STUDIES ON

THE EFFECT OF MAGNESIUM ON BEHAVIOUR OF LATEX

PROJECT WORK DONE BY
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(CANDIDATE CODE: 02 102 007)

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CERTIFICATE

It is certified that project of "Effect of magnesium on behaviour of latex" submitted by Smt.Lisha S.R., M.Sc, Analytical Chemistry, Christian College, Chengannur, for the partial fulfillment of M.Sc in Analytical Chemistry by Kerala University, Trivandrum is a bonafide record of research work conducted at Processing and Quality Control Division of Rubber Board under my guidance. The results obtained have not been used for obtaining any other degree.

Jt.Director (P&QC)

DEPARTMENT OF CHEMISTRY

CHRISTIAN COLLEGE, CHENGANNUR

(Affiliated to the University of Kerala)

CERTIFICATE

Certified that the project report entitled **"Studies on the effect of magnesium on behaviour of latex"** *is the bonafide record of work done by* **Lisha. S. R** *in partial fulfilment of the requirements for the award of the degree of* **Master of Science in Analytical Chemistry** *under the University of Kerala.*

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DECLARATION

I do hereby declare that the project entitled, "Studies on **THE EFFECT OF MAGNESIUM ON BEHAVIOuR OF LATEX**" is the original project work carried out by me under the joint supervision of **Mr. M. Sunny Sebastian**, Joint Director, Central Laboratory, RRII, Kottayam and **Prof. Sophia. K. Philip**, Selection Grade Lecturer, Dept. of Chemistry, Christian College, Chengannur and that it has not previously formed the basis of award of any degree or diploma or any other title.

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LISHA. S.R

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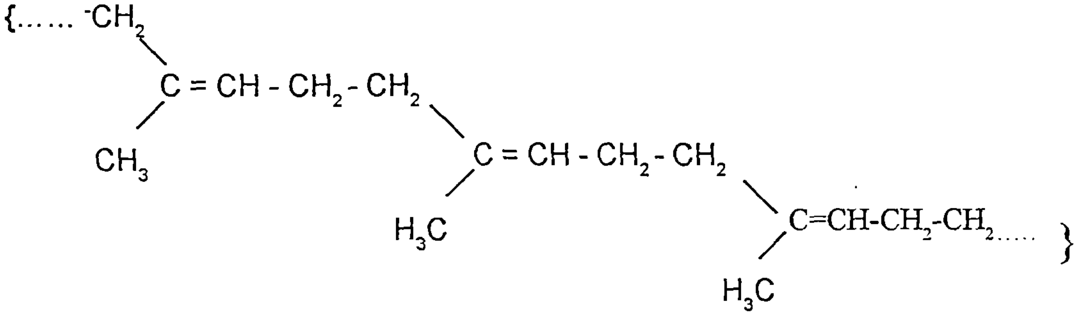
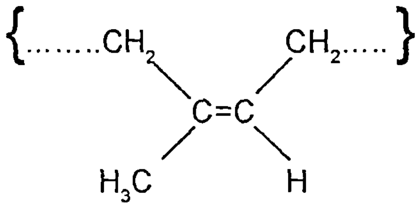
INTRODUCTION

1.1 Natural Rubber

Natural Rubber (NR) is a versatile material which is very useful in our every day life. The use of Natural Rubber ranges from house hold goods to materials for heavy industries. Natural Rubber is obtained as latex from the "*Hevea Brasiliensis*" tree. The polymer contained in the latex is cis-1,4-polyisoprene which has a density of 0.93 gmcm^{-3} at 20°C.The structural formula of polyisoprene $(C_5H_8)n$ is shown below

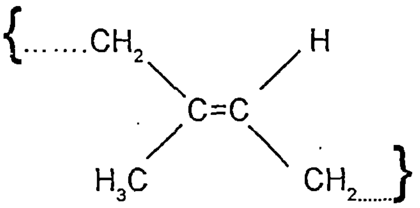


Because of the presence of olefinic carbon atom, cis and trans forms are possible. The transform of polyisoprene is called " Guttapercha". Both cis and trans forms are shown below.



Cis- 1,4- polyisoprene

(Natural Rubber)



Trans – 1,4 - polyisoprene

(Guttapercha)

In Natural Rubber, there is a bending back of successive isoprene units giving the molecule a coiled structure while guttapercha shows straightening structure. It has a refractive index of 1.52 and dielectric constant of about 2.5.

Natural Rubber contains several non-rubber constituents in small quantities like proteins, sugar, phospholipids, lipids etc. Natural Rubber is not a monodisperse. Fresh Natural Rubber latex has a wide particle size distribution ranging from 0.04mm- 3 mm. Natural field latex collected from the tree is marketed as concentrated latex or processed into solid dry rubber. Concentration can be effected by centrifugation, evaporation, or creaming. Dry rubber obtained has the following typical constitution.

Composition	**Dry rubber (%)**
Rubber Hydrocarbon	**93.7**
Protein	**2.2**
Carbohydrate	**0.4**
Natural Lipids	**2.4**
Glycolipid & Phospholipid	**1.0**
Inorganic Constituent	**0.2**
Others	**0.1**

1.1.1 PROPERTIES OF NATURAL RUBBER

If we stretch a rubber band and release immediately, it takes almost its original shape and length. Similarly when a block is compressed and released the block will assume its original shape. In the extent to which to be distorted, in the rapidity of its recovery, in the degree to which it recovers its original shape and dimension rubber is unique. These are requirements of *"rubberiness"*. Another property of rubber is its strength and toughness. A very important quality of rubber is *"building tack"*, ie.,when two fresh surface of milled rubber are pressed together, they coalesce to form a single piece. This makes relatively simple the building of a composite article such as tyre. Some physical properties of natural rubber are shown below.

Parameters	Value
Specific gravity or density	0.91 – 0.92
Refractive index	1.52.
Thermal Conductivity	0.00032 cal/sec . cm.°C.
Heat of Combustion	10700cal/gm
Dielectric strength	1000 volts / ml
Volume resistivity	10.5ohms/k
Power factor (1000 cycles)	0.15 - 0.2
Coefficient of cubical expansion	0.00062/°C
Cohesive energy density	63.7 cal/cc.
Dielectric constant	0.37

Natural latex is a high molecular weight polymer, molecular weight of the order of 10^5 -10^6. This is measured on the basis of osmotic pressure, viscosity measurements, due to depression in freezing point or elevation of boiling point. Average molecular weight can vary from 200,000 to 500,000.

With its wide range of useful properties, natural rubber can be used in a large variety of applications. Major application of natural rubber is especially in the tyre sector. Also natural rubber is used in the carcass as well as in the side wall due to its fatigue superior resistance and low build-up. In commercial vehicles, the amount of natural rubber increases with the size of the tyre. It is also applicable in mechanical goods, engineering products. latex goods and footwear.

1.2 NATURAL LATEX

The plants yield milky suspension of crude rubber called latex. Blackley has defined latex as stable colloidal dispersion of polymeric substance dispersed in aqueous medium. The polymer material may be a polymer of single,small ethylenically unsaturated monomer or co-polymer of two or more monomers. Usually the polymer practicale in the latex has a diameter of less than 1μm, although a few latices do contain a small proportion of larger practicles.The natural latex is cis 1,4- polyisoprene and this hydrocarbon is biosynthesised by a complex process involving some proteins. Latex collected from plantation will have a rubber content of 30-40%. For industrial uses this latex is concentrated to 60% rubber content.

The stability of polymer latex is basically due to the presence of surface active material at the interface between the polymer particle and the aqueous phase. Majority of latices are anionic in character, because their particles carry negative charge.

1.2.1 Natural latex as a colloid

The size of the rubber particles in latex are not uniform, but falls in a range, the range of 20-500nm being not uncommon. The rubber particles are predominantly pear shaped. The distribution of particle size in fresh natural latex is so wide that most of the volume of dispersed rubber in the latex is present in the form of a minority of large particle. Thus less than 4% the particle have diameter above 400nm, however they account for about 85% v/v of the total dispersed rubber. It is possible that these large particles are formed by agglomeration and coalescence of smaller particles.

A major portion of the resin matter in latex consist of phospholipids which are strongly adsorbed on the surface of rubber particles. The rubber particles are further covered by adsorbed protein layer. The adsorbed phospholipids and proteins so overlap in molecular level, that it is difficult to say which component forms the outer layer. The protein latex generally has isoelectric point below 5.0, so that proteins carry negative charge, at about p^H 6.5, the normal p^H of latex. The negative charges on the particle contribute to the coulombic repulsive forces . Also the rubber particles are surrounded by a layer of water molecule due to van der Waals forces. These factors contribute to the stability of the latex .

1.2.2. Composition of Natural Latex

The Chemical composition of freshly tapped Hevea latex is complex when compared to synthetic latices. This is because Hevea latex is a cytoplasm. Hevea latex contains, in addition to rubber hydrocarbon, a large number of non-rubber constituents in relatively small amounts. Many of these are dissolved in the aqueous serum of the latex, others are adsorbed at the surface of the rubber particle and some are the non-rubber particle suspended in the latex.

