STUDIES ON

THE EFFECT OF ADDITION OF SOAP ON STABILITY OF CENTRIFUGED LATEX

PROJECT WORK DONE BY
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CERTIFICATE

It is certified that project of "Effect of addition of soap on stability of centrifuged latex" submitted by Smt.Rachel Oommen, 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.

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DEPARTMENT OF CHEMISTRY

CHRISTIAN COLLEGE, CHENGANNUR

(Affiliated to the University of Kerala)

CERTIFICATE

Certified that the project report entitled **"Studies on the effect of addition of soap on stability of centrifuged latex"** *is the bonafide record of work done by* **Rachel Oommen** *in partial fulfilment of the requirements for the award of the degree of* **Master of Science in Analytical Chemistry** *under the University of Kerala.*

Prof. Sophia K. Philip
Lecturer - in - Charge

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DECLARATION

I do hereby declare that the project entitled, "Studies on **THE EFFECT OF ADDITION OF SOAP ON STABILITY OF CENTRIFUGED 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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Chengannur *Rachel Oommen.*

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CHAPTER - I

INTRODUCTION

1.1 Natural Rubber

Natural Rubber is obtained from certain types of plant species like Hevea Brasiliensis of the family Euphorbiaceae and Gayule; however almost, the whole of rubber is obtained from the former species. Rubber is a polymeric material of high molecular weight which is capable of deformation under stress and resume its original shape when the force is removed. The crop from plantation is a milky white colloid known as latex. Latex is an essentially two - phase system - consisting of a dispersed phase and a dispersion medium. The dispersed phase or discrete phase consists of small particles, normally less than 5μ in diameter, the molecules of which are polymeric in nature. The polymeric substance is large in size and comprises of a basic chemical unit, cis 1, 4 - poly isoprene and is biosynthesized by a complex process involving proteins.

English - Chemist Joseph Priestly while using latex, made an article to rub the pencil marks and gave it the name of rubber which was earlier known as "Caoutchouc". However Christopher Colombus is considered to be the 1st European explorer of Natural Rubber and tropical America is the original home of the tree.

Rubber industry occupies a predominant position in India and world. The commercial plantation of this tree has been in existence for the last 150 years. The plantation industry in India is about a century old. The principal source of natural commercial importance is Hevea Brasiliensis, a tree native to the Amazon rain forests. India stands first in productivity of natural rubber, is the 3rd largest producer of natural rubber and India is the 8th largest rubber consuming country in the world.

1. 2 What is Latex?

Blackley defined "latex as a stable colloidal dispersion of polymeric substance dispersed in an essentially aqueous medium". As stated earlier the polymeric substance dispersed in natural rubber latex is cis 1,4 - poly isoprene. Latex collected from plantation will have a rubber content of 30-40%. For industrial uses this latex is concentrated to 60% rubber content.

1.3 Composition of Natural Rubber Latex

In addition to rubber hydrocarbon and water, natural latex contains several non-rubber substances - both organic and inorganic in origin. Fresh field latex is a whitish fluid of density between 0.975 and 0.980 gml^{-1}, P^{H} from 6.5 - 7.0 and surface free energy from 40-45 ergs cm^{-2}. Typical composition of natural rubber latex is given below.

Constituents	Preparation of % mm of whole latex
Total solids	36
Dry rubber content	33
Proteins	1-1.5
Resin matter	1-2.5
Ash	up to 1
Sugar	1
Water	ad 100

The presence of non-rubber substance is essential either for synthesizing the rubber hydrocarbon or imparting colloidal stability to latex. Other constituents present in the latex have physiological functions in the biosynthesis of rubber hydrocarbon.

1.4 Latex as a Colloid.

The size of rubber particles in latex are not uniform, ie, it is poly disperse, but falls in a wide range particle size distortion in the range of 20-5000 nm; being not uncommon. The distribution of pear shaped particles in fresh natural latex is wide that volume of dispersed rubber in latex is present in the form of a minority of large particles. Large particles are formed by agglomeration and coalescence of smaller particles.

