LOW AMMONIA - BORIC ACID SYSTEM FOR PRESERVATION OF NATURAL RUBBER LATEX

A DISSERTATION SUBMITTED TO THE UNIVERSITY OF KERALA

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE

DEGREE OF

MASTER OF SCIENCE IN CHEMISTRY

by SANDRA GEORGE

CHEMISTRY DEPARTMENT
ALLEPPEY-3

CHEMISTRY

JUNE – 2007

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CERTIFICATE

This is to certify that the work described in this dissertation titled “Low ammonia-Boric Acid system for preservation of Natural rubber latex” is an authentic record of the work done by SANDRA GEORGE Register No 05 125 006 doing MSc programme in Chemistry in S.D.College, Alappuzha under my guidance and supervision.

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Ref.No. P&PD/P&QC/07/PW

03.04.07

CERTIFICATE

This is to certify that the report ***Low Ammonia – Boric Acid System for preservation of Natural Rubber Latex*** is a bonafide record of the work undertaken by **Kum. Sandra George**, M.Sc. Chemistry, S.D.College, Alappuzha under my supervision and guidance, in partial fulfillment of the requirement for award of Masters degree in Chemistry. Also certified that the results obtained in this study have not been used for the award of any other degree or diploma.

Dr.M. Sunny Sebastian,
Joint Director (P&QC)

Date: 27-06-2007

DECLARATION

I do hereby declare that the dissertation titled ***"LOW AMMONIA - BORIC ACID SYSTEM FOR PRESERVATION OF NATURAL RUBBER LATEX"*** is an authentic record of the work done by me in the Department of Chemistry, S.D. College, Alappuzha under the Joint supervision of Dr. M. Sunny Sebastian, Joint Director, Central Laboratory, RRII, Kottayam and Sri. R. Venugopal, Selection Grade Lecturer, Department of Chemistry, S.D. College, Alappuzha and has not been submitted previously for the award of any other degree.

Sandra

SANDRA GEORGE

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Sandra

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SYNOPSIS

Natural rubber is a versatile material which is very useful in our daily life. Natural rubber is obtained as latex from 'Hevea brasiliensis' tree.

Studies on the preservation of natural latex were carried out as the project work. Experiments were done by using ammonia and boric acid. These bacterial preservatives retard the formation of microorganic activity in the latex. The Volatile Fatty Acid number gives an indication of the extent of bacterial activity. Higher the volatile fatty acid number, lower is the latex quality. The volatile fatty acid number is determined by the Markham Still apparatus. The results indicate that a composite system consisting of 0.3% ammonia and 0.4% boric acid can be used for long term preservation of natural latex.

CONTENTS

ABBREVIATIONS

VFA	-	Volatile Fatty Acid
HA	-	High Ammonia
LA	-	Low Ammonia
BA	-	Boric Acid
SPP	-	Sodium pentachlorophenate
ZDC	-	Zinc diethyl dithiocarbamate
LATZ	-	Low Ammonia TMTD Zinc Oxide
TMTD	-	Tetramethyl thiuram disulphide
MST	-	Mechanical Stability Test
ZST	-	Zinc Stability Time
ZOV	-	Zinc Oxide Viscosity
DRC	-	Dry Rubber Content
TS	-	Total Solids

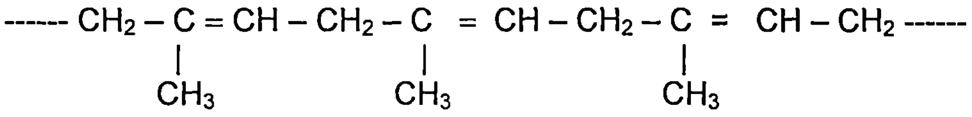
Chapter – I

INTRODUCTION

INTRODUCTION

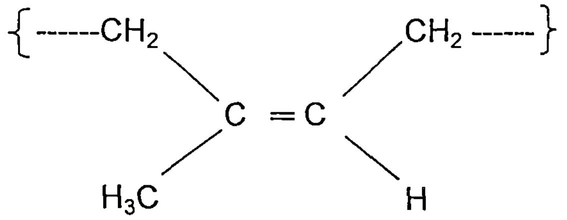
1.1. Natural Rubber

Natural Rubber is a versatile material which is very useful in our everyday 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. This is a native of Brazil and was introduced into tropical Asia in 1876 by Sir Henry Wickham. The polymer contained in the latex is cis-1, 4 – polyisoprene which has a density of 0.93 g/cm^3 at 20°c. The structural formula of polyisoprene $(C_5H_8)_n$ is shown below.

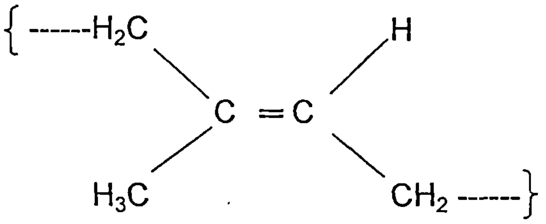


$$\text{------}\,CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH-CH_2\,\text{------}$$

Because of the presence of olefinic carbon atom, cis and trans forms are possible. The trans form 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 gutta-percha shows straightening structure.

Natural Rubber is a high molecular weight polymer with both viscous and elastic properties. Thus the state of natural rubber is referred to as viscoelastic. Natural Rubber contains several non-rubber constituents in small quantities like proteins & sugar, phospholipids, lipids etc. Natural Rubber is not a monodisperse.

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[1].

Typical composition of dry rubber[2] obtained on evaporation of natural latex is shown in table 1.

Table 1 - Composition of Dry Rubber

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. These are requirements of rubberiness. Another property of rubber is its strength and toughness. A very important quality of rubber is "building tack", i.e, 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 in table 2.

Table 2 – Physical properties of Natural Rubber

Parameters	Value
Specific gravity or density	0.91 – 0.92
Refractive Index	1.52
Thermal conductivity	0.00032 cal/s.cm.°c
Heat of combustion	10700 cal/g
Dielectric strength	3937 V/ mm
Volume resistivity	10^{15} ohm.cm
Power factor (1000 cycles)	0.15 – 0.2
Coefficient of cubical expansion	0.00062/°c
Cohesive energy density	63.7 cal/cc
Dielectric constant	2.37

Since natural rubber contains isoprene units, it shows all the reaction of an unsaturated polymer. It gives addition compounds with halogens, ozone, hydrogen chloride and several other reactants that react with olefins. Its combination with sulphur is known as vulcanisation. This reaction converts the plastic properties of raw rubber into elastic properties. Vulcanised rubber has very high tensile strength and comparatively low elongation. Its hardness and abrasion resistance are also high compared to raw rubber.

With its wide range of useful properties, natural rubber can be used in a large variety of applications. Major application of natural rubber is in the tyre sector. Also natural rubber is used in the carcass as well as in the side wall due to its superior fatigue resistance and low heat 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. In addition to these, natural rubber now finds extensive use in soil stabilization, in vibration adsorption and in road making[3].

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 particle in the latex has a diameter of less than 1 µm, although a few latices do contain a small proportion of larger particles. The natural latex is cis 1, 4-poly isoprene and this hydrocarbon is biosynthesized by a complex process involving some proteins, Rubber Elongation Factor (REF). Latex collected from plantation will have a rubber content of 30-40%. For industrial uses this latex is concentrated to 60% rubber content.

The latex is obtained from the bark of the tree by a process known as tapping. It is a process of controlled wounding of the plant in which a thin layer of bark is removed. The latex vessels in the regions of the wound are opened by tapping and latex flows out from the tree which is channelled into a container attached to it.

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 is 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% of 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 absorbed 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 protein carry negative charge, at about pH 6.5, the normal pH 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 Waal's forces. These factors contribute to the stability of the latex[4].

1.2.2. Composition of Natural Latex

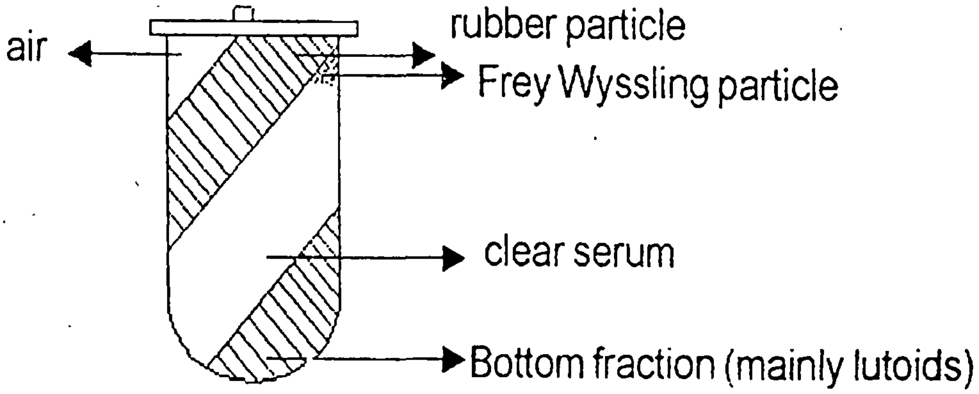
Table 3 – Composition of Natural Latex

Constituent	Proportion / % m/m on whole latex
Total solids	36
Dry rubber	33
Proteinaceous substances	1 – 1.5
Resinous substance	1 – 2.5
Ash	Up to 1
Sugars	1
Water	100

Latex is a white or slightly yellowish opaque liquid with a specific gravity in the range of 0.96 to 0.98 and having a variable viscosity. The chemical composition of freshly tapped Hevea latex is complex when compared to synthetic latices. This is because Hevea latex is a cytoplasm Heveca 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 particles 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 the figure.

