages over sulphur vulcanised latex. Absence of nitrosamines, very low cytotoxicity, low emission of SO_2 and less formation of ashes, transparency and softness(low modulus) and degradability are reported for RVNRL. These advantages come from the fact that RVNR latex does not contain dithiocarbamates, sulphur and zinc oxide. A potential area for RVNR latex is in the medical or food related products. The low modulus of RVNR latex rubber are favourable for gloves that are usually used for a long time. The high temperature stability of radiation vulcanizate (c-c crosslinks) is superior to that of sulphur valcanizate (c-s-c crosslinks) in principle because of the higher bond energy of c-c compared to c-s bond. However there is a decrease in the resistance to thermal oxidative degradation of radiation vulcanizate when it is leached with ammonium solution(40). Elution of natural antioxidants is one of the reasons. Absence of dithiocarbamate that functions as strong antioxidants, is another reason for the poor ageing properties.

Radiation chemistry of natural rubber latex is not clearly understood because latex represents a complex system. Each latex particle contains several hundreds to several thousands of rubber molecules and is protected by a rubbery membrane and by a negatively charged thin film of phospholipid-protein complex. Presence of nonrubbers in latex can influence the speed of radiation vulcanisation(41). A high concentration of nonrubbers in latex to be irradiated is found to reduce the speed of vulcanisation by radiation.

In large scale irradiation, where it is necessary to agitate the latex during irradiation inorder to achieve a homogenous dose, there is ingress of air in the system which may reduce the crosslink density of the film and ultimately result in lower tensile strength. This effect is expected to be more pronounced at lower dose rates. Further research about this aspect is in progress. Inorder to clearly understand the vulcanisation process, it is essential to know the response of network structure to changes in the parameters such as concentration of rubber particles in the latex, addition of various additives and ambient conditions under which irradiation is carried out.

Radiation vulcanization vs conventional vulcanization

In sulphur vulcanization sulphur forms crosslinks between rubber chains whereas in radiation vulcanisation rubber free radicals are produced white form crosslinks. The number of free radicals produced by a substance through exposure to gamma rays depends on its `G' value. The `G' value of a substance is the number of free radicals produced for 100 electrons volts of energy absorbed. The `G' value of natural rubber is 0.5. In radiation vulcanisation programmes small quantities of chemicals with high `G' value are added. These substances are called sensitizers.

Significance of RVNRL

In many rubber products like nipples, catheters, condoms and surgical gloves there is intimate contact of the product with human body. It is advisable to use latex of highest purity in the manufacture of such products. Many chemicals used in rubber vulcanisation show skin irritation Also, some additives in rubber compounding are found to favour the production of nitrosamines. All these can be avoided by using RVNRL. Vulcanization of rubber by sulphur is an energy consuming process. It also needs storage of a number of materials at the factory. In sulphur curing all the ingredients should be added as solutions, dispersions or emulsions. Preparation of these can be avoided by using RVNRL. The main advantages of RVNRL are higher purity, biological compatibility of the products and higher transparency of the articles(40). Improvements are to be made in strength properties of the products prepared from RVNRL. More research work is required to utilise the advantageous properties of RVNRL in the manufacture of rubber products in factories.

Latex Products

There are a number of latex products available in the market for varying applications. But to differentiate them by the field of application will not be very easy due to the innumerable number of products and applications. The conversion of natural rubber latex into a product is accomplished in many ways and a stable colloidal system is maintained until it is converted into a solid product(39). Depending on the method of manufacture there are mainly four types of latex products. They are dipped products, foam products, extruded products and cast products. Other latex products include sprayed articles, bonded products and coated articles.

Dipped products

Latex dipping is a process which have been developed since the end of World War I.

The dipping process consists essentially of 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 thickness of the deposit may be reinforced with subsequent coatings. The process is completed by drying, leaching and vulcanising the deposit. It is usually desirable to form a rolled bead at the neck of the article, inorder to reinforce the thin rubber deposit against tearing.

At present a wide range of rubber products is made by latex dipping. The most practically significant of these are the various types of gloves ie. surgeons gloves, household gloves, electricians gloves and heavy industrial gloves. Other important products include certain types of seamless wellington boot, seamless football bladders, toy balloons and prophylactics.

Dipping methods

Simple dipping

By simple or straight dipping is meant dipping without the assistance of any ancillary aids such as coacervants. The deposits will be very thin unless the latex compound is inordinately viscous.

Single dip

Single dip processes give very thin deposits and for this reason are not widely used. Furthermore, the deposit will be more prone to defects such as pinholes which arise from grease spots and other imperfections on the surface of the former.

Multi dip

Straight dipping is usually practised as a multi dip process allowing partial drying between successive dips. Multi dip processes are use for the production of articles such as prophylactics and usually two dips are given for such products.

Wet coacervant dipping

In this method a fluid coacervant such as acetic acid is used to assist the build up of a deposit. It can be done in two ways, according as the former is dipped first into the coacervant or first into the latex compound.

Dry coacervant dipping

The most popular method of coacervant dipping and widely used of all latex dipping processes is that which involves the use of dry coacervants such as calcium chloride, calcium nitrate, cyclohexylammonium acetate and other salts. The former is first immersed in a solution of the coacervant in a volatile solvent. After withdrawal from the solution the solvent is allowed to evaporate and then the former immersed in the latex and a predetermined dwell time is given.

Heat sensitised dipping

The principle of this type of dipping is to employ a heated former and to compound the latex in such a way that it is heat sensitive. The deposit builds up around the former as heat is conducted away into the surrounding latex. The thickness of deposit depends on the degree of heat sensitivity of latex, temperature of former and heat capacity of the former.

Electro deposition

Since the latex particles usually carry a negative charge, it is possible to assist deposition by causing the particles to migrate towards the former under the influence of a potential gradient. Former must have a positive polarity and this arrangement is known as anode process.

Formers

Various materials are employed for the manufacture of formers. Glazed or unglazed porcelain are used for majority of glove and balloon manufacture. Hollow glass formers are used for prophylactic manufacture. Aluminium and its alloys are used because they are light, strong, unbreakable and unaffected by thermal shock.

Other cheaper materials which have been used for the manufacture of formers include wood, plaster of paris and paper.

Dipping tanks

It is necessary to provide a means whereby the latex compound can be kept in motion and circulated from top to bottom of the tank and back again. This should be provided with lids, so that they may be covered when not in use inorder to retard evaporation of water from the compound. It is also desirable to provide a water jacket to keep the temperature constant.

Dipping machines

There are mainly two types of dipping machines. In the one, the formers move downwards into the latex bath, and in the other, the bath is brought upto the formers. Machines of the moving former type are normally used in conjunction with continuous production assemblies.

Sequence of operations

For a general dipping process the main operations are done in the sequence as follows. Compounding of latex, pretreatment of formers, immersion of former, dwelling, withdrawal, inversion of former, drying, beeding, leaching, dusting, vulcanisation, stripping, inspection and after treatments.

Defects

Pinholes, craters and blisters

The largest number of defects encountered in articles produced by dipping come under this heading. Usual cause is air bubbles entrapped in the latex. Pinholes may be caused through particles of dirt and dust settling on the former.

Webbing

The term is applied to the formation of liquid films or webs between adjacent parts of the same former. The cause may be related to the surface free energy of the latex compound.

Mud cracking

Cracking of the deposit during drying out resembles the drying of mud, hence the origin of the name. Low wet gel strength or cohesive strength which is unable to support the forces of contraction due to drying may be the reason for this defect.

Transverse striations

This may be due to uneven wetting of the former or slow rate of immersion.

Blank spots

May be due to the presence of grease on mould surfaces.

Lumpy deposits

Due to latex skin on the surface of the bath or due to incompletely dried coacervant solution running down the surface of the former.

Condoms - A brief history

The condom can well be denoted as one of the oldest contraceptives. It has been mentioned in the history for the first time in connection with the King of Minos in Knossos on Kreta, that fish bladder can be used for preventing conception. Around 1560 it was reported by the Italian doctor Falloppio that linen bags soaked with medicine can be used for the prevention of infection from sexual diseases which was quite widespread at that time.

In the following century, starting from England via france the condom found widespread use all over Europe. The English doctor Conton after whom the condom was presumably named was at that time considered to be the inventor of the contraceptive. At that time thin intestines of the sheep were used. In the beginning of the 20th century, with the invention of vulcanisation, the condom made of rubber appeared in the market.

For some decades the condom was characterised by large wall thickness and insufficient elasticity, but it developed quickly to become the most popular contraceptive.

Natural rubber latex condoms

Before the establishment of the latex industry in the late 1920's and early 1930's, condoms were made by dipping in rubber solution. Prior to that they have been fabricated from rubber sheet and incorporated a seam. The precise date when rubber condoms were first manufactured is not known. The early condoms were relatively thick and were intended for reuse. Latex condoms were introduced in 1932 by which time latex concentrate had become commercially available in rubber consuming countries. The use of latex enabled condoms to be made lighter and disposable.

The dipping process is used to manufacture latex condoms and formers used are usually made of glass. High quality latex and compounding chemicals are required for condom manufacture because they may otherwise cause skin irritation or other problems.

Natural rubber latex condoms versus other condoms

Natural rubber latex condoms are widely accepted as a contraceptive. There has not been a synthetic product made that has the same strength characteristics as latex condoms. But research is going on in the new prophylactics made of materials other than traditional latex such as thermoplastic elastomers and polyurethane. The makers of the new condoms promise such attributes as increased sensitivity for the user and partner, plus superior protection against sexually transmitted diseases and low toxicity for those allergic to latex proteins. But exactly how big the market will be for the new condoms remains uncertain, especially since none of the condoms have landed in the commercial sector yet. London International Group PLC is one company with a non Latex male condom(42).

AIDS and contraceptives

The Acquired Immuno Deficiency Syndrome or AIDS, was first spotted in 1981 in the USA in a young homosexual male, who had a rare form of cancer notably pneumocystis carinii - a form of pneumonia rare among young men.

Contraceptives were forbidden in the USA in 1873 but condoms were excluded from this ban as it was considered that they prevented infection. AIDS is spreading rapidly world wide particularly in South Asia and Africa. The data published at the first meeting of the United Nations Programme on AIDS (UNAIDS) held in Geneva in July 1995 shows the current status of AIDS and HIV infection. There are 20 million people world wide who have been infected. It is estimated that there are 6000 new infections every day, of the 20 million people carrying the AIDS virus. 4.5 million have full blown symptoms of the disease.

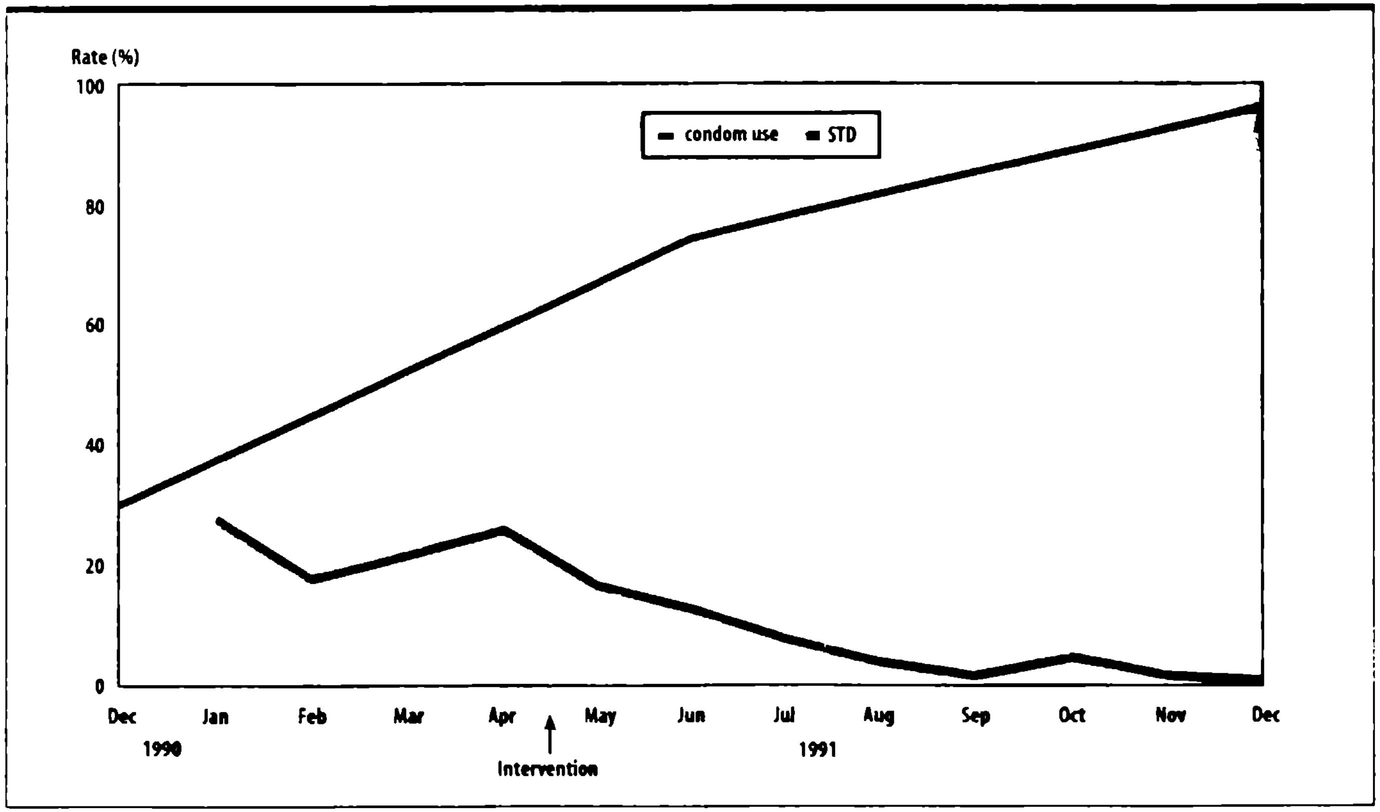
The aids epidemic have greatly increased the demand for condoms in many countries. The initial surge was in 1987-88. Data from a national survey of US drug stores showed that condom sales rose from 240 million annually in 1986 to 299 million in 1988. The global production increased from 4.9 billion units in 1981 to 8.5 billion units in 1990.

To fight against the spread of AIDS quality condoms are needed. The World Health Organisation, The world wide AIDS prevention community and the family planning community are demanding more rigorous standards. They also want condom manufacturers to share the responsibility of fighting the scourge of AIDS.

There is a quite revolution or better yet evolution going on in condom market. With the advent of AIDS condom makers are developing condoms to give consumers more choices and more protection.

According to `very conservative' estimates made by the World Health Organisation about 5 to 7 million Indians could be infected with HIV by the turn of the century. An economic analysis carried out by the United Nations Development Programme (UNDP) has shown that for each Indian suffering from AIDS, direct costs (drug treatment, hospitalisation etc) would approximate to Rs.23,000 ($738). Indirect costs (income foregone because of AIDS related morbidity and mortality) could add upto a staggering Rs.3,15,000 ($10,100). The study estimates that by the year 2000, India could end up spending Rs.34,500 crore on the 1 million AIDS patients. These are all facts relating the economic aspects only and even by considering this the significance of condoms is clear. The chief of WHO's AIDS

Increase in reported condom use and decrease in STDs among sex workers following the introduction of 100% condom use, Pitsanuloke province, Thailand



programme Dr.Michael Merson emphasised that it was better to invest now in controlling the disease rather than to have to spend 10 to 100 times more at a later date.

India has the largest number of people infected with HIV in the world. The way the government and society respond over the next few years will be critical to the way the epidemic develops here. It is also clear that women were most often the causality for no fault of their own. In Africa 70-90% of the women who have the HIV have only one sexual partner.

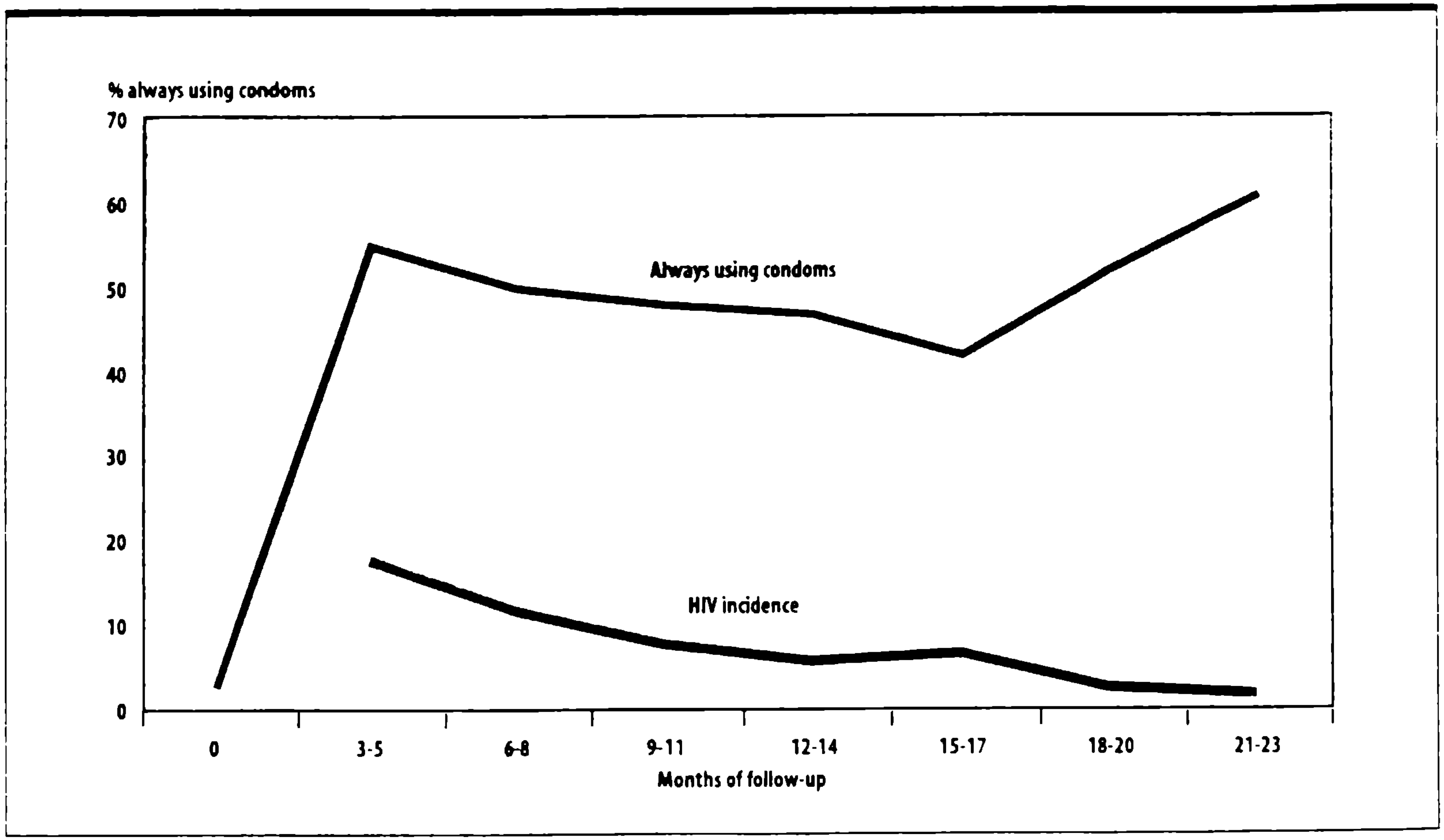
Preventing the transmission of HIV

As part of its role in reviewing and consolidating existing information and knowledge about interventions to prevent the transmission of HIV, Global Programme on Aids (GPA) held a meeting in May 1993 to discuss approaches to AIDS prevention which have proven effective. The aim was to determine which approaches work best, how and why they work, and whether their effects will be lasting. The discussion was centered around 13 selected projects grouped into five themes.

1. AIDS prevention through community- reaching people through social networks.
2. AIDS prevention through condom promotion.
3. Reaching the hard-to-reach.
4. Media campaigns for the prevention of AIDS.
5. Health service based prevention.

Among this AIDS prevention through condom promotion was found practically successful. It was clear that organisations

Increase in reported condom use and decrease in new HIV infections during an intervention among female sex workers in Kinshasa, Zaire



and groups throughout the world have developed innovative projects and two projects in Zaire illustrate the effects very well. Condom sales was increased from half a million in 1987 to 18 million in 1991 among Zaires population. Thus the Zaires population accepted condoms for HIV prevention.

Any strategy promoting safer sex in the general public must ensure that condoms are easily accessible to those at greatest risk of being infected or inflicting others with HIV (eg. men and women who have multiple partners). Despite high HIV/AIDS awareness reported, use of condom remains low in many countries. For example the results of KABP (Knowledge, Attitudes, Beliefs and Practices) studies carried out in late 1980's indicate that sexually active men in many African countries are reporting high levels of multiple partners and low levels of condom use in high risk encounters and more recent surveys and studies indicate that condom use is increasing slowly.

The dependability of condoms

Even though it is established that natural rubber latex condoms can act as a barrier to virus transmission, its dependability in actual practice is being questioned. Even though manufacturers claim the best qualities to their product, the rate of pregnancy even at the condom using period and failure of condoms due to breakage etc indicate that there are quality problems related to the product. Due to the quality requirement by the customers WHO has amended the specifications for condoms. The amendment in October 1991 ensures the condom's fitness for use. Earlier the national standards for condoms have been evolved based on national regulatory requirements or the desire of the industry to improve its product. In general, these standards do not fully take into account the serious consequences of breakage when condoms are used for protection against AIDS nor are designed to deal with storage conditions in tropical and developing countries.

Essential performance criteria

To be effective, condoms must not break during use. If a condom breaks during use, it has failed completely. Breakage puts the user or partner at risk to some extent as if no condoms were used. Freedom from breakage is the most important criterion for quality of condoms.

The second most important criterion is leakage caused by large pores or microscopic holes known as pinholes. These flaws may put the user or partner at some risk, depending upon the size and location of the holes and other factors.

In developing countries or in other circumstances where condoms may be stored for long periods at substandard conditions, shelf stability assumes a very high level of importance. Condoms are perishable goods. When condoms deteriorate, they are much more likely to break during use.

Unfortunately uniformity of strength and elasticity which are indications of the potential for breakage during use have often been ignored.

Because condoms are produced directly from natural materials, they may never be as uniform as synthetic products. But the variations should be within certain limits to avoid the risk of users by limiting to the greatest extent possible those condoms that will break or leak during use.

Limiting condoms that will break during use

The less elastic and strong the condoms the more likely it is to break. By examining the variation in stretch and breaking force of sample condoms, the proportion of weak condoms can be estimated for the whole batch or production lot. Clinical trials have confirmed that weak condoms are more likely to break during use.

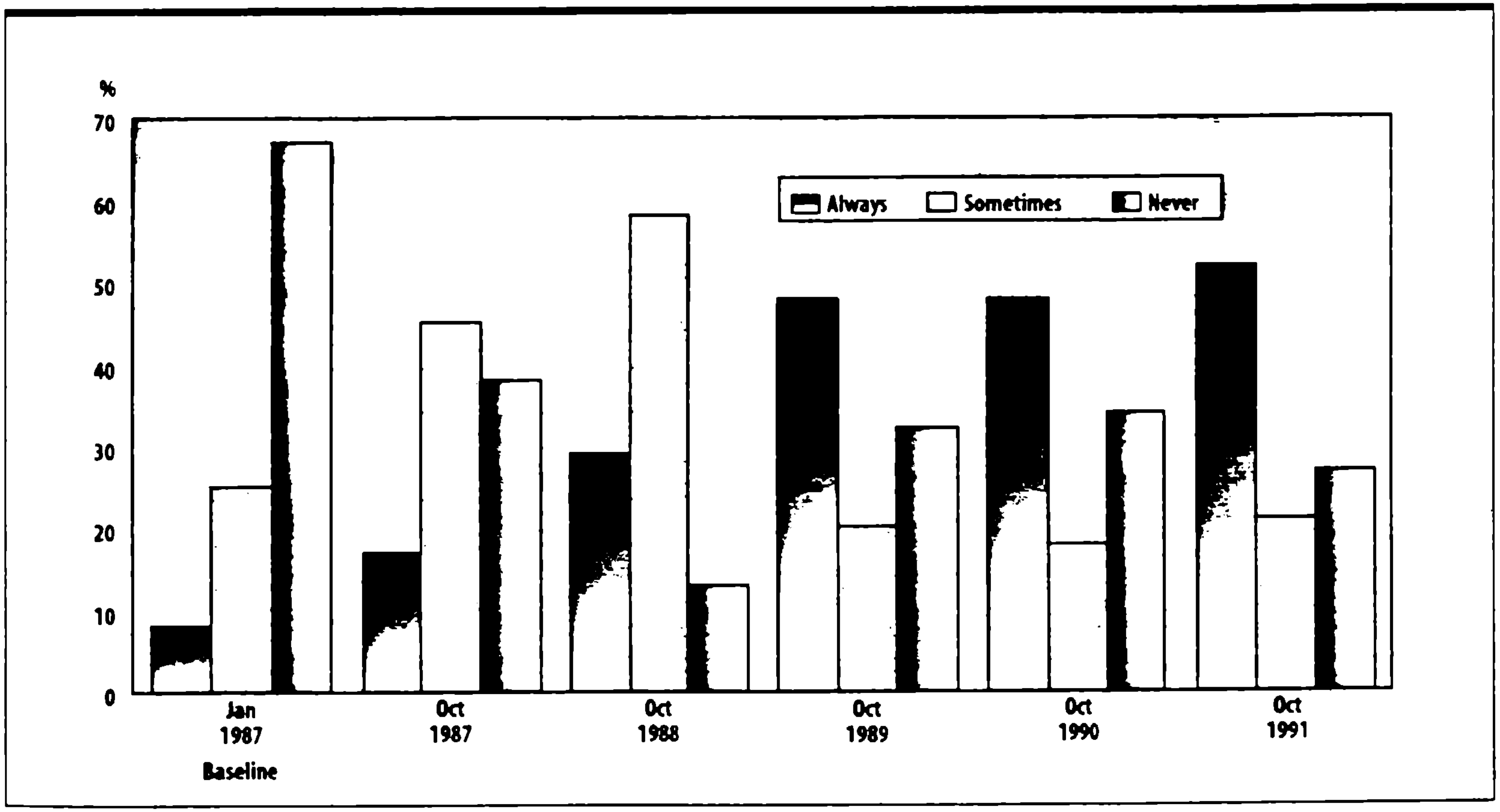
Until a few years ago the emphasis was on the features of freedom from holes and the tensile strength. Later a clear, if not yet quantified, relationship between the volume and pressure at which condoms break under inflation and the incidence of breakage in use has been established. Bursting tests have the advantage of measuring the strength and elasticity throughout the entire length of condom.