Resin matter in latex is phospholipids which are strongly adsorbed on the surface of rubber particles. These are also covered by adsorbed protein layer and it is difficult to say which forms outer layer. The protein in latex has an iso-electric point below 5.0 so that proteins carry negative charge at about P^H 6.5 which is normal p^H of latex. The coulombic repulsive forces are contributed by negatively charged particles in rubber latex. Also rubber particles in latex are surrounded by a layer of water molecules due to van der Waal's forces. All these factors contribute to the colloidal stability of latex.

1.5 Physical properties of Latex

Few hours after tapping, if left unattended, latex thickens and on further keeping the whole mass is coagulated. It is different from coagulation by acids. The former occurs at $P^H > 6$ while the latter occurs at $P^H < 4.8$. Spontaneous coagulation is due to the formation of soaps in latex by saponification. The rubber particles lose their charge and agglomerate by forming insoluble soaps leading to complete coagulation.

1.6 Preservation of Latex.[10]

Why preservation is necessary :

The sterile field latex is contaminated by different types of bacteria. It gradually thickens by bacterial activity leading to spontaneous coagulation and putrefaction. Hence some preservative is necessary to prevent coagulation. This is achieved by adding suitable chemicals.

Attributes of a preservative

1) The chemical that is used as a preservative should be able **to enhance the P^H of latex**. Since the P^H of field latex is about 7, the stability of latex is due to adsorbed proteins and phospholipids and higher fatty acids on the surface of rubber particles.

2) Metallic ions like magnesium can form insoluble products with proteins or higher fatty acid anions will neutralize the negative charges on rubber particles and will destabilize the latex. Thus preservative must be able **to deactivate the harmful metallic ions.**

3) The bacterial contamination in sterile field latex may lead to putrefaction. Using the sugars in latex as substrate, the micro organism liberate volatile fatty acids (VFA) in latex and destabilize it. Therefore the preservative must **destroy the microorganism that lead to putrefaction**.

Ammonia is used as a preservative since it meets all the above requirements. The state of preservation of latex is expressed by its VFA number. It is the number of gms of potassium hydroxide required to neutralize the volatile fatty acids present in a quantity of latex equivalent to 100gm total solids. The VFA number must be in the range of 0.01 - 0.03 for a well preserved latex. However ammonia as a preservative have certain limitations also. To a great extent these have been overcome by several low ammonia systems.

1.7 Concentration of Latex

The low drc of field latex makes it unsuitable for direct application in product manufacturing. Hence field latex is to be concentrated to about drc of 60%. The concentration can be achieved by any of the following methods.

1. Centrifuging
2. Creaming
3. Evaporation
4. Electrodecantation.

Centrifuging and creaming are commercially used at present. Centrifuged latex in India contributes about 85-90% and the remaining by creaming. Evaporated latex is produced in Malaysia in limited amounts and electrodecantation method is only of academic interest.

Why concentration is necessary

The low drc field latex, if employed in latex dipping process, the thickness of the deposit formed will be small. To obtain desired thickness, the number of dips will be more, compound to a high drc latex. Also the strength of wet gel formed from a low drc latex is poor. The cost of transportation of low drc latex is high. These considerations make it necessary to concentrate field latex.

Theory of Centrifuging.

Natural Rubber latex if left undisturbed, cream under gravity and the rate of creaming is given by,

$$V = \frac{2gr^2(d_1 - d_2)}{9\eta}$$

Where,

V - Velocity of creaming

g - Acceleration due to gravity

r - average particle radius.

d_1 - Sp. Gravity of rubber

d_2 - Sp. Gravity of serum

And η - Viscosity of dispersing medium.

In latex concentration by centrifuging, gravitational force, is replaced by a high centrifugal force by centrifugal latex separators.

The latex enters the bowl through a central feed tube, then passes through a distributor to the bottom of the bowl from where it flows through a series of holes on separate discs in to the interior of the bowl. Inside the bowl of a disc type latex centrifuging rotating at a high speed, a mass of latex is broken up into a number of thin conical shells, because of the presence of separator discs. Hence the maximum distance a particle has to travel in order to pass from skim into cream is very small. The cream being the lighter component moves towards the axis of rotation and goes into the cenex gulley. The skim moves away from the axes of rotation and leaves the bowl through orifice formed by regulating screws.