Fresh latex can be separated into four zones, by high speed centrifugation. There are three particulate components in major amount suspended in an ambient serum. These are rubber particle (the main particulate species), the so called lutoids and Frey Wyssling particles. The distribution of the major zones in the centrifuge tube, after high speed centrifugation, is illustrated in fig.(1.1)

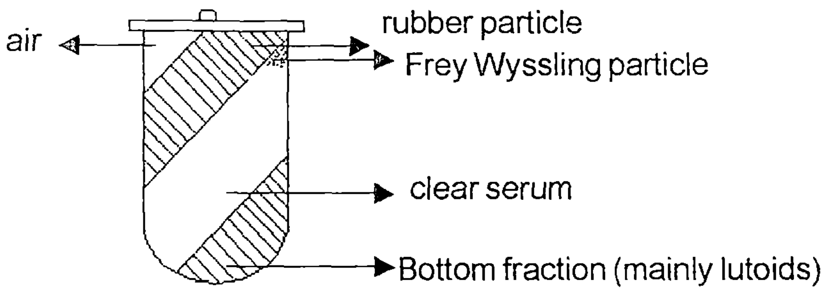


Fig 1.1

The upper most layer contains the rubber particles. Below this layer Frey Wyssling particle, followed by the clear serum zone and finally the bottom fraction which contains predominantly the lutoids.

In fresh latex, rubber particle constitute 25% - 45 % of the volume of the latex. The rubber particle in the fresh latex contains proteins and lipids. The rubber hydrocarbon is predominantly cis-1,4- polyisoprene (at least 99%). The most abundant non rubber particles are the lutoids. Inside the lutoid is an aqueous solution(often called 'β -serum') which contains dissolved substances such as acid, minerals, salt, protein, sugar and a polyphenol oxidase etc. The amount of lutiods present is usually sufficiently large enough to have a marked influence on the viscosity and colloidal property of fresh latex. Frey Wyssling particles are spherical, often bright yellow and of high refractive index. They often appear in clusters. The yellow colour is due to the presence of carotenoid pigments.

1.2.3. Chemical composition

The most abundant non-rubber constituents in fresh latex are proteins, lipids, quebrachitol and inorganic salts,but as would be expected from the cytoplasmic nature of latex, a large number of other substances are present in small amounts.

Proteins

The total protein content of fresh latex is approximately 1%-1.5% of which about 20% is adsorbed on the rubber particles. The adsorbed proteins, together with adsorbed lipids, impart colloidal stability to the latex. The serum from unpreserved latex contains seven electrophoretically distinct protein components. Ammonia preservation for several months reduces the number of electrophoretically resolvable components from seven to two.

α - Globulin and Hevein

αGlobulin is the protein present in the highest concentration in fresh latex serum. It is soluble in salt solution at p^H values away from its isoelectric point, (p^H 4.55) is coagulated by heat and is readily adsorbed at hydrocarbon-water interfaces. The sulphur content is low and there is little phosphorus present. It is precipitated from solution at approximately the same pH as that at which fresh latex is coagulated, suggesting that it is one of the proteins adsorbed on the surface of the rubber particles and thus partly responsible for the colloidal stability of the latex.

Approximately 20% of the dry matter in the bottom fraction of latex from mature trees is water- soluble protein, of which about 70% is hevein It is a low molecular weight protein. Its iso electric point is 4.7 and it contains an abnormally high amount of sulphur (about 5%), essentially all of which is present as disulphide groups in cystine. Hevein is readily soluble in water over a wide range of p^H, including its iso electric point, it is coagulated by heat, and has a molecular wt of about 5000.

Basic Proteins

In addition to the basis proteins in latex serum, several of high isoelectric points protiens (>p^H8.6) have been detected in fresh latex bottom fraction. The basic component has isoelectric point in the region of p^H 10. These basic proteins may have an important influence on the colloidal stability of fresh latex due to the positive electric charge they carry at neutral or slightly alkaline p^H values.

Lipids

Lipids are water insoluble and are concentrated mainly in the rubber phase with smaller quantities in the bottom fraction and in the Frey wyssling particles. Lipids may be divided in to neutral lipids and polar lipids, In Hevea latex the polar lipids are phospholipids. Neutral lipids are acetone soluble but undegraded phospholipids are not. The amount of phospholipid is however, constant at about 1% (on d.r.c). Thus the clonal variation of the total lipid can be ascribed to differences in the content of neutral lipids.

Neutral Lipids

The neutral lipids contain at least 14 substances. These have been classified in to sterols, sterol esters, free highfatty acid, fatty acid esters, wax esters, monoglycerides, diglycerides, triglycerides and phenolic substances. Some of the identified substances include β – sitosterol, and its ester, tocotrienols and arachidic, palmitic, stearic, linoleic and oleic acids. Long chain fatty acids form 6 - 8% of the total lipids in the rubber phase. Sterols constitute 13 - 28% of the natural lipids. The major single component of the neutral lipids of the rubber phase in fresh latex is triglycerides. The main triglyceride contains three furanoid fatty acids. This is a rare triglyceride known in nature.

Phospholipids

The Phospholipids in Hevea latex contains Phosphatidylcholine (or lecithin) as the major component . (about 80%), metal phosphatidates phosphatidy ethanolamine and phosphatidyl-inositol. These are long chain fatty acids esters of glycerophosphoric acid in which the phosphate group may be esterified with choline, ethanolamine, inositol or combined with a metal atom in metal phosphatidates.

Inositols and Carbohydrates

Quebrachitol (methyl inositol) is the most concentrated single component in the serum phase, amounting to about 1% of the whole latex. Small amounts of inositol isomers, sucrose, glucose, galactose, fructose and two pentoses have also been detected. In the absence of adequate preservation, the carbohydrates are metabolized by bacteria and converted to volatile fatty acids. These acids are not present in fresh latex and their concentration in commercial latex is a measure of the degree of bacterial decomposition, which the latex has undergone.

Inorganic constituents

The total concentration of inorganic ions in fresh latex is approximately 0.5% of which more than half normally consists of potassium (0.12-0.25%) and phosphate ions (0.25%). Small amounts of magnesium, copper, iron, sodium and calcium are also present. The relative properties of the ions, which show both genetic and environmental variation can have a marked influence on the colloidal stability of the latex and its concentrates. In particular a high ratio of Magnesium to phosphate ions is often found in latices of low stability.

Natural antioxidants

The presence of materials, which provide antioxidant action to rubber in latex have been identified. The most active substances, are lecithins, amino acids and tocopherols.

Enzymes and Bacteria

Latex contains some enzymes and bacteria also. Spontaneous coagulation of latex is due to their activity.

Other minor constituents of latex include ribose nuclei acid (RNA), pyrophosphate nucleosides and low molecular weight thiols.

Types of Latex

A wide range of polymer latices is available commercially. The principal varieties contain the following polymeric material:

- Natural rubber
- Styrene- butadiene copolymer.
- Chloroprene rubber
- Acrylic (co) polymers
- Vinyl acetate (co) polymers
- Vinyl chloride (co) polymers
- Synthetic cis-polyisoprene
- Butyl rubber

Natural rubber latices are concentrated and purified forms of the latex obtained from the botanical source Hevea brasiliensis, which is cultivated in tropical region. The second and largest group of polymer latices (shown above) consists of the many varieties of synthetic latex that are produced by emulsion polymersation. The third group comprises latices which are made by solution polymerisation and conversion of the polymer solution to a latex.

1.2.5 Collection of Latex

The latex that flow out from the rubber tree on tapping is channeled into a container attached to them. The flow of the latex will continue for about 3 hrs. and. after that it would stop. Latex has to be collected from the field as soon as possible after stoppage of flow of latex, that is absent three hours after the first tree is tapped. Latex from the collection cups is then poured into the collecting buckets and the last traces are wiped out from the cup. The use of lumps of rubber for cleaning out the cups should not be allowed into the latex. If signs of pre-coagulation are observed in the latex, it is necessary to use an anti-coagulant. Ammonia is the anticoagulant suitable for preparation of preserved latex. The tappers should not leave the bucket latex, exposed to sun, as heat increases tendency for fermentation of latex.

The latex should be delivered to the processing factory as rapidly as possible after collection in order to prevent premature coagulation. Aluminium or galvanised iron tanks are used for transporting latex in the case of large estates. Brass fitting must be avoided to prevent contamination of latex with copper. The best way to protect them would be to coat the surface with an inert material which will prevent the latter form coming into contact with the metal. Bitumen based or chlorinated rubber based inner paints are suitable coating for the tank.

Unclean utensils are sources of bacteria resulting in enhanced precoagulation of latex. The latex collection cups, the spouts, the buckets used for collecting latex and all other vessels used in the processing factory should be scrupulously clean to prevent bacterial contamination. It is advisable to clean all latex tanks equipments with a 1% formalin solution or with 0.3% lysol every week.