The standards/specifications for condoms such as WHO September(1992), ISO4074-1, ASTM: D 3492,(1983) and BS.3704(1989) are replaced by WHO June 95,ISO 4074-1-2 ASTM D 3492-(1993) and BS 3704(1989) amendment No.2, 1995 respectively.

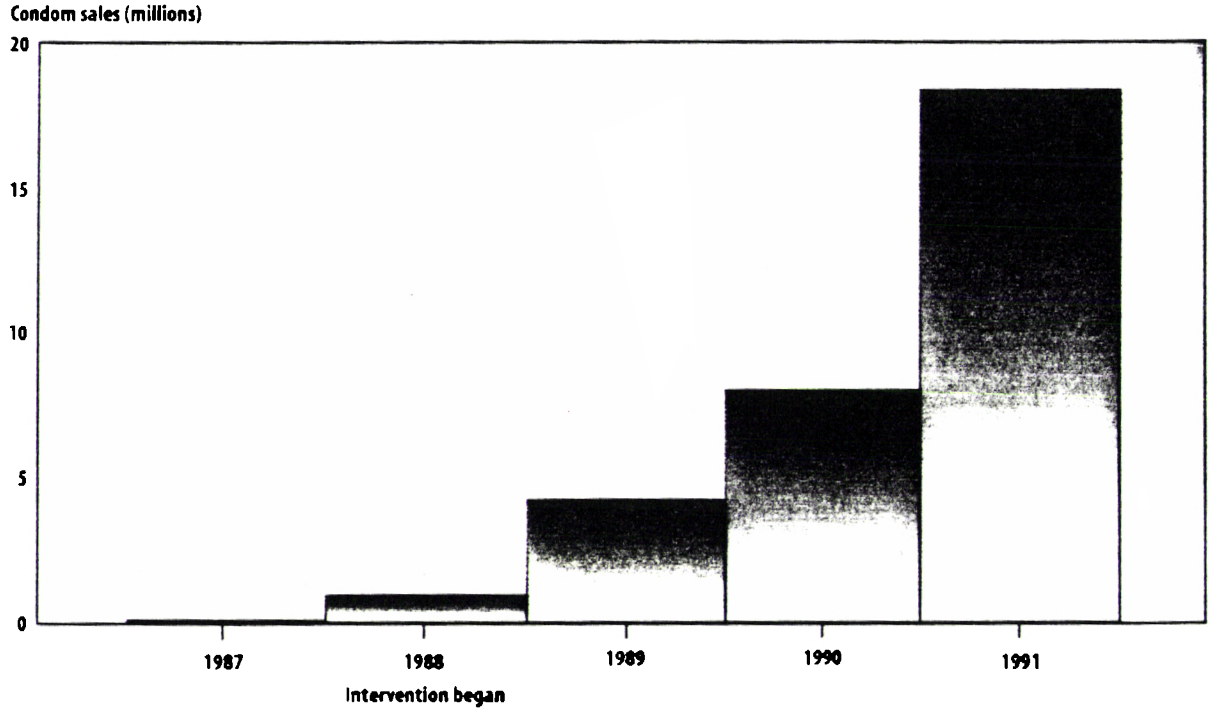
In the new standards the acceptance quality levels (AQL) for absolutely critical parameters such as freedom from holes and bursting volume and pressure are more stringent.

Tensile tests have two major limitations. First, they

Percentage of 17-30-year-olds reporting condom use with casual partners, Switzerland



Increase in condom sales through social marketing in Zaire



measure only a small portion of the condom, usually taken from the middle of the shaft. Therefore they cannot detect flaws in the condom throughout its entire length and especially those at the critical closed end. Secondly, only a small number of samples are tested, sufficient to provide an index of proper formulation and curing. This small sample does not allow for sensitive measurement of uniformity of the batch with respect to strength and elasticity. Air inflation tests have the advantage of testing the entire condom. Also because the tests are relatively simple to perform, they are generally done in large numbers and can provide a sensitive index of the uniformity of the batch or production lot. Both volume and pressure at burst have been shown to correlate with breakage during use.

Limiting condoms that may leak during use

Virtually all standards prescribe a test for freedom from holes. This test is based on filling random samples of condoms with water and looking for leaks. In some countries such as Japan, Korea and some European countries, an electrical conductance test is used whereby sample condoms are filled with conductive solution and dipped into another conductive solution. The flow of electric current across the condom membrane is then measured.

Limiting the rate at which condoms may deteriorate in the shelf

The ways that condoms deteriorate are not yet fully understood. It is known that condoms stored in hot climates without careful climatic control deteriorate much more quickly

Reported condom use by adults in the general population in seven African countries

Country	Reported behaviour
Botswana (Gaborone)	48.2% of men (15-25) used with any partner in past year 69.9% of women (15-25) used with any partner in past year 61.8% of men (15-25) used with casual partners in past year 20.4% of women (15-25) used with casual partners in past year
Burkina Faso (Ouagadougou)	33.0% of men always used in past 6 months 9.0% of women always used in past 6 months
Burundi (Bujumbura)	13.8% of people (men and women) used at least once in past year
Central African Republic (Bangui)	35.4% of men always used in past year with non-regular partner 9.5% of women always used in past year with non-regular partner
Ethiopia (Addis Ababa)	33.4% of adults (men and women) always used in past year
Guinea (Conakry)	2.8% of men currently use with any partner 1.4% of women currently use with any partner
Zambia (urban)	60.0% of post-secondary students (M&W) always use with non-regular partner 16.0% of post-secondary students (M&W) always use with regular partner

than condoms stored in temperate climates. The primary goal of good transport and storage systems for condoms is to keep the products cool and to protect them from sunlight, oxidising agents and mechanical damage. Some countries and ISO prescribe oven ageing tests variously described as "storage resistance" or accelerated ageing. There is very little empirical correlation between the ageing tests and deterioration in the field. A positive result based on these tests is insufficient to guarantee adequate shelf life in the field. However, oven ageing may provide some warning of inappropriate formulation or curing of the latex film.

Scope for the present work

Condoms are widely accepted as a contraceptive for family planning and population control. It is also accepted as the most effective barrier against sexually transmitted diseases, especially AIDS, the incurable disease. But presence of pinholes and low film strength of condoms make it unsuitable for the purpose. Quality improvement of condoms by reducing the pinhole formation and increasing the film strength is thus an essential requirement for population control as well as for preventing the spread of sexually transmitted diseases. Strict implementation of WHO specification of condoms further increases the rejection percentage. This causes higher rejection loss to condom manufacturers because the defects could be identified only at the final stage of processing. If the influence of various factors which cause these defects is known, manufacturers can take remedial measures to reduce the defectives so that rejection loss can be decreased and quality of condoms increased.

Condoms being manufactured from natural rubber latex, its property variations may depend on quality of latex, compounding variables and process parameters. Among the compounding variables, stabilizers, vulcanising chemicals, and antioxidants form the most important class. Process parameters such as ball milling time of dispersion, concentration and temperature of mould cleaning solution, period and temperature of vulcanisation constitute another important class of variables which determine the pinhole formation and properties of condoms. Comparative evaluation of prevulcanised, postvulcanised and radiation vulcanised latex also was found essential to make use of the advantageous properties of these modified latices.

In the present study, it was proposed to conduct experiments to improve the quality of condoms by reducing the pinhole rejection percentage and increasing the tensile properties, burst volume, and burst pressure. Ageing property improvement also was an important target among other parameters. Until a cure for AIDS is found, a high quality latex condom is the only effective device in the prevention of the spread of HIV, AIDS and STD's. Hence it is all the more necessary to have high quality condoms.

CHAPTER II

EXPERIMENTAL TECHNIQUES

MATERIALS

High ammonia centrifuged natural rubber latex whose characteristics are listed in Annexure 1 was used for the study. Low ammonia preserved latex used was LATZ which contain 0.35% ammonia and 0.025 TMTD/ZnO (1:1) prepared at Rubber Research Institute of India. Radiation vulcanised natural rubber latex (RVNRL) used for the studies also was prepared at RRII, Kottayam. Ammonia concentrated acids such as HCl, H_2SO_4, HNO_3 etc, Methyl red, Phenolphthalein, Sodium carbonate, Barium hydroxide, Ammonium sulphate, Acetic acid, Potassium hydroxide, Formaldehyde etc were laboratory grade reagents. Compounding ingredients such as Potassium oleate, Potassium laurate, Poly vinyl alcohol, Emulvin-T (stabiliser based on poly ethylene oxide condensate manufactured by Bayer(India) Limited, Vulcastab VL (stabiliser based on polyethylene oxide condensate manufactured by ICI(India) Limited, Casein, Nocceller TP (sodium di-n-butyl-dithiocarbamate) manufactured by Ouchi Shinko Chemical Industrial Co. Limited, Japan, Setsit-5((Activated dithiocarbamate) manufactured by Vanderbilt Co. USA), Zinc oxide, Zinc mercapto benzo thiazole, Sulphur, Nocrac NS 5 (2,2 methylene 4 ethyl-6 tert-butyl phenol) manufactured by Ouchi Shinko Chemical Industrial Co. Ltd. Japan., Vulcanox HS (poly 2,2,4 trimethyl 1,2 dihydro quinoline) manufactured by Bayer(India) Ltd., Irganox 1010 (penta erythritol-tetrakis-(3-(3',5'-di-tert butyl-4' hydroxy phenyl) propionate)) manufactured by Ciba Geigy, Pentaflex SP(E) (styrenated phenol) manufactured by polyolefin Industries Limited, Vanox SKT (3,5- Ditert butyl 4 hydroxy hydro cinnamic acid triester with 1,3,5 tris (2 hydroxy ethyl) s-triazine-2,4,6 (1H,3H,5H) trione), Vanox MBPC (2,2' methylene bis(4-methyl 6-tert butyl phenol),Darvan no.1 (sodium salt of polymerised alkyl naphthalene sulphonic acid) and Darvan no.2 (sodium salt of polymerised substituted benzoic alkyl sulphonic acid), manufactured by Vanderbilt Co. USA etc were of commercial grade.

METHODS

Analysis of Rubber Latex

Total Solid Content (TSC)

It is the percentage by weight of the whole latex which is non volatile at a definite temperature.

For the determination of TSC (43)about 2 gm of the latex sample is accurately weighed into a petridish. It is made into a thin coating at the bottom of the petridish. It is then dried in an air oven at a temperature at 70±2°c for 16 hrs., cooled in a dessicator and weighed. The process of drying and weighing are continued until concurrent values are obtained.

If W_0 is the initial sample weight, and W is the weight of the residue then, total solid content is calculated as $100xW/W^0$

Dry Rubber Content (DRC)

The dry rubber content of a latex (44)is defined as the percentage by weight of the whole which is precipitated by acetic acid under closely defined conditions.

About 10gm of the well mixed latex sample is accurately weighed to a beaker. It is then diluted with water and 8ml of acetic acid per gram of the sample is gently added with stirring. The solution is kept undisturbed for 15 minutes at a temperature little below boiling. If the serum is milky, rectified spirit is added and stirred. Coagulum is then washed in running water and using hand roller it is made into a thin sheet of 2 mm thickness. The coagulum is dried at 70°C for 16hrs. It is cooled in a dessicator and weighed till constant values are obtained.

If Wo is the initial sample weight and W is the weight of the coagulum obtained, then the dry rubber content is calculated as $100 \mathrm{x} W/W^{o}$.

TOTAL ALKALINITY AS AMMONIUM CONTENT

It is the free alkali content of a latex. About 1 to 3gms of latex sample is weighed and it is titrated against standard acid (0.1N Hcl) using methyl orange as indicator. The test is conducted in water medium. Ammonia content (45) is calculated by the equation

$$\text{Ammonia content} = \frac{V \times N \times 0.017 \times 100}{W}$$

Where 0.017 is the million equivalent weight of ammonia.

V = Volume of acid consumed, N = Normality of acid, W = Weight of acid

$$\text{Total alkalinity} = \frac{\text{Ammonia content} \times 100}{100 - \text{TSC of the sample}}$$

VISCOSITY

Brookfield LV viscometer was used for measuring the viscosity of latex. It consists of a rotating cylinder driven by a synchronous motor through a beryllium-copper torque spring. The viscous drag on the 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 a pointer and scale. The pointer is attached to the cylinder spindle and the scale to the drive spindle above the spring, so that both pointer and scale rotate. While taking the reading, they are clamped together and the rotation stopped when the pointer is opposite a window which is cut out of the casing. A range of speeds and of discs and cylinders is available so that a wide range of viscosity may be covered. Brookfield LV viscometer model DV.II+ version 3.2 also was used for the study.

COAGULAM CONTENT

The material which is retained by a mesh of arbitrary size under specified conditions of test is known as coagulum. The procedure for natural rubber latex is to dilute 200 gm of latex with an equal volume of a 5% alkali soap solution(potassium oleate) and then to filter through a stainless steel gauze of 80 mesh as per ASTM. The coagulum is washed with soap solution until free from latex and then with distilled water until the washings are neutral to litmus. The gauze is then dried to constant weight at 70±2°C. The coagulum content is expressed as a percentage of the weight of the latex sample.

MECHANICAL STABILITY TIME(MST)

By the mechanical stability of a latex is meant its resistance towards those mechanical influences which tend to increase the number and violence of collisions between particles and so tend to coacervate the latex.

Klaxon MST apparatus is used for the measurement of MST. Latex sample is diluted with 1.6% ammonia to adjust the TSC to 55±0.2%.Then 80±0.5 gm is weighed into the sample container and adjusted its temperature to 35±1°C. Placed the sample container in the apparatus so that the distance between the bottom of the container and the circular plate inside is 13±1mm. Then the shaft is rotated at a speed of 14000±200 rpm. End point is taken when the coagulum capable of discrimination by naked eye has begun to generate and the MST is expressed by seconds of the period from beginning of the test to end point. For discrimination of the end point, a drop of sample is taken at the tip of a sampling bar, the end of which is made of a sphere of diameter 2 mm and it is made to fall on the surface of water taken in a dish, then grains of coagulum float scattered on the water surface. Duplicate also is done to confirm the result.

VOLATILE FATTY ACID NUMBER(VFA number)

It is the number of grams of potassium hydroxide equivalent to the steam volatile fatty acids which are produced by the acidification of latex containing 100gm total solids. 50 gms of latex sample of known TSC and DRC is weighed into a beaker. 50ml of Ammonium sulphate solution is added and warmed over a waterbath until it coagulate. Then the serum is pressed out of the coagulum by kneading with a glass rod and 10ml of the serum is transferred into a conical flask. It is acidified with 2ml of dilute sulphuric acid and is introduced into the Markham still apparatus. Few drops of silicone antifoaming agent is also added and the distillate is collected. It is then titrated with barium hydroxide. A blank test is also conducted by substituting 20ml of water for 50gm of concentrated latex.

Volatile Fatty Acid Number(46) is calculated using equation;

$$\text{VFA Number} = \frac{\dfrac{56.1 \times V \times N}{1000}\left[50 + W\left(\dfrac{100 - DRC}{100D}\right)\right] 100 \times 100}{10 \times 50 \times TSC}$$

Where V = Volume of Ba(OH)2 used

N = Normality of Ba(OH)2 used

W = Weight of latex taken

TSC = Total Solids Content

D = Density of Serum

POTASSIUM HYDROXIDE NUMBER (KOH Number)

The KOH number is defined as the number of grams of potassium hydroxide equivalent to the acids present as ammonium salts in a quantity of latex containing 100gm of solids.

Weigh to the nearest 0.1gm into a 400cm^3 beaker a quantity of latex containing approximately 50gm of TSC. Alkalinity is adjusted to 0.5$\pm$ 0.1% ammonia calculated on waterphase by adding the required quantity of formaldehyde solution.

$$\text{Weight of 5\% HCHO to be added to reduce the total alkalinity by 5\%} = \frac{\text{Weight of latex } (100 - \text{TSC})(\text{TA} - 0.5)}{189}$$

where TA - Total alkalinity

Dilute the latex with water to about 30% total solids.

Water to be added = 166.7- wt. of sample + wt. of HCHO

where 166.7 is the total quantity of sample to be taken for testing.

Insert the electrodes to the latex and slowly add 5 cm^3 of the KOH solution. Resultant equilibrium pH reading is recorded and KOH solution addition is continued in $1cm^3$ increments recording the equilibrium pH after each addition until the end point has been passed. Then KOH number(47) is calculated.

$$\text{KOH number} = \frac{561 \times V \times N}{W \times TSC}$$

where V - Volume of KOH at end point

N - Normality of KOH

W - Weight of sample.

pH VALUE AT 25°C

pH of a latex sample(48) is measured using standard pH meter as per clause 6 of ISO 976-1977(E)

ZINC OXIDE VISCOSITY

This test is used for the assessment of the ability of a latex to resist the effects of chemical destabilisation with zinc oxide. Principle is to determine the change in viscosity which occurs when a latex is compounded with zinc oxide under standard conditions.

320 gms of latex sample was taken and the viscosity of the sample at 25°C is noted. Then 5gms of 40% zinc oxide (approximately 1 phr) is added to the sample and viscosity is noted after 5 minutes when temperature is kept at 25°C. The sample is kept as such for 60 minutes and again tested for zinc oxide viscosity (ZOV), Zinc oxide heat stability time (ZHST) and Zinc oxide Mechanical Stability Time(ZMST)

Zinc oxide Heat Stability Time(ZHST) For this 50 cc of latex is placed in a water bath at 90±2°C and it is stirred at a constant speed. Time taken for complete coagulation of the sample is found out.

Zinc oxide Mechanical Stability time(ZMST) Latex sample is heated to 35±1°C and 80 gm of the sample is sieved through an 80 mesh and tested for MST using Klaxon MST apparatus.

PREPARATION OF DISPERSION

All solid compounding ingredients were added to latex in the form of dispersion. Here a 50% mixed dispersion containing all solid compounding ingredients was prepared by ball milling for 72

h. To study the effectiveness of ball milling particle size analysis also was done using a Malvern 1 M 120 particle size analyser. The particle size is based on the principle of laser ensemble light scattering. It can be used to measure particles of size varying from 0.1 to 600 μm. Depending on the size range of the particles, lenses of focal length such as 45mm, 100mm and 300mm can be used. These lenses can measure size ranges of 0.1 to 80 μm, 0.5 to 180μm and 1.2 to 600μm respectively.

The light scattered by the particles and the unscattered remainder are incident onto a receiver lens known as range lens. This operate as a fourier transform lens forming the diffraction pattern of the scattered light at its focal plane. The unscattered light is brought to a focus on the detector and passes through a small aperture in the detector and out of the optical system. The total laser power passing out of the system in this way is monitored allowing the sample volume concentration to be determined.

As material flows through the beam the measured light scattering is continuously changing forming the instantaneous integral of the material illuminated by the analyzer beam. By making many measurements of the detector readings(sweeps) and averaging over many such sweeps of the detector, it is possible to build up an integral light scattering characteristic based on millions of individual particles.

COMPOUNDING

Compounding of latex was done as per the formulation given for each compound and the order of addition of ingredients also was followed as in the respective formulations. After the addition of each ingredient 1% ammonia solution was used to wash the container so that complete transferring of the ingredient is ensured. Stirring was also done continuously to get a uniform mix without any agglomeration or settling.

MATURATION

A period of 16 h was given for maturation of the compound.

PREVULCANISATION

The compounded latex was heated in a water bath to 55°C for 8 hours with continuous stirring. The container was kept closed to prevent the escape of ammonia by evaporation. The total solid content of the latex was determined and it is reduced to 48 using 1% ammonia solution. Viscosity measurements were made before and after dilution.

MOULDING

Moulding of condoms was done by straight dipping method. Glass formers were cleaned thoroughly using soap solution and dried. It is then dipped in the diluted latex to form a very thin deposit of latex over it. A period of 20 seconds for immersion, 10 seconds as dwelling time and 30 seconds for withdrawal was the usual time schedule. After the first dip, the former was inverted and rotated to get a uniform deposit of latex. It is then dried by rotating over a hot plate. Twenty formers were given their first dip and then started the second dip one by one. The period of immersion, dwell time and withdrawal were same as for first dip. Edge rolling was done by hand to form an intact bead which prevents, the deposit from tearing while stripping and testing.

VULCANISATION AND STRIPPING

After drying, the deposit along with the former is kept in an air oven at 80°C for 30 minutes. Then it is cooled and stripped using french chalk powder.

CONDITIONING

The stripped condoms were conditioned for 24h at room temperature.

TEST FOR LEAKAGE

These tests were carried out by following the procedures given in BIS 3701(1985).

Air leakage test was conducted by inflating the condom with air to a diameter of 150mm and by examining them for the presence of pinholes. The examination of the inflated condom was completed within a minute.

Water leakage test was conducted by filling the condom with 300ml of water at room temperature. It was then suspended for 1 minute to detect any visible leakage through the condom wall. The condom was then rolled over an absorbent paper after closing its open end by twisting it near the rim. The paper was inspected for signs of leakage.

TEST FOR PINHOLES

Electronic testing was carried out to detect presence of pinholes in the product.

Products were placed tightly on the test moulds of automatic pinhole testing machine. It was then dipped in a wetting solution 25mm below the bead line of the product.

The wetting agent is a 0.1% solution of alkyl sulfo succinate in water kept at 70°C. The solution helps the powder on the product to be wiped off and it will penetrate through holes present facilitating permeation of the electrolyte to enable positive detection of the pinhole.

DETECTION OF PINHOLE

By dipping the covered products on the test mould into the detecting tank the electrolyte will penetrate through existing pinholes to make direct contact with the test mould. Then a constant electric current is applied between the test mould and electrolyte solution. The variation in voltage due to the degree of resistance is detected by the inspecting control device in the detection board to determine the presence of pinhole. Pin switches linked to the products to determine the existence of pinholes are hit by a detecting solenoid if there is a pinhole. Subsequently these pin switches are sensed to classify the defectives later in the classification process. The electrolyte in the detecting tank is a 0.1% solution of sodium hydrogen carbonate maintained at 40-50°C by a water jacket for cooling and a steam pipe is equipped inside the tank for heating purpose.

After dipping in the detection tank it is washed by passing through a water tank kept at 45 to 65°C. It is then dried by radiation heaters and hot air in the drying chamber kept at 60-100°C. Sponge will wipe off the water on the teat of products.

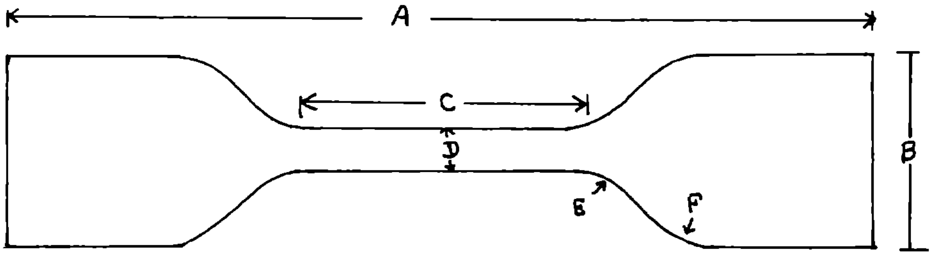
Products are then rolled up using sponge disc and are classified into good and defective, according to the position of pin switches.

TEST FOR TENSILE PROPERTIES

MODULUS, TENSILE STRENGTH AND ELONGATION AT BREAK

These tests were carried out using a Zwick universal testing machine (UTM) model 1474(1980). The machine consists of a load frame and an electronic control unit. Load measuring device is load cell fixed at the top of the load frame. Below the load cell is a moving platform driven by a continuously variable speed motor. The speed of movement of the platform can be varied according to the requirement. Grips suitable for dumb bell specimens are fixed on the load cell and the moving platform. During testing the specimen is subjected to stretching at constant speed. Force and elongation are continuously monitored by the electronic unit. Test specimens were kept at ambient temperature. Thickness measurement was carried out using a micrometer the foot of which exerts a pressure of 200 g/cm^2 on the rubber. Bench mark of 20mm was given at the middle neck portion of the dumb bell test piece. Since the width of the breaking neck portion is constant, the area of cross section is calculated using the thickness measured. Velocity of movement of crosshead of the machine was adjusted to 500 mm/minute. Modulus at 500% elongation, elongation at break and tensile strength can be calculated for each sample.

DIMENSIONS OF DUMB-BELL TEST PIECE IN mm.



A - Overall length minimum 115

B - Width of ends 25±1

C - Length of narrow parallel portion 33±2

D - Width of narrow parallel portion 6.0 to 6.1

E - Small radius 14±1

F - Large radius 25±2

Tensile strength is calculated by dividing the load at break by the initial area of cross section of the test piece. Results of the dumb bell test piece which breaks outside the neck portion are avoided.

Modulus (M_{500}) was calculated by dividing the load at 500% elongation by the initial area of cross section. Elongation at break was calculated by subtracting the bench mark distance from the final elongation and expressed it as a percentage of the initial distance.

TEST FOR BURST VOLUME AND BURST PRESSURE

These tests were carried out as per ISO 4074/6-1984(E). Enersol automated condom inflation tester was used for the testing. In this test a constant length of the condom was inflated with clean air at a rate of 0.4 to 0.5 dm^3/s. Test was conducted at ambient temperature of 25°C and at ambient pressure of 100 Kpa. Its bursting volume and bursting pressure were directly obtained from the burst volume tester.