1.8 Centrifugal process

Different types of centrifuges are used for concentration of latex. Of these, the most widely used type is the Alpha Laval (LRB 510 and Alpha Laval 2000) from Sweden , (fig. I),. Recently a machine ICF LC 540 / LC 440 made in India has also been introduced. The basic design of the different makes is similar. The machine consists of a rotating bowl in which a set of concentric conical metallic separator discs are enclosed.

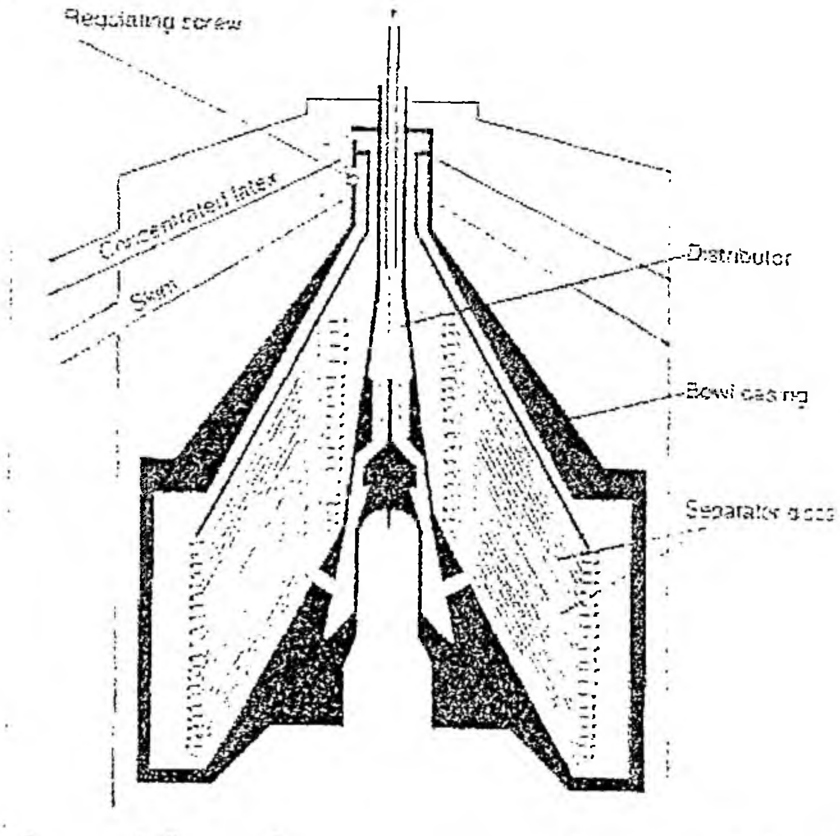


Fig. 1. Diagrammatic section of latex centrifuge bowl, indicating the path of latex [illegible]

Fig I - Centrifuging machine.

Field latex is sieved through a 60 mesh sieve and bulked in the bulking tank and homogenised by stirring, either manual or mechanical. A representative sample is drawn for testing DRC, NH_3, VFA number and magnesium content. Based on the magnesium content, calculated quantity of diammonium hydrogen phosphate is added to the latex to precipitate the magnesium.

$$Mg^{+2} + NH_3 + HPO_4^{-2} \longrightarrow Mg(NH_4)PO_4$$

The latex is then left undisturbed for the precipitation of magnesium ammonium phosphate and other sedimentable impurities to settle as sludge.

The sedimented latex is then fed to the centrifuge where the field latex is separated to concentrated latex of DRC 60% or above and skim latex of DRC about 5% or less.

The concentrated latex is ammoniated further during the process. The cenex in the tank is homogenised and tested for DRC and ammonia. A solution of lauric acid as ammonium laurate is added to the latex at a level of about 0.02 - 0.025 % to increase the mechanical stability of latex. Cenex is ammoniated to about 0.8% and finally diluted to DRC slightly above 60% by adding water. Finally a representative sample is tested for all parameters as per 5430 - 1981.