Figure 1 – Composition of Latex



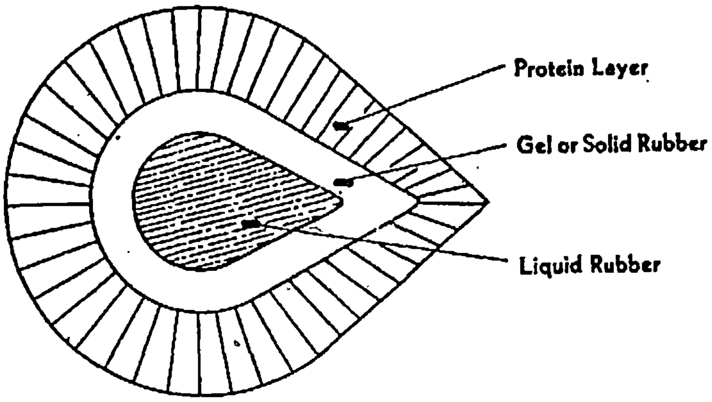
The uppermost layer contains the rubber particles. Below this layer Frey Wyssling particle, followed by the clear serum zone and finally the bottom fraction which contains predominantly the lutoids.

In fresh latex, rubber particle constitute 25% - 45% of the volume of the latex. The rubber particle in the fresh latex contains protein 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 the 'β-serum') which contains dissolved substances such as acid, minerals, salt, protein, sugar and a polyphenol oxidase etc. The amount of lutoids 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[5].

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.

Figure 2 – Latex particle[6]



a. 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 contain seven electrophoretically distinct protein components. Ammonia preservation for several months reduces the number of electrophoretically resolvable components from seven to two.

b. α - Globulin and Hevein

α - Globulin is the protein present in the highest concentration in fresh latex serum. It is soluble in salt solution at pH values away from its isoelectric point, (pH 4.55) is coagulated by heat and is readily adsorbed at hydrocarbon – water interfaces. The sulphur content is low and there is little phosphorous 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 protein adsorbed on the surface of the rubber particle 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 isoelectric 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 pH, including its isoelectric point, it is coagulated by heat, and has a molecular weight of about 5000.

c. Basic proteins

In addition to the basic proteins in latex serum, several of high isoelectric points proteins (>pH 8.6) have been detected in fresh latex bottom fraction. The basic component has isoelectric point in the region of pH 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 pH values.

d. 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 into 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.

e. Neutral lipids

The neutral lipids contain at least 14 substances. These have been classified into sterols, sterol esters, free high fatty acid, fatty acid esters, wax esters, monoglycerides, diglycerides, triglycerides and phenolic substances. Some of the identified substances include β-sito sterol, 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.

f. Phospholipids

The phospholipids in Hevea latex contains phosphatidylcholine (or lecithin) as the major component (about 80%), metal phosphatidates phosphatidyethanolamine 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.

g. 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 metabolised 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.

h. 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.

i. 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.

j. Enzymes and Bacteria

Latex contain same enzymes and bacteria also. Spontaneous coagulation of latex is due to their activity. Other minor constituents of latex include ribose nucleic acid (RNA), pyrophosphate nucleosides and low molecular weight thiols[7].

1.2.4. Synthetic Latices

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

Styrene – butadiene latex
Butyl Polymer
Polychloroprene
Chloroprene latex
Nitrile
Silicone
Thiokol
Acrylic (co) polymers
Cis poly butadiene

Poly urethanes

Vinyl acetate (co) polymers

Acrylates

Chloro Sulphonated polymers

Vinyl Chloride (co) polymers

Polyethylene

Fluro-Hydrocarbon

Synthetic cis – polyisoprene

Acrylonitrile – butadiene (co) polymer

Ethylene propylene copolymer

Ethylene propylene terpolymer[8]

1.2.5 Collection of Latex

The latex that flows out from the rubber tree on tapping is channelled into a container attached to them. The container can be coconut shells or glazed earthern wares. Generally coconut shells are used. The spouts and buckets are made of galvanized iron. The flow of latex will continue for about 3 hours and after that it would stop.

Figure 3 – Collection of rubber latex in rubber plantations

Latex has to be collected from the field as soon as possible after the stoppage of flow of latex, that is about 3 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. If signs of pre-coagulation are observed in the latex, it is necessary to use an anticoagulant. Ammonia is the anti coagulant suitable for preparation of preserved latex. The tappers should not leave the buckets containing latex exposed to sun as heat increase tendency for fermentation of latex.

The latex should be delivered to the processing factory as rapidly as possible after collection inorder to prevent premature coagulation. Aluminum galvanized iron tanks are used for transporting latex in the case of large estates. Provision of a large man hole facilitating thorough cleaning of the tank, each day has to be given. The outlet tap is kept at the bottom of the tank. Brass fittings must be avoided to prevent contamination of latex with copper. Iron tanks, if unprotected will contain some rusty matter which will contaminate the latex. The best way to protect them would be to coat the surface with an inert material which will prevent the latex from coming into contact with the metal. Bitumen based or chlorinated rubber based inert paints are suitable coatings for the tank.

Unclean utensils are sources of bacteria resulting in enhanced pre-coagulation 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 and equipments with a 1% formalin solution or with 0.3% lysol every week[9]

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 membrane having relatively large pores, such as filter paper. The characteristic properties are the motion of the particles, the electric charge which they carry and the manner in which light is transmitted through the solution and reflected from them. The colloidal particles are observed to be in continous motion in irregular paths. This motion, characteristic 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 viscous fluid substance and provided on the exterior of the elastic shell with a layer of protein, soap and other protective materials. The solid content of fresh hevea 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 pH 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[10].

1.2.7 Anticoagulants

Anticoagulants are chemicals added to latex to prevent pre-coagulation. For preparation of preserved latex, ammonia is used as the anticoagulant. The use of anticoagulant is mostly required during rainy seasons as the tapping panel and coconut shells are contaminated with rain water which leads to more bacterial attack of latex and eventual pre-coagulation of it.

For preparation of stock solution, dissolve 1 kg of ammonia gas into 100 litres of water or dilute 50ml of 20% ammonia solution to 1 litre with water. For every 10Kg of latex, use 100ml of the stock solution. A few drops of anticouagulants are previously added into the coconut shells during tapping and the rest of the amount is added into the collection buckets when it is half full. Anticoagulants should never be added to empty buckets[11].

1.2.8 Spontaneous Coagulation of Latex

Fresh Hevea 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, ie., 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 Coagulation method

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 cause 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 aluminum and other metals are very active coagulants for latex, the aluminum ions in this case being adsorbed by the latex particles and neutralizing negative electric 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 neutralisation 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 silico fluoride, which may be added to the latex in small amount 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 silico fluoride may be used to cause delayed coagulation. Magnesium sulphate, ammonium sulphate, formaldehyde, diphenyl guanidine and salts of divalent metals have been used for this purpose[12].

1.2.10. PRESERVATION OF LATEX

Why preservation is required

Natural rubber latex is a negatively charged colloidal dispersion of rubber particles in an aqueous serum. The presence of non rubber constituents like proteins, carbohydrates etc in latex make it a suitable medium for growth of microorganisms. Because of the proliferation of microorganisms, organic acids are produced and these decrease the stability of latex. The latex gets putrified with the development of bad smell and finally coagulates. This is called spontaneous coagulation which 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 preservative. Preserved latex may be either field latex or concentrated latex.

Attributes of a Preservative

The stability of latex is mainly due to adsorbed proteins, phospholipids and higher fatty acids on the surface of rubber particles. The isoelectric point of the adsorbed protein is about 4.5. The pH of latex, as it comes out of the tree is about 7. Hence the chemical that is used as preservative should be able to enhance the pH.

Anions of higher fatty acids and proteins impart negative charges to the individual rubber particles, the coulombic repulsive forces between the individual particles prevent the agglomeration of the dispersed particles. Metallic ions like magnesium, which can form insoluble products with proteins or higher fatty acid anions, will neutralize the negative charges on the rubber particles and will tend to destabilize the latex. The preservative must be able to deactivate the harmful metallic ions.

The sterile latex, as soon as it comes out of the tree gets contaminated with bacteria. By the time the latex is collected, the microbial population reaches about 10^5 to 10^6 /ml. Using the sugars in latex as substrate, the microorganisms liberate volatile fatty acids (VFA) in latex and tend to destabilise it.