TEST FOR ELECTRICAL RESISTANCE

For electrical resistance measurement condoms were filled with a conducting solution and placed inside the conducting medium through which electricity is passed. Electrical resistance offered by the condom wall was measured using the japanese industrial standard machine.

The JIS Tester consists of chain conveyor with 424 product holders and chain conveyor for electrodes with 14 electrodes. Detecting tank is filled with 1% sodium chloride solution and can be moved up and down. Service tank for sodium chloride solution is provided with automatic level controller with alarm system. Rotary supply tank, stripping and drying line, and detecting instrument are the other attachments.

To carry out the testing the required resistance value is selected and set as reference. The print/stop key is selected for print position. Products are fixed on the product holder one by one and as the chain advances the solution from the service tank is poured into the products through a rotary supply tank. The supply of the solution is controlled by the proximity photo sensors timing pulses which in turn controls the ON/OFF of the solenoid valve. Feeding delay and feeding quantity are set by the timers. The conveyor advances to detecting tank. There the electrode is inserted inside the product containing sodium chloride solution so that pinhole can be detected by the detecting device, pin contact of each electrode contacts to the slide contactor. If there is any pinhole the resistance will be low and this value will be printed in red ink (value below reference resistance) and the buzzer sounds with a glow of the lamp. Then the product is removed and tested visually for pinholes. Products having higher than reference resistance are stripped out using rotary disk brush, and are received in a separate tank. The values are printed in black ink. The electrodes contain zinc sulphate solution, zinc rod and agar-agar.

The reference resistance can be set according to the thickness of the condom wall and required electrical resistance.

TEST FOR AGEING RESISTANCE

Accelerated ageing test was carried out to study the ageing properties of condoms. The test consists in subjecting test pieces to controlled deterioration by air at an elevated temperature and at atmospheric pressure after which tensile properties, burst volume, burst pressure etc were measured.

The air oven was provided with slow circulation of air and the temperature of the oven was thermostatically controlled so that the test pieces are kept with ±1°C of the specified ageing temperature. 70°C was the selected temperature for ageing. Duration of ageing was varied for different studies. When the ageing period is over it is taken out and kept for not less than 16 hrs and not more than 96hrs in a strain free condition and then used for physical property measurements.

CHAPTER III

STUDIES ON THE EFFECT OF STABILIZER SYSTEMS

INTRODUCTION

Natural rubber latex being a dispersion of polyisoprene in an aqueous medium, stabilizers or surface active substances are important among the compounding ingredients. Whenever a latex is brought into contact with solids, liquids or gases of large surface area, sufficient additional stabilizer should be present to prevent the transfer of soap from the rubber particles to the new interface, otherwise flocculation of the latex is liable to occur. In all commercial latices particle aggregation is prevented or retarded by an adsorbed film of one or more surface active compounds surrounding the polymer particles. There are a number of latex stabilizers available for various purposes. Based on this function they are known as wetting agents, dispersing agents, dispersion stabilizers, emulsifiers, foam promoters, foam stabilizers etc. Being surface active materials, these can cause frothing in latex which may lead to formation of pinholes in dipped goods especially in thin products like condoms. Tests on porosity of condoms have shown that they can be a barrier to HIV cytomegalovirus or hepatitis B virus(49-51) if it is properly made to be free from holes and have adequate strength and elasticity. The extent of frothing depends on the type of stabilizer and its dosage. Latex stabilizers also influences the wet gel strength of films. Reports on the effect of fatty acid soaps on mechanical stability of natural latices are available(29).

During the manufacture of latex condoms, mechanical forces are applied and the possibility of destabilization exists. The control of mechanical stability is therefore of considerable importance. Various chemicals are added during processing of latex which requires, high chemical stability also for the latex. Thus the selection of suitable stabilizer system play an important role in determining the quality and rejection percentage due to pinholes of condoms.

In the present work, six different commercially available stabilizers were selected to study their effect on NR latex condoms.

EXPERIMENTAL

Materials

Natural rubber latex containing 60% rubber prepared by centrifuging was used. Stabilizers selected for the study were casein, potassium oleate, potassium laurate, polyvinyl alcohol, Emulvin-J (stabilizer based on polyethylene oxide condensate manufactured by Bayer(India) Limited and Vulcastab VL (stabilizer based on polyethylene oxide condensate manufactured by ICI(India) Limited which were of commercial grade.

Methods

Raw latex quality was ensured by analysing the parameters given in annexure I. Compounding of latex was done using the formulation given annexure III. Casein-Potassium oleate system was the control. Compounded and matured latex was prevulcanised and diluted to 47 total solids content and double dipped condoms were prepared. Compounding and sample preparation were continued by varying the concentration of stabilizers. Casein was selected as primary stabilizer when all other stabilizers were used as secondary. Then potassium oleate was used as primary stabilizer when all others were secondary. Thus the effect of both control stabilizers were studied in different systems. Products were analysed for water leakage, air leakage and pinhole formation according to standard procedures specified. Promising stabilizer systems were selected for further studies to analyze their effect on physical properties of condoms.

RESULTS AND DISCUSSION

Effect of stabilizer system on rejection due to pin holes

When the quality of condoms were assessed in terms of pin hole rejection rate, it was found that casein-potassium laurate system is much better compared to all other systems. The control compound with 0.02 phr each of casein and potassium oleate gave 8.5% rejection due to pin holes while the same concentration of casein-potassium laurate system gave only 2.5% rejection.

A stabilizing system was found essential as otherwise the rejection rate was very high(25%) as indicated by sl.no.27 in table 1. Potassium oleate alone was also highly undesirable as the pin hole rating was substantially high(18.75%) as indicated by sl.no.1 in 2.

Latex being a dispersion of polyisoprene in an essentially aqueous medium, stabilizers play a vital role in keeping the system stable. Since in all latex applications stirring or pumping and usually addition of compounding materials are involved, mechanical and chemical stability are essential. Stirring of latex causes a rapid movement of the polymer particles with many collisions between them. Even when not being stirred, the particles because of their colloidal size undergo brownian motion and move rapidly in a limited space with frequent collisions(52). The large particles with their slower motion will either cream to the top or settle to the bottom, depending on the specific gravity of the polymer relative to that of water. Thus they become tightly packed. Obviously, The particles if not properly stabilized or separated from each other, tend to adhere together and floc or microcoagulum forms. In extreme cases, the particles may coagulate into solid mass. Chances for microcoagulation will be higher without a surface active agent. Any stabilizer can contribute to reduce the microcoagulation tendency. This may be the reason for the reduction in pin hole rejection rate from 25% to 18.75% observed at 0.02phr potassium oleate alone in the system(table 2). When casein was also added at 0.02phr level, rejection rate was further reduced to 8.75% as indicated by the control system(sl.no.4, table 1). When the concentrations of casein and potassium oleate in the control compound was changed to study their individual effect it was noted that even in the absence of potassium oleate rejection rate was less compared to compound containing potassium oleate. Also it was observed that as the concentration of potassium oleate increased the rejection rate also increased. Casein was used as primary stabilizer and its concentration was kept constant at 0.02phr, when these observations were made.

Normally when a surface active agent is added chances for frothing will be higher. Bubbles present in the dipping compound can lead to pin holes in the moulded latex film or it can lead to a weak spot. Increased frothing effect of potassium oleate may be contributing to the increased pin hole rejection values at higher concentration of oleate. It was already been reported that as chain length of fatty acid component of a soap increases, its foaming efficiency increases(53). As lauric acid is having lower chain length, it causes less frothing.

The higher fatty acid soaps are known to affect the stability and cure of natural rubber latex. Addition of small amounts of higher fatty acid soaps have been shown to greatly improve the mechanical stability of latex with an optimum effect when the alkyl chain length of the HFA soap contains 9 to 11 carbon atoms(54,55). The lower rejection rate of compounds containing potassium laurate compared to potassium oleate could thus be attributed to the lower frothing tendency and improved mechanical stability caused by the laurate soap(29). The crosslinking potential in accelerated sulphur compounds is also affected by the amount of HFA present(56). Presumably these acids form part of the activator system by solubilizing zinc(57). It was shown that (58) the milligrams of laurate soap present in whole latex concentrate correlate(at a 99% confidence level) with a decrease in mechanical stability on the latex concentrate. But it is known that laurate soaps added to latex concentrates increase mechanical stability of the latex. Reasons for the difference in behaviour of added and original laurate soaps are not known. Perhaps the distribution between the rubber and the aqueous phase is different for the added and original soaps, or perhaps the distribution of the soap on the surface of the latex particles is different.

The effect of stabilizers on pinhole rejection rate with casein as primary stabilizer was also studied. Potassium laurate and Vulcastab VL were found to reduce pin hole rejection rate compared to the control compound. Thus they can replace potassium oleate to reduce rejection rate due to pin holes. Polyvinyl alcohol and Emulvin T were having more or less the same effect as that of potassium oleate. But compounds containing polyvinyl alcohol gave increased viscosity values.

The same stabilizers when used in combination with potassium oleate as primary stabilizer it was found that the compound containing potassium laurate behaved almost the same way as the control. Potassium oleate- polyvinyl alcohol combinations were not found better than the control. Viscosity of the compound was found to be increasing with increasing concentrations of polyvinyl alcohol. Potassium oleate-Vulcastab VL system were found to be inferior to the control system with respect to pin hole formation.

EFFECT OF CASEIN-POTASSIUM LAURATE SYSTEM ON PHYSICAL PROPERTIES

Based on the results obtained from the pin hole rate studies the stabilizer system most suitable was the combination of casein and potassium laurate. Therefore this system was considered for further studies.

Physical properties such as tensile strength, elongation at break, modulus, burst volume and burst pressure, electrical resistance etc were determined. Ageing resistance also was measured for the different concentrations of the selected stabilizer system and the control. Maximum percentage retention of tensile strength was found for potassium laurate-casein system compared to the other systems as is seen from table 3. It is reported that rubber soluble soaps formed from oleic acid and lauric acid can react with accelerators during vulcanization to enable them to exert their full effect but oleic acid is reported to have detrimental effect on ageing(59). The differences in ageing properties of condoms observed for potassium laurate casein system when used in place of potassium oleate-casein system may be due to this difference between oleic and lauric acids. Elongation at break values were more or less the same for all the systems. Modulus at 500% elongation also was compared for all concentrations of the system. Burst volume and burst pressure values (table 4) showed that dependable values were observed for casein-potassium laurate system. Electrical resistance was found comparable for all the systems. Reasons for the difference in physical properties observed when different stabilizer systems were used is not fully understood. These stabilizers may be having different mechanisms of action. Usually water molecules are hydrogen bonded to the surfactant molecules, forming an additional hydrated, protective layer around each particle(60)

The surfactant molecules have limited solubility in water and those not adsorbed on the particles usually exist in the water phase as micelles, ie, fairly large, charged aggregates of long chain electrolyte(61). The critical micelle concentration (CMC) is the concentration of electrolyte in the water phase at which micelles begin to form(62). The surfactant molecules in the water phase are in equilibrium with the adsorbed surfactant molecules on the particles. Any appreciable dilution of the latex will therefore, rob surfactant from the particles resulting in possible destabilisation of latex, if the adsorbed surfactant, before dilution is just barely adequate for stabilization.

As soap is added to latex, surface tension will drop rapidly at first and then more slowly when the particles are saturated.

The choice of surfactant is largely dependant on the application involved. Too much or the wrong kind of surfactant might interfere with the knitting together of the particles during application, resulting in poor cohesion or adhesion.

The pH of the system can have an important effect on stability. Although many anionic surfactants will impart stability over a wide pH range, certain compounds added to the latex may cause destabilization unless added within a narrow pH range. Soaps such as potassium oleate lose their stabilizing ability as the pH is lowered and then revert to fatty acids.

Destabilization or coagulation can be achieved by dehydration of the particles ie, removal of water of hydration associated with the surfactant molecules, neutralization of the charge on the adsorbed soap or depletion of the surfactant from the particle surface. The simplest form of dehydration is drying of latex to form a polymer film which is practised by the condom manufacturers.

As condoms being very thin, are much affected by the microcoagulum, froth and the stabilizing capacity of the surface active material present in the latex compound. Interaction of these substances with other compounding ingredients and latex particles also influence the ultimate properties of the condoms. From the studies conducted it was found that different stabilizers can vary the pin hole formation rate and physical properties of condoms.

CONCLUSIONS

1. It can be concluded that potassium laurate is a better replacement for potassium oleate at the same concentration of 0.02phr as a secondary stabilizer along with 0.02phr of casein in latex compound for condoms.
2. Among the stabilizer systems studied potassium laurate-casein system and Vulcastab VL-casein system were found to give reduced pin hole formation rate.
3. Presence of potassium oleate along with other stabilizers enhanced the pinhole formation rate and reduced the physical properties of condoms.

3. Among the different stabilizer systems studied Casein-Potassium laurate combination was the most effective system for obtaining lowest pin hole rejection rate and highest physical properties for condoms.

Table 1

Effect of stabilizer system on pinhole formation
(Casein as primary stabilizer)

Sl. No.	Concentration of secondary stabilizer (phr)		Percentage rejection due to		
			Air leakage	Water leakage	Pinhole
1.	Potassium oleate	Nil	7.5	7.5	7.5
2.		0.01	7.5	7.5	7.5
3.		0.015	5.0	7.5	7.5
4.		0.02	7.5	7.5	8.75
5.		0.025	10	10	16.0
6.		0.03	10	12.5	16.25
7.	Potassium laurate	0.01	5	7.5	7.5
8.		0.015	3.75	3.75	3.75
9.		0.02	0	2.5	2.5
10.		0.025	2.5	2.5	2.5
11.		0.03	2.5	0	2.5
12.	Poly vinyl alcohol	0.01	7.5	7.5	8.75
13.		0.015	5.0	7.5	8.75
14.		0.02	8.75	7.5	8.75
15.		0.025	10.0	10.0	11.25
16.		0.03	12.5	12.5	12.5
17.	Emulvin T	0.01	5.0	10.0	10.0
18.		0.015	7.5	7.5	7.5
19.		0.02	7.5	7.5	8.75
20.		0.025	5.0	7.5	7.5
21.		0.03	5.0	5.0	7.5
22.	Vulcastab VL	0.01	10.0	5.0	10.0
23.		0.015	7.5	5.0	6.25
24.		0.02	5.0	5.0	6.25
25.		0.025	5.0	5.0	5.0
26.		0.03	5.0	5.0	6.25
27.		Nil	25	10.0	25.0

* Casein at 0.02 phr was used as primary stabilizer in all the cases except in Sl.No.27 where no stabilizer was used.

Table 2

Effect of stabilizer system on pinhole formation
(Potassium oleate as primary stabilizer)

Sl. No.	Concentration of secondary stabilizer (phr)		Percentage rejection due to		
			Air leakage	Water leakage	Pinhole
1.	Casein	Nil	18.75	18.75	18.75
2.		0.01	18.75	18.75	18.75
3.		0.015	7.5	7.5	10.0
4.		0.02	8.75	7.5	8.75
5.		0.025	5.0	7.5	7.5
6.		0.03	5.0	7.5	7.5
7.	Potassium laurate	0.01	8.75	7.5	8.75
8.		0.015	6.25	5.0	6.25
9.		0.02	7.5	7.5	7.5
10.		0.025	10.0	5.0	10.0
11.		0.03	16.0	10.0	16.0
12.	Polyvinyl alcohol	0.01	11.25	5.0	11.25
13.		0.015	8.75	7.5	8.75
14.		0.02	5.0	8.75	8.75
15.		0.025	5.0	8.75	8.75
16.		0.03	7.5	7.5	8.75
17.	Emulvin T	0.01	11.25	10.0	11.25
18.		0.015	10.0	5.0	10.0
19.		0.02	7.5	7.5	8.75
20.		0.025	11.25	10.0	11.25
21.		0.03	8.75	7.5	8.75
22.	Vulcastab VL	0.01	13.75	10.0	13.75
23.		0.015	11.25	10.0	11.25
24.		0.02	10.0	7.5	10.0
25.		0.025	8.75	5.0	8.75
26.		0.03	7.5	7.5	10.0

0.02 phr of potassium oleate was used as primary stabilizer in all the cases.

Table 3

Effect of stabilizer system on tensile properties of condoms

Concentration of		500% Modulus (MPa)	% retention*	Tensile strength (MPa)	% retention*	Elongation at break(%)	% retention*
Potassium oleate	Casein						
Nil	Nil	6.5	70.92	15.97	50.09	769	93.62
0.02	Nil	6.5	71.84	19.33	57.42	788	92.63
	0.01	6.5	70.81	19.54	57.83	792	92.04
	0.015	7.0	67.52	19.73	65.88	800	92.62
	0.02	8.0	67.88	20.91	68.25	798	92.0
	0.025	8.0	67.75	20.0	69.0	800	92.62
	0.03	8.0	67.91	20.3	68.44	807	92.19
Potassium oleate	Potassium laurate						
0.02	0.01	7.5	78.66	19.3	57.6	779	93.7
	0.015	7.5	77.33	19.5	59.1	782	94.37
	0.002	7.8	76.92	19.7	61.4	781	94.87
	0.025	8.0	75.75	19.6	69.2	794	91.30
	0.03	8.0	75.00	19.8	69.8	800	91.37
Casein	Potassium oleate						
0.02	Nil	7.5	70.48	20.0	71.00	792	93.56
	0.01	8.0	69.59	19.73	65.88	788	92.5
	0.015	8.0	68.41	19.90	65.82	800	93.75
	0.02	8.0	67.82	20.91	68.75	798	92.0
	0.03	8.0	66.44	19.78	69.81	800	93.62
Casein	Potassium laurate						
0.02	0.01	7.5	73.33	20.5	70.73	800	93.12
	0.015	8.0	75.00	20.92	72.19	799	92.36
	0.02	8.0	73.75	21.18	74.59	806	92.92
	0.025	7.9	73.94	21.16	74.19	800	92.37
	0.03	8.0	76.25	21.18	74.12	805	93.41

* % retention after ageing at 70°C for 168 h.

Table - 4

Effect of stabilizer system on BV, BP and Electrical resistance of condoms.

Concentration of stabilizers		Burst volume (litres)		Burst pressure (KPa)		Electrical resistance (% of condoms above 10MΩ)	
Potassium oleate	Casein	Original	% Retention	Original	% Retention	Before ageing	After ageing
Nil	Nil	24.8	60.8	0.9	55.55	90	90
0.02	Nil	26.8	58.58	1.0	60.0	92	90
0.02	0.01	29.9	53.51	1.0	60.0	93	93
0.02	0.015	31.2	51.60	1.1	63.63	99	98
0.02	0.02	31.8	50.31	1.4	57.14	99	99
0.02	0.025	32.0	51.56	1.4	57.14	98	97
0.02	0.03	32.0	51.25	1.3	61.50	98	99
Potassium oleate	Potassium laurate						
0.02	0.01	30.8	50.0	1.0	70	91	90
0.02	0.015	31.0	51.29	1.0	75	92	92
0.02	0.02	30.0	53.33	1.1	68.18	93	90
0.02	0.025	28.9	54.67	1.2	66.66	97	95
0.02	0.03	29.1	54.64	1.4	57.14	96	94
Casein	Potassium oleate						
0.02	Nil	29.8	50.33	1.2	66.66	93	93
0.02	0.01	29.5	51.18	1.2	62.5	93	92
0.02	0.015	29.4	53.06	1.4	57.14	92	90
0.02	0.02	31.8	50.31	1.4	57.14	94	93
0.02	0.025	31.8	50.0	1.3	53.84	93	92
0.02	0.03	29.4	54.42	1.2	66.66	94	94
Casein	Potassium laurate						
0.02	0.01 32	50.0	1.4	64.28	64.28	96	95
0.02	0.015 32.3	54.17	1.4	71.42	71.42	96	96
0.02	0.02 34.4	54.94	1.5	66.66	66.66	98	98
0.02	0.025 34.8	54.02	1.5	73.33	73.33	99	100
0.02	0.03 33.9	53.09	1.4	78.57	78.57	100	99

CHAPTER IV

STUDIES ON THE EFFECT OF VULCANISING SYSTEMS

INTRODUCTION

Rubber vulcanisation is the most important discovery in rubber technology. Vulcanising system is the quality determining factor of any product among the compounding variables. Strength properties of condoms are very sensitive to the vulcanising system used. Sulphur is the usual vulcanising agent for natural rubber and along with accelerators and activators it forms the vulcanising system. Accelerators not only accelerate the vulcanising process, but also influence the properties of the finished product, because the type and dosage of accelerators affect the network structure of the rubber vulcanisate, which in turn determines the physical, mechanical, chemical and service properties of the product(63). Vulcanisates obtained by using binary accelerator systems are found to have superior physical and chemical properties(64,65). Dithiocarbamates, thiazoles and xanthates are the main accelerators used in latex processing.

In the present study, sulphur being the vulcanising agent, its effect on properties of condoms, by varying its concentration, was studied. Accelerators used were two dithiocarbamates (Setsit-5 and Nocceller TP(NTP)) and one Thiazole type accelerator(ZMBT). Different concentrations and combinations of these vulcanising accelerators with sulphur and zinc oxide were used as the vulcanising system to study their effect on tensile properties, burst volume, burst pressure and ageing characteristics of condoms.

EXPERIMENTAL

Materials

High ammonia centrifuged natural rubber latex, whose characteristics are listed in annexure-1 was used for the study. Casein, Potassium oleate, Ammonia, Sodium-di-N-butyl dithiocarbamate (Nocceller TP, Ouchi Shinko Chemical Industrial Co., Japan), Activated dithiocarbamate (Setsit-5, Vanderbilt, USA), Zinc oxide, 2,2-Methylene 4-Ethyl 6-Tert-butyl Phenol (Nocrac NS-5,Ouchi Shinko Chemical Industrial Co., Japan), Sodium salts of polymerised substituted sulphonic acid (Darvan 1 and 2, Vanderbilt, USA), Zinc salt of Mercaptobenzothiazole (ZMBT) and Sulphur were of commercial grade.

Methods

Solid compounding ingredients such as sulphur, Zinc oxide, Nocrac NS-5, Darvan 1 and 2 were ball milled for 72h to prepare a 50% composite dispersion. A 35% dispersion of ZMBT was prepared and used for the work. Ammonia was used as 25% and 1% solutions as required. Potassium oleate was used as a 20% solution and casein as 10% solution. Setsit-5 and Nocceller TP, being water soluble accelerators, were added directly into latex and stirred thoroughly. Order of addition and dosage of the compounding chemicals were as shown in Annexure 3. The latex compound was prevulcanised at 55°C for 8h and then it was diluted using 1% ammonia solution to a total solids content of 48%. Glass formers were used to dip mould condoms by straight dipping. Double dipped products were dried and then vulcanised at 80°C for 30 minutes in an air oven. After vulcanisation it was cooled to room temperature and stripped from the formers using french chalk powder.

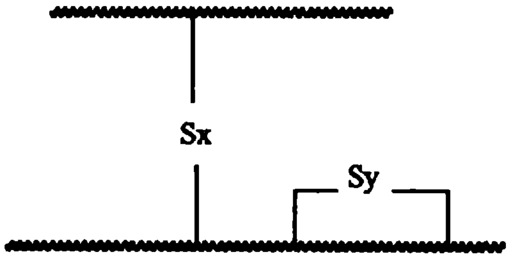
Different vulcanising systems were tried to prepare condoms by the method described and their effect on tensile properties, burst volume, burst pressure, ageing properties etc were studied in each case. The samples were conditioned in the laboratory for 24h before testing. Tensile properties such as tensile strength, modulus at 500% elongation, elongation at break etc were studied using an Instron tensile tester model 1474 according to ASTM 412(1980). Burst volume and burst pressure were tested as per ISO 4074/6-1984(E). Ageing was carried out in an air oven at 70°C for a period of 168h and ageing resistance was assessed in terms of percentage retention of various properties after ageing.

RESULTS AND DISCUSSION

1. Effect of sulphur level

The effect of different levels of sulphur on the properties of condoms is shown in table 1. As sulphur level increases modulus and tensile strength increases steadily. A reasonable increase in the burst volume and burst pressure has also been observed as the sulphur level is increased. The increase in the burst volume in inspite of the higher modulus at higher sulphur levels(Table 1a). However, ageing resistance decreases as the sulphur level increases(Fig.1).

In sulphur vulcanisation of NR, mono and polysulphidic linkages are formed between polymer chains. As sulphur level increases, crosslink density increases, which is reflected in the modulus values. During rubber vulcanisation using sulphur crosslinks and cyclic structures of the following type are formed.



Generally x in an efficient accelerated curing system is about 1 or 2 with little or no cyclic groups formed. In efficient systems x equals upto 8 and many cyclic structures are formed.

For most rubbers, one crosslink for about each 200 monomer units in the chain is sufficient to provide a suitable vulcanised product(66). It is these amounts of cyclic sulphur(y) and the excessive sulphur in the crosslinks(x) which contribute to the poor ageing properties of the sulphur vulcanisates. It is well known that in NR a high sulphur vulcanising system leads to formation of predominantly polysulphidic crosslinks which are more flexible and hence can cause higher elongation and tensile strength(67). However these polysulphidic crosslinks are more thermolabile and hence ageing resistance of vulcanisates prepared using higher sulphur levels is poor. The sulphur level was varied in the case of Setsit-ZMBT accelerator combination as well (Table 1.b). Here again it was observed that modulus and tensile strength increases as the sulphur level increases. Burst pressure also increases with the sulphur level, but burst volume is not affected much. However it is worth noting that ageing resistance is not adversely affected by the higher levels of sulphur as was observed in the Setsit-NTP-sulphur combinations (Fig.1).

2. Setsit-ZMBT combination

The control formulation used in this study is having a combination of Setsit and NTP at 0.5 and 0.2 phr respectively. When Setsit was used alone and in combination with ZMBT noticeable changes in properties were observed. Modulus increased steadily when increasing dosage of ZMBT was used with 0.5phr of Setsit, indicating an increased level of crosslinking(Table 2). Tensile strength also increased, although not so markedly as in the case of modulus. Elongation, however, decreased marginally. All these changes indicate that a combination of Setsit and ZMBT imparts a tighter cure to rubber than the control. This is reflected again in the burst pressure values. However, burst volume is less when this combination is used. It may also be noted that with Setsit alone, burst volume registers a higher value.