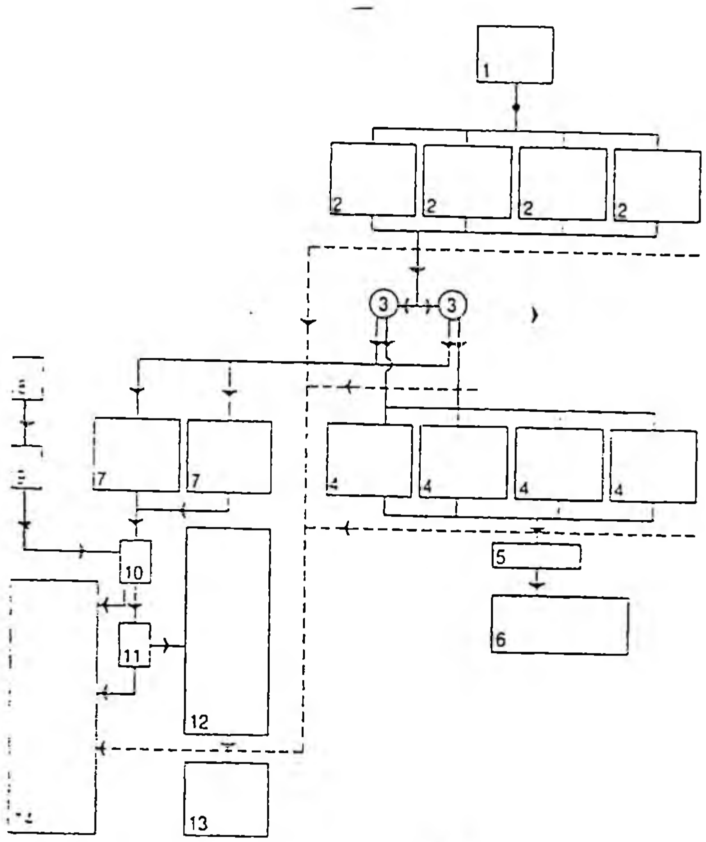


Fig. 2. Flow diagram of latex centrifuging plant

1. Tanker
2. Field latex storage tanks
3. Centrifuging machines
4. Concentrate storage tanks
5. Drum filling
6. Store
7. Skim latex collection tanks
8. Concentrated sulphuric acid storage tank
9. Sulphuric acid dilution tank
10. Skim coagulation tank
11. Crepe unit
12. Crepe drying shed
13. Skim crepe packing/storage
14. Effluent treatment plant

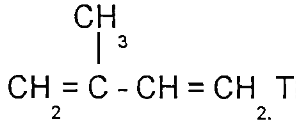
.... Wash water line

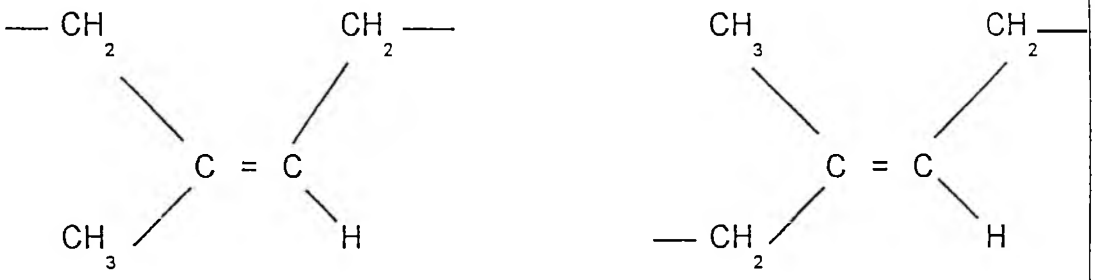
2. Composition of Natural Rubber

Natural Rubber consists of high proportion of rubber hydrocarbon about 95 - 98% having lower quantity of proteins, resins and other non rubber constituents. Typical composition of constituents in dry natural rubber is