All the above requirements are met by ammonia. P^H of ammoniated latex is about 9.8 to 10.2. Metals like magnesium are precipitated as hydroxide or as magnesium ammonium phosphate in the presence of externally added phosphate or that are generated in latex by hydrolysis of phospholipids. Microorganisms are killed by ammonia at concentrations above 0.35%, the rate of annihilation depending on ammonia concentration. Further, ammonia is a readily available chemical and can be easily handled. Hence ammonia was used as a preservative for several decades.

The state of preservation of latex is expressed by its VFA number. VFA number is defined as the number of grams of potassium hydroxide required to neutralise the volatile fatty acids present in a quantity of latex equivalent to 100g total solids. For a well preserved latex, VFA number is low, say in the range of 0.01 – 0.03, when it is freshly processed.

Limitations of High Ammonia (HA) Latex

1. Increase in VFA of HA latex during storage

It is generally observed that even in the case of a well preserved latex there is a steady increase in VFA number during storage. This is attributed to the activity of some bacteria which build up resistance to ammonia in latex, that is, a still stronger biocide is needed for the long term preservation of latex. However, for a well preserved latex, the increase in VFA number during storage is very small.

2. Latex stability during long term storage

The mechanical and chemical stability of concentrated HA latex increases during storage and attains a maximum value in 20-30 days. The high stability is maintained more or less constant for about another one month or so and then slowly declines. Concentrated latex needs a reasonably high stability for atleast 6 months or so.

3. **Surface skin formation**

   HA latex concentrate readily forms a surface skin on exposure to air, as the preservative ammonia escapes from the surface.

4. It is a common practice to allow latex compound to mature say for 1-4 days, for the better behaviour of compounded latex during product manufacture. Ammonia preserved natural latex undergoes a marked and progressive thickening when compounded with sparingly soluble zinc compounds, especially zinc oxide. After a sufficient time has elapsed the latex may gel. The rate of this thickening and subsequent gelation increase markedly with temperature.

5. Ammonia interferes with the gelation of natural rubber latex by sodium silico fluoride, during latex foam manufacture by the Dunlop process. This is because ammonia provides a source of hydroxide ions which have to be removed by the reaction with the H^+ ions generated by the hydrolysis of silico fluoride anions before the pH can be reduced to a value at which gelation can occur. It is therefore necessary to reduce the ammonia content in HA latex to a low level, prior to the use of silico fluoride as delayed action gelling agent.

6. The consumption of coagulant in dipping process and during the extrusion of latex thread will be high as the ammonia content in the compounded latex increases.

7. When HA latex is deammoniated prior to compounding for foam manufacture, the air in the factory floor is contaminated. Also some rubber will be lost by adhering to the walls of the deammoniation device.

Considering these drawbacks, it was thought advisable to have a preservation system, with lesser amount of ammonia, the reduction in ammonia content being compensated by some other biocides.

The table below gives the major low ammonia system that were introduced during the fifties.

Table 4 – Major Low Ammonia System

Sl. No.	Preservation System	Preservatives used
1	LA – SPP	0.2% ammonia + 0.2% sodium pentachlorophenate
2	LA – BA	0.2% ammonia + 0.2% boric acid + 0.05% lauric acid
3	LA – ZDC	0.2% ammonia + 0.1% zinc diethyl dithiocarbamate + 0.05% lauric acid

Several other systems containing different rubber accelerators and oximes were also tried.

However the above 3 systems failed to have any serious impact on the latex industry. The major drawbacks of the systems were:

1. High toxicity and poor film colour in the case of LA-SPP latex.
2. Low MST and poor storage stability in the case of LA-ZDC latex.
3. Poor chemical stability to added zinc oxide and slow cure in the case of LA-BA latex.

LATZ Latex

To overcome the above said drawbacks of low ammonia latices, composite preservation system containing ammonia, TMTD and zinc oxide was introduced in 1975. This latex, now popularly known as LATZ, use the following chemicals for preservation.

Ammonia - 0.2 – 0.3%
TMTD - 0.0125%
ZnO - 0.0125%

TMTD (tetra methyl thiuram di sulphide) and Zinc oxide being water insoluble are added to latex as fine dispersion by ball milling.

LATZ system of preservation can be applied to both field latex and concentrated latex. Also there is a practice of using this low ammonia system for field latex preservation and after centrifugal concentration the concentrated latex is marketed as HA latex.

Typical raw latex properties of LATZ are given in the table. Typical figures for HA latex are given for comparison.

Table 5 – Latex properties of LATZ System

Sl. No.	Property	HA	LATZ
1	TSC %	61.74	61.76
2	DRC %	60.10	60.12
3	NRS %	1.64	1.64
4	Alkalinity as ammonia %	0.68	0.21
5	PH	10.65	10.08
6	VFA No.	0.07	0.05
7	KOH No.	0.63	0.58
8	MST (Sec)	1168	1131
9	ZST (Sec)	223	352
10	Viscosity (cps)	77	70
11	Nitrogen on TS%	0.29	0.28

Several of the drawbacks associated with the HA latex are eliminated/minimised in LATZ latex.

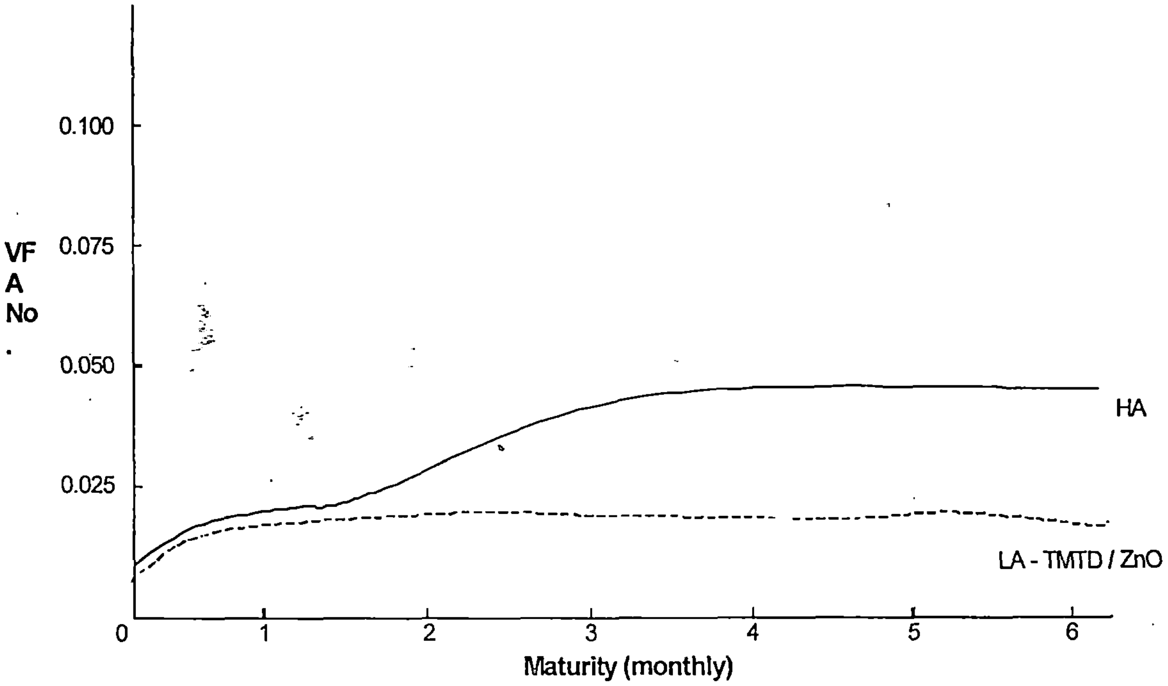
Properties of LATZ latex

LATZ latex has excellent preservation and storage properties. The table below gives the VFA number and microbial population of centrifuged latex after storage for one month and the figure gives the type of variation during a period of 6 months, for both HA and LATZ latex, prepared from the same bulk of field latex.