The most striking feature of this accelerator combination is the significant improvement in ageing resistance over the control. Retention of properties such as modulus, tensile strength, burst volume and burst pressure after ageing is considerably higher than in the control. It is therefore, inferred that this combination not only promotes a tighter cure, but causes formation of predominantly shorter sulphur linkages. It may also be noted that ZMBT is having a mild antioxidant action in NR vulcanisates(68).

The proportion of these two accelerators was tried in the reverse order with a higher dosage of ZMBT. The results are summarised in Table 3. It is observed that modulus and tensile strength of these combinations are in general better than those realised with the Setsit-ZMBT combinations described in the previous paragraph. However, burst volume and burst pressure values are slightly inferior. Ageing resistance of both the combinations are more or less comparable.

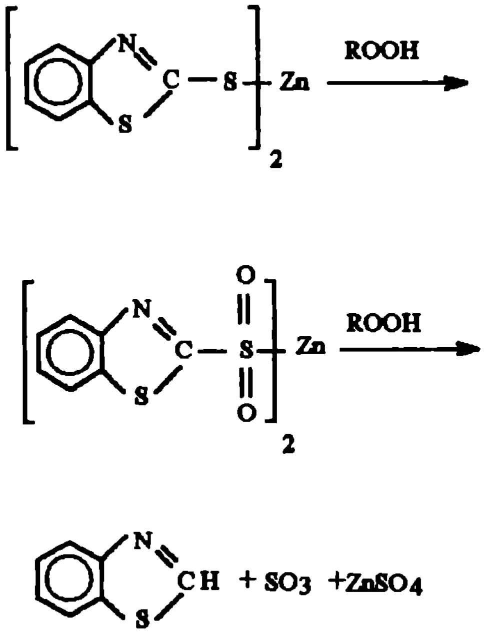
3. NTP-ZMBT combinations

With NTP alone the modulus is relatively low. So is the burst pressure. However tensile strength, elongation and burst volume are marginally higher than those of the control. Combinations of NTP and ZMBT are found to be contributing to higher modulus and tensile strength, but lower burst volume and pressure(Table 4). In ageing resistance, these combinations are slightly better than the control, but not as good as the Setsit-ZMBT combinations. In general, it could be concluded that these combinations are more or less comparable to the control, Setsit-NTP combination.

4.ZMBT-NTP combinations

These combinations were tried to explore the benefits of using a predominantly thiazole based accelerator combination on the overall balance of properties. The results are given in Table 5. It is observed that these combinations are better than the control in many respects. Modulus, tensile strength and burst volume are found to be significantly better than those of the control, although burst pressure is slightly inferior, but still within specifications. ZMBT alone was tried, but the properties are not much different from those of the control. A combination of 0.5phr of ZMBT and 0.3phr of NTP was found to be optimum. Ageing resistance, as assessed from the percentage retention of various properties, was also found to be improved when these combinations of accelerators are used. In this respect also 0.5/0.3 ZMBT/NTP combination was found to be optimum.

Accelerating activities of various dithiocarbamates differ considerably(69) and this may be the reason for the difference in properties observed when Setsit and NTP were used in equal quantities along with ZMBT. Although thiazoles are insufficiently active to be used on their own for latex work, they do function as secondary accelerators along with dithiocarbamates giving vulcanisates of higher modulus(6). The most suitable thiazole accelerator for latex work is ZMBT(70). The activity of ZMBT was confirmed by the increased modulus values as given in Tables 2,3 and 4. It is also reported(68) that properly compounded Mercaptobenzothiazole vulcanisates give flatter cure curves than those containing most other types of accelerators. They maintain strength properties even when considerably overcured. Mercaptobenzothiazole itself is also an excellent antioxidant(68) and hence the compounds in which it is used show better ageing resistance. The better ageing properties observed in Tables 2,3,4 and 5 could be due to the special properties of ZMBT as reported. The mechanism of antioxidant action of ZMBT has been investigated(71) and has been shown to involve the formation of the stable zinc benzthiazole sulphinate which acts as a reservoir for sulphur trioxide which(together with H_2SO_4) is an effective catalyst for the nonradical decomposition of hydroperoxides(72). This mechanism is analogous to that proposed earlier(73) for the action of the zinc dialkyl dithiocarbamates.



The low mechanical strength of condoms when dithiocarbamate type accelerators alone were used could be attributed to the peaky cure exhibited by them which causes reversion of vulcanisates even under slight overcuring conditions. When part of the dithiocarbamate type accelerator was replaced by thiazole type, this disadvantage was minimised. Since ZMBT also has reversion resistance it naturally improves the ageing characteristics of vulcanisates.

CONCLUSIONS

1. Quantity of sulphur and type of accelerators were found to affect the tensile properties, burst volume and burst pressure of condoms.
2. Among the different accelerator combinations studied, Setsit-ZMBT and NTP-ZMBT combinations were found to impart high mechanical strength to condoms.
3. Setsit-ZMBT system was found to give maximum ageing resistance to condoms compared to the other accelerator combinations.
4. Increase in concentration of sulphur increased mechanical strength of condoms at the expense of ageing resistance.

TABLE 1

EFFECT OF SULPHUR LEVEL

a. Setsit-NTP accelerator combination

Properties	Sulphur Level (phr)			
	0.5	1.0	1.5	2.0
500% Modulus (MPa)	7.0	7.5	8.0	8.5
Tensile strength (MPa)	18.66	19.58	20.91	21.89
Elongation at break (%)	764	778	791	798
Burst volume (litres)	27.8	29.5	31.8	34.5
Burst pressure (KPa)	0.9	1.1	1.4	1.6

b. Setsit-ZMBT accelerator combination

Properties	Sulphur Level (phr)			
	0.5	1.0	1.5	2.0
500% Modulus (MPa)	8.0	9.0	9.9	10.5
Tensile strength (MPa)	20.23	21.25	21.37	22.44
Elongation at break (%)	791	793	789	804
Burst volume (litres)	30.0	31.5	29.8	30.6
Burst pressure (KPa)	1.0	1.1	1.4	1.3

TABLE 2

SETSIT-ZMBT COMBINATION

Properties	Accelerator dosage					
	Setsit	0.5	0.5	0.5	0.5	0.3
	ZMBT	Nil	0.2	0.4	0.6	0.6
500%% Modulus (MPa)		8	9	9.9	10.8	10.6
Tensile strength (MPa)		19.59	19.81	21.37	21.44	21.19
Elongation at break (%)		800	795	789	781	780
Burst volume (litres)		34.1	29.8	24.8	29.0	28.9
Burst pressure (KPa)		1.2	1.3	1.4	1.4	1.5
% Retention of modulus		68.8	70.9	84.5	86.4	86.1
% Retention of tensile strength		84.68	85.51	85.07	81.62	81.17
% Retention of elongation at break		98.3	98.1	97.3	95.1	95.5
% Retention of burst volume		79.2	82.3	82.5	72.9	69.9
% Retention of burst pressure		86.9	88.1	89.9	77.8	78.1

Table 3

ZMBT-SETSIT COMBINATIONS

Properties	Accelerator level						
	Setsit	Nil	0.1	0.2	0.3	0.2	Nil
	ZMBT	0.5	0.5	0.5	0.5	0.7	1.0
500% Modulus (MPa)		9	8.9	8.8	8.7	9.3	9.5
Tensile strength (MPa)		20.10	21.40	22.30	22.50	23.40	21.9
Elongation at break (%)		802	786	783	795	778	789
Burst volume (litres)		31.0	30.2	27.6	26.3	26.9	30.8
Burst pressure (KPa)		1.0	1.0	1.3	1.3	1.2	1.1
% Retention of modulus		74.1	76.9	77.4	79.0	77.1	77.0
% Retention of tensile strength		85.57	84.57	82.06	81.77	76.92	77.6
% Retention of elongation at break		94.2	98.0	97.8	96.7	99.0	98.5
% Retention of burst volume		61.7	70.8	81.9	85.4	73.3	69.1
% Retention of burst pressure		68.7	67.9	72.4	79.1	67.8	68.7

Table 4

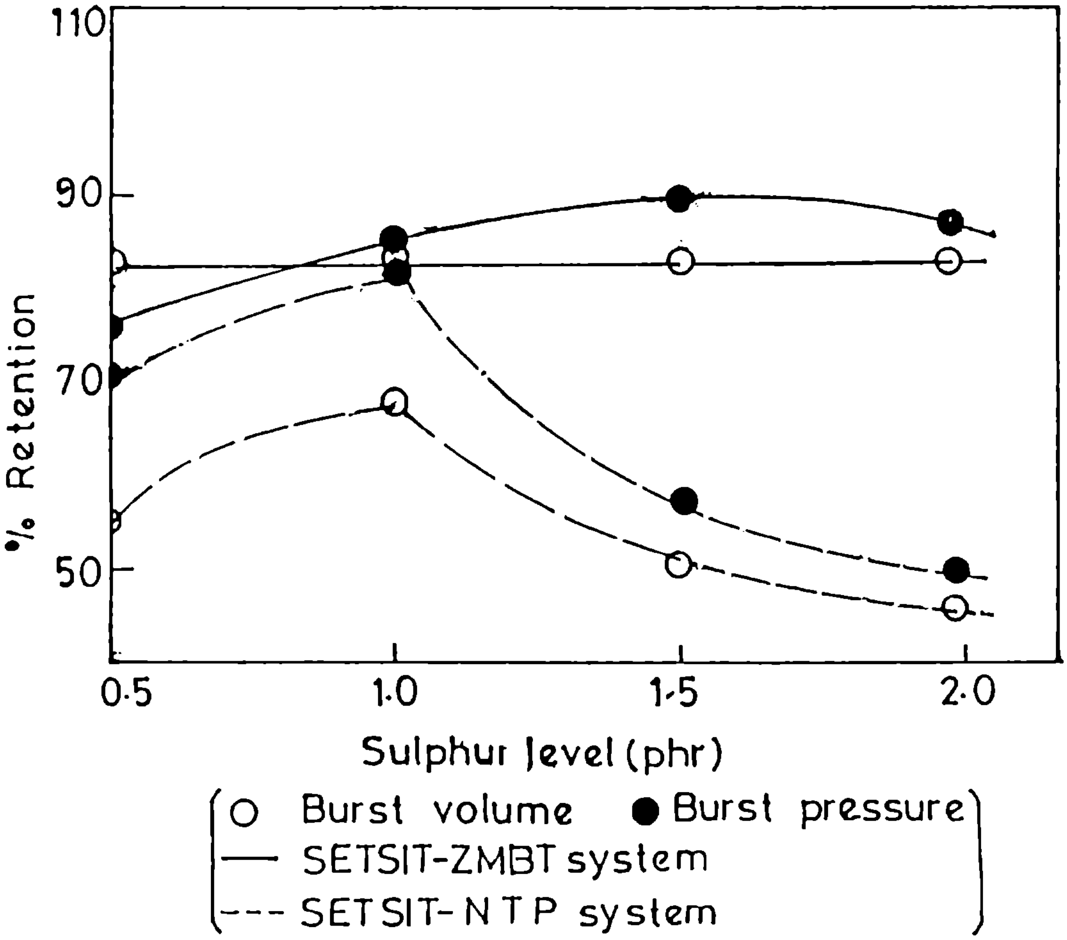
NTP-ZMBT COMBINATIONS

Properties	Accelerator level						
	NTP	0.5	0.5	0.5	0.5	0.8	0.8
	ZMBT	Nil	0.1	0.2	0.3	Nil	0.2
500% Modulus (MPa)		7.5	8.5	8.7	8.8	8.5	8.7
Tensile strength (MPa)		21.43	20.98	22.01	22.97	21.33	22.25
Elongation at break (%)		811	808	803	779	774	790
Burst volume (litres)		33.5	33.1	28.7	29.8	31.5	27.5
Burst pressure (KPa)		1.1	1.0	0.95	1.2	1.0	1.15
% Retention of modulus		65.7	69.8	70.1	73.3	67.9	71.6
% Retention of tensile strength		76.52	78.98	79.23	80.38	78.81	80.14
% Retention of elongation at break		99.1	99.1	96.2	97.0	95.8	97.0
% Retention of burst volume		56.71	59.21	61.1	59.9	57.8	59.3
% Retention of burst pressure		69.8	71.9	75.4	76.1	68.8	74.4

Table 5
ZMBT - NTP Combinations

Properties	Accelerator level						
	NTP	Nil	0.1	0.2	0.3	0.2	0.3
	ZMBT	0.5	0.5	0.5	0.5	0.7	0.7
500% Modulus (MPa)		9.0	8.8	8.7	8.7	9.7	9.5
Tensile strength (MPa)		20.10	21.80	22.50	22.0	23.10	23.00
Elongation at break (%)		790	789	788	793	785	788
Burst volume (litres)		31.0	29.9	32.1	34.8	35.9	36.1
Burst pressure (KPa)		1.0	1.1	1.2	1.2	1.3	1.30
% Retention of modulus		74.1	75.6	75.9	76.8	76.8	76.7
% Retention of tensile strength		85.57	79.81	81.77	82.7	77.48	76.95
% Retention of elongation at break		97.4	96.0	97.9	97.7	93.8	94.2
% Retention of burst volume		61.70	63.40	64.8	98.1	60.4	61.8
% Retention of burst pressure		68.7	66.8	70.1	71.4	65.3	66.1

FIG.(1). EFFECT OF SULPHUR LEVEL ON AGEING RESISTANCE



CHAPTER V

EVALUATION OF DIFFERENT ANTIOXIDANTS FOR NR LATEX CONDOMS

INTRODUCTION

Ageing, the unwanted deterioration in the physical properties of a polymer due to the action of heat, radiation, oxygen, ozone or mechanical work either separately or in combination of a latex product cannot be prevented, but it can be retarded. Antioxidants are used for retarding this deterioration so that the life of product can be extended.

The subject of antioxidants for rubber was first extensively reviewed by semon and Duffraise (74). Since then a number of outstanding reviews have been written(75-82). There is a comprehensive literature on the role of antioxidants which prolong the lifetime of rubber products in recent publications(83-86). Although ageing of natural rubber and rubber vulcanizates has been the subject of a large number of investigators(87-89),reports on ageing of dipped NR latex products are very few.

In the present study, condoms were found to show varying degrees of ageing resistance in different conditions and formulations of manufacture. Eventhough much has been learned about the action of antioxidants under various conditions, the selection of the proper antioxidant system for a given latex and for a given product may depend on empirical observation in laboratory testing.

For the comparative evaluation, six commercial antioxidants were selected and their effect on properties and ageing characteristics of latex condoms were investigated.

EXPERIMENTAL

Materials

60% centrifuged high ammonia latex whose characteristics are given in annexure 1 was used for the study. Low ammonia (LATZ) type also was used for comparative evaluation. Its characteristics are given in annexure- 2. Different antioxidants used were Vulkanox HS (poly 2-2-4 trimethyl 1,2 dihydroquinoline) manufactured by Bayer India Ltd, Irganox 1010 (Penta erythritol- tetrakis- (3-(3' 5'-d; tert butyl 4 hydroxy phenyl) propionate) manufactured by Hindustan Ciba Geigy, Pentaflex SP (styrenated phenol) manufactured by Polyolefins Industries Ltd, Vanox SKT (3,5- di- tert butyl 4 hydroxy cinnamic acid triester with 1,3,5 tris(2 hydroxy ethyl) s-triazine- 2,4,6- (1 H,3H,5H) trione) and Vanox MBPC (2,2' methylene bis (4 methyl 6-tert butyl phenol) manufactured by Vanderbilt Co. USA, and Nocrac NS 5 (2,2 methylene bis 4 ethyl 6 tert butyl phenol) manufactured by Ouchishinko Chemical Industrial Co. Ltd, Japan.

Methods

Compounding of latex was done as per the formulation given in annexure 3. Maturation period of 24 hours was given for the latex compound before starting the prevulcanisation. Prevulcanisation period of 8 hours was given at 55°C after which it was analyzed for total solids content and diluted to 48 TSC using 1% ammonia solution and condoms were dipmoulded. Double dipped condoms were prepared by straight dipping method. Post vulcanisation at 80°C for 30 minutes was conducted in an air oven and after cooling to room temperature, they were stripped using french chalk powder. 24 hours conditioning period was given and then they were tested for physical properties and ageing characteristics.

Results and Discussion.

All the six antioxidants studied (Vulkanox HS, Irganox 1010, Pentaflex SP, Vanox SKT, Vanox MBPC and Nocrac NS-5) were found to have beneficial effects on the ageing properties of condoms. It was found that presence of some antioxidant is essential to retain the properties of condoms after ageing.

Protection of rubber using antioxidants.

The active hydrogen in an olefin is the one in the alpha position with respect to the double bond since the radical formed on its removal is stabilised by resonance. In its simplest form the accepted scheme for uninhibited hydrocarbon oxidation is;

Initiation Production of $R^\bullet$ or $RO^\bullet_2$ radical

$RH \longrightarrow R^\bullet + H^\bullet$

Propagation

$R^\bullet + O2 \longrightarrow ROO^\bullet$

$ROO^\bullet + RH \longrightarrow ROOH + R^\bullet$

Termination

$2R^\bullet_2 \longrightarrow$ }
$R^\bullet + ROO^\bullet \longrightarrow$ } Non radical products
$ROO^\bullet + ROO^\bullet \longrightarrow$ }

Scheme for inhibited hydrocarbon oxidation is

$RH \text{ --> } R^{\bullet} + H^{\bullet}$

$R^{\bullet} + O_2 \text{ --> } ROO^{\bullet}$

$ROO^{\bullet} + RH \text{ --> } ROOH + R^{\bullet}$

$ROOH \text{ --> } RO^{\bullet} + O^{\bullet}H$

$RO^{\bullet} + RH \text{ --> } ROH + R^{\bullet}$

$^{\bullet}OH + RH \text{ --> } H_2O + R^{\bullet}$

Here the original free radical has gone through a single reaction cycle giving a degraded rubber (ROH) and three new free radicals ($R^{\bullet}$)(auto catalysis)

Inhibitor reacts in the following manner(66).

$R^{\bullet} + AH \text{ --> } RH + A^{\bullet}$

$ROO^{\bullet} + AH \text{ --> } ROOH + A^{\bullet}$

$RO^{\bullet} + AH \text{ --> } ROH + A^{\bullet}$

ROOH + AH --> Harmless fragments.

A* is incapable of propagating the chain reaction. Thus the antioxidant AH protects rubber from degradative reactions.

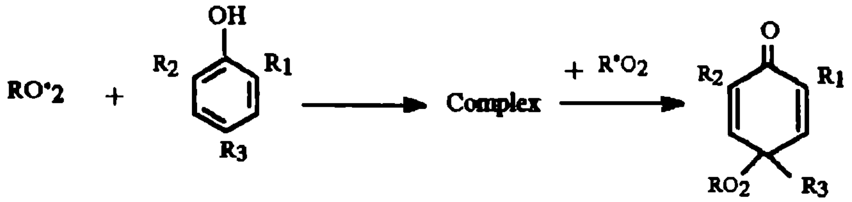
Vulkanox HS

It was found that Vulkanox HS at 0.5 phr and above this level could improve the ageing characteristics of condoms with respect to tensile, Burst volume and Burst pressure properties. At 0.25 phr level it is not at all effective and burst volume value was found to decrease slightly. At higher concentrations of Vulkanox HS

(1phr) the condoms were having some discoloration. Amine type antioxidants are usually hydrogen donors and terminate kinetic chains by hydrogen transfer to form ROOH from $RO_2^{\bullet}$ radicals. The newly formed antioxidant radical can terminate a second chain. There is some evidence that amines act both as chain breakers and peroxide decomposers. Shelton and Cox (90) studied the oxidation of vulcanised rubber and found it necessary to invoke both chain transfer and peroxide decomposition in their reaction mechanism. Capp and Hawkins(91) showed that amines would react with tertiary hydroperoxides with reactivity decreasing in the order tertiary>secondary >primary and with aromatic amines being less reactive than aliphatic. In this study since only Vulkanox HS was studied among the amine type, the comparison of different amine type antioxidants is beyond the scope of this work. The ability of amines to act as radical trap has been discussed by Furukava et al(92). He showed that there is an excellent correlation between the oxidation potential of an amine and the relative tensile strength of a gum natural rubber containing the amine where TSo and TS are the tensile strengths before and after 48 hours oven ageing at 100°C. The good tensile property retention after ageing of condoms at 70°C for 168 hours may be due to the favourable oxidation potential of Vulcanox HS at the ageing condition. It is reported that (93) Vulkanox HS can be prepared by polymerising 2,2,4 trimethyl dihydroquinoline which is obtained by the reaction between aniline and acetone in presence of acid. Increasing concentrations of Vulkanox HS upto 1phr level was found to improve the ageing properties. 0.75 phr & 1 phr were found to impart almost same property retention.

Pentaflex SP

Phenolic antioxidants are well known in latex formulations due to the nonstaining property. Hindered phenols are presently used as radical trapping agents. Pentaflex SP at varying concentrations of 0.25 to 1 phr were tried in latex condoms and found that 1 phr level of pentaflex give maximum tensile strength and burst volume whereas modulus was maximum at 0.75 phr. Percentage retention of all these properties were maximum at 1 phr level. It is well established that (94,95) the hindered monophenols deactivate two $RO2^{\bullet}$ radicals for each molecule. The mechanism by which they do this has been the subject of much debate. Hammond et al(96) finding the oxidation rate to be first order in peroxy radical and half order in inhibitor concluded that formation of a complex between phenol and phenoxy radical was rate determining.

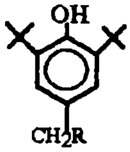


Hydrogen abstraction process is considered as the rate determining step of oxidation. Shelton and Vincent(97) studying the oxidation of purified polyisoprene demonstrated that replacing hydrogen in 2,6 di-t-butyl phenol by deuterium resulted in an increase in rate.

Howard and Ingold(98) showed that replacing hydroxyl hydrogen in a monophenol by deuterium increases the rate of oxidation of hydrocarbons in solution by a factor of 6-10. So the Pentaflex SP may be acting as antioxidant by this hydrogen abstraction mechanism. Steric hindrance is provided for hindered phenols by bulky substituents in positions on the ring ortho or para to the hydroxyl group. Styrene unit provide the steric hindrance in Pentaflex SP. These bulky substitutes can influence the specificity of the phenols by blocking phenoxy radicals from abstracting hydrogen atoms from organic substrate.

Vanox MBPC and Nocrac NS-5(Hindered phenols)

In this study hindered bisphenols such as 2,2 methylene bis(4 methyl 6tert butyl phenol) ie. Vanox MBPC and 2,2 methylene bis (4 ethyl 6 tert butyl phenol) ie Nocrac NS-5 were found to have comparable efficiency with respect to antioxidant action when measured in terms of percentage retention of quality parameters of condoms after ageing. Percentage retention of burst pressure was found to show a reversion effect when Nocrac NS-5 was used in increasing concentrations(0.25 to 1phr) whereas all other properties show better ageing characteristics compared to lower concentrations of the antioxidant. But the original burst pressure value was maximum at 1 phr level of Nocrac NS-5. 0.5 and 0.75 phr levels were almost similar in imparting the antioxidant efficiency. Modulus values were maximum for 0.75 phr and 1 phr levels of Nocrac NS-5. But Vanox MBPC gave same values of modulus even at 0.5 phr level. Tensile strength, Burst volume and burst pressure values and their retention after ageing also increased gradually with increasing concentration of Vanox MBPC. The term hindered phenol is used to designate any phenol which has tertiary alkyl substitutes in both orthopositions. Phenols which have less bulky substituents are refered to as partially hindered phenols. A hindered phenolic antioxidant also contains a group in the paraposition which greatly influences its activity. It is well known that the antioxidant activity is greatly reduced with parasubstituent branching from normal to secondary to tertiary(37). Consequently the term hindered phenolic antioxidant has come to be used primarily for hindered phenols which have a methylene linkage in the paraposition and which are represented by;



The monophenols are more volatile compared to bisphenols and because of this usually bisphenols are preferred as antioxidants in stereoregular elastomers. The effectiveness of a number of bisphenols in enhancing the induction period during the air oxidation of white oil was explained by Low(100). Grindburg et al(101) in his studies, compared the effectiveness of alkane bisphenols and he found compound of ortholinked bisphenols such as 2,2 bis(4-hydroxy phenyl butyl phenol) and styrenated 2,2-bis(4 hydroxy phenyl propane) were more effective compared to the paralinked bisphenols of their analogues. The higher retention properties such as burst volume, burst pressure and tensile properties after ageing of condoms may be attributed to this advantageous ortholinkage in the hindered bisphenols, ie. Nocrac NS-5 and Vanox MBPC. In the case of colour development also ortholinked bisphenols were reported to have superiority over paralinked counterparts. Among the two, Nocrac NS-5 was found less discolouring compared to Vanox MBPC. Kemperman(102) has studied the relative effect on physical properties and colour development on NR vulcanizates of a number of bisphenols and confirmed the result. According to him changes in the alkyl substituents which decrease the activity are;

a. An increase in the size of the para group.

b. A decrease in the size of the ortho group.

c. A progressive replacement of the hydrogen atoms of the methylene bridge with alkyl groups.

An exception to these generalisations is 2,2' isobutylidine bis(4 methyl 6-tert butyl phenol) which has high activity and causes no discolouration.