Composition	%
Rubber Hydrocarbon	93.7
Protein	2.2
Carbohydrate	0.4
Neutral lipid	2.4
Glycolipids & phospholipids	1.0
Inorganic constituents	0.2
Other	0.1
Total	100.00

3. Chemistry of Natural Rubber[4]

It is found that chemical composition of natural rubber is $(C_5H_8)_n$. The basic unit being isoprone is 2 methyl-1, 3 butadiene.  $CH_2=C(CH_3)-CH=CH_2$. The monomer units undergo 1,4 addition. Polymerised 2 methyl - 1, 3 - butadiene has one double bond unit for each C_5H_8 group. Thus two spatial arrangements, cis and trans are possible

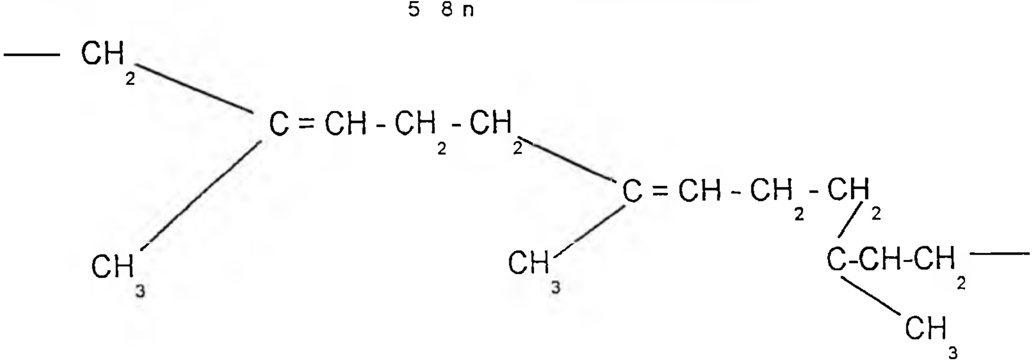


Cis

Trans

(Alternate configuration of isoprene monomer)

Later on, it was found that isoprene can be polymerized into natural rubber having chemical formula as $(C_5H_8)_n$ and structural formula as



Cis 1-4- Poly isoprene

Natural rubber has very important non-rubber constituents such as protein, sugar and fatty acids which act as natural antioxidants and activators to curing. Unstretched rubber shows broad diffusion bands when examined by X-rays. The main source of variation in natural rubber hydrocarbon is due to difference in molecular weight and the degree of cross-linking of molecules or gel content.

4. Different Forms of Natural Rubber

Liquid latex or dry field coagulum are not used as such for the manufacture of rubber goods. So processing of the latex / coagulum into different marketable form is necessary. This permits suitable type of rubber for a given product. Latex can be processed into different forms such as

4. a. Ribbed Smoked Sheets (RSS)

This is the oldest form of processed natural rubber. The field latex is sieved to remove dirt and other contaminants. Then diluted it to 15% with water. The diluted latex is transferred to coagulation tanks of dishes. Eventhough coagulation can be brought in by different ways such as by addition of chemicals (like acids or metallic salts), natural coagulation and also by assisted biological coagulation in RSS processing is effected by additing dilute formic acid or acetic acid. After storage for several hours, the thick coagulum is pressed on plain rollers to squeeze out latex serum. The pressed coagulum is washed well while sheeting. It is then compressed by using the grooved rollers which helps faster drying of the sheets due to increased surface area. These sheets are dried for about 4-5 days in smoke house at a temperature of 40 - 60°.

4. b. Air dried sheets (ADS)

ADS are produced in the same manner as that of RSS, but are dried in hot air currents without the use of smoke. The temperature inside the chamber is controlled thermostatically. The air dried sheets has a light amber colour.

4. c. Crepe rubbers.

Crepe rubbers are produced from fresh latex coagulum, field coagulum, and / or cuttings of RSS. When this is passed through crepers, a lace like rubber is obtained. Different types of crepe rubbers are pale crepe, sole crepe, brown and blanket crepes. Crepe rubbers are classified according to the starting material used. Drying of crepe is done either in air drying sheds or in heated drying chambers. The hot air at 33 -35 °C is circulated in the drying chamber.