Table 6 – Properties of centrifuged latex

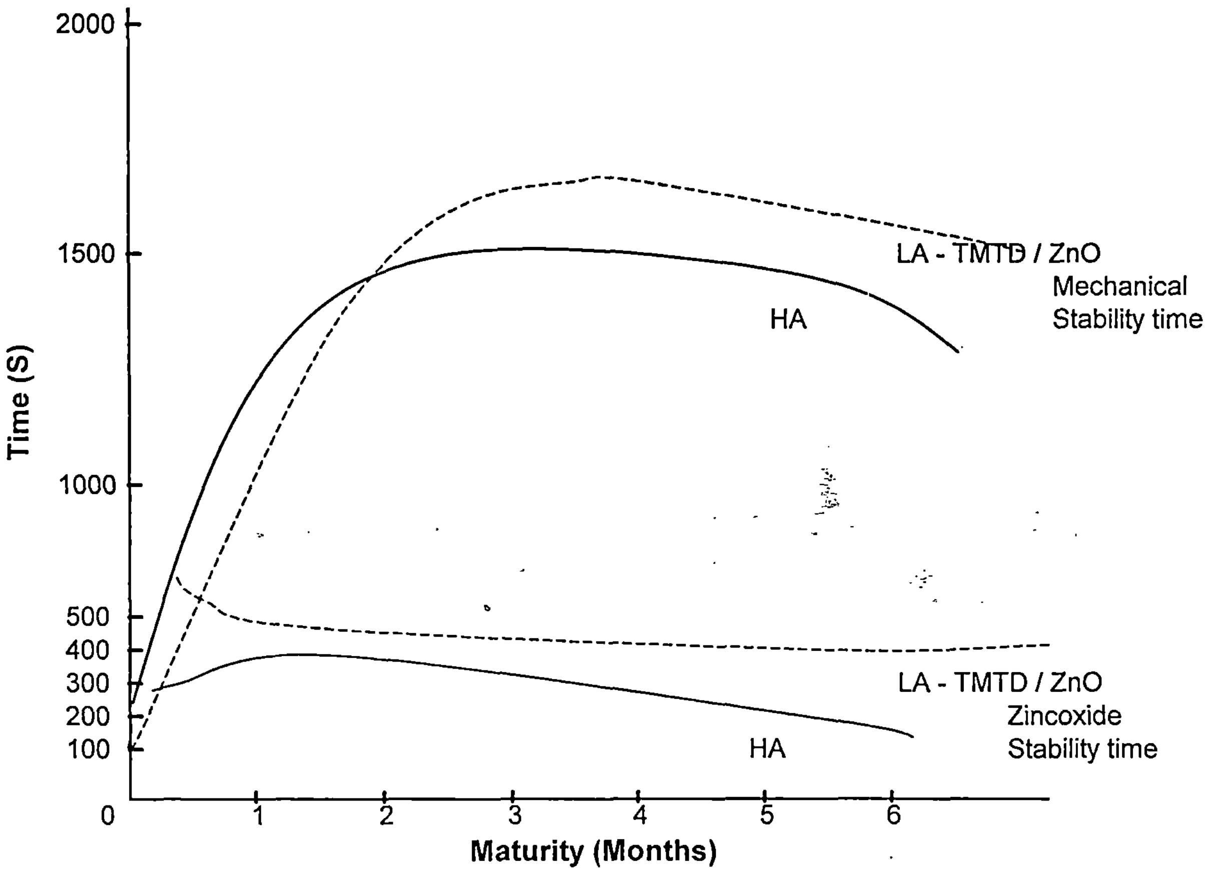
Property	HA	LATZ
VFA number	0.05	0.01
Bacterial count (log/ml)	2.78	nil

Figure 4 – Volatile fatty acid number development



The MST of both HA and LATZ latex reaches a maximum value in about a month time. In the case of HA latex, MST remains more or less constant for about 2 months or so and slowly declines. However, for LATZ latex, there is practically no fall in MST when stored for about 6 months. The absence of fall in MST for LATZ latex may be due to lesser hydrolysis of proteins and absence of viable bacteria. During storage, generally the ZST of LATZ latex is better than that of HA latex. The variation of MST and ZST during storage of both HA and LATZ latices are given in the figure.

Figure 5 – Latex stability and maturity



LATZ performs well in Zinc Oxide Viscosity (ZOV) tests. It is also highly suitable for applications where high shear is involved. LATZ latex gives a light coloured film, good compound behaviour and excellent precure and vulcanizable properties. The latex is eminently suitable for a broad range of application including dipped goods, foam, latex adhesive, binder and carpet backing.

Reasons for the superiority of LATZ system as a preservative

A preservative for natural latex should be alkaline and this function is done by ammonia, which is normally added up to 0.2 – 0.3%. The preservative should be a powerful bactericide, but ammonia at this level has only weak bactericidal activity. There are thiol groups in the serum of natural latex, originating from sulphur containing proteins or amino acids like cysteine and glutathione. TMTD reacts with these thiol groups to give dithio carbamic acid. Zinc ions reacts with dithiocarbamic acid to form zinc dimethyl monothio carbamate, which is a very powerful bactericide. Further TMTD protects the proteins and keeps it in the native state and prevents it from being denatured. Denatured protein is attacked by alkali and proteolytic enzymes, while native protein is not attacked. The protein is kept in the native state, by the TMTD, reacting with the thiol groups in proteins to form mixed disulphides.

The most important sugar in latex is sucrose, present at 0.1 to 1% on the weight of latex and is converted by the enzyme invertase to glucose and fructose. These lower sugars are converted by bacteria to volatile fatty acids, especially acetic acid. The enzyme invertase contains a thiol group and TMTD reacts with it, by thiol-disulphide interchange and inactivates the enzyme. Thus TMTD functions as an enzyme poison.

Finally, those bacteria which build up a resistance to ammonia, are mainly proterolytic bacteria such as Bacillus subtittis, which produce the enzyme proteoses which degrades the proteins. These proteoses are also thiol containing enzymes and TMTD reacts with them.

Thus, LATZ system provides excellent short/long term preservation to natural latex. From the above discussions it is clear that LATZ latex has definite technical advantages over HA latex, and the Indian latex industry can very well accept this raw material[13].

1.2.11. <u>Concentration of latex</u>

Natural rubber latex exudes from the tree with a dry rubber content of 30 to 40% the average being 33%. It is therefore, uneconomical to transport preserved field latex over large distances. The normal procedure is to concentrate it to about 60% dry rubber content. The transportation of such concentrates is clearly more economic. Further more, many important processes require a high DRC latex concentrate of minimum 60% rubber content as the main raw material. An example is manufacture of latex foam rubber. Additionally, latex concentrates are more uniform in quality and have a higher degree of purity.

Concentration of natural rubber latex can be usually achieved by any of the following methods.

1. Centrifuging
2. Creaming

Centrifuging is the most popular and widely used technique for the manufacture of concentrated latex. This is because, the quality of the concentrate is excellent for use in the manufacture of any type of latex product.

But the cost of centrifuged latex is high and it is not possible for small manufactures to invest on a very costly machine like the latex centrifuge.

Creaming of latex is done with the use of material known as creaming agents. This process is simple and involves only simple machinery and low power consumption. Hence small scale latex goods manufacturers can produce concentrated latex by this technique[14].

1.2.12. 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 latter stages of the process.

Commercial application 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 tearing, 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' gloves, household gloves, electricians' glove and heavy industrial gloves, etc.

Interest in the possibility of using polymer latices as components of drug delivery systems has arisen from the conjunction of three considerations: (1) the possibility that the taking of the drug can thereby be facilitated; (2) the possibility that the rate of release of the drug into the body can be controlled; (3) the possibility that the drug can be 'targeted' by making the latex particles immunospecific. It has been claimed that acetylsalicylic acid which has been immobilized on negatively charged latex particles can readily be administered orally, and that the acetylsalicylic acid is then slowly released into the alimentary canal if the bond by which the drug is attached to the particle surface is capable of being cleaved by acid-catalysed hydrolysis. It has further been claimed that the release reaction can be catalysed by hydrogen ions the concentration of which has been enhanced in the vicinity of the negatively charged particles surface. Interest has also been shown in the possibility of physically entrapping drugs in latex particles, with the intention that subsequently the drug should be slowly released into the patient. The smaller the latex particle, the faster was found to be the rate of subsequent release. The order in which the drug and the latex were combined did not affect the rate of release, nor did the use of a dicarboxylic acid such as succinic acid, as an entrapment facilitator.

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 threads and rubberized hair are examples. Polymer latices are also utilized in paper treatment, such as beater addition, saturation of the dry paper, surface coating of paper etc[15].

REVIEW OF LITERATURE

The Volatile Fatty Acid Number test was developed by Philpott and Sekar. Their observations, published in 1953, form the basis of the current test method.

The formation of volatile fatty acid anions in fresh natural rubber latex is illustrated by E.H. Lowe.

Blackley has defined volatile fatty acid number as the number of grams of potassium hydroxide equivalent to the anions present as salts of steam - volatile acids in a quantity of latex which contains 100 grams of total solids.

Studies on the Improvements in the preservation of latex was done by Sekar. K.C. Hevea latex concentrate containing less than 0.5% and more than 0.15% ammonia is preserved by the addition of a selenium alkyl dithiocarbamate (e.g. selenium diethyl dithiocarbamate). Between 0.01% and 0.1% of a surfactant (e.g. ammonium laurate) also may be added.

Another invention by Lowe J.S and Taysum. D.H relates to the preservation of latex and latex concentrates by the addition of antibiotics. Known latex preservatives permit the survival of bacteria. Antibiotics, e.g. penicillin, streptomycin, oxytetracycline, chlortetracycline and chloramphenicol, are claimed as preservatives for natural rubber latex and these can be sprayed on the tapping panel, poured into the tapping cup, or added to the latex at the collecting station. The latex is then concentrated and a detergent, which may or may not be bactericidal, or stabilising soap is added to increase its mechanical strength

Another study by Sekar. K.C and Morris. J.E relates to the preservation of natural rubber latex, both on short or long term basis. On a short-term basis, anti-coagulants are added to the latex prior to the making of sheet and crepe, and temporary preservatives are added to it prior to the preparation of concentrate. On a long-term basis, it is for the preservation of latex concentrates during shipment and storage prior to use. The temporary preservation of fresh latex is of importance in avoiding blemishes in sheet rubber produced from the latex, particularly bubbles and dark colourations. The additives of this specification, ammonia and boric acid are superior to formaldehyde and ammonia in that a sheet of light colour is produced[16].