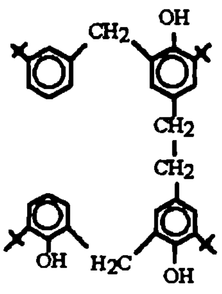
An outstanding characteristic of these hindered bisphenols is their ability to retard the oxidation of rubber products which are contaminated with copper(103). Vanox MBPC (2,2 methylene bis(4 methyl 6-tert-butyl phenol)) is a copper ion deactivator which acts by the propagation inhibiting mechanism. The deactivation of metal ions by chelation operates by

1. A steric effect which blocks the hydroperoxide from the co-ordination sites on the metal ion and;

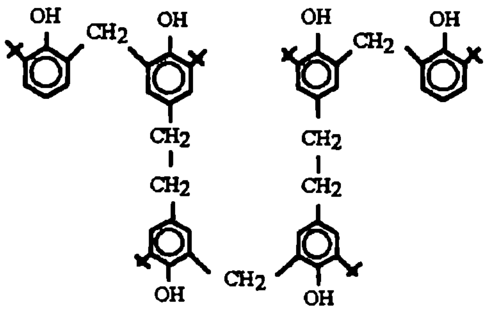
2. An electronic effect which preferentially stabilizes one of the metal oxidation states(104).

However chelation is not always effective and can sometimes enhance metal ion activity particularly if co-ordination is incomplete and causes an unfavourable change in redox potential(104-106). This hindered bisphenol(Vanox MBPC) outperform most amine and phenolic antioxidants in this application. Only the highly staining p-Phenylenediamines are as effective as these bisphenols. The exact mechanism by which they function remains unclear. Extensive studies were conducted to understand the mechanism of their action.

Unlike the hindered phenols, 2,2 methylene bis-4 methyl 6-tert-butyl phenol does not give a primary phenoxy radical. The primary radical is detected by Electron Spin Resonance spectroscopy(ESR) only when it is complexed with metal ions(107). Oxidation of these hindered bisphenol with less than equimolar amounts of tert-butyl hydroperoxide gives dimer(II) and trimer(III) analogous to the dimers of hindered phenols together with dark brown products(108).

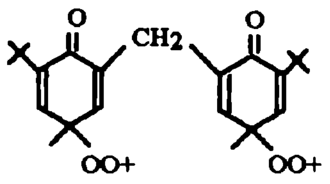


II

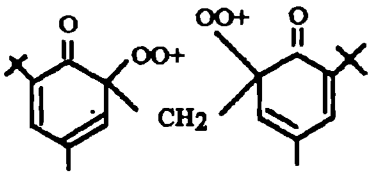


III

Both these compounds are antioxidants. The dimer equals the monomer in activity while the trimer is somewhat less effective. The implication is that although the phenoxy radical is not stable, it is converted into other active materials such as methylene bisdimers, rather than to inert quinol ethers. This overall process would result in the termination of two phenoxy radicals. Furthermore, since Taimr and Posppisil found that excess tert-butyl hydroperoxide is required to give the alkyl peroxy cyclohexadienones(IV and V). These peroxide initiators should not form, form during inhibited autoxidation(109), but the thermal stabilities and relative rates of formation of these products have not been determined.

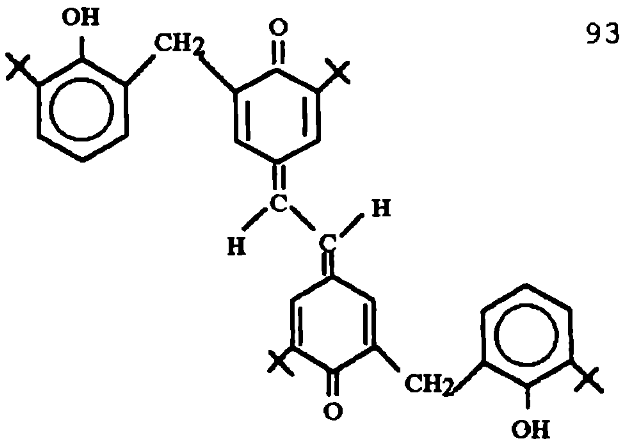


IV



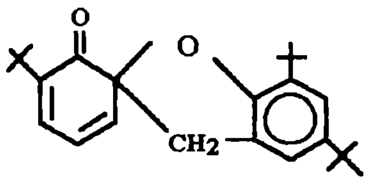
V

The dark products which are responsible for the discoloration were found to contain the highly conjugated and coloured stibene quinone(VI) and the corresponding compound from the trimer(III).



VI

Dimer formation is prevented when the p-methyl group is replaced by a tert-butyl group, and this compound gives a thermally stable spiroquinol - ether(VII) oxidation(110).



VII

2,2 methylene bis 4 methyl 6 tert butyl phenol is widely used as a stabilizer for synthetic rubbers, gel inhibitor of SBR and in light coloured rubber products. The ethyl analogue (Nocrac NS-5) is comparatively somewhat less discolouring and also less active. This was confirmed by the antioxidant efficiency with lower concentrations of Vanox MBPC in place of slightly higher concentrations of Nocrac NS-5 to impart comparable values for modulus, tensile strength and burst volume of NR latex condoms.

Irganox 1010 and Vanox SKT

Irganox 1010 and Vanox SKT found to impart maximum retention properties to aged condoms compared to other antioxidants. Esters of phenol substituted acids can improve ageing characteristics of polymers and the alkyl hydroxy phenyl acid ester was found to be effective in improving the original burst volume, tensile strength and burst pressure of condoms and their retention percentage. So it can be assumed that its protection mechanism started in the processing stage itself if the condoms were slightly over cured. The actual mechanism by which these antioxidants impart better ageing properties compared to other antioxidants are not well understood. Patel (111) have compared the effectiveness of more complex phenols with that of a typical bisphenol and monophenol in stabilizing unvulcanised EPDM, BR and emulsion SBR. Penta erythritol tetrakis- 3-(3'5'-di tert butyl 4 hydroxyphenyl) propionate (Irganox 1010) was found to be five times more effective in stabilizing EPDM at 150°C than either 2,6 di tert butyl 4 methyl phenol or 2,2 methylene bis 4-methyl 6-tert butyl phenol. This results supports the comparatively superior efficiency of Irganox 1010 and Vanox SKT over other antioxidants. 0.5 phr of these two antioxidants were found to retain 77 to 79 percentage of the original tensile strength after ageing for 168 hours at 70°C whereas 1 phr of these antioxidants increases the value still higher. This was an additional advantage since for dipped articles higher percentage of solid compounding ingredients may not be so desirable due to the chances for pinhole formation. Less quantity of more efficient compounding chemicals will be always desirable as far as the quality aspects are concerned. Burst pressure retention values registered a remarkable improvement compared to all other antioxidants studied.

Combination of antioxidants

Synergistic effects of combination of compounding ingredients are well known in rubber technology. In the field of antioxidants, the most common synergistic combinations are mixtures of antioxidants operating by different mechanisms. For example combinations of peroxide decomposers with propagation inhibitors are commonly used. Similarly, combinations of metal chelating agents with propagation inhibitors are used in ceratin elastomers. However synergistic combinations of structurally similar antioxidants are also known, particularly combinations of phenol. Scott(112) has given a detailed discussion of synergism.

Combination of Pentaflex SP and Vanox SKT

Among the antioxidants studied it was noted that PentaflexSP imparts lower ageing properties compared to bis phenols, Vanox SKT, and Irganox 1010. But when 0.25 phr of Pentaflex was used along with 0.25 phr Vanox SKT in a formulation, the efficiency of the combination increased even higher than that imparted by the most effective antioxidants at still higher concentrations. The most efficient Vanox SKT reported a maximum original burst volume of 40.5 at 0.5 phr and 38.5 at 1 phr level. But when the combination of 0.5 phr each of Pentaflex SP and Vanox SKT were used, the original burst volume was 44.8 and the percentage retention was 80.7

It is well established that synergistic combinations of compounding ingredients can reduce the quantity requirement in rubber formulations. Mahoney in his review(113) discusses the synergistic behaviour of hindered and unhindered phenols attributed to the regeneration of the nonhindered phenol(AH) by hydrogen abstraction from the hindered phenol (BH).

$$A' + BH \rightarrow AH + B'$$

The equilibrium in this reaction is far to the right side since the OH bond energy of BH is much lower than that of AH. Termination occurs by the combination of the stable hindered phenol radicals. Since Vanox SKT have both phenolic group and ester group it can sometimes give the reactions of a hindered phenol with a very bulky hindering substituent. Ditert butyl 4 hydroxy cinnamic acid tri ester with 1,3,5 tris (2 hydroxy ethyl) s-triazine- 2,4,6-(1H,3H,5H)trione can thus enhance the overall quality of condoms when used alone and in combination with less effective antioxidant such as Pentaflex SP. Other disadvantages such as high volatility of monophenols and discolouring tendency of bisphenols and amines etc also can be reduced by using combinations of them with Vanox SKT.

Combination of Vulkanox HS and Noorac NS-5

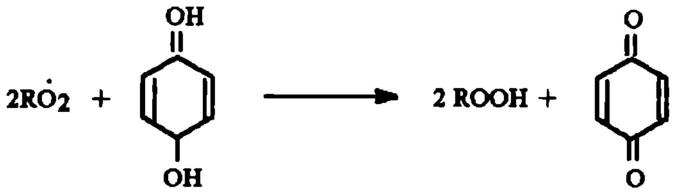
It is well established that when two antioxidants one a free radical inhibitor and other a hydroperoxide decomposer are used in combination the overall effect is more than additive. Here an amine type antioxidant which is poly 2,2,4-trimethyl 1,2 dihydro quinoline known as Vulkanox HS was used in combination with an ortholinked bisphenol. Nocrac NS-5 was very effective in retaining the ageing characteristics of condoms. Vulkanox HS was having a discolouring tendency at higher concentrations and this could be reduced by replacing a part of it by Nocrac NS-5. Eventhough bisphenols also were reported to have a slight discolouring tendency, the combination did not show any such discoloration. Retention percentage of burst volume, burst pressure and tensile properties of condoms after ageing was very low for Vulkanox HS alone even at 1 phr level which even discoloured the condoms. But when 0.5 phr of Vulkanox HS was replaced with 0.5 phr of Nocrac NS-5 the retention percentage of tensile strength increased from 68.9 to 82.5 and that of burst volume and burst pressure increased from 73.00 and 64.50 to 80.70 and 80.80 respectively. The difference observed explains the synergistic behaviour of the antioxidant combination.

Nocrac NS-5 in LATZ Latex

Effect of Nocrac NS-5 in LATZ latex also was studied in comparison with that of high ammonia latex at 0.5 phr level it was found that original values of tensile strength remained same while modulus, burst volume, burst pressure and elongation at break were higher for LATZ latex condoms. Percentage retention of all these properties also were higher in LATZ latex while tensile strength retention was lower for LATZ latex condoms. So it can be concluded that the effect of antioxidants vary with the particular characteristics of the polymer and with particular field of application.

DISCUSSION

Oxygen in conjunction with thermal, radiant or mechanical energy is the principal cause of elastomer ageing and it is well established that antioxidation of hydrocarbons is a free radical chain process involving the cleavage of C-H bonds rather than addition of oxygen to the double bond of an olefin(114). Phenols have definite protective action especially the hydroxy derivatives of conjugated or condensed ring structures and polyhydroxy phenols. This was confirmed by the efficient antioxidant protection observed by all the phenolic type antioxidants studied. Condoms being very thin and light coloured, the nonstaining phenolic type antioxidants can only be used effectively. It is confirmed that(115) phenols and amines react with RO2 radicals formed during the oxidation of NR and do not react with R' radicals. Bickel and Kooyman showed(116) that for hydroquinone each mole of inhibitor reacted with two initiator radicals.



This is an example of how phenolic antioxidants terminate chain reactions by hydrogen abstraction.

$$RO^{\bullet}_2 + AH \rightarrow ROOH + A^{\bullet}$$

Eventhough the mechanism of action of the phenolic antioxidants used may be same, the difference in the efficiency may be due to some other reasons. It is reported(117) that a linear relationship exists between the oxidation-reduction potentials of a series of phenols and the logarithm of their relative antioxidant efficiencies. The oxidation-reduction potentials of Nocrac NS-5 and Vanox MBPC may be similar as with the chemical structures which contribute to the similar antioxidant efficiency in NR latex condoms. Irganox 1010 and Vanox SKT were having same substituent group which is 3,5 ditert butyl 4 hydroxy phenyl group. Both the antioxidants were having similarity in structure and bulkiness and they may also be having similarity in oxidation-reduction potentials which gives comparable antioxidant activity in NR latex condoms.

The difference in antioxidant activity of Nocrac NS-5 in LATZ and HA latex confirms the fact that the selection of proper antioxidant system for a given latex and for a given product depend on empirical observation in laboratory testing.

CONCLUSIONS

1. Among the six different antioxidants studied, Vanox SKT and Irganox 1010 were the most efficient in retaining the properties of natural rubber condoms.
2. Bisphenolic antioxidants such as Nocrac NS-5 and Vanox MBPC were having higher antioxidant efficiencies compared to pentaflex SP and Vulcanox HS which are antioxidants of monophenolic and amine type respectively.
3. Least efficient antioxidants such as pentaflex SP and Vulkanox HS when used in combination with Vanox SKT and Nocrac NS-5

respectively, were found to give improved ageing resistance and less discolouration, due to their synergistic effect in NR latex condoms.

4. It was found that the effect of antioxidant (Nocrac NS-5) on condoms vary with the type of latex used (LATZ and HA) for the condom manufacture.

Table - 1
Effect of Vulkanox HS and Pentaflex SP on quality of condoms

Concentration of A/O (phr)	Modulus at 500% E		Tensile strength (MPa)		E.B (%)		Burst volume (Litres)		Burst pressure (KPa)	
	B	% ret.	B	% ret.	B	% ret.	B	% ret.	B	% ret.
Vulcanox HS										
0.25	7.50	61.80	22.10	69.10	811.00	96.10	29.80	69.50	1.30	61.00
0.50	7.50	63.40	23.00	71.40	791.00	96.00	31.40	71.00	1.70	62.00
0.75	7.50	66.40	23.10	69.80	820.00	94.80	34.50	73.00	1.60	63.80
1.00	7.50	70.40	23.20	68.90	813.00	93.30	36.40	73.00	1.80	64.50
Pentaflex SP										
0.25	7.50	60.00	21.90	68.10	789.00	94.00	30.40	68.70	1.60	55.50
0.50	7.50	62.40	22.00	67.90	785.00	95.10	30.60	69.80	1.40	68.10
0.75	8.00	63.10	22.50	70.10	794.00	96.80	31.80	71.60	1.80	69.90
1.00	7.50	64.50	22.70	74.80	798.00	95.40	33.10	79.70	1.80	71.80

B - Before ageing
% Ret - % retention after ageing at 70°C for 168h.

Table - 2

Effect of Nocrac NS-5 and Vanox MBPC on quality of condoms

Concentration of A/O (phr)	Modulus at 500% E		Tensile strength (MPa)		E.B (%)		Burst volume (Litres)		Burst pressure (KPa)	
	B	% ret.	B	% ret.	B	% ret.	B	% ret.	B	% ret.
Nocrac NS-5										
0	7.50	60.00	22.00	65.00	785.00	90.80	30.90	65.00	1.60	59.80
0.25	7.50	62.10	22.30	70.50	781.00	92.00	32.10	70.40	1.60	59.90
0.50	7.50	62.80	23.50	73.40	795.00	93.50	34.00	72.40	1.70	61.10
0.75	8.00	64.00	23.50	75.10	790.00	90.80	36.10	73.00	1.80	62.40
1.00	8.00	65.50	24.00	76.80	795.00	92.80	38.90	73.90	2.00	60.80
Vanox MBPC										
0.25	7.50	63.00	23.00	71.10	795.00	95.00	31.10	69.80	1.60	62.10
0.50	8.00	63.40	22.90	74.00	794.00	94.00	33.00	71.10	1.70	64.00
0.75	8.00	64.10	24.00	75.80	800.00	95.00	37.00	72.80	1.80	64.10
1.00	8.00	65.40	24.10	77.10	798.00	92.90	37.50	73.90	2.10	65.40

B - Before ageing

% ret - % retention after ageing at 70°C for 168h.

Table - 3
Effect of Vanox SKT and Irganox 1010 on quality of condoms

Concentration of A/O (phr)	Modulus at 500% E		Tensile strength (MPa)		E.B (%)		Burst volume (Litres)		Burst pressure (KPa)	
	B	% ret.	B	% ret.	B	% ret.	B	% ret.	B	% ret.
Vanox SKT										
0.25	8.0	64.80	23.50	76.90	801.00	95.50	39.10	74.00	1.80	59.10
0.50	8.0	65.00	24.10	77.10	799.00	94.10	40.50	74.40	2.00	62.40
0.75	8.0	67.00	24.00	79.40	805.00	94.40	38.50	77.10	2.00	68.00
1.00	8.0	70.00	24.50	80.00	800.00	90.10	38.50	80.80	1.90	80.00
Irganox 1010										
0.25	8.0	67.00	22.90	75.10	800.00	94.80	38.30	73.80	1.60	70.00
0.50	8.0	67.80	23.40	79.40	798.00	94.10	40.30	75.10	1.70	70.90
0.75	8.0	69.10	24.10	80.40	803.00	90.80	40.20	75.60	2.10	80.40
1.00	8.1	71.10	24.50	81.80	811.00	91.00	39.80	80.90	2.10	80.90

B - Before ageing
% ret - % retention after ageing at 70°C for 168h.

Table - 4
Effect of antioxidant combinations on quality of condoms

Concentration of A/O (phr)	Modulus at 500% E		Tensile strength (MPa)		E.B (%)		Burst volume (Litres)		Burst pressure (KPa)	
	B	% ret.	B	% ret.	B	% ret.	B	% ret.	B	% ret.
Pentaflex SP + Vanox SKT										
0.25+0.25	8.00	80.00	24.00	80.80	810.00	95.40	39.10	75.60	2.00	60.40
0.50+0.50	8.00	84.50	24.80	84.50	808.00	96.00	44.80	80.70	2.00	80.80
Vulcanox HS + Nocrac										
0.25+0.25	8.00	75.40	23.80	77.90	790.00	93.40	40.80	79.60	18.0	71.40
0.50+0.5	8.00	78.50	24.50	82.50	802.00	96.60	41.20	82.40	2.00	82.40

B - Before ageing
% ret - % retention after ageing at 70°C for 168h.

Table - 5
Effect of Nocrac NS - 5 in (LATZ) and (HA) latices

Type of latex				
LATZ latex		HA latex		
Properties	Original value	% retention	Original value	% retention
M500 (MPa)	8.5	74	7.5	62.8
T.S (MPa)	23.5	68	23.5	73.4
E.B (%)	788	94	795	93.5
Burst volume (litres)	38.4	74	34.0	72.4
Burst pressure (KPa)	1.8	78	1.7	61.1

* % retention after ageing for 168 hrs at 70°C

CHAPTER VI

INFLUENCE OF PROCESS VARIABLES ON QUALITY OF NR LATEX CONDOMS

INTRODUCTION

Eventhough natural rubber latex condoms are widely accepted as a contraceptive and as a barrier against sexually transmitted diseases, they are not having 100% reliability in effecting their purpose. Presence of pinholes in condoms makes them unsuitable for use. Variation in film strength and other physical properties of condoms also cause breakage of condoms and thus fail to serve their requirement. Process variables such as ball milling time of dispersions, concentration and temperature of mould washing solution, period and temperature of prevulcanisation of latex compound, period and temperature of final vulcanisation of condoms, all may be having some influence on pinhole formation and other properties of condoms. During the inspection of final product, each condom is electronically tested for the presence of pinholes and only those which pass the test are further processed. The important quality parameters of condoms, as specified by WHO are listed in annexure 4. When strict compliance to these specifications is resorted to, further rejections are possible. Since the defects could be identified only at the final stage of processing of the product, manufacturing industries face the problem of high rejection rate. In this context, it is necessary to have an awareness of the influence of various process variables on quality of NR latex condoms, so that the rejection rate may be reduced by taking remedial measures in the initial stages of processing itself.

It is well known that for latex compounds, the particle size of dispersions and droplet size of emulsions should be comparable to that of rubber particles(118). This is required for a uniform distribution of the ingredients in latex(119,120,121,122). As condoms are manufactured by straight dipping technique, the surface quality of formers have a direct influence on the quality of condoms. The soap solution used for cleaning the formers should have adequate concentration. Temperature of the cleaning bath also influences the degree of cleanliness and the properties of condoms. Time and temperature of prevulcanisation and post vulcanisation also are of much importance as far as the final properties of condoms are concerned.

Inspite of the significant influence of the above mentioned variables on the quality of condoms and the extent of pinhole rejection rate, systematic investigations on these aspects have not been reported.

In this work the effect of ball milling time, concentration and temperature of mould cleaning solution, temperature and period of prevulcanisation and final vulcanisation on quality parameters of condoms and pinhole rejection rate has been studied.

EXPERIMENTAL

Materials

High ammonia centrifuged natural rubber latex, whose characteristics are listed in annexure I, was used for the study. Casein, potassium oleate, ammonia, sodium di-N-butyl dithiocarbamate (Nocceller TP, Ouchi Shinko Chemical Industrial Co., Japan), activated dithiocarbamate(Setsit-5, Vanderbilt, USA), Zinc oxide, 2,2 methylene 4-ethyl 6-tert-butyl phenol (Nocrac NS-5, Ouchi Shinko Chemical Industrial Co., Japan), sodium salts of polymerised substituted sulphonic acid (Darvan No.1 and 2, Vanderbilt, USA) alkyl aryl polyether type mould washing agent and sulphur were of commercial grade.

METHODS

Ammonia was diluted to 25% and 1% solutions, potassium oleate and casein were used as 20% and 10% solutions respectively. Dispersions of solid ingredients were prepared by ball milling. Ball milling was carried out for 72h to prepare a 50% composite dispersion of all solid ingredients except when the effect of ball milling time was studied. Particle size distribution of the composite dispersion was assessed using a Malvern IM 120 particle size analyzer. The ingredients were added in the order given in annexure - 3. Soluble ingredients such as Nocceller TP and Setsit-5 were directly added to latex and stirred well. Prevulcanisation of latex was done by heating the compound at 55°C for 8h under stirring. In the studies of the effect of prevulcanisation on quality of condoms, the time and temperature of prevulcanisation was varied. After prevulcanisation, latex was diluted using 1% ammonia solution to a total solids content of 48%. Condom samples were produced by straight dipping technique using glass formers. Double dipped products were prepared and vulcanisation was done in an air oven at 80°C for 30 minutes. For the studies of the effect of time and temperature of vulcanisation on quality of condoms the parameters were varied and the resulting products were analyzed. After the final vulcanisation, condoms along with the mould were cooled to room temperature and stripped from the mould using french chalk powder.

After 24h conditioning the products were tested for pinholes, tensile strength, burst volume and burst pressure. Air leak and water leak tests were carried out as per IS 3701-1985(123). Electronic testing was conducted to detect pinholes. Burst volume and burst pressure tests were carried out as per ISO 4074/6-1984(E). Ageing was conducted in an air oven at 70°C for 168h. Tensile strength, elongation at break and modulus at 500% elongation were determined using a Zwick universal testing machine model 1474 according to ASTM 412(1980).

RESULTS AND DISCUSSION

Effect of ball milling time

It was found that as the ball milling time increased particle size decreased upto 72h and then it marginally increased. The specific surface area also increased upto 72h and then decreased as is shown in Table 4. The exact reason for the slight increase in particle size beyond 72h ball milling is not clear. Probably, under conditions of prolonged ball milling there is a tendency for reagglomeration of particles. During the course of ball milling, there has been a steady change in the particle size distribution towards the lower range as is clearly indicated in fig.1. Table 1 also indicates that pinhole rejection percentage was maximum for the highest particle size dispersion and it gradually decreases with decreasing particle size. The percentage of condoms having pinholes was 55 when the ball milling time was 1h while it was only 10 when the ball milling time was 72h. In the case of tensile strength, burst volume and burst pressure a gradual increase was observed upto 72h ball milling and a slight decrease beyond that. It was reported(24) that size of sulphur particles is of great importance for the crosslinking reaction. The high tensile strength, modulus and burst volume obtained at 72h ball milling could be attributed to the optimum level of crosslinking obtained by the fine particle size dispersion of sulphur and other ingredients.

Effect of mould cleaning

When different concentrations of mould cleaning soap solution were used, it was observed that as the concentration of soap was increased from 0.1 to 0.7% tensile strength showed a slight increase while burst volume and burst pressure improved considerably. It was also observed that pinhole rejection percentage was reduced from 12.5 to 8.75 when the soap concentration was increased from 0.1 to 0.5 and then it increased to 10 for a concentration of 0.9%. It reveals that an optimum concentration of soap can reduce the quantity of rejected condoms by ensuring a cleaner mould. However, excess of soap can have adverse effect as well. Presence of dust, dirt, grease etc on the mould surface can produce pinholes or weak spots in the latex film. With thorough cleaning of the mould using an adequate level of soap, this can be minimised and latex pick up becomes uniform and this may be the reason for the improved burst volume and other properties observed as is shown in Table 2. A higher than the optimum level of soap might cause frothing of latex which could lead to more pinholes. It may be noted from Table 3 that the efficiency of mould cleaning increased when the temperature of the bath was raised from 20 to 60°C as is evidenced by the values of pinhole rejection rate and other properties. All the strength properties of condoms improved steadily with increasing temperature of mould cleaning bath. A higher temperature is always helpful in removing grease from mould surface and a grease-free mould is uniformly wetted by the latex compound leading to better properties.

Effect of prevulcanisation

As the prevulcanisation time was increased from 4 to 12h the pinhole rejection rate increased and a maximum was reached at 10h of prevulcanisation. Modulus at 500% elongation and tensile strength increased with increasing temperature of prevulcanisation and a maximum value was obtained at 10h. But it was noted that ageing resistance decreased as the prevulcanisation time increased as is evident from fig.2a. Retention of properties after ageing was adversely affected as the prevulcanisation time increased. Burst volume and burst pressure were maximum at 6h of prevulcanisation. However, retention of these properties after ageing was poorer with increasing time of prevulcanisation.

The temperature of prevulcanisation also has a significant influence on the properties of condoms. Table 5 indicates that pinhole rejection rate increases steadily with increasing prevulcanisation temperature. Modulus at 500% elongation, burst volume and burst pressure passes through a maximum at 50°C. Tensile strength was found to decrease marginally with increasing temperature of prevulcanisation. Ageing resistance also decreased when the temperature of prevulcanisation was increased(Fig.2b).