Anticoagulants

Anticoagulants are chemicals added to latex to prevent precoagulation. For preparation of preserved latex, ammonia is used as the anticoagulant. The use of anticoagulants is mostly required during rainy season as the tapping panel and collection cups are contaminated with rain water which lead to more bacterial attack of latex and eventual precoagulation of it.

For preparation of stock solution dissolve 1kg of ammonia gas in to 100 litres of water or dilute 50 ml of 20% ammonia solution to 1 litre with water. For every 10 kg of latex, use 100 ml of the stock solution. A few drops of anticoagulants are previously added in to the collection cups during tapping. Anticoagulants should never be added to empty buckets.

1.2.6 PROPERTIES OF LATEX

Latex is a colloidal system consisting of a suspension or emulsion of rubber particle in an aqueous medium. The term *"colloid"* is applied to any suspension or emulsion in which the particles are too large to pass through a parchment membrane, *but which are small enough to pass through a filtering member having relatively large* pores, such as filter paper. The charesteristic properties are the motion of the particles, the electrical charge, which they carry, and the manner in which light is transmitted through the solution and reflected from them. The collodial particles are observed to be in continuous motion in irregular paths. This motion, characteristics of colloids, is termed "Brownian Movement". Natural latex shows lyophilic character, i.e., lyophilic colloids absorb molecules of the liquid medium to form a layer around each particle so that their effective size is greatly increased. The particles have a diameter of approximately 0.25 microns. The particles are consisted of a tough and some what elastic outer shell filled with visceous fluid substance and provided on the exterior of the elastic shell with a layer of protien, soap and other protective materials. The solid content of fresh heavea latex may vary from 30 – 45% depending upon the sources, and in certain instances even wider variations have been noted, depending upon the age of the tree, the tapping method, the season, and the particular part of the tree which was tapped. When latex is coagulated to form crude rubber some of the non – rubber materials are separated from the rubber, and a portion is left dissolved in the aqueous medium or serum of the latex. Most type of polymer latices are mildly alkaline with a p^H in the vicinity of 10. They differ considerably in viscosity, depending on their solid content and particle size distribution.

The most outstanding property of natural rubber latex is its high wet-gel strength that is especially beneficial in the manufacture of dipped or unsupported products. Many synthetic latices are tailored to particular application and, therefore, have specific properties, for example adhesion or solvent resistance.

1.2.7 PRESERVATION OF LATEX

Why preservation is required

Natural rubber latex is negatively charged colloidal dispersion of rubber particle in an aqueous serum. The presence of non – rubber constituent like proteins, carbohydrates etc. in the latex make it a suitable medium for growth of micro – organisms. Because of the proliferation of micro – organisms, lower organic acids especially acetic acids are produced and these decrease the stability of latex. The latex gets putrefied with the development of bad smell and finally coagulates. This is called spontaneous coagulation that takes place within a period of 6 – 12 hours after tapping. Hence if latex is to be kept for longer periods, bacterial activity should be suppressed. This is accomplished by the addition of preservatives. Preserved latex may be either field latex or concentrated latex.

Preservatives

Various chemicals are used as preservatives among which ammonia is of prime importance.

Attributes of a preservative

The essential requirements of a chemical to function as a preservative are given below.

1) The primary requirement of any preservative is that it should preserve latex against spontaneous coagulation and putrefaction. It should destroy or inactive micro-organisms.

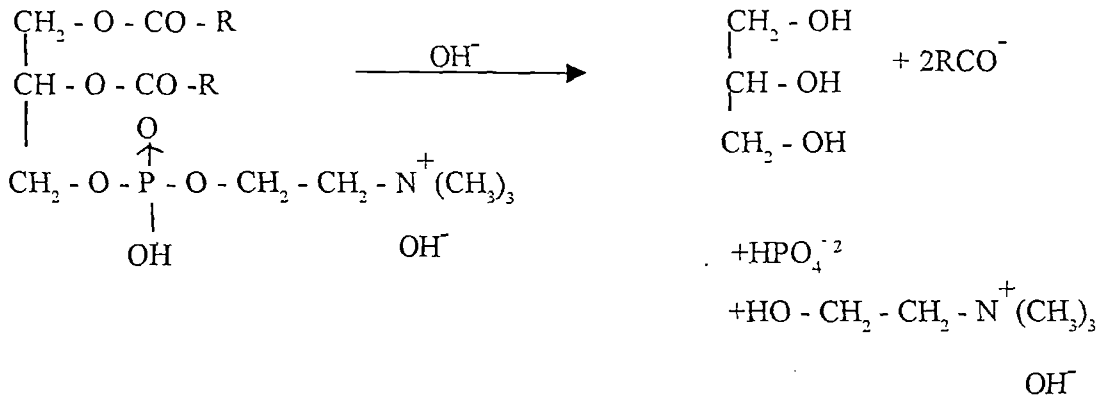
2) It should increase the colloidal stability of latex. This can be achieved by increasing the P^H of latex and hence the preservative should preferably be an alkali.

3) It should deactivate or remove traces of metal ions present in latex. Magnesium stimulates bacterial proliferation and it also accelerates chemical coagulation. Hence magnesium has to be removed from latex for efficient preservation

4) It should not be harmful to people and should not have adverse reaction on rubber containers of latex and should be cheap, readily available and convenient to handle.

Ammonia as a preservative – H A latex

In presence of ammonia, the density of the bound electrical charge on the rubber particle and electro kinetic potential of the interface between rubber particle and the aqueous phase are increased, thereby increasing the colloidal stability of latex. In presence of ammonia, the phospholipids in latex undergo slow hydrolysis, liberating higher fatty acids (HFA). The HFA anions are strongly surface active and add to the colloidal stability of latex.



Ammonia is a very effective bactericide if the level exceeds 0.35 m/m on the whole latex. Ammonia is able to deactivate some metallic ions, the most important among these being the precipitation of Magnesium in presence of orthophosphate anions.

$$Mg^{+2} + NH_3 + HPO_4^{-2} \longrightarrow MgNH_4PO_4$$

Some other polyvalent metallic ions are precipitated as hydroxides. The auxiliary requirements stated earlier are also satisfied by ammonia. Hence ammonia is utilised as a common preservative for latex. When ammonia alone is utilized as a preservative its content is about 0.7 - 0.8 % and this latex is known as high ammonia latex.

Limitations of Ammonia as a preservative

A major disadvantage of ammonia as a preservative is that it interferes with certain established latex process. Thus ammonia latex undergoes progressive and marked thickening when compounded with zinc compound like zinc oxide. In presence of ammonia and ammonium ions zinc forms zinc ammine complexes, having low stability constants and decomposes to form insoluble zinc soaps leading to destabilization of latex. In latex foam manufacture by Dunlop process, approach to gelling p^H is delayed by the liberation of hydroxyl ions from ammonium hydroxide. Hence latex has to be deammoniated to about 0.2% prior to compounding. High ammonia latex when deammoniated , the factory floor is polluted and there will be loss of rubber in the deammoniation tank. High ammonia latex, when used for dipping process, generally consumes more of coagulant. Because of the pungent nature, ammonia is difficult to handle.

When ammonia alone is used as bactericide, a small fraction of the microbial population in latex attains resistance to ammonia. This can lead to gradual increase in volatile fatty acids (VFA) of high ammonia latices. The formation of a surface skin is frequently a troublesome feature of high ammonia latex, when compounded.

1.2.8 COAGULATION METHODS

The rubber particles in normal or concentrated latex are suspended in an aqueous medium in which is dissolved or suspended a variety of substances such as proteins, sugars, alcohols and fatty acids and small amounts of complex organic materials. The rubber particles have a negative electric charge and are covered with colloidal system. As a result the latex does not coagulate except when some of these factors are changed; for example. the neutralization of the charge on the particles or the destruction of the protective coating by bacterial or chemical action.

Preserved latex is coagulated by many organic liquids, metal salts, acids etc. Metal salts causes direct coagulation of fresh latex, but with preserved latex they cause either flocculation or coagulation, depending upon the concentration in which they are used.

Coagulation may be completely affected by the adsorption of metal ions, particularly those of the divalent or trivalent group. Salts of aluminium and other metals are very active coagulants for latex, the aluminium ions in this case being adsorbed by the latex particles and neutralizing negative electrical charge. Protective agents, which assure stabilization of the latex particle against coagulation by acids, may not be affected against coagulation by multivalent ions.

Passing an electric current through latex may also bring about coagulation. In this case the negative latex particles move to the positive electrode (anode) where their charge is neutralized and they deposit in coherent form.

Another type of coagulation is that consisting of neutralization of ammonia by the addition of a non-coagulant, such as formaldehyde. Ammonia reacts to form a non – ionized material and the concentration of protective hydroxyl ions is decreased with consequent reduction in stability of the latex. In this instance there is also a reaction between the formaldehyde and the latex proteins to decrease their stabilizing effect.