To prevent putrefaction, auto coagulation and development of high VFA's in natural rubber latex, preservatives are used. Studies of Ng chew sum[17] show usage of various commercial chemicals for latex preservation.

Another study on the requirements of an ideal preservation for natural rubber latex was done by Dr. M. Sunny Sebastian[18]. Latex preservation systems involves the use of low ammonia and a non polluting secondary preservative or low ammonia and a synergistic mixture of two or more preservatives. For long term preservation, LATZ system was found to be more effective.

Chapter – 2

EXPERIMENTAL TECHNIQUES

EXPERIMENTAL TECHNIQUES

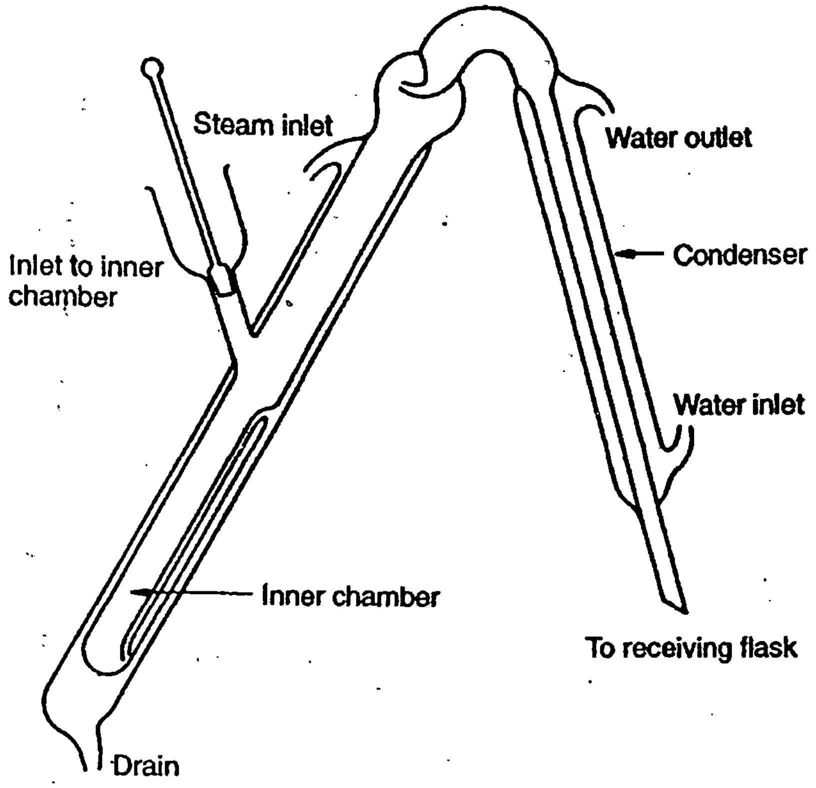
2.1. Materials used

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

2.2. Equipment used

Markham still Apparatus[19]

Figure 5 - Illustrating the Markham Semi-micro still for carrying out the steam-distillation step of the determination of volatile fatty acid number



2.3. Chemicals used

Glacial acetic acid

Ammonium Sulphate

Barium hydroxide

Potassium hydrogen phthalate

Antifoaming agent – silicon type

Phenolphthalein indicator

2.3.1. Preparation of 2% acetic acid solution

Dissolve 2ml glacial acetic acid in water and make up to 100 ml.

2.3.2 Preparation of 30% Ammonium sulphate

Dissolve 30g ammonium sulphate in water and make up to 100 ml.

2.3.3. Preparation of 0.02 N Barium hydroxide solution

3.5g of barium hydroxide is dissolved in ~~500~~ 1000ml water.

2.3.4. Preparation of 0.02N potassium hydrogen phthalate

1.0211g of potassium hydrogen phthalate is dissolved in water and made up to 250ml.

2.3.5. Standardisation of Barium hydroxide

Barium hydroxide solution is standardized by potassium hydrogen phthalate using phenolphthalein as indicator. End point is the appearance of pale pink colour.

Experiment No: 1

Determination of Dry Rubber Content (DRC)

Apparatus

Balance (Max wt = 200g)

Conical Flasks (50ml, 250ml)

Beaker (250ml)

Rollers

Oven

Reagents

2% acetic acid solution.

Procedure

Weigh about 15g of the well mixed sample accurately to 1 mg in a 250ml beaker from stoppered conical flask. Add about double the amount of water for both field latex and concentrated latex, and well mix. Keep the diluted latex for 15-20min. Add about 2 to 3 ml of acetic acid per gram of sample with gentle stirring. Keep the solution undisturbed for about 15 minutes in a water bath, if the serum remains milky add about 5ml of rectified spirit per gram of the sample and gently stir. When the serum is clear filter the serum through Whatman No. 1 filter paper. Collect any small particular of coagulum by rubbing with main bulk. Thickness of the coagulum is reduced to about 1mm either by hand roller or other devices such as mechanical roller. Wash the coagulum with running water with at least six changes of water. Dry the coagulum at a temperature of approximately 70 ± 2°C. Cool in a dessicator and weigh. Determination must be duplicated.

Calculations

$$\text{DRC} = \frac{W_1}{W_2} \times 100$$

W_1 = Weight in grams of dried film.

W_2 = Weight in grams of latex sample taken[20].

Table 7.a - Determination of DRC

Sample	Weight in grams of latex taken (W_2)	Weight in grams of dried film (W_1)	DRC = $\frac{W_1}{W_2} \times 100$
1	10.9304	3.4350	31.4261
2	12.8614	4.0432	31.4367

Mean DRC = 31.43

Table 7.b - Determination of DRC

Sample	Weight in grams of latex taken (W_2)	Weight in grams of dried film (W_1)	DRC = $\frac{W_1}{W_2} \times 100$
1	15.4968	4.6124	29.7635
2	12.2346	3.6444	29.7876

Mean DRC = 29.77

Experiment No. 2

Determination of Total Solids (TS)

Apparatus

Balance (max wt 200g)

Conical flasks (50 ml)

Petridishes (60 mm diameter)

Oven

Reagents

Nil

Procedure

Take about 20ml of the well mixed sample in a stoppered conical flask. Weigh to the nearest 0.01g. Pour about 2g of the sample into previously weighed petridish of about 60mm. diameter and weigh to obtain the weight of latex taken from the difference. Swirl the petridish gently to ensure that latex covers the bottom of the dish. Dry the test portion in an air oven at a temperature of 70°C for 16 hours. (cool in a dessicator and weigh as quickly as possible). Repeat the drying operation until the loss in weight is less than 1mg during a period of 30 months for temperature between 70°C and 75°C.

Calculations

$$\text{Total solid percent by weight} = \frac{W_1}{W_2} \times 100.$$

W_1 = Weight in grams of dried film.

W_2 = Weight in grams of latex sample taken for test[21].

Table 8.a - Determination of TS

Sample	Weight of petridish in grams (W_a)	Weight of petridish of dry film in grams (W_b)	$W_1 = W_b - W_a$	Weight of latex taken W_2 grams	TS% by weight = $\frac{W_1}{W_2} \times 100$
1	18.241	18.645	0.404	1.139	35.4697
2	18.290	18.718	0.428	1.216	35.1973

Mean TS = 35.33

Table 8.b - Determination of TS

Sample	Weight of petridish in grams (W_a)	Weight of petridish of dry film in grams (W_b)	$W_1 = W_b - W_a$	Weight of latex taken W_2 grams	TS% by weight = $\frac{W_1}{W_2} \times 100$
1	18.9525	19.7078	0.7553	2.2549	33.4959
2	18.2383	18.8593	0.6210	1.8500	33.5676

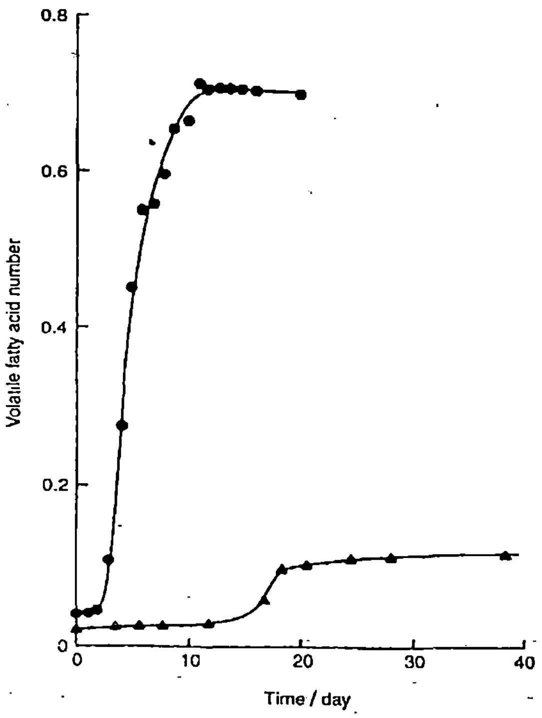
Mean TS = 33.53

Formation of the anions of volatile fatty acids

The principal facts relating to the formation of the anions of the volatile fatty acids, and to the microorganisms responsible for their formation, appear to be as follows:

1. The natural rubber latex in the latex vessels is believed to be substantially free from bacteria.
2. Bacterial infection of fresh natural rubber latex can arise from many sources, such as the atmosphere the bark of the tree and the utensils used for the tapping process. An annulus of bacteria and coagulated rubber particles may form around the top of the severed latex vessels, causing infection of any latex which subsequently flows from the tree.
3. The manner in which the voltatile fatty acid anions develop in fresh natural rubber latex is illustrated by results reported by Lowe[22].