During prevulcanisation of latex both crosslinking and main chain scission may become comparatively more significant when the reaction is carried out for a longer period and/or at a higher temperature. Strength properties in general, improves as the extent of prevulcanisation increases. However, after the maximum crosslinking has taken place, any further increase in temperature or time or both causes reduction in strength properties on account of chain scission reactions. It is also worth noting that as the vulcanisation of latex takes place within the individual rubber particles, the surface hardness of the particles increases during vulcanisation. This reduces the chances for interparticle fusion, which is one of the factors contributing to the low strength of films prepared from prevulcanised latex. Therefore, in order to achieve maximum strength it is essential to optimise time and temperature of prevulcanisation. The exact reasons for the adverse effect of time and temperature of prevulcanisation on pinhole rejection rate are not clear. It is possible that the viscosity of the latex compound increases during prevulcanisation. A higher viscosity of the latex causes more air entrapment leading to increased pinhole formation.

During ageing also both crosslinking(post-curing) and chain scission take place. As the crosslinking reaction has already been completed and all the vulcanising ingredients fully used up, further heat treatment can cause only chain scission leading to drop in strength properties.

Effect of final vulcanisation

In the manufacturing process condoms are subjected to a final vulcanisation at an elevated temperature for a predetermined time. Tables 6 and 7 show the effect of time and temperature of final vulcanisation on properties of condoms. It is observed from Table 6 that 20 minutes is the optimum period for vulcanisation at 80°C. Properties such as modulus, tensile strength, burst volume and burst pressure attain maximum values in 20 minutes. Beyond this period, most of the properties drop. Ageing resistance also decreases significantly beyond this period.

From Table 7 it is noticed that 70°C is the optimum temperature for final vulcanisation of condoms if the duration is fixed as 30 minutes. Strength properties attain maximum values at this temperature and then decreases at higher temperatures. Pinhole rejection rate was found to increase with increasing temperature of final vulcanisation. It is possible that the microlevel air bubbles expand and burst at the higher temperatures leading to larger number of pinholes.

The accelerators used in the compound are dithiocarbamate type which give a peaky cure. Also the latex used was already prevulcanised before the dipping process. Therefore, the longer final vulcanisation time and higher temperature might be causing reversion and this could be the reason for the sudden decrease in tensile strength and burst volume values especially after ageing(Figs.2c and 2d). It is an established fact that the amount of combined sulphur in rubber vulcanisate is a linear function of heating time(125). The rate of reaction between rubber and sulphur also depends on the temperature at which the mixture is heated. Hence the variation in strength properties noted at higher time and temperature of prevulcanisation and final vulcanisation could be due to the difference in combined sulphur content and a higher crosslink density.

CONCLUSIONS

1. Properties of condom improve and pinhole rejection rate decreases as the ball milling time of the composite dispersion increases, the optimum period being 72h. Particle size of the ingredients decreases considerably during ball milling.

2. Optimum concentration of mould cleaning soap solution is in the range 0.5-0.7% and its temperature 60°C.
3. Time and temperature of prevulcanisation and final vulcanisation are interrelated in determining the final product properties.

Table 1

Effect of ball milling time of composite dispersion on quality of condoms

Ball milling time (hrs)	Average particle size (um)	Average specific surface area (m²/cc)	Pinhole rejection (%)	Modulus at 500% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Burst volume (litres)	Burst pressure (KPa)
1	14.12	4.62	55	7.5	16.1	750	17.9	0.7
24	2.48	6.86	47	7.7	17.0	774	18.8	0.8
48	1.21	10.39	26	8.0	19.2	786	29.9	1.0
72	0.5	15.56	10	8.5	20.9	799	31.8	1.4
120	0.7	12.81	10	8.0	19.5	788	30.9	1.2

Table 2

Effect of concentration of mould cleaning bath

Concentration of soap solution (%)	Pinhole rejection (%)	Modulus at 500% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Burst volume (Litres)	Burst pressure (KPa)
0.1	12.5	7.7	19.9	760	30.5	1.0
0.3	10.0	7.9	20.1	765	31.0	1.2
0.5	8.75	8.0	20.9	790	31.8	1.4
0.7	8.75	8.1	21.0	799	34.2	1.4
0.9	10.0	8.0	20.8	798	35.0	1.3

Table 3

Effect of temperature of mould cleaning bath on quality of condoms

Temperature of bath (°C)	Pinhole rejection (%)	Modulus at 500% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Burst volume (Litres)	Burst pressure (KPa)
20	12.5	7.9	20.0	754	28.9	0.9
30	12.5	7.9	20.1	785	30.4	1.0
40	10.0	8.0	20.91	791	31.8	1.4
50	10.0	8.2	21.4	781	33.0	1.4
60	8.75	8.2	21.7	788	33.5	1.2

Table 4

Effect of prevulcanization time (Temp: 55°C)

Prevulcanization time (hrs)	Pinhole rejection (%)	Modulus at 500% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Burst volume (Litres)	Burst pressure (KPa)
4	7.5	8.0	18.8	789	33.8	1.2
6	8.75	8.0	19.4	811	33.9	1.4
8	10.0	8.0	20.9	798	31.8	1.4
10	12.5	8.1	21.1	813	30.9	1.4
12	12.5	8.4	21.0	810	30.8	1.4

Table 5

Effect of prevulcanization temperature (Time: 8 h)

Prevulcanization temperature (°C)	Pinhole rejection (%)	Modulus at 500% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Burst volume (Litres)	Burst pressure (KPa)
45	8.75	7.8	21.0	799	32.3	1.3
50	8.75	8.0	20.9	811	32.0	1.4
55	10.0	8.0	20.95	792	31.8	1.4
60	11.25	7.9	20.3	787	30.1	1.3
65	12.5	7.8	20.3	778	29.8	1.3

Table 6

Effect of final vulcanization time (Temperature: 80°C)

Vulcanization time (minutes)	Pinhole rejection (%)	Modulus at 500% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Burst volume (Litres)	Burst pressure (KPa)
10	8.75	8.4	20.90	809	30.6	1.4
20	10.0	8.4	21.0	800	32.1	1.4
30	10.0	8.0	20.9	798	31.8	1.4
40	10.0	7.9	20.1	765	28.1	1.3
50	10.0	7.9	18.8	764	26.8	1.1

Table 7

Effect of final vulcanization temperature (Time: 30 minutes)

Vulcanization temperature (°C)	Pinhole rejection (%)	Modulus at 500% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Burst volume (Litres)	Burst pressure (KPa)
60	10.0	8.0	21.3	813	30.0	1.4
70	10.5	8.0	21.3	800	32.4	1.4
80	10.0	8.0	20.9	798	31.8	1.4
90	12.5	7.8	20.4	789	31.5	1.3
100	12.5	7.8	19.9	785	30.4	1.2

FIG.1. EFFECT OF BALL MILLING PERIOD ON PARTICLE SIZE

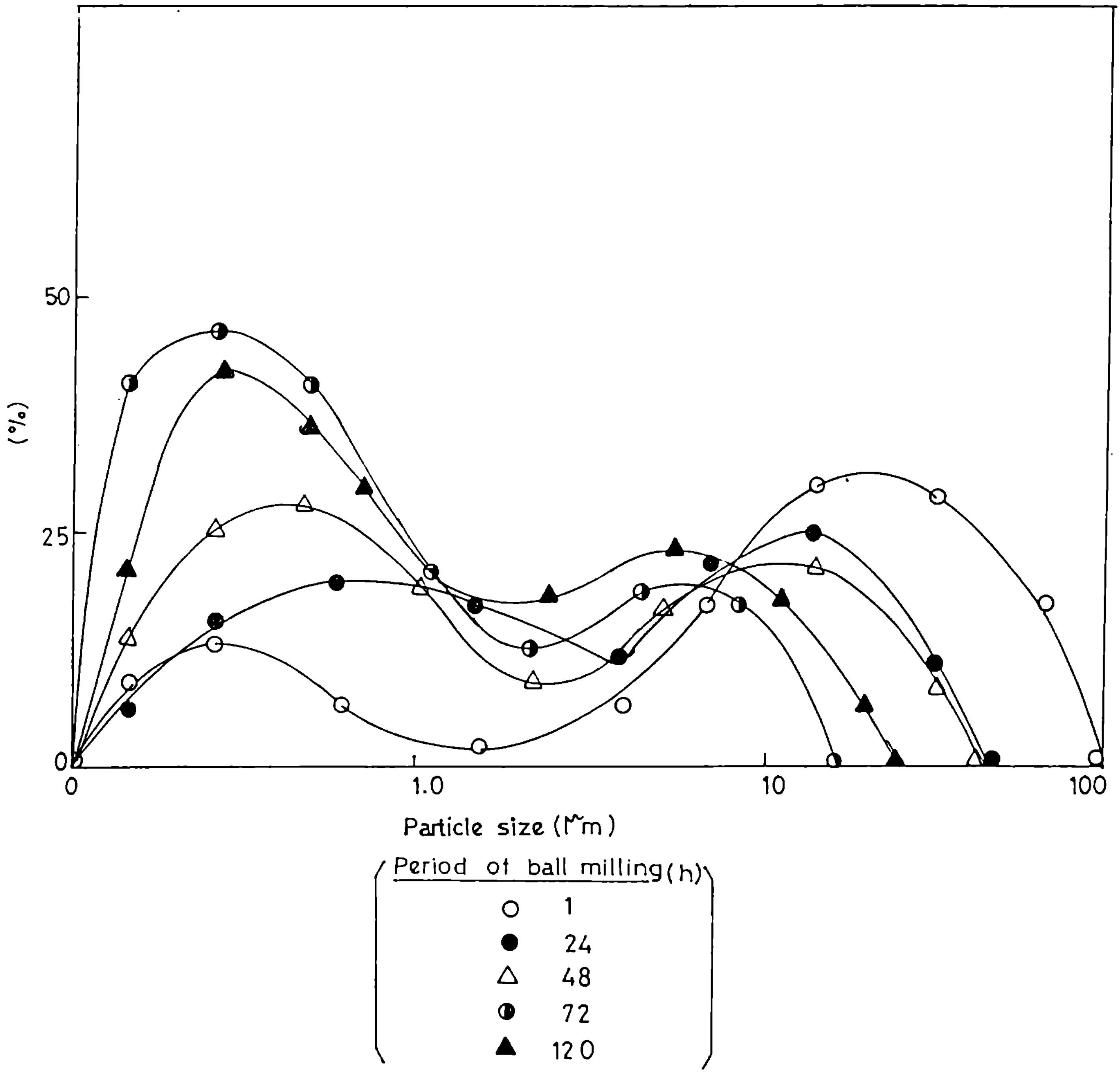
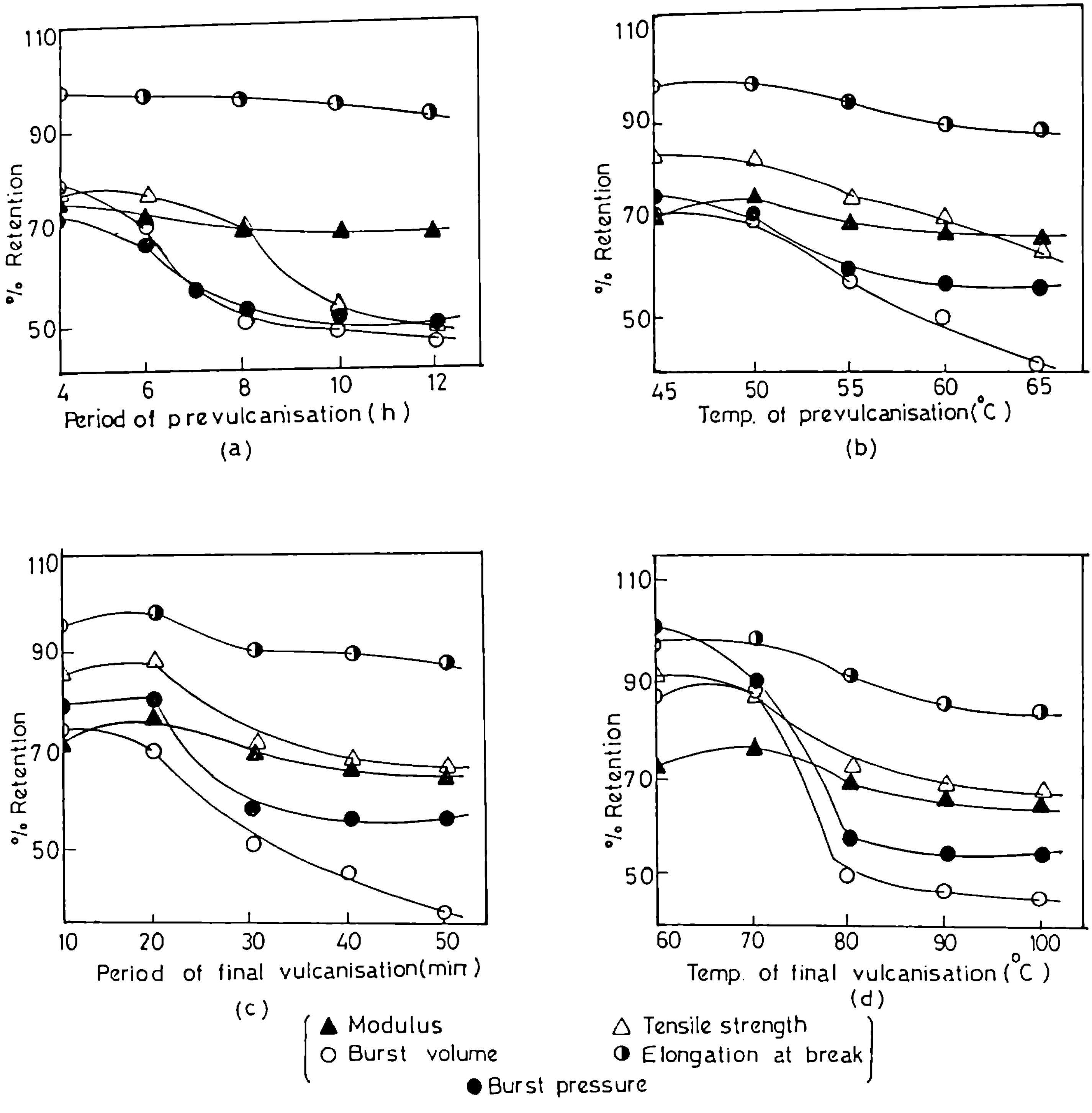


FIG.2. EFFECT OF PROCESS VARIABLES ON % RETENTION OF PROPERTIES



(a)

(b)

(c)

(d)

CHAPTER VII

COMPARATIVE STUDY OF POSTVULCANISED, PREVULCANISED AND RADIATION VULCANISED NR LATEX CONDOMS

INTRODUCTION

For any product manufacture the most important criteria which determine its quality is the raw material used. As far as latex products are concerned, modified forms of latex can significantly change the product properties. Prevulcanised and radiation vulcanised latices were developed to make use of their advantageous properties.

It is well known that certain accelerators used for vulcanisation of rubber latex produce nitrosamine, a carcinogenic substance during vulcanisation. As the safety requirement for use of rubber products are becoming more stringent it is time to look for an alternative which is technically and economically viable. Development of RVNRL is an answer to this search(126-128). In addition to the absence of carcinogenic nitrosamines RVNRL is reported to have low cytotoxicity and high transparency.

Use of prevulcanised latex also have certain advantages over post vulcanised latex film. Effective control of ultimate physical properties may be exercised before articles are manufactured from it. Also the time for final vulcanisation may be reduced. But contradictory reports are there regarding the rate of crosslinking observed during prevulcanisation in the latex phase and those occurring in post vulcanised films(129-131). There is a general consensus among latex technologists that the rate of prevulcanisation is much faster than the rate of postvulcanisation under otherwise identical conditions(132). There is no reliable reports regarding the effect of prevulcanised, post vulcanised and radiation vulcanised NR latex on the quality of condoms.

In the present study the properties of these three latices and their influences on quality of condoms is compared with respect to pinhole rejection rate, tensile properties, burst volume, burst pressure and ageing characteristics.

EXPERIMENTAL

60% low ammonia(LATZ) latex was used for the study. Compounding was done as per the formulation given in Annexure 3. Solid ingredients were added as a 50% mixed dispersion and water soluble liquid ingredients were added as such. After giving a maturation period of 24 hours prevulcanisation of the latex compound was done by heating the compound for 8 hours at 55°C in a constant temperature water bath. Radiation vulcanisation of the latex was conducted at rubber research institute of India after compounding it as per the following formulation.

60% latex	167
10% KOH	2
nBA	1
CCl_4	1

0.1% ammonia water was also added in the required quantity. Maturation time of 2 hours was given and irradiated using γ rays in a γ chamber for 2.5 Mrad radiation dose.

Rheological behaviour of unvulcanised, prevulcanised and radiation vulcanised latices were compared by measuring the viscosities using a Brookfield LV viscometer model DVII+ (spindle no.2). Temperature dependence of these viscosities also was noted by measuring it at different temperatures. Shear rate was varied by using different rates of rotations of the spindle. Total solid content of the latices were reduced to 48 and condoms were dipmoulded using glass formers.

Post vulcanised condoms were prepared by dip moulding and were given a vulcanisation time of 30 minutes at 80°C in an air oven. Condoms from prevulcanised latex was dipmoulded similarly and were also given a post vulcanisation for 30 minutes at 80°C. Radiation vulcanised latex condoms were kept in an air oven at 70°C for 5 hours for complete drying. Stripping of condoms from the mould was done using french chalk powder. After conditioning for 24 hours at room temperature the products were tested for various quality parameters. Effect of stabilizers and antioxidant also were studied by suitably compounding latices for this purpose.

RESULTS AND DISCUSSION

General characteristics of the postvulcanised, prevulcanised and radiation vulcanised latices.

Table 2 can explain certain drawbacks and advantages of these latices in comparison with one another. Total solids contents are almost similar. A slightly higher TSC was observed for prevulcanised latex. Viscosity also increased for prevulcanised latex. Radiation vulcanised latex registered a maximum viscosity of 79 cps. It may be due to the crosslink formation in both these latices. Maximum heat stability time showed by radiation vulcanised latex indicate a lower extent of vulcanisation. prevulcanised latex gave very low HST and it may be due to the prolonged time of prevulcanisation given for the latex. MST also showed the high stability of RVNRL compared to other two latices. pH values were same for prevulcanised and radiation vulcanised latices and it was 1 unit lower than the post vulcanised latex. This may be due to the escape of ammonia from these two latices during stirring and processing.

Rheological behaviour of the latices

As far as the quality of dipped latex products are concerned, the rheological behaviour of the latex is of much influence. Brookfield viscosity studies (table 4) showed that prevulcanised latex give higher viscosity values than post vulcanised(unvulcanised) latex. The difference in these values were higher at low shear rates whereas at high shear rates eventhough there was difference it was not much apart. This may be explained by the secondary valence bond theory as reported by Blackley(133). Low shear rates may not break these weak bonds but at higher shear rates these effects may be reduced by breaking of these bonds. Eventhough it is believed that during prevulcanisation vulcanisation reaction takes place in each of the individual latex particles without altering their state of dispersion appreciably, the actual mechanism is not yet fully understood. But the increase in viscosity with increasing prevulcanising time is in agreement with the already reported results(134). So it can be assumed that some rearrangement of the latex particles to affect the state of dispersion may be taking place during prevulcanisation. Temperature dependence of the viscosity also was noted for all the three, viz. postvulcanised, prevulcanised and radiation vulcanised latices. As the temperature increases viscosity was found to decrease both for low and high shear rates (12 & 60 rpm). Minoura & Asao observed that as the irradiation of latex continues the viscosity decreases sharply at first, passes through a minima and then increases(135).

Effect on pinhole formation

It was noted that pinhole rejection percentage of condoms was highest for postvulcanised condoms and lowest for RVNRL condoms (table 4). Prevulcanised latex gave intermediate values for pinhole rejection rate. Solid compounding ingredients present in the latex may cause pinholes if they are not properly reduced in size and dispersed. Sometimes reagglomeration of the dispersed particles is possible and this can cause pinholes in the dried film. RVNRL does not contain such dispersion and this may be a reason for the low pinhole rejection rate observed. It was already noted in the studies of stabilizing system that, potassium oleate added as a stabilizer is effective in producing pinholes due to the formation of froth in the latex. These bubbles present on the mould surface may break while heating in the oven and forms a pinhole at that point. In case of prevulcanised latex these bubbles might have escaped during 8 hours of stirring and heating for prevulcanisation. RVNRL does not contain any oleate and so it naturally will be producing less pinholes. In addition to this the drying temperature given for RVNRL condoms was only 70°C whereas for other two types it was 80°C. Oily substances if present on the mould surface may reduce the wetting of mould by latex and this also can give low resistance when tested in the electronic testing machine. Liquid ingredients added as accelerators may sometimes be reducing the wetting tendency eventhough they are considered as water soluble substances. Atmospheric dust particles can also produce pinholes in condoms. Ageing of condoms prepared from all the three types of latices does not have any influence on the rejection percentage due to pinholes (table 5,6).

Influence of stabilizer system

(a) Potassium oleate - casein system

Effect of potassium-oleate casein system in different latices for condom manufacture was studied and it was observed that pinhole rejection percentage was maximum for post vulcanised latex condoms and minimum for radiation vulcanised latex. Radiation vulcanised latex already contains KOH which was added before its irradiation. So this was an additional stabilizer for this latex. Even before the addition of the stabilizer system RVNRL was having a pinhole rejection percentage of 11.5 and it could be reduced to 10 by the addition of potassium oleate casein system (table 4&5). Modulus values does not get affected by the presence of potassium oleate - casein system. Tensile strength of post vulcanised film was same before and after the addition of the stabilizer whereas prevulcanised and radiation vulcanised latex condoms showed a slight increase in tensile strength. Burst volume values of all the three latices were improved by the presence of this stabilizer system. Burst pressure value was same for post vulcanised condoms, but other two types of latices gave improved burst pressure values on the addition of potassium oleate - casein system. It was found essential to add stabilizers to reduce the pinhole rejection percentage and for improved physical properties.

(b) Potassium laur ate - casein system

Potassium laur ate - casein system was found to reduce the pinhole rejection percentage of all the three types of latex condoms. Post vulcanised, pre vulcanised and radiation vulcanised latices gave only 5% rejection when this stabilizer system was used. Ageing did not affect the rejection percentage due to pinholes. Tensile strength of radiation vulcanised latex increased slightly while for the other two latices not much difference was observed. Burst pressure values did not show any variation with the change in stabilizer system, except for prevulcanised latex condoms where the burst pressure decreased from 1.8 to 1.6 for potassium laur ate - casein system. But this decrease was within the specification of WHO for condoms.

(c) Polyvinyl alcohol - casein system

Percentage rejection of condoms due to pin holes was intermediate to those of the other two stabilizer systems. But on ageing the condoms for 168 hours at 70°C the percentage rejection was more compared to those before ageing. Polyvinyl alcohol - casein system was found to increase the viscosity of the latex compound during processing. But this system was found to increase the tensile strength of radiation vulcanised latex condoms, while that of post vulcanised and pre vulcanised latices were slightly lowered. Burst volume and burst pressure values were not much affected.

Comparing all the three stabilizer systems it can be concluded that potassium laurate - casein system improves the overall quality of latex condoms compared to other stabilizer systems. Comparative evaluation of the stabilizer systems in high ammonia latex are given in chapter 3. Eventhough a slight decrease in burst pressure value were noted for RVNRL condoms, it was within the specified limits of WHO. So considering all aspects of the condom property potassium laur ate - casein system was found essential to increase the quality of latex condoms manufactured from postvulcanised, prevulcanised and radiation vulcanised latices.

Effect on tensile properties, burst volume and burst pressure

In the comparative evaluation, post vulcanised condoms gave maximum tensile strength and burst volume compared to condoms from prevulcanised and radiation vulcanised latex. Burst pressure was maximum for condoms prepared from prevulcanised latex. RVNRL condoms were inferior to both prevulcanised and postvulcanised latex condoms with respect to tensile, burst volume and burst pressure properties. Modulus at 500% elongation was maximum for prevulcanised latex condoms while tensile strength showed a low value compared to that of postvulcanised latex condoms. The low tensile strength of prevulcanised latex condoms than that of postvulcanised may be due to the non homogeneous nature of the film as reported by Porter (136). Low wet gel strength of prevulcanised latex (132) also can cause reduction in burst volume and tensile properties of condoms due to the deformations that might have taken place in the wet condition. It has been reported that in the vulcanisation of dry rubber as the vulcanisation temperature becomes lower, the chances for the formation of polysulfidic type linkages are high (137). So the higher polysulfidic linkages in the prevulcanised latex condoms may be attributed to the low prevulcanisation temperature (55°C). It is also reported that tensile strength and modulus are improved only upto a certain extent of prevulcanisation and above that level the properties decrease (138). Difference in the particle nature during drying of the film also may cause variations in strength properties of prevulcanised and post vulcanised latex films. Loss of water takes place during drying of film to bring the particles in a close packed configuration. Deformation of the particles with an increase in area of contact accompanied by further loss of water also takes place leading to the formation of a continuous film. During prevulcanisation, flocculation may be taking place and these flocculated particles may be preventing the close packing of particles during drying of condoms. Prevulcanised latex condom showed similar modulus values for M300 compared to postvulcanised condoms. But the M500 values were higher for the former. This behaviour can be explained with the help of secondary valence bond theory. According to this theory(133), the coherence of films from prevulcanised latex derives mainly from the totality of secondary valence bonds, which come into being between the molecules of each pair of particles as the latex is dried down and the particles come close to one another. As a result of vulcanisation reaction probably all of the molecules of any one particle will be linked to one another, so that the particle itself may be regarded as one giant single network. Whilst the secondary valence bonds set up between any two molecules of adjacent particles will be very weak, the totality of such forces between two adjacent particles will be appreciable since they are scaled up by the total number of rubber molecules present in each particle. Initial low modulus(M300) is due to the molecules in the region of overlap moving independently of one another so that the behaviour is similar to that of unvulcanised rubber. The increasing stiffness observed at 500% extension is considered to be due to the increasing lack of independence of the molecules in the region of overlap of particle. Low burst volume and tensile strength of condoms from prevulcanised latex is thus in agreement with the reported(133) results of properties of prevulcanised films.