A type of coagulation widely used in the technical applications of latex consists in the use of a material such as sodium silicofluoride, which may be added to the latex.in small amounts without causing any immediate coagulation. On standing for a period of time, depending upon the amount added, coagulation takes place. This is termed “delayed coagulation” . A number of substances other than sodium silicofluoride may be used to cause delayed coagulation. $MgSO_4$, $(NH_4)_2SO_4$, H-CHO, diphenylguanidine and salts of divalent metals have been used for this purpose.

Spontaneous coagulation of Latex

Fresh Heavea latex can be kept as fluid only for a few hours. A few hours after tapping, latex thickens and on further keeping the whole mass is coagulated, i.e. the rubber is coagulated from the latex which is effected by adding acetic acid to the diluted latex. The spontaneous coagulation is believed to be due to formation of soaps in latex by the saponification of organic glycerides and lipids. The soap anions strongly adsorb on rubber particle surface. They then react with magnesium and calcium ions forming insoluble soaps. The rubber particle thus loses their charge and agglomerate leading to complete coagulation.

1.2.9 APPLICATIONS OF LATEX

In general, latex is more expensive on dry basis than its dry polymer counterpart. However, since it is a liquid, it is usually easier to process. Furthermore a number of process, such as latex backing of carpets, can be readily automated. Latex polymer also tend to have better physical properties and to be less prone to contamination. However, use of polymer latices is restricted to the manufacture of thin articles or components (up to 0.2mm thick), or thicker products with an intercommunicating cellular structure, because of the need to remove water in the later stages of the process. The cost of water removal, and the attendant effects of shrinkage, are important, and sometimes limiting factors, in latex processes.

Commercial applications of polymer latices are most varied. In the carpet industry, considerable quantities of latex are used for anchor coats, secondary backing and gel and no-gel foam backing. Other major latex applications are in binders for non-woven fabrics, papers and woven textiles. In non-woven fabrics, the polymer phase is also used as an adhesive. Latices are also used in a variety of processes for impregnating textiles. In such process, the object is to cause the latex polymer to penetrate a pre - existent textile structure in such a way as to enhance such properties as increase resistance to teaving, resilience, wet strength etc. Latex surface coating are widely used in water-thinned paints. The development of latex-based paints has been described as the biggest advance in paint technology since the introduction of cellulose nitrate. Dipping processes with latex is used for the manufacture of various types of gloves: surgeons' glove, household gloves, electricians' glove and heavy industrial gloves etc. Other important products made by latex dipping include certain types of seamless Wellington boot, seamless football bladders and toy balloons. Latex moulding, especially the production of hollow casting, makes a large number of products. Latex adhesives are used in a wide range of different industries. Two of the most important fields of application for latex adhesives are the binding of paper and leather. Although latex adhesives may be used to combine certain hard adherents such as metals, glasses, ceramic tiles etc, it is difficult to ascertain the extent of application in this connection. There are so many applications, of which latex thread and rubberized hair are examples.

Polymer lattices are also utilized in paper treatment, such as beater addition, saturation of the dried paper, surface coating of paper etc.

1.2.10. EFFECTS OF MAGNESIUM ON BEHAVIOUR OF LATEX

Fresh field latex contains metallic ions like Mg and Ca, which affect the spontaneous coagulation. The process of spontaneous coagulation may be accelerated by the addition of small amounts of fatty acid soaps. The addition of large amount causes a retardation of the process. The range of soap addition over which the coagulation time is minimum depends upon the amount of Ca and Mg. If these are absent, then unpreserved latex may be kept in a fluid condition for many days until putrefaction set in. The spontaneous coagulation is supported by two theories. The first supposed that the effect is due primarily to the development of acidity through microorganisms interacting with various non-rubber constituents. The second ascribes the effect to the liberation of fatty acid anions through the hydrolysis of several of the lipid substances present in the latex. Such anions are then thought to be adsorbed on to the surface of the rubber particles, possibly partially displacing adsorbed protein. Then they interact with metallic ions such as those of Ca and Mg present in the latex initially or gradually released by the action of enzyme for insoluble Magnesium/Calcium soaps, thus recovering the stability of latex.

1.2.11. REMOVAL OF MAGNESIUM

Fresh field latex contains about 60% water, 30% rubber components and lower percentages of proteins (1 – 1.5%) lipids (1 – 1.25%) and minerals. Ammonia is added as a preservative to prevent putrefaction. Thus Mg ions and phosphate ions present in the field latex combine with ammonia to form a precipitate of Magnesium ammonium phosphate.

$$Mg^{+2} + NH_3 + HPO_4^{-2} \longrightarrow Mg\ NH_4PO_4$$

The precipitate sediments as sludge together with any sand, dirt or bark which may be present in the latex.

Some latices do not contain sufficient phosphate to ensure the complete precipitation of Mg. The Mg:PO_4 ratio is to some extent a clonal characteristic, although large variations exist with clones. Some clones give latex in which this ratio is high. The ammonia preservation tends to be low and variable stability because of the residual magnesium ions. Its mechanical stability is very low; its viscosity at a given solid content is high, and its gelling p^H is high. These abnormalities are accentuated during the wintering period. The abnormality of Glenshiel 1 latex is unfortunate because this clone is particularly high – yielding.

Adverse Mg:PO_4 ratios are usually associated with an excess of Mg ions rather than with a deficiency of phospho lipids, it is significant that abnormal latices do not appear to be deficient in this substance.

Madge, Collier and Peel (1950) have shown that small addition of water soluble phosphates (such as diammonium hydrogen orthophosphate or tetra sodium phosphate) improves the mechanical stability of Glenshiel 1 latex, up to the point where the added phosphate is roughly equivalent to the residual magnesium. Further additions then cause the stability to fall again. The addition of water- soluble phosphate to a normal concentrate brings about an immediate reduction in stability. These effects are illustrated in the figure (1.2) given below.

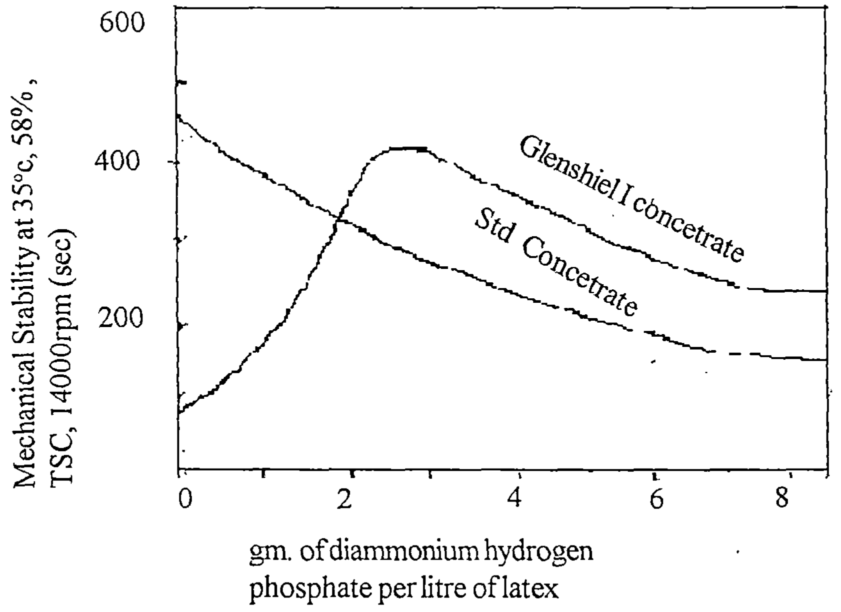


Fig.1.2

Effect of a water soluble phosphate upon the mechanical stability of natural rubber latices [after Madge, Collier and Peel(1950)]

The addition of water-soluble phosphate to Glenshiel 1 latex also has the effect of reducing its gelling p^H to a normal value.

1.2.12. GELATION OF NATURAL LATEX

Latex gelling may be described as a homogenous coagulation. The rubber particles in latex are irreversibly and uniformly associated and continuous aqueous phase of the latex is totally enclosed and uniformly distributed throughout the interstices of the continuous rubber phase. A latex gel is termed strong after gelling is complete; the product still containing all the water has a good tensile strength and a measure of elastic recovery. It is called weak, if the gel is easily deformable and readily broken by small tensile forces. A pasty gel is a self-evident description.

The two basic gelling systems that are of interest in the production of latex foam rubber are:

1) The heat gelling system, in which the latex is conditioned by sensitizing agents and an inversion of phase is brought by the application of heat.
2) Delayed action gelling system, in which an inversion of phase takes place in predetermined and controllable time interval after the addition of the gelling agent without any substantial change in temperature.

It will be appreciated that a rise in temperture will accelerate (2) or prolonged storage could in certain cases lead to incipient gelling system normally used in (1).