Figure 7 - Development of voltaic fatty acid anions in fresh (points●) and ammonia-preserved (points▲) natural rubber latex.



After a short induction period, the concentration of these anions increase rapidly over a period of a few days, until a stage is reached after which very little further increase occurs. These characteristics suggest an enzyme catalyzed process. It is presumed that the enzymes are of bacterial origin. The eventual decline of the rate of formation of the volatile fatty acid anions to effectively zero implies either that the substrate for the process has become exhausted, or that enzymes have become deactivated.

4. The manner in which the volatile fatty acid anions form in ammonia – preserved natural rubber latex is also shown in the figure. It is qualitatively similar to that in which they develop in the fresh latex. However, the induction period is longer, and the increase in the concentration of these anions during the period of rapid formation is greatly reduced.

5. The substrate for the formation of the volatile fatty acid anions is believed to be the various carbohydrates which are present in the aqueous phase of the latex. Additional anions are formed if sugars, notably glucose, are added to the latex, However, Lowe has stated that quebrachitol is not a substrate. Amino acids stimulate the formation of the volatile fatty acid anions, probably by activating the sugars, rather than by acting as substrates themselves. The initial stage of the process whereby volatile fatty acid anions are formed may be the formation of a sugar – amino acid complex. Citric 2-hydroxy –1, 2, 3 – propane tri-carboxylic acid and malic (1-hydroxy –1, 2-ethane dicarboxylic) acids also have a stimulating effect.

Protein do not appear to be substrates in themselves, but, by partial hydrolysis to amino acids, may bring about activation of other substrates.

6. The formation of the volatile fatty acid anions is progressively inhibited by increasing concentrations of ammonia[23].

Experiment No. 3

Determination of Volatile Fatty Acid (VFA) Number

Apparatus

Balance (max wt. = 200g)

Beaker (250 ml)

Water bath

Markham semi-micro still apparatus

Burette (10ml x 0.01)

Pipette (10ml)

Reagents

30% Ammonium sulphate aqueous solution.

50% Sulphuric acid aqueous solution.

Standardised Barium hydroxide solution (0.02 N)

Antifoaming agent - Silicon type.

Procedure

Weigh about 50g to the nearest 0.1g of known dry rubber and solids content into a beaker. Add 50ml ammonium sulphate solution and stir the mixture warming over a water bath until the latex thickens and coagulates. Press the serum out of the coagulum by kneading with a glass rod or pestle and filter through a dry filter. Introduce 10ml of the serum by pipette to the Markham still apparatus with steam passing through the outer jacket of the apparatus (steam outlet open) into the inner tube. Also add 2ml 50% sulphuric acid and 2 drops of antifoaming agent. Pass steam gently first then close the steam outlet fully and continue distillation at a rate of approximately 200ml per hour until 100ml of distillate collects. Titrate the distillate with standardised $Ba(OH)_2$ solution. The $Ba(OH)_2$ solution is standardized with potassium hydrogen phthalate.

Calculations

$$\text{VFA Number} = \frac{0.55 \times N \times V\ (202 - DRC)}{TS}$$

N = Normality of $Ba(OH)_2$.

V = Volume in ml of $Ba(OH)_2$[24].

Chapter – 3

LOW AMMONIA – BORIC ACID SYSTEM FOR LATEX PRESERVATION

LOW AMMONIA – BORIC ACID SYSTEM FOR LATEX PRESERVATION

3.1. Volatile Fatty Acid (VFA) Number

The Volatile Fattty Acid (VFA) number is defined as the number of grams of potassium hydroxide equivalent to the anions present as salts of steam-volatile acids in a quantity of latex which contains 100grams of total solids.

The Volatile Fatty Acid number test was developed by Philpott and Sekar. Their observations, published in 1953, forms the basis of the current test method.

The principal steam – volatile acids, the anions of which are assayed by the procedure for determining VFA number, are formic, acetic and propionic. Of these, acetic is the most prominent. The anions are formed by the action of microorganisms, especially bacteria, upon certain of the carbohydrates which are present in the aqueous phase of the latex. Ammonia and other bactericidal preservatives retard the formation of these anions. For this reason, the VFA content of an ammonia preserved natural rubber latex gives an indication of the extent of microorganic activity which has occurred during the time since the latex exuded from the tree. Boric acid appears to be particularly effective as an inhibitor of the formation of volatile fatty acid anions. There is good evidence that the VFA content of the latex in the vessels of the tree is almost zero. Higher the VFA number of natural rubber latex, the lower is the latex quality.

In outline, the VFA number of natural rubber latex is determined by separating the constituents of the aqueous phase from a specified mass of latex, and then subjecting those constituents to steam distillation after acidification by addition of a strong acid. Because acids such as acetic acid are weak, their anions are converted to the free acid by acidification with a strong acid. After separation by steam distillation, the volatile fatty acids are assayed by titration with standard aqueous alkali solution.

Philpott and Sekar developed two methods of estimation.

1. One which involved a macro scale constant volume steam distillation for which the aqueous phase from an acid-coagulation process was preferred.
2. A second procedure which involved a micro scale total – recovery steam distillation, in which the aqueous phase was obtained by the use of ammonium sulphate as a neutral coagulant. The slow, even colloidal destabilization of natural rubber latex which is effected by this reagent was found to be especially convenient.

The following additional comments may be noted.

1. The success of the semi-micro scale procedure for determining the VFA number depends upon the recovery of steam – volatile acids being effectively complete.

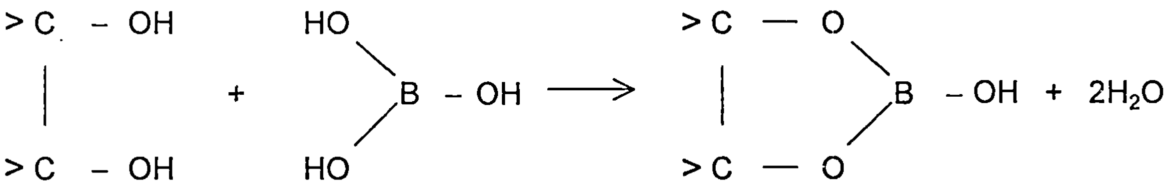
2. According to Philpott and Sekar the acidity of the liquid which is being distilled should be at least 1.5N, because ammonium sulphate solutions of lower acidity tend to release traces of ammonia during steam distillation.
3. The reason why barium hydroxide is used as the alkali for the titration is that any carry-over of liquid into the distillate is immediately revealed by the appearance of turbidity in the titration vessel when the barium hydroxide solution is run in, caused, of course, by the precipitation of barium sulphate.

Boric acid appears to be particularly effective as an inhibitor of the formation of the volatile fatty acid anions. The low concentrations of these anions in ammonia-preserved natural rubber latex which contains boric acid as a secondary preservative has been attributed to a number of causes. These include.

a. Inhibition of the enzymes which catalyze the formation of the volatile fatty acid anions.
b. Deactivation of the microorganisms which produce the enzymes which catalyse the formation of the volatile fatty acid anions.
c. Sequestration, by chelate complex formation, of the carbohydrates which function as substrates for the formation of the volatile fatty acid anions, thereby preventing the formation of the requisite sugar – amino acid complex.

d. The possible ability of borates to inhibit a switch from the krebs cycle to a cycle which results in the formation of the volatile fatty acid anions.

As regards explanation (c), it is well known that boric acid can interact with the hydroxyl groups attached to adjacent carbon atoms in carbohydrate molecule as follows.



As regards explanation (d), this carries the implication that the anions of non-steam volatile fatty acids of higher molecular mass than the volatile fatty acid anions may be formed instead of the latter[25].

3.2. Experimental

In processing of concentrated latex, it is a usual practice to store latex for a few days, sometimes even a month or two or even more. For long term preservation of natural latex, the LATZ system was found to be more effective than HA system. However, LATZ system had the following drawbacks.

- The chemical stability of concentrated latex and its compounded latex generally show lower chemical stability.
- TMTD (tetramethyl thiuram disulphide) is likely to generate harmful nitrosamines in latex products.

In this study, boric acid was used as the secondary preservative.

Two major trials were conducted

- ☐ In the first trial, ammonia concentration was held constant at 0.2% and concentration of boric acid was varied, in the concentration range 0 to 0.6% .
- ☐ In the second case, boric acid concentration was held constant at 0.4% and the concentration of ammonia was varied.