Reasons for low strength properties of RVNRL is not yet fully investigated. Crosslinks formed in RVNRL should be superior to that of sulphur vulcanisate in strength and temperature stability because of the higher bond energy of C-C bond in RVNRL compared to C-S bond of sulphur vulcanisate. But practically the reverse was observed. It is well known that presence of radical scavengers such as oxygen can retard the crosslinking reaction especially at low doses. The ingress of air in the system while agitating the latex during irradiation can reduce the crosslink density. Since the radiation vulcanisation was done at a low dose the oxygen might have acted as mentioned above. The extent of vulcanisation also was low which is indicated by the high heat stability value. The nonrubber particles present may affect the fusion behaviour of rubber particles. All these parameters may be contributing to the lower values of modulus, tensile strength, elongation at break, burst volume and burst pressure of RVNRL condoms. Other reported work on RVNRL also gave lower values for physical properties of films(127,128).

Effect of thermo oxidative ageing and action of antioxidant.

Different periods of ageing at a constant temperature of 70°C was given for sample condoms prepared without using any antioxidant and with the use of a bisphenolic antioxidant, Nocrac NS-5; which was used in all the control compounds. In the case of postvulcanised latex condoms the decrease in tensile properties and burst volume were less compared to those of prevulcanised and radiation vulcanised latex condoms. Low ageing properties of prevulcanised latex may be due to the higher polysulfidic linkages formed at the prolonged heating period of latex at 55°C for prevulcanisation. In the case of dry rubber also as the vulcanisation temperature becomes lower, the chances for the formation of polysulfidic type linkages are high(137). In the studies conducted by Parks and Lorenz(139) it was observed that oxygen uptake become greatest in the polysulfidic network compared to mono and disulfidic linkages. They attributed this to initiation of oxidation by perthiyl radicals formed on polysulfide scission and to activation of hydrogen atoms by cyclic sulfides. Lal(140) has made similar observations and showed that removal of polysulfides by treatment with triphenyl phosphine results in reduced rates of oxidation. The situation has been clarified by Bell and Cuneen(141) who studied the oxidation of protected and unprotected vulcanisates of highly purified natural rubber and unpurified NR, ie,RSS-1 (ribbed smoked sheet rubber). Low interparticle fusion of prevulcanised latex as reported(134) may also help to reduce the tensile properties as well as burst volume of condoms. This again will be reflected in the low ageing properties of condoms. Reduced tensile properties of radiation vulcanised latex was already established(127,128). Ageing properties of radiation vulcanised NR latex film also is very poor which is in agreement with the results of K.Makuuchi. But the antioxidant Nocrac NS-5 was found to improve the ageing properties of condoms with respect to tensile strength, elongation at break and burst pressure. The effect was more pronounced at longer ageing periods where the properties of condoms breaks the boundaries of the specifications of WHO. So the study is of much relevance with respect to quality improvement of condoms. Stabilization against thermal oxidation has been reviewed in considerable detail by Shelton(142,143) Ingold(144) and Denisov(145). But the effect of antioxidants in particular application vary with the type of product and their service conditions. Ambelång et al(146) has reviewed the properties of a number of stabilizers for use in vulcanisates. As far as NR latex condoms are concerned;ortho linked bisphenolic type(Nocrac NS-5) was found very effective in improving the burst volume, burst pressure and tensile properties such as modulus, tensile strength and elongation at break. Grindberg (147) in his studies compared the effectiveness of alkane bisphenols and he found compounds of ortholinked bisphenols were more effective compared to paralinked bisphenols of, their analogues. So it can be confirmed that the higher retention percentage of tensile strength, burst volume and burst pressure of all the three types of latex condoms were due to the better antioxidant activity itself. Another observation is that in the case of post vulcanised latex condoms, even after 24 hours ageing tensile strength and burst volume values were having 110 and 108 percentage retention respectively(table 8). This result indicated that they might not have attained the maximum vulcanisation in the vulcanisation period given. In the case of prevulcanised latex reversion might have started, since these are already fully vulcanised. Breakage of polysulfidic linkage was another expected reason. RVNRL condoms were having elongation at break values nearer to those of other two latex types. Tensile strength was much below, but could be improved slightly with the addition of antioxidants, but cannot meet the specification of WHO for condoms(Table 10). Burst pressure also was found to decrease well below the specification limits on ageing. So, as far as the quality parameters are stringent with NR latex condoms, much improvement has to be made in the radiation vulcanised latex film properties to compete with postvulcanised and prevulcanised latex condoms.

CONCLUSIONS

1. Post vulcanised latex condoms were found to have better physical properties and ageing characteristics compared to prevulcanised and radiation vulcanised latex condoms.
2. Presence of potassium laurate-casein stabilizer system and an antioxidant(Nocrac NS-5) were found essential for better physical properties and their retention after ageing.
3. Rheological properties of the post vulcanised, prevulcanised and radiation vulcanised rubber latices were found to vary with the variations in temperature and shear rate.
4. Pinhole rejection percentage of RVNRL condoms were lower than those of post vulcanised and prevulcanised latex condoms whereas physical properties and ageing characteristics were inferior to them.

Table -1

Characteristics of postvulcanised, prevulcanised and radiation vulcanised Latices.

Properties	Postvulcanised Latex	Prevulcanised Latex	Radiation Vulcanised Latex
Total solids content (TSC) % by mass	53.00	55.00	53.00
Viscosity at 28°C(60 rpm)	33.00	62.00	79.00
Heat Stability Time (HST) at 90°C (Seconds)	528.00	268.00	900.00
Volatile fatty acid number (VFA)	....	....	00.02
Mechanical Stability Time (MST)	1200.00	880.00	1300.00
pH at 28°C	10.00	09.00	09.00

Table -2

Compounding formulation	Dry weight (phr)
Centrifuged(LATZ) latex (60% rubber)	100.00
Potassium oleate	00.02
Casein	00.02
Ammonia	00.28
Nocceller TP	00.20
Setsit - 5	00.50
Zinc oxide	00.90
Nocrac NS - 5	00.50
Sulphur	01.50
Darvan No.1	00.045
Darvan No.2	00.045

Table - 3

Rheological behaviour of the latices

		Brookfield Viscosity (CPS)										
Type of latex	Period of pre vulcanisation (h)	Temp (°C)	40	40	35	35	30	30	25	25	20	20
		rpm	12	60	12	60	12	60	12	60	12	60
Post vulcanised latex	0		56	27	50	30	81	41	99	50	110	59
Pre vulcanised latex	2		60	30	80	38	90	48	110	52	112	61
do	4		64	32	81	50	93	52	112	53	118	68
do	6		69	36	84	56	95	58	118	59	120	74
do	8		75	39	85	63	100	66	120	73	126	80
Radiation vulcanised latex	0		119	68	136	73	156	84	186	91	191	100

Table -4

Properties of the latices before the addition of the test stabilizer systems.

	Type of Latex		
	Post vulcanised	pre vulcanised	Radiation vulcanised
Pin hole rejection (%)	12.5	14	11.5
M500 (MPa)	8	8.5	7
Tensile strength (MPa)	25	23	18
Burst volume (Litres)	38.6	34.8	29
Burst pressure(KPa)	1.6	1.6	1.2

Table -5

Effect of Potassiumoleate-Casein stabilizer system on condoms of different latices

Type of Latex						
Properties	Post vulcanised		Pre vulcanised		Radiation vulcanised	
	Before ageing	% retention after ageing	Before ageing	% retention after ageing	Before ageing	% retention after ageing
Pinhole rejection (%)	12.5	100.0	11.25	100.0	10.0	100.0
M500 (MPa)	8.0	76.0	8.50	74.0	7.0	69.5
Tensile strength (MPa)	25.0	75.0	23.50	68.0	19.5	66.5
Burst volume (Litres)	41.0	73.0	38.40	74.0	30.8	63.5
Burst pressure (KPa)	1.6	75.0	1.80	78.0	1.5	55.3

Ageing was done at 70°C for 168h

Table - 6

Effect of Potassium laurate-Casein stabilizer system on condoms of different latices

Properties	Type of Latex					
	Post vulcanised		Pre vulcanised		Radiation vulcanised	
	Before ageing	% retention after ageing	Before ageing	% retention after ageing	Before ageing	% retention after ageing
Pinhole rejection (%)	5.00	100.0	5.00	100.0	5.00	100.0
M500 (MPa)	8.0	80.0	8.00	78.0	7.0	68.9
Tensile strength (MPa)	25.3	78.5	23.00	70.0	20.0	68.7
Burst volume (Litres)	40.0	74.0	39.1	76.0	32.4	64.8
Burst pressure (KPa)	1.8	73.0	1.60	78.5	1.5	59.8

Ageing was done at 70°C for 168h

Table - 7

Effect of Poly vinyl alcohol -Casein stabilizer system on condoms of different latices

	Type of Latex					
Properties	Post vulcanised		Pre vulcanised		Radiation vulcanised	
	Before ageing	% retention after ageing	Before ageing	% retention after ageing	Before ageing	% retention after ageing
Pinhole rejection (%)	8.75	110.0	8.75	112.0	6.25	100.0
M500 (MPa)	8.0	76.5	8.00	74.8	7.0	63.0
Tensile strength (MPa)	24.3	75.8	22.60	74.0	20.5	67.5
Burst volume (Litres)	38.4	75.5	38.50	76.2	30.5	64.4
Burst pressure (KPa)	1.8	74.0	1.70	79.2	1.4	60.0

Ageing was done at 70°C for 168 hours

Table - 8

Effect of thermooxidative ageing on post vulcanised latex condoms.

properties	Without antioxidant						With antioxidant (Nocrac NS-5;0.5phr)					
	Before ageing	% retention of properties after ageing period (h)					Before ageing	% retention of properties after ageing period (h)				
		0	24	48	96	168		0	24	48	96	168
M500 (MPa)	7.5	100	100	93	76	73	8.0	100	100	95	80	76
T.S (MPa)	24.5	100	110	88	77.5	73.2	25	100	100	96	88	75
EB(%)	800	100	100	100	96	93	796	100	100	98	96	95
BV (litres)	38.8	100	108	94	83	68	41	100	99	92	84	73
BP (KPa)	1.6	100	100	92	81	71	1.6	100	95	85	78	75

Table -9

Effect of thermooxidative ageing on pre vulcanised latex condoms

properties	Without antioxidant						With antioxidant (Nocrac NS-5;0.5phr)					
	Before ageing	% retention of properties after ageing period (h)					Before ageing	% retention of properties after ageing period (h)				
		0	24	48	96	168		0	24	48	96	168
M500 (MPa)	7.5	100	100	94	78	70	8.5	100	100	95	85	74
T.S (MPa)	23.0	100	96	89	73.0	65.5	23.5	100	100	100	84	68
EB(%)	788	100	99	98	91	90	788	100	100	98	97	94
BV (litres)	38.4	100	94	92	80	62.5	38.4	100	100	98	90	74
BP (KPa)	1.6	100	94	92	84	70	1.8	100	100	96	89	78

Table -10

Effect of thermooxidative ageing on Radiation vulcanised latex condoms

properties	Without antioxidant						With antioxidant (Nocrac NS-5,0.5phr)					
	Before ageing	% retention of properties after ageing period (h)					Before ageing	% retention of properties after ageing period (h)				
		0	24	48	96	168		0	24	48	96	168
M500 (MPa)	6.5	100	100	84.5	71.2	58.5	7.0	100	100	96.5	78.5	69.5
T.S (MPa)	18.9	100	94.0	85.0	71.0	54.5	19.5	100	89.5	86.3	71.5	66.5
EB(%)	730	100	95.0	91.0	90	89.5	764	100	98.0	93.5	93	91.5
BV (litres)	30.3	100	88	74.3	68.5	59.4	30.8	100	90.0	89.5	71.5	63.5
BP (KPa)	1.3	100	95.0	89.0	68.5	55.3	1.5	100	95.0	89.5	67.1	55.3

Chapter VIII

SUMMARY AND CONCLUSIONS

The effect of compounding variables and process parameters which significantly affect the pinhole formation and physical properties of condoms, have been studied in detail in the present thesis. The important findings are summarised here below.

Stabilizer systems

Among the stabilizer systems studied, casein-potassium laurate system was found most suitable for condom manufacture. This system gives lower rejection percentage due to pinholes and are able to improve physical properties of condoms. Vulcastab VL also was effective in reducing the pinhole formation when used with casein. Tensile strength retention after ageing was maximum for casein-potassium laurate system. Elongation at break,modulus at 500% elongation, electrical resistance etc were comparable for all the systems. Burst volume and burst pressure values were also higher for casein-potassium laurate system compared to casein-potassium oleate which was the control system. The higher fatty acid soaps are known to affect the stability and cure of natural rubber latex. Addition of small amounts of higher fatty acid soaps have been shown to greatly improve the mechanical stability of latex with an optimum effect when the alkyl chain length of the HFA soap contains 9 to 11 carbon atoms(54,55). The lower rejection rate of compounds containing potassium laurate compared to potassium oleate could thus be attributed to the lower frothing tendency and improved mechanical stability caused by the laurate soap(29)

Vulcanising system

Vulcanising system is the most important compounding variable which could affect the physical properties and ageing characteristics of condoms. Influence of sulphur concentration in the formulation was studied keeping all other parameters constant. It was found that tensile strength, elongation at break, modulus etc increased but ageing resistance was decreased. Burst volume and burst pressure of condoms also increased inspite of the increase in modulus with higher sulphur level. It is well known that in NR a high sulphur vulcanising system leads to formation of predominantly polysulphidic crosslinks which are more flexible and hence can cause higher elongation and tensile strength(67). However, these polysulphidic crosslinks are more thermolabile and hence ageing resistance of vulcanisates prepared using higher sulphur levels is poorer. But when accelerator combination was varied ageing resistance also was improved. Setsit-NTP accelerator combination gave low ageing resistance whereas Setsit-ZMBT combination improved the ageing resistance. Setsit-ZMBT combination was found to give a tighter cure than Setsit-NTP and this was observed in the burst pressure values also. The higher retention of tensile properties, burst volume and burst pressure of compounds containing ZMBT may be due to the antioxidant activity of ZMBT. NTP-ZMBT combination also gave higher tensile strength, and modulus but burst volume and burst pressure were lower. Ageing resistance was better than the control system, but was not as good as the

Setsit-ZMBT combination. When the concentration of ZMBT was higher in NTP-ZMBT combination it gave increased values for burst volume modulus and tensile strength. A combination of 0.5 phr of ZMBT and 0.3 phr of NTP was found to be optimum for this system. The low mechanical strength of condoms when dithiocarbamate type accelerators alone were used could be attributed to the peaky cure exhibited by them which causes reversion of vulcanisates even under slight overcuring conditions. But when ZMBT was used instead of one dithiocarbamate, the properties improved due to the antioxidant action of ZMBT. Also thiazole type accelerators are reported to give flatter cure curves(68) than most other types of accelerators. They maintain properties even when considerably overcured. Hence it is desirable to use combination of thiazole type and a dithiocarbamate type accelerator for condom manufacture.

Antioxidants

Six antioxidants were analyzed to study their effect on condoms. It was found that an antioxidant is essential to retain the properties of condoms after ageing.

Vulkanox HS, the amine type antioxidant used was efficient in retaining the properties when added at 0.5phr and above this level. But higher concentrations were having a discolouring effect.

Pentaflex SP which is a phenolic antioxidant also was efficient at 1phr level to impart comparable tensile strength and burst volume. But the ageing characteristics were much below compared to Nocrac NS-5 which was the control.

Vanox MBPC and Nocrac NS-5 both bisphenolic type antioxidants were having similar structure and hence same antioxidant efficiency. Vanox MBPC was effective in imparting maximum values of modulus at 0.5phr level whereas Nocrac NS-5 gave the maximum values at 0.75phr level only. Tensile strength, burst volume and burst pressure values and their retention after ageing increased gradually with increasing concentration of these antioxidants. Ortholinked bisphenols are reported to be more effective than paralinked analogues. The higher retention properties such as burst volume, burst pressure and tensile properties after ageing of condoms may be attributed to this advantageous ortholinkage in the two antioxidants, Nocrac NS-5 and Vanox MBPC. Colour development also was lower for ortholinked bisphenols.

Among the six antioxidants studied Irganox 1010 and Vanox SKT were having maximum antioxidant efficiency. 0.5phr of these antioxidants were able to improve the burst volume, tensile strength and burst pressure of condoms than all the other antioxidants. Both these antioxidants are esters of phenol substituted acids. The mechanism of action of these antioxidants is not known. But chemically similar compounds are reported to have very high antioxidant efficiency in elastomers. 1phr level of these antioxidants could increase the activity still higher. Combination of Pentaflex SP and Vanox SKT and that of Vulkanox HS and Nocrac NS-5 were having synergistic effect in imparting better ageing characteristics to condoms. The discolouring tendency of Vulkanox HS also was reduced by replacing a part of it with Nocrac NS-5.

Process variables

Ball milling time of dispersion was found to affect the pinhole formation of condoms. As the ball milling time increased, the particle size of solid ingredients decreased gradually and at 72 hours of ball milling optimum was obtained. Above this period, a slight increase in the size of particles was observed and this may be due to the reagglomeration of dispersed particles. Physical properties of condoms also was higher when lower particle size dispersions were used for compounding. It was reported(124) that size of sulphur particles is of great importance for the crosslinking reaction. The high tensile strength, modulus and burst volume obtained at 72h ball milling could be attributed to the optimum level of crosslinking obtained by the fine particle size dispersion of sulphur and other ingredients.

Temperature and concentration of mould cleaning soap solution also influences the quality of condoms. A higher than optimum level of soap may lead to frothing and pinhole formation. Optimum temperature of the mould washing solution may be helpful in removing grease, oil etc from the surface of the mould. Thus if these parameters were not optimum, presence of oily substances on the mould surface may lead to the formation of weak spots or pinholes in condoms.

Period and temperature of prevulcanisation and final vulcanisation also significantly influences the physical properties and rejection rate due to pinhole of condoms. Burst volume and burst pressure were maximum at 6 hours of prevulcanisation. Then it decreases with increasing period of prevulcanisation. Pinhole rejection rate was found to increase with increasing temperature of prevulcanisation. 50°C was found optimum for obtaining higher modulus at 500% elongation, burst volume and burst pressure. Ageing resistance also decreased when the temperature of prevulcanisation was increased. The adverse effect at higher period and temperature of prevulcanisation may be due to more air entrapment, at higher viscosity, obtained during prevulcanisation. Breaking of polysulphidic linkages also might have started during ageing, which were formed as a result of prolonged heating at low temperatures of prevulcanisation.

Final vulcanisation temperature was found optimum at 70°C when duration was kept at 30 minutes. Still higher temperatures of vulcanisation was found to increase the pinhole rejection rate. It is possible that the microlevel air bubbles expand and burst at the higher temperatures leading to large number of pinholes. Adverse effect on properties such as tensile strength and burst volume of condoms at higher temperatures and longer periods of vulcanisation may be due to reversion taking place in presence of dithiocarbamate type accelerators. Hence the temperature and period of prevulcanisation as well as final vulcanisation are interrelated in determining the final quality of NR latex condoms.

Postvulcanised, Prevulcanised and Radiation vulcanised NR latex condoms

Using LATZ latex, condoms were prepared in three different ways. Latex was compounded and postvulcanised condoms were prepared in one case. In another case the latex compound was given a prevulcanisation before the dipping process. Radiation vulcanisation of latex was carried out in the third case. Rheological characteristics at different temperatures and shear rates, effect on pinhole formation, influence of different stabilizer systems and effect of the presence of antioxidant in these latices were studied. Thus a comparative evaluation of the three modified latices were carried out with respect to tensile properties, burst volume, burst pressure and ageing characteristics of condoms.

Viscosity values were higher for radiation vulcanised and prevulcanised latices compared to post vulcanised latex. But the viscosity difference was higher at low shear rates. But increase in temperature was found to decrease the difference.

Pinhole rejection percentage was higher for post vulcanised latex and lowest for RVNRL condoms. Absence of any compounding dispersion in RVNRL may be contributing to the low pinhole formation rate. Presence of an additional stabilizer, KOH, may also be contributing to the lower rejection due to pinholes. But in the case of prevulcanised latex the froth might have escaped while prolonged heating for 8 hours and this may be the reason for comparatively low rejection rate due to pinholes of prevulcanised latex than postvulcanised.

Presence of a stabilizer system in all the three latices were found to increase the quality of condoms with respect to low pinhole formation and higher physical properties. Among the three stabilizer systems studied, casein-potassium laurate combination was most effective in reducing the pinhole formation and improving the tensile and burst volume properties. Polyvinyl alcohol-casein system increased the viscosity of latex compound and pinhole rejection percentage of aged condoms was higher compared to unaged in presence of this stabilizer system. Potassium oleate-casein system was inferior due to high pinhole formation rate and lower physical properties compared to potassium laurate-casein system. Hence casein-potassium laurate system was found suitable for condoms of all the three types of latices.

With respect to tensile strength and burst volume of condoms of the three latices, postvulcanised condoms were superior over other two types. RVNRL condoms were having very low physical properties and this result is in agreement with those of previous workers(40). Presence of nonrubber particles which affect the fusion behaviour of latex may be a reason for their low strength. High heat stability and mechanical stability of RVNRL indicate a low extent of vulcanisation and this also may be contributing to the low physical properties. Breaking of polysulphidic linkages formed during prevulcanisation latex might be reducing the properties of condoms prepared from prevulcanised latex. Low wet gel strength of prevulcanised latex also may be contributing to the comparatively low properties of the prevulcanised latex condoms.

Thermooxidative ageing of condoms of the three modified latices and the effect of antioxidant in them were studied. It was noted that presence of an antioxidant is essential in all these latices to obtain improved ageing characteristics. Nocrac NS-5, the bisphenolic type antioxidant was used for the comparative evaluation. Post vulcanised latex condoms were found better in ageing resistance compared to prevulcanised and RVNRL condoms. Low temperature vulcanisation of rubber is reported to increase the chance of formation of polysulphidic linkages(120). Prevulcanisation of latex compound at 55°C may be the reason for the high rate of formation of polysulphidic linkages and during ageing they may break easily to reduce the strength properties of condoms. Ageing characteristics of RVNRL is also found very poor as reported by Makuuchi(40). But Nocrac NS-5 was found to improve the ageing characteristics of RVNRL with respect to tensile properties and burst volume. But the retention properties were much below after ageing. Hence further work is required in the field of RVNRL to make use of its advantageous properties without sacrificing the physical properties and ageing characteristics of the vulcanisate.

CONCLUSIONS

1. Potassium laurate-casein combination was found to be the most suitable stabilizer system for NR latex condoms.

2. Quantity of sulphur and type of accelerators were found to affect the tensile properties, burst volume and burst pressure of condoms.

3. Setsit-ZMBT and ZMBT-NTP combinations were found to impart high mechanical strength to condoms compared to NTP-Setsit control system.

4. Ageing resistance of condoms improved when one of the dithiocarbamate type accelerator in the combination was replaced by thiazole type accelerator.

5. Increase in concentration of sulphur increased mechanical strength of condoms at the expense of ageing resistance.

6. Presence of an antioxidant was found essential to improve the ageing characteristics of NR latex condoms.

7. Among the six different antioxidants studied, Vanox SKT and Irganox 1010 were found most suitable for NR latex condoms to retain their physical properties after ageing.

8. Ortholinked bisphenolic type antioxidants were having higher antioxidant efficiencies compared to Pentaflex SP and Vulkanox HS which are antioxidants of monophenolic and amine type respectively.

9. Synergistic effect also was observed when combination of

Vulcanox HS and Nocrac NS-5; and Pentaflex SP and Vanox SKT; were used in latex compounding.

10. Antioxidant effect of Nocrac NS-5 was found to vary with the type of latex used. This was observed when the antioxidant was tried in both LATZ and HA latex for condom preparation.

11. Increased ball milling time of dispersions upto 72h could decrease the particle size of ingredients which improved the mechanical properties of condoms also increased with a reduction in pinhole rejection rate.

12. Concentration and temperature of mould cleaning soap solution was also found to affect the quality of condoms. For the alkyl aryl polyether type mould cleaning agent, optimum concentration was 0.5-0.7% and temperature around 60°C.

13. Period and temperature of prevulcanisation and final vulcanisation are interrelated in determining the final properties of latex vulcanisates.

14. Post vulcanised latex condoms were found to have better physical properties and ageing characteristics compared to prevulcanised and radiation vulcanised latex condoms.

15. Presence of potassium laurate-casein stabilizer system and an antioxidant(Nocrac NS-5) was found essential for better physical properties and their retention after ageing.

16. Rheological properties of the post vulcanised, prevulcanised and radiation vulcanised natural rubber latices were found to vary with the variations in temperature and shear rate.

17. Pinhole rejection percentage of RVNRL condoms were lower

than those of post vulcanised and prevulcanised latex condoms where as physical properties and ageing characteristics were inferior to them.

Use of natural rubber latex condom as a contraceptive is widely accepted for family planning and hence the control of population. In the context of increasing incidence of the incurable disease(AIDS), the use of high quality condoms is the only healthy way to prevent or reduce the risk of being infected with the causative virus of the disease. Significance of the research studies conducted thus lies in the ultimate goal of achieving population control and for the prevention of the spread of sexually transmitted diseases through the use of high quality NR latex condoms. General findings of this study may be applicable for the quality improvement of other rubber products also.