4. d. Technically specified rubber (TSR)

Technically specified rubber is a modern form of marketable rubber and can be produced from field coagulum, latex and or from both. Production of TSR involves a series of operations like initial size reduction, creping final size reduction, washing, drying etc. and produced in bales and graded following National or International standards. (IS 4588 or ISO 2000).

4. e. Preserved field latex

The sterile field latex is preserved using ammonia as preservative to avoid putrefaction.

4. f. Centrifuged Latex[3]

The ammoniated field latex after mixing with diammonium hydrogen phosphate is kept undisturbed overnight, then magnesium ammonium phosphate and other impurities settle down as sludge and are removed .By centrifuging field latex is separated into the concentrated latex and the skim latex and collected separately.

5. Properties of Natural Rubber.

5a. Physical and Technological properties of NR:-

The hydrocarbon content in natural rubber is about 94%. The non-rubber substances although present only in low concentrations influence the physical and chemical properties of hydrocarbon polymer. The properties of Natural Rubber depends very much upon the state of cross-linking.

Natural rubber is an amorphous solid insoluble in water. It is elastic and elasticity greatly increases after vulcanization. Being a hydrocarbon, rubber is not resistant to organic solvents such as kerosene, petrol or benzene. It slowly swells up by impregnating the solvent and then forms a viscous and sticky solution. It has high degree of stiffness. Specific gravity of raw rubber at $0^{\circ}C$ is 0.950 and 0.934

at 20°C. Specific gravity at room temperature is 0.92. Heat of combustion is 10700 cal /gm. The coefficient of cubical thermal expansion is 670×10^{-6} /°C.

5b. Chemical Properties of Natural Rubber

Natural rubber slowly oxidises on exposure to air. When heated in air it softens and then burns to form water and carbondioxide. On heating rubber at very high temperature in the absence of air a liquid known as oil of rubber is obtained as a result of liquefaction of rubber. The rubber powder - abraded reacts with hydrogen gas in presence of a catalyst to form fully saturated hydrocarbon of the formula $(C_5H_{10})_n$ known as hydro rubber. It decolourises Bromine water to form tetra bromide $C_{10}H_{16}Br_4$. It forms ozonide with ozone and reacts with hydrochloric acid.

Another property of rubber is its strength and toughness. An important quality of rubber is building tack when two fresh surfaces of milled NR are pressed together, they coalesce to form a single piece. This makes simple the building of composite articles.

6. Rubber product manufacturing methods

Four major steps involved in the conversion of natural rubber for product manufacturing include.

a) Mastication

During mastication, rubber molecules are mechanically broken down. It reduces the molecular weight and makes the natural rubber compatible for the compounding ingredients. It is done by applying mechanical shear forces between the warm rollers. During the process the natural rubber loses its reversibility and turns mouldable. Chemical peptisers can be used to increase level of kneading / mastication and it can improve technological characteristics.

b) Compounding.

Compounding means the mixing of rubber fillers with compounding ingredients like curatives, antioxidants etc so as to impart the desired properties to the final product suitable for particular purpose. Compounding for making the desired product are incorporated by different methods such as mixing, calendering, extruding etc.

c) Shaping

In the case of rubber products having continuous profile such as tube, tyre tread, channels etc shaping operation is carried out separately. Extruders and calenders are the major shaping machines. Calender consists of a barrel inside of which there is a screw which can be rotated in desired rpm. The rubber compound which spread in the machine is then led to the other and it is then passed through a die having desired product profile. The product is collected and vulcanized separately by different methods.