The way in which a latex gels and the characteristics of the formed gel can influence the physical properties of the final product- for example: its size, modulus and tensile strength.

When gelling processes are used in manufacture, particularly the delayed action gelling processes it is desirable for the path of gelling to be definite and reproducible. In other words, the thickening stage should be progressive and to a reproducible pattern and the actual gelling point should be sharp and distinct.

This results in reproducibility of cycle time and product properties. In foam manufacture, in which other reactions are taking place simultaneously with the gelling reaction and balanced systems always involved, a controlled and reproducible gelling path is obviously advantageous.

Assuming that no mixing additions have been made that interfere with gelling conditions, differences in latex quality can themselves lead to physical difference in gelling path. Reference has been made to the large variation in the magnesium phosphate ratio in various clonal latices. If the excess of Mg in certain cases is not controlled, a fluctuating viscosity is observed as the p^H falls during gelling, due presumably to the early precipitation of Magnesium soaps. Such latex can form a pseudogel at a high p^H, which reliquefies as the p^H falls.

With certain type of high stability latex such as those preserved with low ammonia and sodium pentachlorophenate, the gel with sodium silicofluoride at room temperature can be pasty and ill defined. It will be seen that castor oil soap and zinc oxide when added separately to a latex gelled with sodium silicofluoride have little influence on the wet gel strength but together they increase the wet gel strength considerably.

It is not unreasonable to expect therefore that; as both gellation and vulcanization are rate processes, the vulcanization of wet gels initially in different states of formation, both in kind and degree, can lead to differences in the physical properties of the vulcanized product.

Certain types of gel exhibit pronounced synthesis after formation, i.e, an exudation of part of the serum originally included in the interstices of the wet gel. The extent of such synthesis before vulcanization can influence the size and properties of the final product. An extreme case where loss of water is positively prevented is that of a gel - formed from a latex ebonite mixing. If such a gel is cured under water no water in the gel escapes and a fully microporous ebonite is obtained on drying out. The micropores are formed where water was previously resident in the gel and the rigidity of the cured ebonite resist any tendency to shrink on drying. The strength of the hot, wet gel after vulcanization is of great importance in mould opening process, which may be mechanized. This applies particularly to foam rubber manufacture where moulding may be fairly complicated in shape .

CHAPTER II

MATERIALS AND METHODS

2.1 MATERIALS USED

Field latex used for experimental purpose was received from the latex collecting unit in Rubber Research Institute of India, Kottayam.

Typical composition of natural latex

Ingredient	%
Total solid content	41.5
Dry rubber content	36
Proteinous substance	1.4
Natural lipids	1.0
Phospho lipids	0.6
Ash	0.5
Inositols & carbohydrate	1.6
Other nitrogen Compound	0.3
Water	58.5

2.2 INSTRUMENTS USED

The viscosity of the latex can be determined by using Brook field viscometer.

The Brook field viscometer

This instrument is a technical viscometer, which is widely used for the measurement of the latex viscosity. It consists of a rotating member, which is usually a cylinder driven by synchronous motor, through a

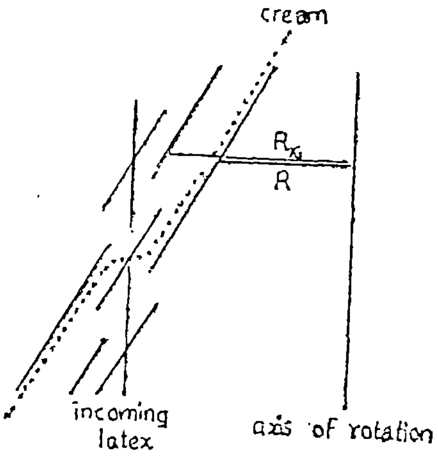
Beryllium-copper torque spring. The viscous drag on the cylinder causes an angular deflection of the torque spring, which is proportional to the viscosity of the fluid, in which the disc is rotating. The torque and therefore the viscosity is indicated by means of a pointer and scale. The pointer is attached to the cylinder spindle and the scale to the drive spindle above the spring, so that both pointers and scale rotate. To obtain a reading, they must be clamped together and rotation stopped when the pointer is opposite a window, which is cut out of the carrying. For this reason, it is always possible to flow continuously, the course of viscosity changes due to temperature or associated with non- Newtonian behavior. The calibration is normally based upon the immersion in fluid contained in a 600ml beaker. A range of speed and of disc and cylinder is available, so that a wide range of viscosity may be covered. The shear rate is not definable in a viscometer of this type, in which a single element rotates in a mass of fluid of rather indefinite extent. The Brookfield viscometer is somewhat similar to concentric annular space. As is general to such an instrument, the distribution of shear rate depends very much upon the flow characteristics of the fluid, which fills the annular space. Brookfield viscometer readings are affected by turbulence and to a certain extend by the angle of immersion of the spindle.

CENTRIFUGATION

The most commonly used centrifuges are the Alpha-Laval machines, the principle of which is illustrated in fig (2.1) and (2.2).

The ammoniated field latex centers the centrifuge bowl, through a central feed tube, and then passes through a distributor to the bottom of the bowl, where it flows through a series of holes in to the interior to the bowl. The rotating mass of latex is broken up in to a number of thin conical shells, within the bowl, which rotates at high speed. The effect of these disc in facilitating separation is illustrated in fig (2.1). The rubber rich concentrate flow inwards towards the axis of rotation and hence empties from the bowl through holes into a stationary gully. The skim being more dense on the other hand flows outwards from the axis of rotation and leaves the bowl through an orifice which is formed by a regulating screw, the skim screw. The skim passes out of the centrifuge through a second stationary gully.

The bowl rotates at speeds of about 6000rpm;at this particular speed, the corresponding centrifugal acceleration at a point 6 inches from the axis of rotation is approximately 6160g. A well balanced bowl is very necessary if such high acceleration are to be obtained without any mishap.



Illustrating the effect of separator discs.

Fig. 2.1

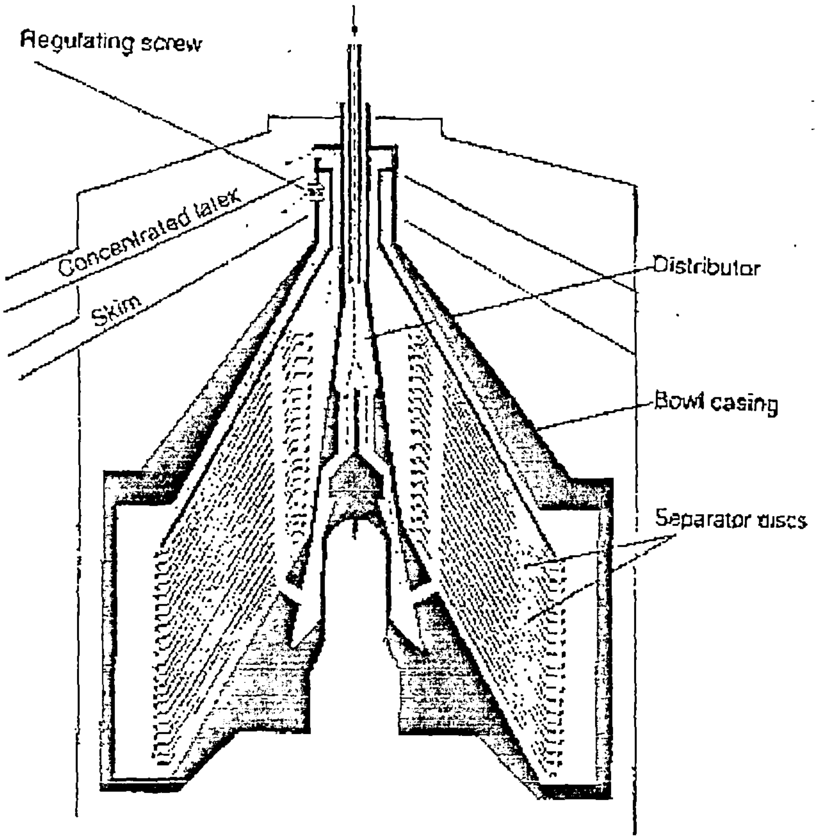


Fig 2.2. Diagramatic section of latex centrifuge bowl. indicatig the path of latex (Blackley, 1997)

2.3 CHEMICALS USED

(1) 10% Diammonium hydrogen phosphate(D A H P)

(2) 40% Zinc oxide (ZnO) dispersion

(3) P^H-10 Buffer solution.

(4) 0.005M Ethylene diammine tetra acetic acid(E D T A)

(5) Eriochrome black T

(6) Magnesium sulphate $MgSO_4.7H_2O$

2.3.1 Preparation of 10% solution of DAHP

Molecular mass of Diammonium hydrogen phosphate; $(NH_4)_2HPO_4$ being 132, about 10 gm of DAHP is weighed out accurately into a 100ml standard measuring flask, dissolved in water and made upto the mark.