CHARACTERISTICS OF CHEMICALS

Casein

Appearance - White/slight yellow
Fat - 5% Maximum by weight
Ash - 4% Maximum by weight
Moisture - 12% Maximum by weight
Nitrogen - 14.5% Maximum by weight
Copper - 5ppm Maximum

Potassium oleate

Appearance - Yellow opaque liquid
Active content - 20+1
pH - 11+1.5
Free alkali - 0.05% Maximum
Insoluble matter
against alcohol - 0.1% maximum

Pentaflex SP

Active content - 30% Min. by weight
pH - 6.5 - 8.5
Emulsion stability- Good or a slight layer formation at the top which disappears on gentle shaking
Specific gravity - 1.08

Nocrac NS-5 **(2,2 methylene bis(4-ethyl 6-tert-butyl phenol))**

Appearance	White or greyish white powder
Melting point	115 deg.c.min.
Ash	0.3% max
Heating loss	0.5% max
Specific gravity:	1.0

(made by Ouchi Shinko Chemical Industrial Company Ltd.Japan)

Sulphur

Appearance	Light yellow powder
Moisture	1% max.
Residue on 100% mesh sieve:	Nil
Residue on 200% mesh sieve:	0.5% max
Ash content	1% max. by weight
Sulphur content (Purity)	96% min. by weight
Dispersion in water	Early dispersible

Zinc oxide

Appearance	White powder
Zinc oxide content:	99% min. by weight
Cupric oxide	Nil
Metallic zinc	Nil

Ignition loss	1% max. by weight
Insoluble matter against HCl	0.1% max. by weight
Heavy metals (as lead)	0.03% max.
Impurity	Nil
Carbonic acid	A little quantity

ZMBT(Zinc mercaptobenzothiazole)

Physical form	-	Yellowish powder
Specific gravity	-	1.72 max.
Moisture	-	0.5 max.
Fineness (63 microns)	-	0.3 max.
Solubility	-	Not easily soluble in petroleum spirit, benzene, CCl_4, methylene chloride, ethyl alcohol, ethyl acetate and acetone Practically insoluble in water.

Mould washing soap (Aryl alkyl polyether type)

Physical appearance	Colourless liquid
Cloud point (1% aqueous soln.)	61±3 deg.c
pH of 1% aqueous soln.:	6-7.5
Specific gravity at 25°C:	1.05 ± 0.005
Percentage solids	98±2

Darvan No.1

(Sodium salt of polymerised alkyl napthalene sulfonic acid)

Appearance	Dark yellow powder
Content	85% min.
Moisture	10% max.
pH(1% solution)	8.02-10.5

Darvan No.2

(Sodium salt of polymerised substituted benzoic alkyl sulfonic acid)

Appearance	Dark brown powder
Content	85% min.
Moisture	10% max.
pH(1% solution)	8.00-10.5

Nocceller T.P

(Sodium di-n-butyl-dithiocarbamate)

Appearance	light yellow or reddish brown semi transparent liquid
The oil matter	1 % min.
Solubility	soluble in water
Specific gravity	1.09-1.14(at 20 deg.C)
Content	50.0% min.
Free alkali	1.3% max.

(Made by Ouchi Shinko Chemical Industrial Co.Ltd.Japan)

Setsit-5

(Activated dithiocarbamate)

Appearance	Amber coloured liquid
Specific gravity	1.01±0.02
Flashing point	54 deg.C
Solubility	Soluble in water

(Made by Vanderbilt Co.USA)

REFERENCES

1. D.C.Blackley High Polymer Latices Vol.1 Maclaren & Sons Ltd, London 214-240 (1966)

2. P.B.Dickenson Proc.Nat.Rubb. Prod. Res. Ass. Jubilee Conf., Cambridge. Maclaren and sons Ltd. London., (1964)

3. W.A.Southorn , and J.B.Gomez , J.Rubb.Res.Inst. Malaya 23(1).15, (1970)

4. B.L.Archer and B.G.Andley. Adv. Enzymol. 29,221(1967)

5. L.Bateman, Chemistry and Physics of rubber like substances, p. 43-60 Maclaren and Sons Ltd. London(1963)

6. A.Karunakaran , G.F.J.Moir, and S.J.Tata Proc. Nat. Rubb. Res. Conf., KualaLumpur. (1960)

7. W.W.Bowler, Ind.Engg.Chem, 45. [illegible] (1953)

8. J.R. Wan Wazer, J.W.Lyons, K.Y. Kim and R.E. Colwell, Viscosity and flow measurement, Inter sciences, Newyork 6 (1966)

9. K.F. Gazeley, A.D.T. Gorton and T.D. Pend le, Natural Rubber Science and Technology, A.D.Roberts, Ed, MRPRA, Oxford University Press, London 71, (1988)

10. Kothandaraman,R. Unpublished data. Rubber Research Institute of India.

11. Mc Gavack John. 1959. The preservation and concentration of Hevea latex. Rubb.Chem.Technol. 32: 74,(1960)

12. Rhodes, Edgar. Latex preservatives. Some preliminary experiments with sodium pentachlorophenate. 'Santobrite' J.Rubb.Res.Inst. Malaya 8(3) 324-30 (1938)

13. Philpott,M.W. New presevatives for rubber latex. Rubb.Dev. 11(2) 47-50 (1958)

14. Angove,S.N. Preservation of NR latex concentrates part II. Evaluation of various oximes as secondary preservatives. Trans. IRI, 40: 257-61 (1964)

15. Angove,S.N. Preservation of NR latex concentrate part III. Evaluation of micellaneous rubber accelerators as secondary and teritiary preservatives. Trans. IRI. 41:136 (1965)

16. Sekar K.C. Inhibition of volatile acid formation in preserved NR field latex for concentration by centrifuging and creaming. Rubb.News. 15.(6)

17. Mathew.N.M., Leelamma Vargese, Kothandaraman, R and Thomas E.V. Presentation of concentrated NR latex with methylamine Rubb. Bd Bull. 66 13: 58-65 (1976)

18. David craig, Rubber chemistry and technology 30,1343(1957)

19. Bateman,L; Moore;C.G, Porter,M; and Saville B, chemistry of vulcanization, chapter 15, The chemistry and physics of rubber like substances. Ed. Bateman L, London. Maclaren (1963)

20. A.Y.Coran, Science and Technology of Rubber, Frederic. R; Erich, Ed; Rubber Division of ACS, 291-335 (1978)

21. L.Bateman, J.I.Cunneen, C.G.Moore, L.Mullins and A.G.Thomas in L.Bateman, ed; The chemistry and physics of rubber like substances, Maclaren, London 715 (1963)

22. W.Hofmann, Vulcanization and vulcanizing agents, Maclaren, London, 5, (1967)

23. J.R.Wolfe Jr. T.L. Pagh, and A.S.Killian, Rubber chem. Technol. 41(5) 1329(1968)

24. L.Bateman, R.W.Glazebrook, and C.G.Moore, J.Appl.Polymer Sci. 1,257 (1959)

25. M.Porter; "The chemistry of the sulphur vulcanization of Natural rubber"; A.V.Tobolsky, ed; The chemistry of sulfides,Interscience publishers, a division of John Wiley & sons, NewYork, (1968)

26. E.M.Madge, Trans.Inst.Rubb. Ind.28,207, (1962)

27. E.W.Madge, H.M.Collier and I.H. Duckworth, Trans. Inst. Rubb. Ind. 13,15,(1952)

28. E.G.Cockbain and M.W.Philpott, "The chemistry and physics of rubber like substances". L.Bateman. Ed, Ch.4 (1963)

29. T.D.Pendle and A.D.T.Gorton, The mechanical stability of natural latices, Rubb.chem.Technol. 986, 51(1978)

30. J.R. Shelton in W.L. Hawkins ed.,Polymer stabilization, Wiley Interscience, NewYork, Ch-2, (1972)

31. J.C.Ambelong et al., Rubber Rev., Rubber. chem. Technol, 36,1497 (1963)

32. Geer, India Rubber World, 55, 127 (1916)

33. S.D. Sutton IRI Trans, 27, 193 (1951)

34. Humphreys, N.C.H and W.C Wake, IRI Trans 25, 334 (1950)

35. Y. Minoura and M. asoa J. Appl. Polym. Sci 5, 40 (1961)

36. K. Makuuchi M. Hagiwara J. Appl. Polym. Sci., 29 965 (1984)

37. K. Makuuchi and K. Tushima "Radiation Vulcanisation of Natural Rubber LAtex with Acrylic Monomers" Intern. Rubber Conference Kualalampur, Malaysia (1985)

38. K. Makunchi and V. Markovik "Radiation Processing of Natural Rubber LAtex" IAEA Bulletin, 33 No.1, 25 (1991)

39. K.F. Gazeley, A.D.T. Gorton and T. D. Pendle, Natural Rubber Sci. Technol. A. D. Robertz, Ed. MRPRA, Oxford University Press, London 100 (1988)

40. K.Makunchi and K. Tsushima "Improvement of Ageing Properties of Latex Rubber Vulcanised with Radiation Vulcanisation" J. Soc. Rubber Ind. Japan 61, 710 (1988)

41. Linzad N.J. Radiation vulcanization improves purity, quality, Rubber Asia March-April 41-43 (1996)

42. Rubber and Plastics News, 14 February(1994)

43. ISO 124-1974(E)

44. ISO 126-1982(E)

45. ISO 125-1982(E)

46. ISO 506-1974(E)

47. ISO 126-1982(E)

48. ISO 976-1977(E)

49. R.Glass,M.Vessy and P.Wiggins,Contraception,10,591-98(1974)

50. C.A.M.Reitmeijer, J.W.Krebs, P.M.Feorino and J.N.Judson, Journal of American Medical Association, 259(12),1851-53(1988)

51. S.Katznelson, W.L.Drew and L.Mintz, Journal of Infectious diseases, 150,155-57(1984)

52. R.D.Dean, Modern Colloids, D.Van Nostrand Co; New York p.35(1948)

53. J.D.Miles and J.Ross, Journal of Physical Chemistry, 48,280(1944)

54. I.S.F.Chen and C.S.Ng, Rubb.Chem.Technol. 57,243(1984)

55. D.C.Blackley, bt.A.A.Nor. Aisah and R.Twaits, Plast. Rubber. Mater. Appl. 4,77(1979)

56. L.Bateman, C.G.Moore, M.Porter and B.Saville, in L.Bateman(Ed.); "The Chemistry and Physics of rubber like substances", Maclaren and sons, London, Ch.15 p.496(1963)

57. E.G.Cockbain and M.W.Philpott, in L.Bateman(Ed); "The Chemistry and Physics of rubber like substances", Maclaren and sons, London, Ch.4,p-94(1963)

58. B.L.Archer, D.Barnard, E.G.Cockbain, P.B.Dickenson and A.I.Mcmullen, in L.Bateman(Ed); "The Chemistry and Physics of rubber like substances", Maclaren and sons, London, Ch.3,p.55(1963)

59. Carrol C.Davis and John.T.Blake, The Chemistry and Technology of rubber, Reinhold Publishing Corporation, 330,West Forty Second Street, New York, p.745(1937)

60. D.C.Blackley, High Polymer Latices Vol.1 Palmerton Publishing Co. New York p.20(1966)

61. H.Merken and D.Phillips, Rubber Age 96,863(1965)

62. R.D.Dean, Modern Colloids, D.Van Nostrand Co., Inc., New York p-217(1948)

63. G..Blokh, "Organic accelerators in the Vulcanisation of rubber, IPST, Jerusalem, 261-266(1968)

64. M.M.Das, D.K.Basu, A.K.Choudhiri, Kouthuk Gummi, Kunststoffe, 36(7), 569-71(1983)

65. B.A.Dogadkin, B.A.Shershnev, Rubb.Chem.Technol. 35(1),1-56, (1962)

66. Maurice Morton (ed;) "Rubber Technology" Van Nostrand Reinhold Co; 450 West 33rd Street, New York 100(01)(1973)

67. N.J.Morrison and M.Porter, Rubb.Chem.Technol. 57,63(1984)

68. Carrol.C.Davis and John.T.Blake, "The Chemistry and Technology Corporation, 330 West Fortysecond Street, New York, USA,p.300(1937)

69. D.C.Blckley, High Polymer Latices, Vol.I, Maclaren and Sons, London, p.176(1966)

70. Ibid idem p.80-81

71. M.J.Husbands and G.Scott, Eur.Polym.J. 15,879(1979)

72. ~~71~~. M.J.Husbands and G.Scott, Eur.Polym.J. 15,249(1979)

73. I.D.Holdsworth, G.Scott and D.Williams; J.Chem.Soc. 4692(1964)

74. C.C.Davis and J.T.Blake, eds; Chemistry and Technology of rubber, Reinhold publishing corp; New York,1937.

75. W.O.Lundberg, ed. Autoxidation and Antioxidants VolI&II. Interscience Publishers, a division of John Wiley and sons, Inc,New York,1961

76. K.U.Ingold, Chem.Rev. 61,563-589(1961)

77. J.R.Shelton, Rubber Chem.Technol. 30,1251-1290(1957)

78. J.R.Shelton, Soc.Paint Technol. 34,590-602 (1962)

79. G.Scott, Chem.Ind.London 82, 271-281(1963)

80. H.C.Bailey, Ind.Chemist, 38,215-222(1962)

81. B.Baun and A.L.Perun, SPE. J. 18,250-259(1962)

82. J.C.Ambelong, R.H.Kilone, O.M.Lorenz, C.R.Parks, C.Wadelin and J.R.Shelton, Rubb.Chem.Tech. 36,1497(1963)

83. W.L.Hawkins, Polymer stabilization, Wiley-Interscience, NewYork,1972.

84. J.E.Stuckey, in Developments in polymer stabilization, I Gerald Scott,ed; Applied science, London, chap.3 1979.

85. G.Scott,ed; Developments in polymer stabilization-4 Applied science, London 1987.

86. H.H.G.Jellinek,ed; Aspects of Degradation and stabilization of polymers, EI Sevier, Amsterdam,1978.

87. E.M.Bevilaqua, R.J.Conley, Ed; in Thermal stability of polymers, Marcel Dekker, New York,1970.

88. J.R.Shelton, D.L.Allara and W.L.Hawkins,eds; Adv.chem.ser. 169, American chemical society, Washington,D.C., 1978.

89. A.K.Bhowmick, S.Rampalli, and D.Melntyre, J.Appl.Polm.Sci., 30,2367(1985).

90. J.R.Shelton & W.L.Cox Ind.Eng.chem; 46,816(1954).

91. C.W.Capp and E.G.E.Hawkins, J.Chem.Soc., 4106(1953).

92. J.Furukawa et al; in R.C.Gould, ed., Stabilization of polymers and stabilizers processes, Adv.Chem.Ser. 85, American chemical society, Washington D.C, P-110 (1968)

93. Reddlelein and Thurm, Ber; 65,1511(1932)

94. T.W.Compbell and G.M.Coppinger, J.Am.Chem.Soc. ,74,1469(1952)

95. A.F.Bickel and E.C.Kooyman, J.Chem.Soc., 3211(1953)

96. G.S.Hammond et al., J.Am.Chem.Soc., 77,3233(1955)

97. J.R.Shelton and D.N.Vincent., J.Am.Chem.Soc., 85,2433(1963)

98. J.A.Howard and K.U.Ingold, Con.J.Chem., 40,1851(1962); 41,1744,2800,(1963); 42,2324(1964)

99. J.R.Dunn and J.Scanlan in L.Bateman(ed;) The Chemistry and Physics of rubber like substances, Maclaren and sons, London, Ch.18(1963)

100. H.Low, Ind.Eng.Chem,Prod. Res.Dev., 5,80(1966)

101. A.A.Grindberg , Kauch Regina, 26(3) 22,(1967) in Russia Sov.Rubb.Technol., 26(3) 24(1967) English Translation.

102. T.Kempermann, Paper given at ACS, Division of Rubber Chemistry, Cleveland,Ohio, October 1971; Published as Bayer Technical Notes for the Rubber Industry, No.45(1972)

103. Rubber Additves, Antioxidant 2246, Technical Bulletin, American Cyanamid Co; Bound Book.N.J.

104. A.J.Chalk and J.F.Smith, Trans Faraday Soc. 53,1235(1957)

105. C.J.Penderson, Ind.Eng.Chem.41, 924(1949)

106. T.J.Wallace, R.M.Skomoroski and P.J.Lucchesi, Chem.Ind.84 1764(1965)

107. A.Tkac and L.Omelka, J.Polym.Sci. 40,105(1973)

108. L.Zikmund, Eur.Polym.J., 8,83(1972)

109. Taimer, J.Pospisil, Angew.Makromol.Chem. 28,13(1973)

110. E.Muller, A.Schick, R.Mayer and K.Scheffler, Chem.Ber., 93,2649(1960)

111. A.R.Patel , J.Appl.Polym.Sci., 16,2751(1972)

112. Gerald Scott, Atmospheric oxidation and antioxidants, Elsevier Publishing Co. Inc; NewYork(1965)

113. L.R.Mahoney, Angew.Chem., Int.Ed., 8,547(1969)

114. Robert.F Mausser, Rubb. India, AIRIA,37(1) 9-15 (1985)

115. E.V.Reztsova and G.V.Chbarova, Dokl.Akad. Nauk,USSR, 170(2) 383(in Russia) 1968

116. A.K.Bickel and E.C.Kooyman, J.Chem.Soc. 32,64(1955)

117. J.L.Bolland and P.Tenhave, Discuss Faraday Soc., 2,252(1947)

118. D.C.Blackley, High polymer latices, Vol.I, Maclaren & Sons Ltd., London, p.135(1966).

119. A.D.T.Gorton and T.D.Pendle, N.R.Technol., 12,21(1981).

120. A.D.T.Gorton and T.D.Pendle, N.R.Technol., 12,1(1981).

121. British standards 3900, Determination of fineness of grind, 1983.

122. A.D.T.Gorton and T.D.Pendle, proc. Eml.polym. conf., PRI, London,June 1982.

123. Beaurau of Indian Standards, 3701(1985).

124. B.Garner, F.Danes, D.Delaunay(Lab, Termocinetique, ISITEM, 44087, Nantes,France) Thermochim. Acta,222(1), 115-25(Fr) (1993).

125. D.S.Pence and J.Young, Kolloid,11, 38(1912).

126.Y.Minoura and M.Asao, J.Appl.Poly.Sci. 5,401(1961)

127. K.Makuuchi and M.Hagiwara, J.Appl.Poly.Sci. 29,965(1984)

128. K.Makuuchi and K.Tsuhima.,International Rubber Conference, Kualalumpur, Malaysia(1985)

129. Loh ACP Ph.D. thesis. Council For National Academic Awards, 1982

130. D.C.Blackley, proc.Int.Rubb.Technol. Conf. Penang 1988

131. M.Porter, Rubb.Chem.Technol. 40,866(1967)

132. K.F.Gazely , A.D.T.Gorton ,T.D.Pendle in "Natural Tubber Science and Technology" (Roberts AD ed, Oxford Univ. Press. 89(1988)

133. D.C.Blackley,High Polymer Latices Vol.1 Maclaren & Sons Ltd, London 399-400(1966)

134. N.R.Peethambaran and Tessy K. George. J.Appl.Poly.Sci. 40,1627-1636(1990)

135. Minoura and Asao, in D.C. Blackley, ed;High Polymer Latices Vol.1 Maclaren & Sons Ltd, London, 390,(1966)

136. M.Porter, Int. Rubb. Technol. Conf. Penang (1988)

137. C.T.Loo, Int.Rubber Conf.,Kuala Lumpur,1975

138. G.H.R.Weir,NR Technol.,10,80(1979)

139. C.R.Parks and O.Lorenz, Ind.Eng.Chem., Prod.Res.Dev., 2,279(1963)

140. J.Lal, J.Polym.Sci. C,16,3391(1968)

141. C.L.M.Bell and J.I.Cuneen, J.Appl.Polym.Sci. 11,2201(1967)

142. J.R.Shelton,Rubber Chem.Technol.; 45,359(1972)

143. J.R.Shelton, in W.L.Hawkins, ed; Polymer Stabilization, Wiley Interscience,Newyork, Ch.2,1972.

144. K.U.Ingold, in R.F.Gould ed; Oxidation of organic compounds, Adv.Chem.Ser. 75-1, American Chemical Society, Washington D.C., p.296 1968

145. E.T.Demisov, Russ.Chem.Rev., 42,157(1973)

146. J.C.Ambelang, R.H.Kilone, O.M.Lorenz, C.R.Parks, C.Wadelin and J.R.Shelton, Rubber Chem. Technol., 36,1497(1963)

147. A.A.Grindberg; Sov.Rubber Technol.,26(3), 24(1967)

ANNEXURE - 1

Characteristics of Centrifuged HA Latex	
Appearance	Clear milky white without grey yellow
Total solids content (TSC) (% by mass)	61.5 (max.)
Dry rubber content (DRC) (% by mass)	60% (min.)
Non-rubber content (TS-DRC) , (% by mass)	1.2 (max.)
Total alkalinity as ammonia (in the aqueous phase) (% by mass)	1.72-2.3
Viscosity at 25°C (cps)	150 cps (max.)
Mechanical stability time (seconds)	1000 (min.)
Volatile fatty acid number	0.04 (max.)
Coagulam content (% by mass)	: 0.1% (max.)
Potassium hydroxide number	0.5 (max.)
pH value at 25°C	10.5 - 11
Zinc oxide viscosity (max.)	20% thickening at 25°C (max.) (after 5 minutes of 1phr zinc oxide addition). 22% thickening at 25°C (max.) (after 5 minutes of 1phr zinc oxide addition).
Zinc oxide stability (sec.)	120 - 210
Zinc oxide heat stability time	250 - 350 at 90±2°C (after 60 minutes of 1phr zinc oxide addition).

ANNEXURE - 2

Characteristics of (LATZ)	
Total solids content (TSC) (% by mass)	61.00
Dry rubber content (DRC) (% by mass)	60.00
Non rubber solids (TS - DRC)	01.50
Ammonia Content (%)	00.35
Viscosity at 25°C (CPS)	79.00
Mechanical stability time (Seconds)	1600
Volatile fatty acid number (VFA No)	00.01
Potassium hydroxide number (KOH No)	00.56

ANNEXURE - 3

Compounding formulation (Control)	(phr)
Centrifuged Natural Rubber latex (60% rubber)	100
Ammonia	0.28
Casein	0.02
Potassium oleate	0.02
Nocceller TP	0.20
Setsit - 5	0.50
Zinc oxide	0.90
Nocrac NS - 5	0.50
Sulphur	1.50
Darvan No.1	0.045
Darvan No.2	0.045

ANNEXURE - 4

WHO specification for latex condoms

Specification	Inspection level	Method	Limits	AQL (%)
CRITICAL SPECIFICATIONS				
1. Air Burst Volume(a)	G-1	ISO 4074-6	Minimum (litres): $w^2/150$	1.0
Pressure(a)	G-1	ISO 4074-6	1kPa	1.0
Volume (b)	80 condoms/ batch	ISO 4074-6	Mean (litres): $w^2/100$	--
Pressure (b)	80 condoms/ batch	ISO 4074-6	1kPa	--
2. Freedom from holes	G-1	ISO 4074-5	No leakage	0.25
3. Package integrity	S-3	WHO Specs. 2.1.3(ii)	Inflate 1 minute	2.5
SPECIFICATIONS BASED UPON PROGRAMME REQUIREMENTS				
1. Width	S-2	ISO 4074-3	53/49mm±2mm (individual) ±1mm (batch av.)	1.0
Length	S-2	ISO 4074-2	180/170 mm minimum	1.0
2. Thickness	S-2	WHO Specs. 2.2.2(ii)	0.06 mm±0.02 mm	1.0
3. Lubricant quantity and viscosity	S-2	WHO Specs. 2.2.3(ii)	450±100mg (of which 20-60mg is cornstarch powder); 200=350 centistokes	4.0
4. Package condition and markings	S-3	WHO Specs. 2.2.4(ii)	Free from defects	2.5

(a) - before oven conditioning, (b) - after oven conditioning.

(contd...)

ANNEXURE - 4 contd.

Specification	Inspection level	Method	Limits	AQL (%)
GENERAL SPECIFICATIONS				
1. Latex	N/A	V.I.	Natural rubber, no grit or discoloration, no toxic or harmful substances	0
2. Bead	N/A	V.I.	Intact and integral with condoms	0
3. Shape	N/A	V.I.	Parallel-sided, reservoir tip	0
Texture	N/A	V.I.	Smooth	0
4. Colour	N/A	V.I.	No added colour	0
Clarity	N/A	V.I.	Translucent	0
5. Dressing and compounding materials*	N/A	V.I.	Non-deleterious, harmless, non-irritant	0
6. Odour	N/A	V.I.	Odourless	0
Taste	N/A	V.I.	Tasteless	0
7. Packaging	N/A	V.I.	Laminate with metal 8 microns minimum thickness	0
8. Workmanship*	N/A	V.I.	Condoms and packaging free from defects; manufacturer to follow GMP	0
9. Consumer packs	--	--	--	--
10. Inner boxes			Contents; marking; materials construction; and workmanship; as specified	
Exterior Shipping Cartons	S-3	V.I.		2.5

V.I. Where this is shown under "Method", testing for the property is by visual inspection

N/A Not applicable (indicates that no specific sample is taken for this test)

* Indicates that objective evidence is required that the specification is being adhered to.

ANNEXURE - 5

Dimensions of Sample Condoms

Width (mm)	52 - 54
Length (mm)	170
Thickness (mm) (Single wall)	0.05 - 0.07
Edge roll thickness (mm)	1 - 1.6

PUBLICATIONS

List of Publication based on the work

1. Research paper on **"Studies on the effect of stabilizer systems on quality of condoms"** is communicated for publication in **Journal of Elastomers and Plastics**. This paper was partly presented in Natioanal Rubber Conference (RUBTECH-94), organised by IRI, Kerala branch at cochin on 14th & 15th November,1994 and was published in the proceedingd of the conference.
2. Research paper on **"Studies on the effect of Vulcanising system on quality of NR latex condoms"** is communicated for publication in **Journal of Appied Polymer Science**.
3. Research paper on**"Influence of process variables on quality of NR latex condoms"** is communicated for publication in **Rubber Chemistry and Technology**.

Publication of the author in related field

1. Research paper on **"Ageing characteristics of natural rubber containing a flame retardant additive"** was presented in an International rubber conference held at Bangalore in 1992 and the same paper was published in **Indian Journal of Natural Rubber Research**.