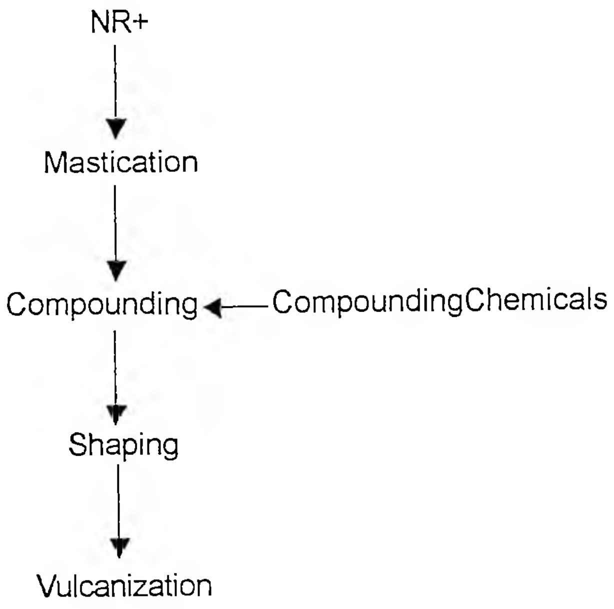
d) Vulcanization

By vulcanization the compound and shaped rubber gets better strength and technological properties. Here rubber in plastic state is converted into the elastic state and this is brought about by the cross-linking of macromolecules at their reactive sites and hence known as cross-linking. Rate of reaction can be enhanced by accelerators.

Vulcanization is carried out by heating crude rubber in presence of sulphur or dipping it in a solution of S_2Cl_2 in CS_2. It depends upon (i) amount of sulphur used - ie, by increasing the amount of sulphur, the rubber can be hardened. (ii) Temperature (iii) Duration of heating. Usual temperature range to bring out the process to reasonable extent is 140 -160°C But for practical purposes a temperature of 150°C is selected.

In addition to sulphur other substances such as sulphur monochloride, selenium, tellurium, zinc oxide, benzoyl peroxide, polysulphide polymers etc can be used as vulcanizing agents. N- cyclohexyl benzthiazyl sulphenamide (CBS) is used as an accelerator which can increase the rate of chemical reaction between sulphur or other vulcanizing agents and rubber.

Flow diagram for Rubber product manufacturing process is shown below :-



7. Techniques of Vulcanization

Vulcanization can be carried out by press curing, open steam curing, hot air curing, lead press curing and liquid bath curing. Compression moulding is the simplest process in press curing.

8. Methods of Vulcanization

8 a. Non-Sulphur vulcanization

It is initiated by a free radical source involving generation of a free radical from a curing agent such as organic peroxide or abstraction of beta - hydrogen atom with respect to C=C by the free radical formed.

8 b. Sulphur vulcanization

In this rubber is heated with sulphur in presence of an accelerator such as aldehyde, amine, thiocarbamate, thiazoles etc. The rate of vulcanization is low if sulphur alone is used. So these accelerators alone or in combination makes it possible to vulcanize rubber within any desired time and temperature.

9. Applications of Natural Rubber Latex

a) Latex dipping process is employed for making wide range of rubber products such as various types of gloves, seamless wellington boot ,seamless football bladders ,toy balloons and prophylactics .

b) A large number of products are made by latex moulding especially hollow castings .

c) Latex foam rubber is another product manufactured out of liquid latex , in which the cells are either all intercommunicating or partly intercommunicating and partly non - intercommunicating.

d) Another application of this polymer latices is in textiles. By the process of latex spreading, a coherent, impervious film of polymer over one surface of the textile is formed. The polymer latices act as binder for non woven fabrics. Another use is in connection with carpet manufacture.

e) Latex is used in surface coating systems especially in oil - bound washable distempers.

f) Latex adhesives are used in wide range of different industries. It is used in the binding of paper and leather.

g) Latex bonded fiber pads are prepared from natural latex . [It comprises hair and other large diameter fibers in the form a random web, the fibers being bonded together at their points of contact by droplets of latex]. Latex is also used in paper treatments and in the manufacture of rubber threads.

h) Another important application of latex is in the field of engineering technology, ie, in the manufacture of latex cement composition in surface of roads

i) Rubber latices have been proposed to use as binders for asbestos breaklining materials.

j) Latex is used in the sealing of cans for the preservation of food stuffs. Used in the insulation of copper conductors and as stabilizers for sandy soils.

10 Scope and objective of the present study

The objective of the present studies was to find the effect of adding an anionic soap potassium laurate on stability and viscosity of centrifuged latex.

The stability measurements involve two types of studies - mechanical stability and chemical stability.