Chapter – 4

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

3.1 Effect of Variation of boric acid concentration in latex on VFA development

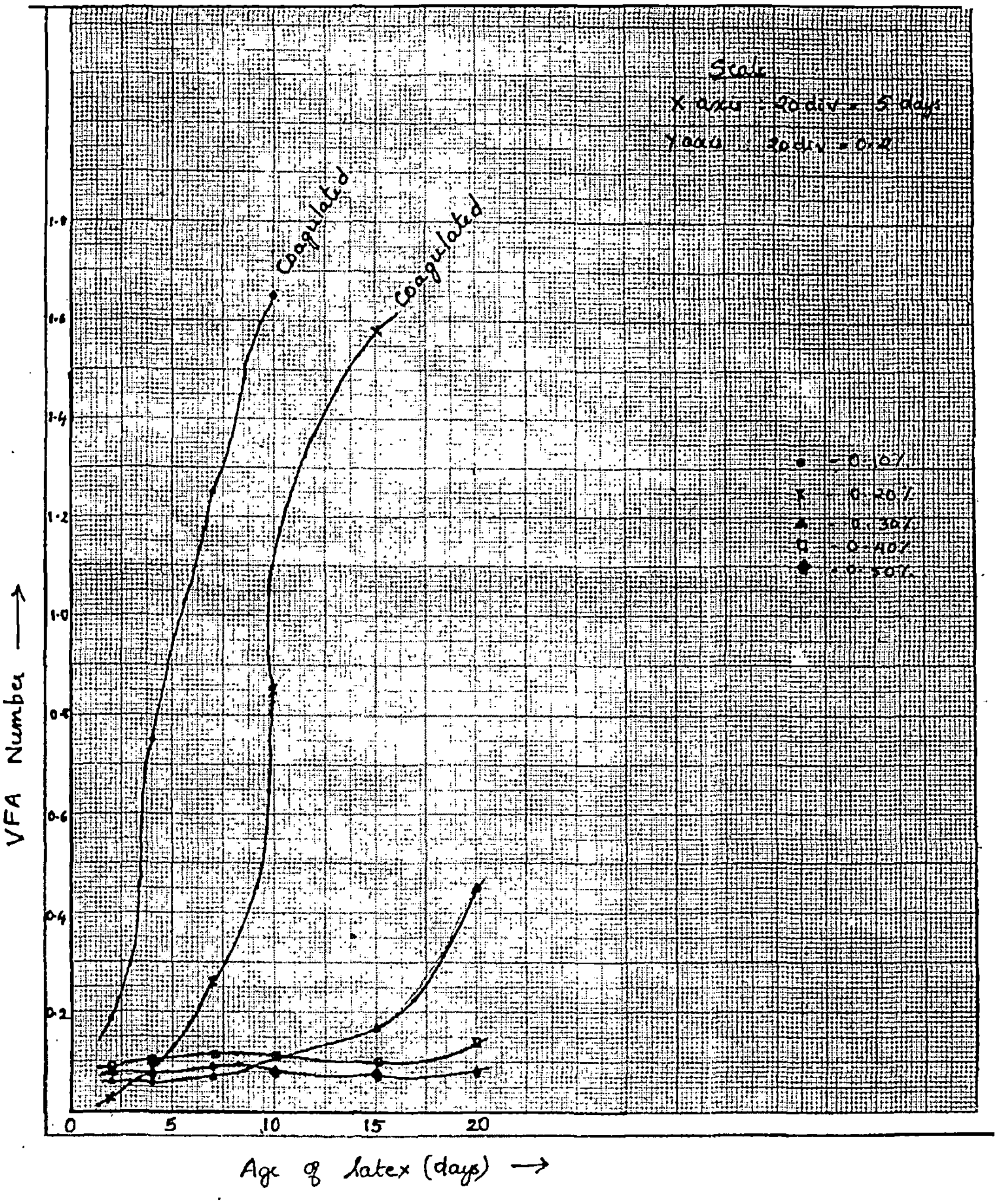
With 0.2% Ammonia, concentration of boric acid is varied and VFA number of the latex is determined.

Table 9.a - Determination of VFA No.

	VFA Number
Fresh latex	0th day
	0.0794

Concentration of Boric acid %	Volatile Fatty Acid (VFA) Number					
	2nd day	4th day	7th day	10th day	15th day	20th day
0.1%	0.1954	0.7511	1.2540	1.6588	Coagulated	Coagulated
0.2%	0.0366	0.0916	0.2626	0.8507	1.5873	Coagulated
0.3%	0.0611	0.0672	0.0727	0.1134	0.1712	0.4539
0.4%	0.09770	0.1043	0.1194	0.1134	0.108	0.1480
0.5%	0.081	0.0872	0.0872	0.0879	0.0893	0.0882

Figure 8.a - Effect of Variation of boric acid concentration on the state of preservation of latex



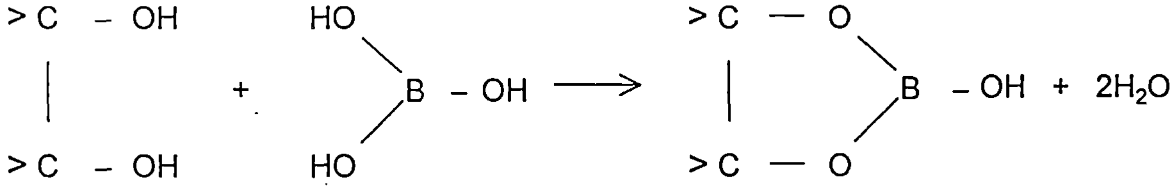
The results obtained in the study are presented in Figure-8.a. The results indicate that at concentrations of 0.1% & 0.2% boric acid, the latex coagulated after a few days of storage. However, beyond a concentration of

0.4%, there was practically no effect on further increase in concentration of boric acid.

The low concentrations of these anions in ammonia-preserved natural rubber latex which contains boric acid as a secondary preservative has been attributed to a number of causes. These include.

a. Inhibition of the enzymes which catalyze the formation of the volatile fatty acid anions.
b. Deactivation of the microorganisms which produce the enzymes which catalyse the formation of the volatile fatty acid anions.
c. Sequestration, by chelate complex formation, of the carbohydrates which function as substrates for the formation of the volatile fatty acid anions, thereby preventing the formation of the requisite sugar – amino acid complex.
d. The possible ability of borates to inhibit a switch from the krebs cycle to a cycle which results in the formation of the volatile fatty acid anions.

As regards explanation (c), it is well known that boric acid can interact with the hydroxyl groups attached to adjacent carbon atoms in carbohydrate molecule as follows.



As regards explanation (d), this carries the implication that the anions of non-steam volatile fatty acids of higher molecular mass than the volatile fatty acid anions may be formed instead of the latter.

3.2 Effect of variation in the concentration of Ammonia in latex to control VFA in latex containing boric acid

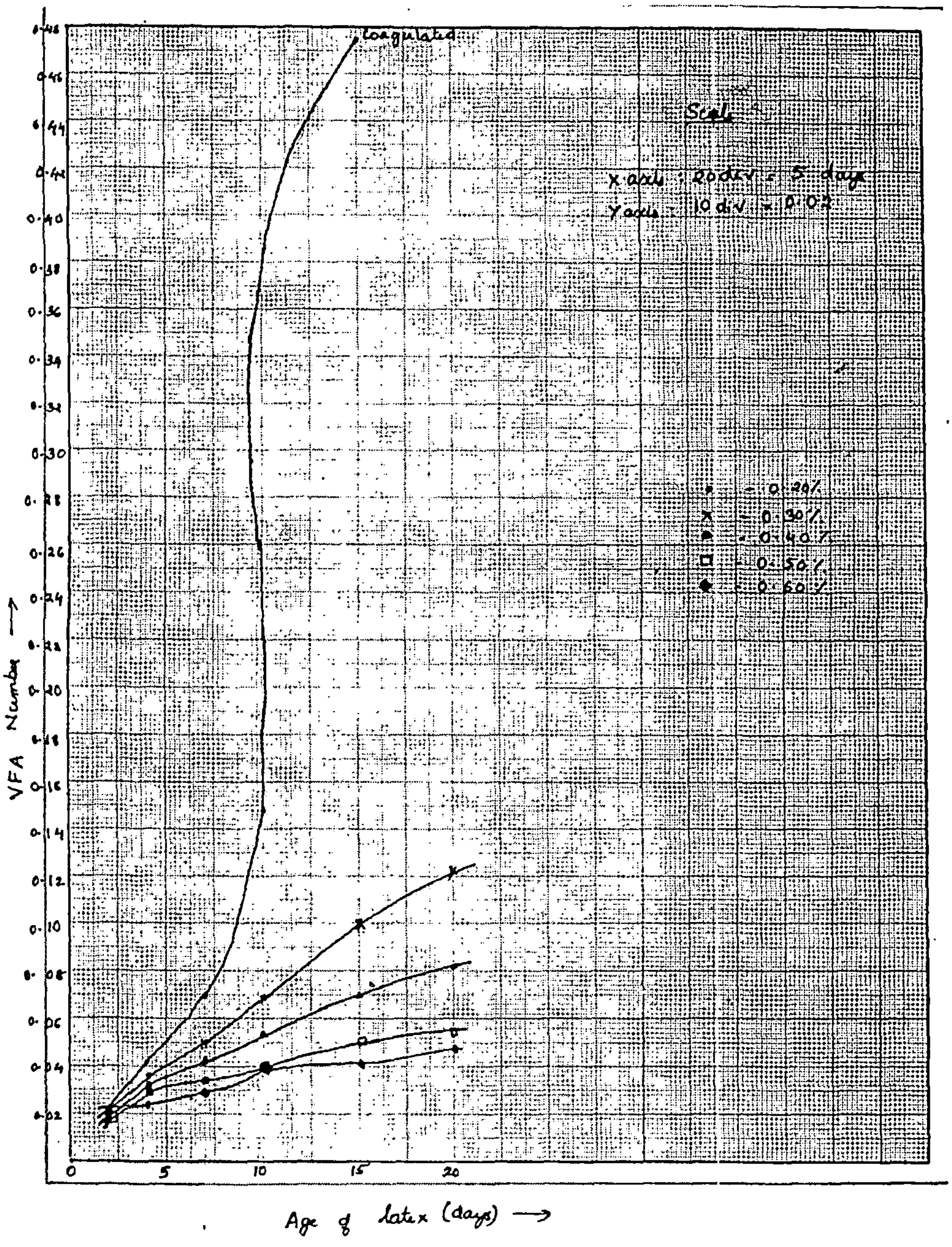
With 0.4% boric acid, concentration of Ammonia is varied and the VFA number is determined.