2.3.2 Estimation of Magnesium

Principle:-

Magnesium in latex is estimated by a complexometric titration. The estimation is based on the reaction.

$$Mg^{2+} + H_2Y \longrightarrow MgY + 2H^+$$

A Standard solution of $MgSO_4.7H_2O$ is prepared and the given EDTA is standardised using Eriochrome black T as the indicator. In presence of metal ion, the indicator gives wine red colour in the P^H range 10. At the end point, all the metal ions are converted to metal EDTA and the free indicator is liberated, which has blue colour.

Reagents:-

Standard solution of EDTA(0.005M)

Dissolved 1.86 gm of EDTA salt in water and made up the solution to one litre. Standardised using 0.005M $MgSO_4$ solution .(1.2324 gm $MgSO_4.7H_2O$ in one litre)

P^H - 10 Buffer solution

17.5 gm of Ammoniumchloride is dissolved in 144ml liquid ammonia and diluted to 250ml.

Eriochrome black T indicator

Prepared by grinding 0.2gm of Eriochrome black T [solochrome black T] and 50 gm of A.R.KCl.

Calculations.

Weight of latex = 12.7585gm.

Weight of $MgSO_4$ = 0.3108gm

20ml $MgSO_4$ $\equiv$ 20.7mlEDTA

10ml latex $\equiv$ 3ml EDTA

$$\text{Molarity of EDTA} = \frac{0.005 \times 20}{20.7} = 0.0048\text{M}$$

$$\text{Weight of magnesium in the latex} = \frac{24.32 \times 3 \times 0.0048 \times 1000 \times 100}{12.7585 \times 10}$$

$$= 274.48 \text{ mg/lit.}$$

$$= \underline{\underline{0.027448\ \%}}$$

Procedure:-

Took 5 to 10 gm of well mixed latex sample in a stoppered conical flask. Weighed to the nearest 0.01gm.Transferred about 4 to 5 gm of latex into a 100 ml standard flask using funnel and weighed to obtain the weight of latex, added by difference. Made upto the mark.10 ml of the solution is pipetted out into 300ml distilled water taken in a 500 ml beaker. 10 ml of buffer solution is added. Added a pinch of indicator and tiltrated against 0.005M EDTA from burrette. Colour changes from wine red to blue

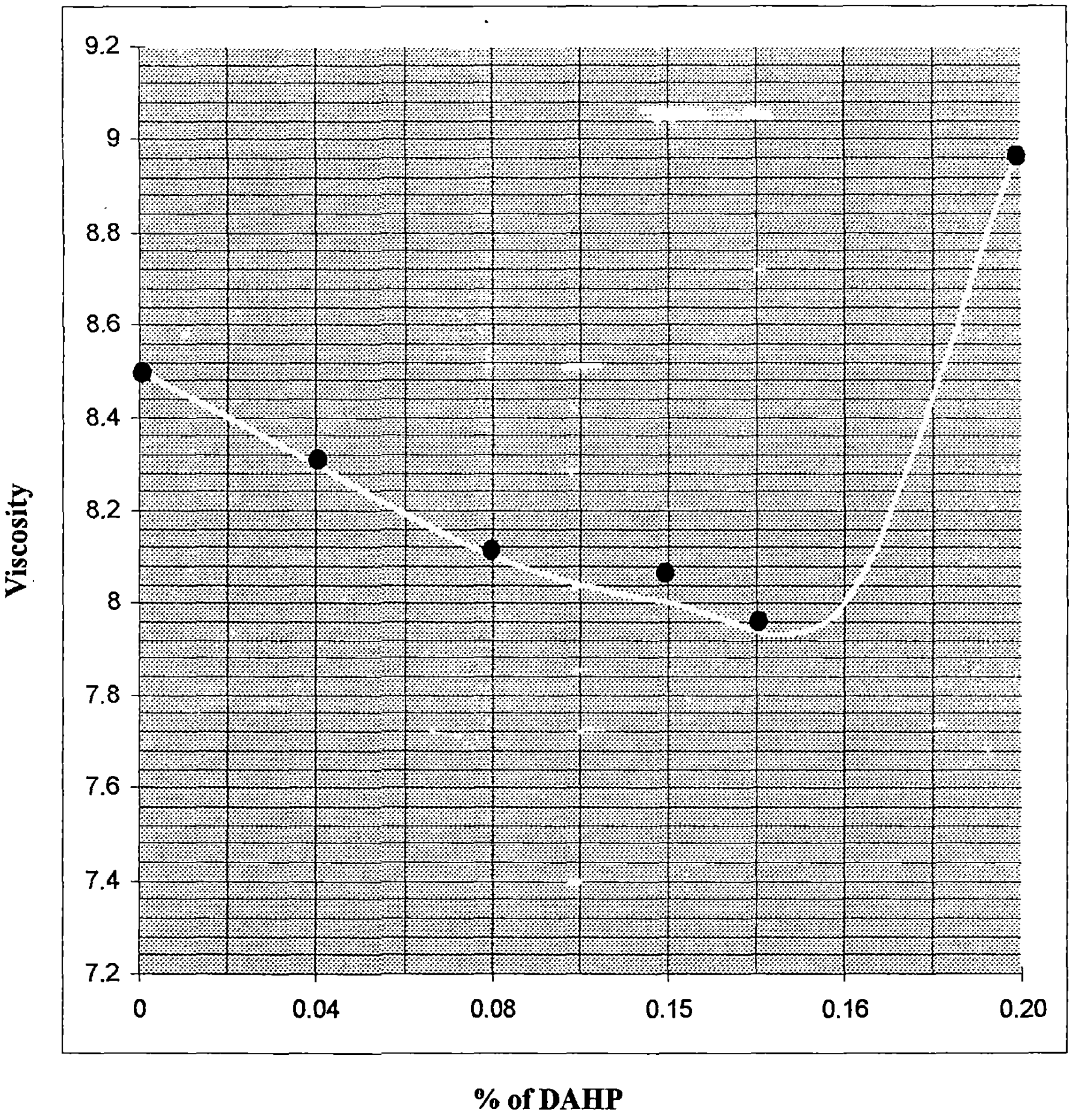
$$\text{Weight of magnesium in the latex(mg/lit)} = \frac{24.32 \times V \times M \times 1000 \times 100}{M \times 10}$$

M - molarity of EDTA

V - volume of EDTA(ml)

W - weight in gm of latex.

$$\text{Mg \% wt} = \frac{12.6 \times M \times V}{W}$$


9.2
9
8.8
8.6
8.4
8.2
8
7.8
7.6
7.4
7.2
Viscosity
0
0.04
0.08
0.15
0.16
0.20
% of DAHP

2.4 Removal of Magnesium from the latex

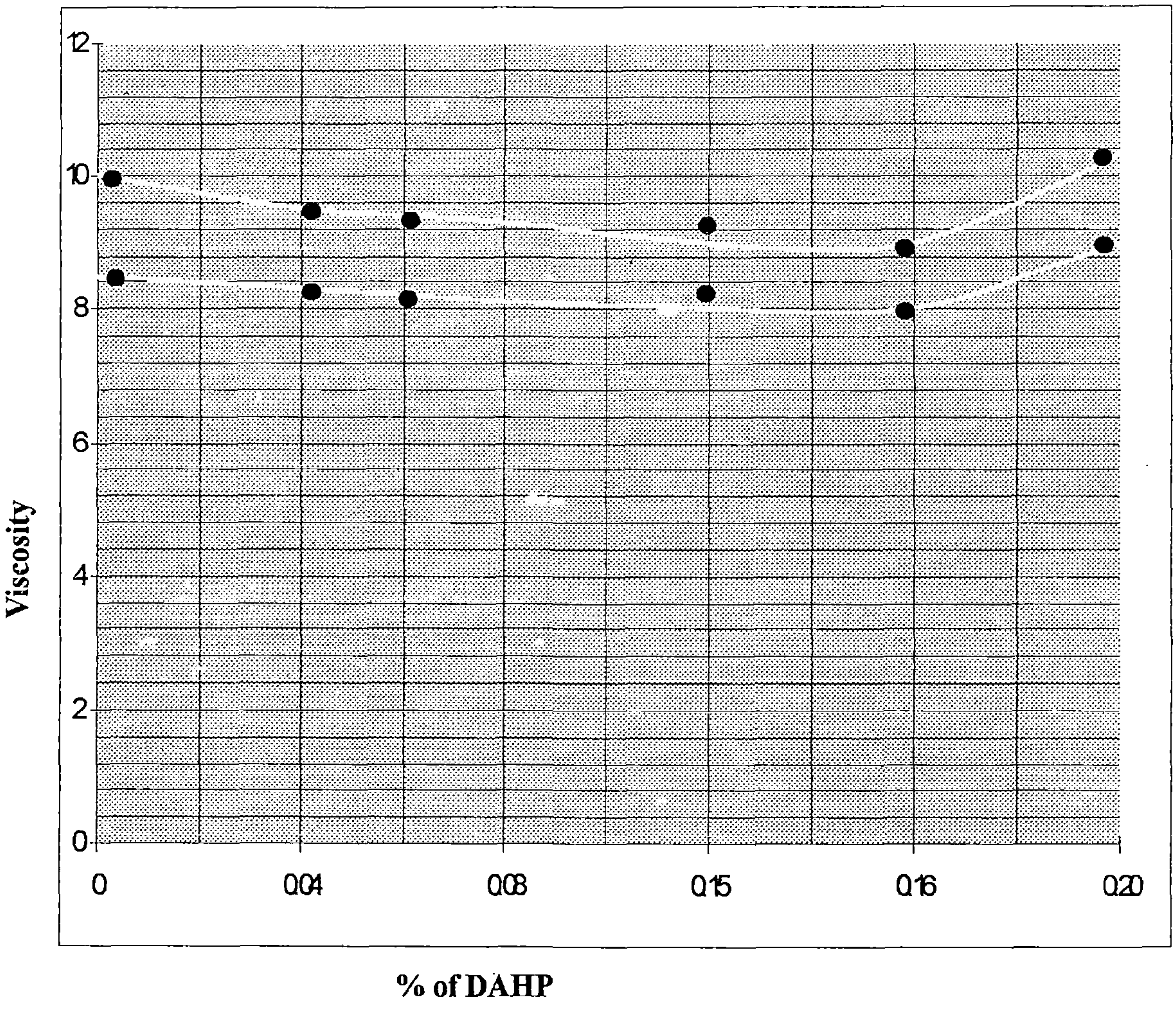
Weighed 250 gm field latex . Seived and taken in 6 separate beakers.Added 10% DAHPin 0,1,2,3.75,4,5,....ml in these beakers. Well mixed the sample and kept undisturbed for 24 hrs to settle Magnesium as Magnesium ammonium phosphate(sludge).After one day decanted the latex and took 220 gm from it.and found the viscosity using Brookfield viscometer.