Table 9.b - Determination of VFA Number

Fresh latex	VFA Number
	0th day
	0.0276

Concentration of Ammonia %	Volatile Fatty Acid (VFA) Number					
	2nd day	4th day	7th day	10th day	15th day	20th day
0.2%	0.02262	0.04262	0.0710	0.1483	0.4774	Coagulated
0.3%	0.02262	0.036	0.0521	0.068	0.105	0.12
0.4%	0.02016	0.03453	0.0425	0.0540	0.07014	0.0821
0.5%	0.02016	0.03061	0.0354	0.0415	0.0502	0.0559
0.6%	0.02262	0.026	0.0310	0.0401	0.042	0.048

Figure 8.b - Effect of variation of Ammonia concentration on the state of preservation of latex

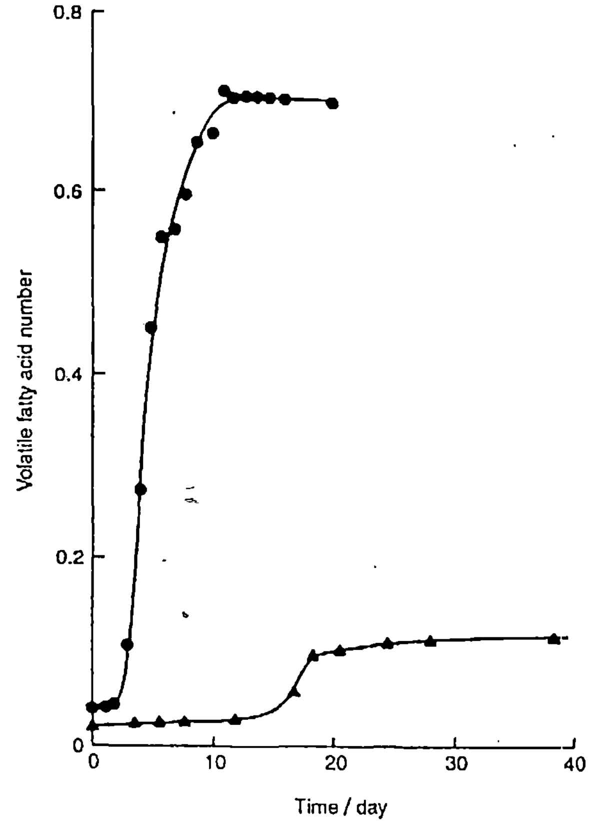


The results obtained in the study are presented in the figure-8.b. The results indicate that at 0.2% concentration of ammonia, the latex coagulated on the 20th day. However beyond a concentration of 0.3% of ammonia containing

0.4% boric acid practically no effect was observed on the colloidal stability of latex. No increase in VFA number was observed.

The manner in which the volatile fatty acid anions develop in fresh natural rubber latex is illustrated by results reported by Lowe.

Figure 9 - Development of volatile fatty acid anions in fresh (points●) and ammonia-preserved (points▲) natural rubber latex.



After a short induction period, the concentration of these anions increases rapidly over a period of a few days, until a stage is reached after which very little further increase occurs. These characteristics suggest an enzyme catalyzed process. It is presumed that the enzymes are of bacterial origin. The eventual decline of the rate of formation of the volatile fatty acid anions to effectively zero implies either that the substrate for the process has become exhausted, or that enzymes have become deactivated.

The manner in which the volatile fatty acid anions form in ammonia – preserved natural rubber latex is also shown in the figure. It is qualitatively similar to that in which they develop in the fresh latex. However, the induction period is longer, and the increase in the concentration of these anions during the period of rapid formation is greatly reduced.

The substrate for the formation of the volatile fatty acid anions is believed to be the various carbohydrates which are present in the aqueous phase of the latex. Additional anions are formed if sugars, notably glucose, are added to the latex, However, Lowe has stated that quebrachitol is not a substrate. Amino acids stimulate the formation of the volatile fatty acid anions, probably by activating the sugars, rather than by acting as substrates themselves. The initial stage of the process whereby volatile fatty acid anions are formed may be the formation of a sugar – amino acid complex. Citric 2-hydroxy –1, 2, 3 – propane tri-carboxylic acid and malic (1-hydroxy –1, 2-ethane dicarboxylic) acids also have a stimulating effect. Protein do not appear to be substrates in themselves, but, by partial hydrolysis to amino acids, may bring about activation of other substrates.

The formation of the volatile fatty acid anions is progressively inhibited by increasing concentrations of ammonia.

Chapter - 5

CONCLUSION

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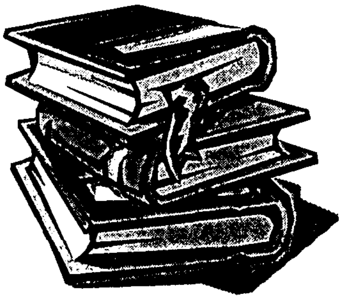
Following conclusions are derived from the above study.

- ☐ Boric acid in presence of ammonia, can function as a secondary preservative for natural rubber latex. Optimum concentration is found to be 0.4%.
- ☐ For effective control of VFA in latex, in presence of 0.4% boric acid, a minimum of 0.3% ammonia is necessary for long term preservation.
- ☐ A composite system consisting of 0.3% ammonia and 0.4% boric acid is recommended for long term preservation of natural latex.



REFERENCE

REFERENCES

1. ***Rubber Engineering.*** Indian Rubber Institute Tata McGraw-Hill Publishing Company Ltd., New Delhi. p 419-421.
2. Reference 1. p 425.
3. ***Rubber Grower's Companion*** *2007.* p 57.
4. Reference 3. p 33
5. D.C. Blackley, ***Polymer Latices Science and Technology Types of Latices.*** Second Edition Volume 2. Chapman & Hall, London. p 78-99
6. Carrol C. Davis, John T. Blake, ***The Chemistry and Technology of Rubber.*** Book Department Reinhold Publishing Corporation New York, USA (1937). p 604.
7. Reference 6. p 600-602.
8. Reference 3. p 53
9. Dr. E.V. Thomas, ***Composition, Collection and Preservation of Field Latex. Training Manual Rubber Goods Manufacture from Latex.*** Rubber Board, Kottayam. p 1-3.
10. R.J. Noble, ***Latex in Industry*** Second Edition (1953)
11. Reference 9. p 3
12. A.D. Roberts, Natural Rubber Science And Technology. Oxford University Press (1988).
13. Dr. M. Sunny Sebastian, ***Comparison of Properties of HA and LATZ*** **Latices.** Paper presented at Seminar on ***LATZ LATEX*** In Mumbai.

Department of Processing & Product Development, Rubber Board (1998). p 11-17.

14. Dr. K.S. Gopalakrishnan, ***Concentration of Latex. Training Manual Rubber Goods Manufacture from Latex*** Rubber Board, Kottayam. p 8
15. D.C. Blackley, ***Polymer Latices Science And Technology Application of Latices*** Second Edition volume 3: Chapman & Hall, London (1972). p 618.
16. Malaysian Rubber Board. http://www.lgm.gov.my/general/patents.html.
17. ***RRIM Training Manual on Latex and Rubber Analysis.*** Rubber Research Institute of Malaysia. Kuala Lumpur (1979).
18. Reference 13
19. D.C. Blackley, ***Polymer Latices Science And Technology Fundamental Principles*** Second Edition. Volume 1: Chapman & Hall, London. p 451.
20. Reference 19. p 420-421
21. Reference 19. p 418-419
22. E.H. Lowe, ***Transactions of the Institutions of the Rubber Industry*** (1959)
23. D.C. Blackley ***Natural Latices*** First Edition Volume 1. p 108-112
24. Reference 19. p 421-422.
25. Reference 19. p 447-448, 452.