% of DAHP	viscosity (cps)
0	8.5
0.04	8.3
0.08	8.1
0.15	8.0
0.16	8.0
0.20	9.0

Table 2.1

2.4.1 Zinc oxide viscosity

Six samples of seived latex containing varying quantities of DAHP were taken in 250 ml beakers.Each sample contained 220gm of seived latex and viscosity of each sample was noted at temperature of 25°C.Then 3.5gm of 40% ZnO was added to each of the sample and allowed to stand for one hour.Again determined the viscosity of each sample using Brookfield viscometer. The results are shown in table 2.2.A graph was plotted connecting percentage of DAHP(in presence of ZnO) against viscosity .The viscosity first decreased with increase in the conc. of DAHP and after reaching an optimum concentration it increases.


12
10
8
6
4
2
0
Viscosity
0
0.04
0.08
0.15
0.16
0.20
% of DAHP

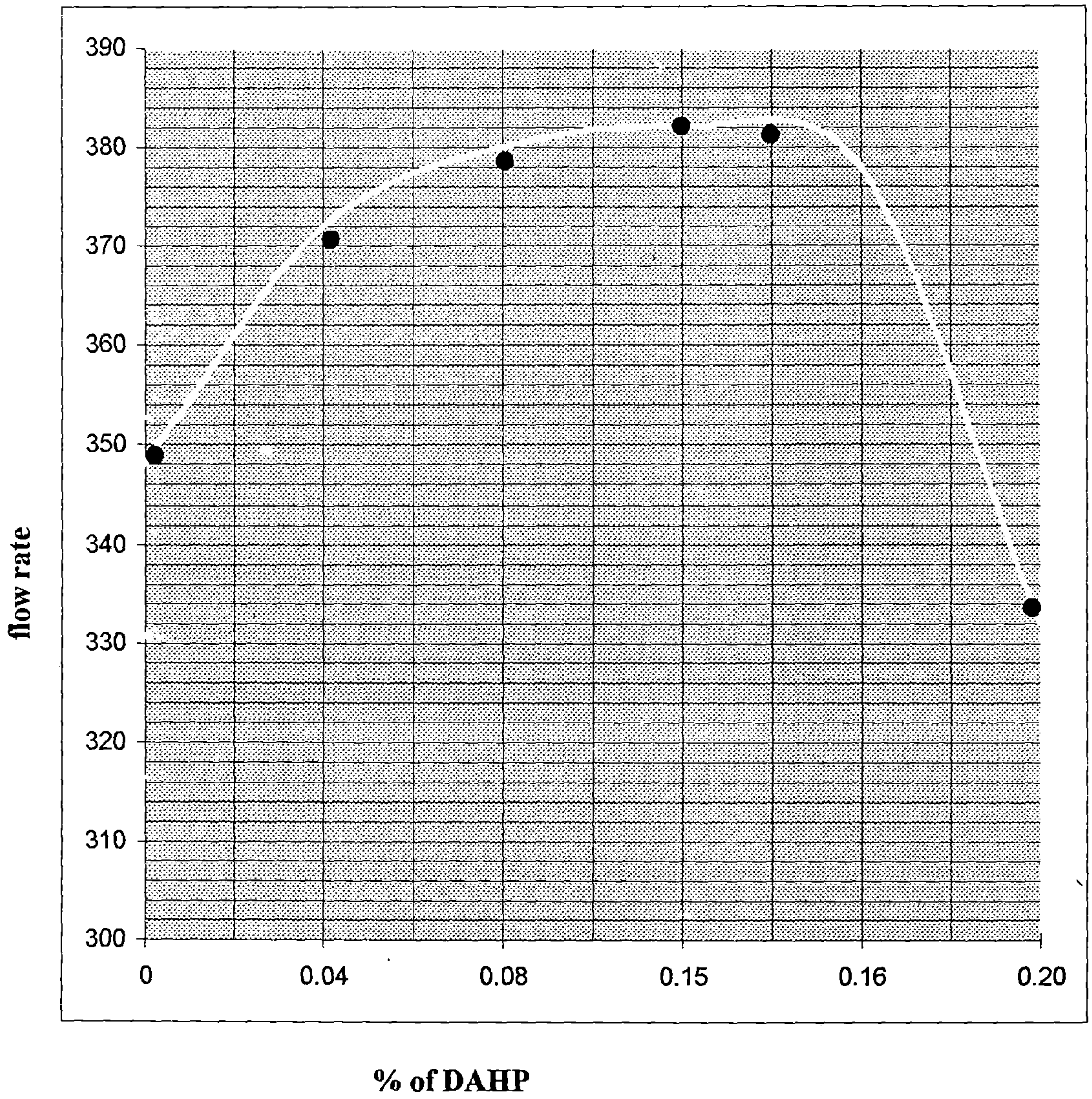
% of DAHP	viscosity in presence of ZnO(cps)
0	10
0.04	9.5
0.08	9.3
0.15	9.0
0.16	9.0
0.20	10.3

Table 2.2

2.4 Effect of viscosity of latex on processing concentrate by centrifuging

Field latex is seived through a 60 mesh sieve and bulked in the bulking tank and homogenised by stirring. Varying quantities of DAHP are added to precipitate magnesium. The latex is then left undistributed for the precipitated Magnesium ammonium phosphate and other sedimental impurities to settle as sludge.

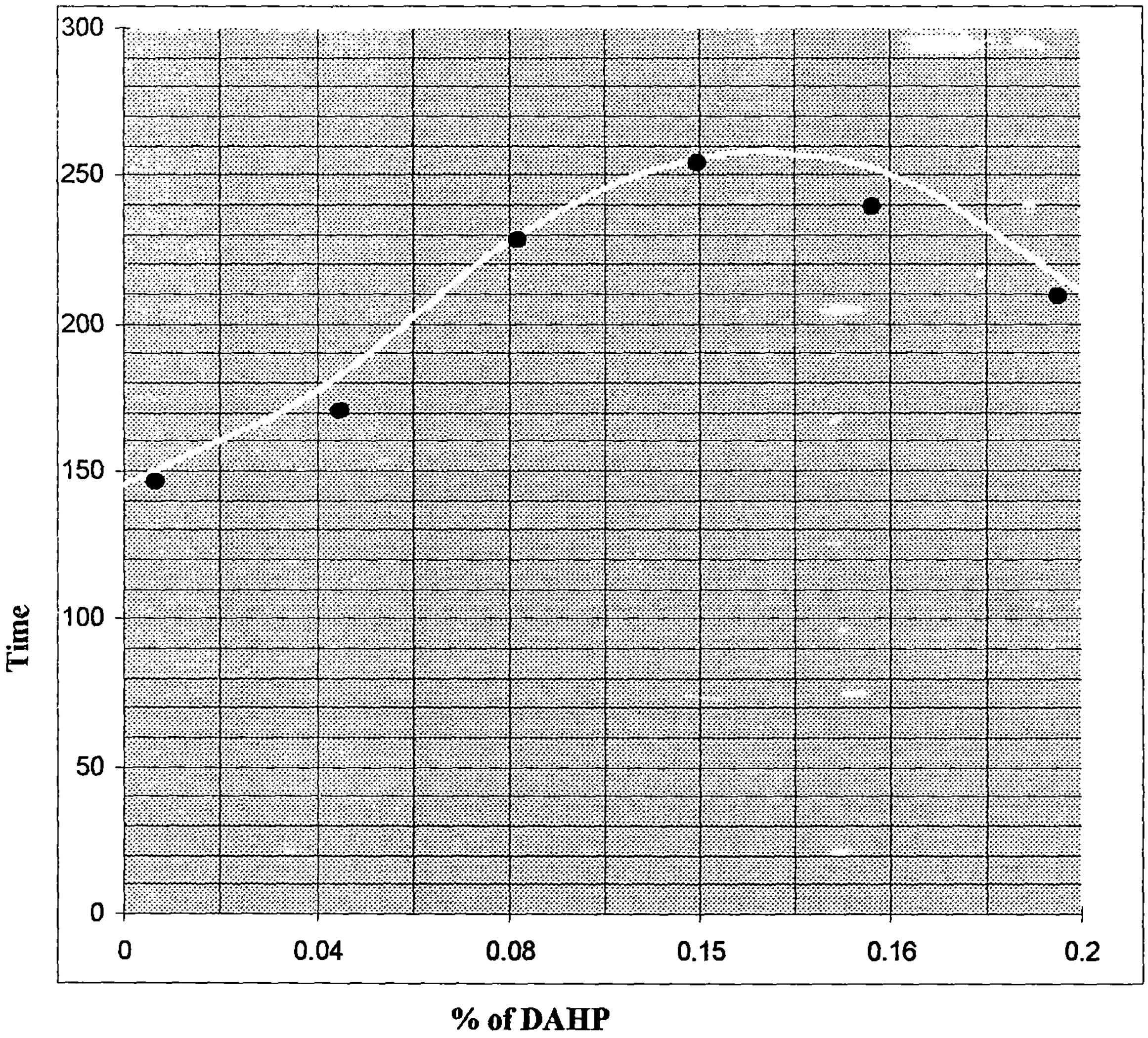
The sedimental latex is then fed to the centrifuge. The most commonly used centrifuges are the Alpha-Laval machines The machine consist of a rotating bowl having concentric conical metallic separator disc. Latex enters the bowl, through a feed tube and passes to the bottom of the bowl. A series of small holes on the separator disc, positioned at definite distance from the centre, allow the latex to get distributed and broken up into a number of thin conical shell within the bowl,


390
380
370
360
350
340
330
320
310
300
flow rate
0
0.04
0.08
0.15
0.16
0.20
% of DAHP

which rotate at high speed. When machine runs the cream centrifuges inwards to the axis of rotation and then empties from the bowl through the holes into a stationary gully. The skim flows outwards from the axis of rotation. The flow rate of latex at varying concentration of DAHP is noted. Clogging time of centrifuge is also noted. The results are shown in tables 2.3 & 2.4. A graph is plotted between % of DAHP and flow rate, and another graph is against clogging time of latex. Each graph shows a maximum at optimum concentration of DAHP.

% of DAHP	**Viscosity**	**flow rate(kg/hr)**
0	8.5	348
0.04	8.3	372
0.08	8.1	380
0.15	8.0	382
0.16	8.0	378
0.2	9.0	332

Table 2.3


Time
300
250
200
150
100
50
0
0
0.04
0.08
0.15
0.16
0.2
% of DAHP

% of DAHP	**viscosity**	**time of clogging of centrifuge(sec)**
0	8.5	145
0.04	8.3	177
0.08	8.1	228
0.15	8.0	256
0.16	8.0	250
0.2	9.0	211

Table 2.4

CHAPTER III
RESULTS AND DISCUSSION

The very importance of magnesium to phosphate ratio will be understood, when it is remembered that on ammoniating fresh latex insoluble magnesium-ammonium phosphate is precipitated as a sludge. The amount of sludge depends on the concentration of magnesium as well as phosphate present in the field latex. The sludge largely removed on standing (sedimentation) and the importance of magnesium to phosphate ratio in this process having thus established. The precipitation of excess magnesium in the latex is not complete, will contain some magnesium, which will subsequently form insoluble magnesium ammonium phosphate, as a result of its reaction with the phosphate obtained from phospholipid hydrolysis

The addition of diammonium hydrogen phosphate prevents delayed sludge formation and increases stability due to ionic effect. However a large increase in the concentration of ions in natural latex will cause partial or total destabilization through suppressions of the electrical double layer surrounding rubber particle and interference with hydrogen layer. This effect is utilized in coagulant dipping,leather board, paper board manufacture and to some degree in plaster casting.

In the first experiment, the magnesium content in the given latex is calculated and it is about 0.027 %. After adding varying quantities of DAHP to the latex for the precipitation of Magnesium ammonium phosphate, a graph is plotted between the percentage of DAHP and viscosity of the latex. With increase in concentration of DAHP, the viscosity first decreased and reached a minimum point, then increased. Viscosity bears an inverse relation to stability of latex, ie higher viscosity means lower stability. Magnesium when present in latex is ionic form, can neutralise two negative charges on latex particles. Hence when the content of Magnesium decreases viscosity reduces and reaches a minimum value.

The presence of ZnO also increases the viscosity of the latex in comparison with percentage of DAHP only. A graph is plotted between viscosity and percentage of DAHP in presence of ZnO. In this case, the viscosity first decreased and after reaching minimum point, it increased.

The viscosity of the latex vary as between different sources. The presence of ammonia causes some decrease in the viscosity as compared with fresh latex. It is some times necessary to make an increase in the viscosity of latex bath, especially in simple dipping process, where the thickness of the deposit depends largely upon the viscosity of the latex. At present a wide range of rubber products are made by latex dipping, possibly the most practically significant of these are various types of gloves, and a number of products like catheters, balloons, nipples etc. Also centrifuged latex concentrates are used for the production of extruded thread, adhesives and for a myriad of other products.

The control of the thickness of rubber deposited in the dipping operation is important. The three main variables affecting deposit thickness are the immersion or dwell time, the viscosity of latex compound and the nature and the concentration of the coagulant. The dwell time has a greater effect on the deposit thickness especially at short times.

If the latex is passed through the centrifuging bowl, as the concentration of DAHP increases, the flow rate increases and reaches a maximum point, when DAHP has optimum concentration and then decreases, ie the deposition of rubber occurs. Removal of the centrifuges covers must be carried out only when the bowl comes to complete rest. If the flow rate increases, the bowl changing occurs only at 45 min. ,thus we can save our time and increase the production rate.

CONCLUSION

The Magnesium present in the latex is precipitated as Magnesium ammonium phosphate by the addition of diammonium hydrogen phosphate. Viscosity of latex vary with variation in concentration of diammonium hydrogen phosphate. At the optimum concentration of diammonium hydrogen phosphate, viscosity has a minimum value. The addition of Zinc oxide increases the viscosity of latex. In the case of centrifugation, the flow rate is maximum when the concentration of DAHP is optimum in which case the viscosity of latex has minimum value. Time of clogging of centrifuge is maximum when the latex contain optimum concentration of DAHP. From the above points, we can conclude that optimum concentration of diammonium hydrogen phosphate added to a latex is very effective in latex viscosity.

REFERENCE

1. D.C **Blackley** – Polymer Latices : Science and Technology vol. I.
2. D.C **Blackley** - Polymer Latices : Science and Technology vol. II.
3. Mc. **Roberts** - Natural Rubber Science and Technology- Rubber research institute of Malaysia.
4. E.W . **Madge** – Latex foam Rubber.
5. H.P **Stevens** and W.H **Steven** – Rubber Latex.
6. K.O. **Calvert** - Polymer Latices and Their Application.
7. R . J. **Noble** – Latex in Industry.
8. Latex and Rubber Analysis – RRIM Training mannual and analytical Chemistry.
9. Rubber Processing Machinery and Maintenance – RRIM Training mannual On Analytical Chemistry.
10. Natural Rubber Process - RRIM Training mannual and analytical Chemistry.
11. Maurice Marton - Introduction to Rubber Technology.
12. Modern ruber chemicals & rubber product technology - SIRI Board of consultants & Engineers.
13. K.A Grosch & P. N. Suift - Rubber chemistry & Technology.
14. C.W. Thomson & H.Howrah - Rubber Developments
15. H.S Lim & S. Sethu - Proceeding of the Rubber Research Institute of Malaysia, planter's conference, 1974, Kualalampur.
16. P.S.R. Rao, C.K.John and C.S Ng - Proceeding of RRIM Planter's conference. 1976. Kualalampur.
17. C.K.John - Proceeding of National Work shop on Latex and latex products. 1983. Kualalampur.
18. T.D. Pendle and A.D.T Gorton - Rubber Chemistry and [illegible]