If latex has high chemical stability, ie, latex performs well in zinc oxide viscosity (ZOV) tests, it is highly suitable for application where high shear is involved. And also stability measurements can give an idea about the latex that whether it is suitable for a broad range of appliations including dipped goods, latex adhesives, binder, carpet backing etc.

Anionic soap if added to the latex in small amounts can improve the mechanical stability of centrifuged latex. MST measurements can be used to study the behaviour of latex under high shear and consequently to get an idea of its behaviour in application like foam rubber products.

The scope of viscosity measurement finds application in the field of dipping process by which manufacturing of different rubberized materials such as gloves, balloons, condoms etc can be carried out. Latex dipping is a process in which thin walled polymer products are produced by first immersing the former in a latex which has been suitably compounded and then subsequently slowly withdrawing the former from the latex in such a way as to leave a uniform deposit upon the former. Thickness of deposit can be increased by repetition of the process. From the viscosity studies, one can understand how much viscous the latex is for a particular purpose.

CHAPTER - II

EXPERIMENTAL TECHNIQUES

MATERIALS & METHODS

1. Materials used

1. 1. Centrifuged Latex

Centrifuged latex used for experimental purpose was received from the centrifuging factory, Rubber board, Kottayam.

Typical properties of centrifuged latex used.

	Parameter	Value
1.	Dry Rubber Content (DRC - %)	60
2.	Total solid contents	61.7
3.	KOH number	0.80
4.	Viscosity (25°C) cps	84
5.	Ammonia content (%)	0.66
6.	Mechanical stability time (MST)	847
7.	Volatile fatty acid No.	0.04
8.	Specific gravity	0.945
9.	Odour (Boric acid test)	No putrefaction

1.2 Ingredients / Chemicals used.

Lauric acid, potassium Hydroxide, zinc oxide (4%)

Preparation of 5% potassium Laurate solution.

Weighed accurately 4.2g of Lauric acid and mixed with about 50ml water and heated on a water bath. Added KOH (~1.2gm) solution to this and made up to 100ml.

2. Test Methods

2.1 Preparation of the latex sample.

Weighed accurately 250 gm each of centrifuged latex having TS 60% in six separate beakers. Added lauric acid to the extent of 0, 0.005%, 0.01%, 0.015%, 0.02% and 0.025%. Addition is as 5% potassium laurate (soap) solution to each latex. Mixed the soap and latex well and kept undisturbed for a day and tested the effect of addition of soap on stability and viscosity of centrifuged latex.

2.2 Determination of total solid content (TS)

Took about 20ml of well mixed sample in a stoppered conical flask. Weighed to the nearest 0.01gm. Poured about 2gm of sample into previously weighed petridish of about 60mm diammeter and weighed to obtain the weight of latex taken from the difference. Swirled the petridish gently to ensure that latex covered the bottom of the dish. Dried the test portion in an air oven at a temperature of 70°C for 16 hours. Cooled in a desiccator and weighed as quickly as possible. Repeated the drying and weighing operation until the loss in weight is less than 1mg between consecutive weighings when dried at temperature between 70 - 75°C

Calculation.

$$TS \ \% \text{ by weight} = \frac{w_1}{w_2} \times 100$$

Where w_1 - wt. in gms of dried film.

w_2 - wt. in gms of sample taken for test.

2.3 *Determination of Dry Rubber Contents (DRC)*

Reagents :- 2% acetic acid solution

Weighed about 15gm of the well mixed latex sample (about 10gm if it is concentrated latex) accurately to 1mg into a 250ml beaker from stoppered conical flask. Added equal amounts of water (for centrifuged latex double amount per gm). Added about 2-3 ml of acetic acid per gm of sample with gentle stirring. Kept the solution undisturbed for about 15min in a waterbath till the serum is clear. Added about 5ml of rectified spirit per gm of sample and gently stirred, if the serum was not clear on heating. When the serum is clear, filtered the serum through Whatmann no.1 filter paper. Collected any small particles of coagulum by rubbing with main bulk. Thickness of the coagulum is reduced to about 2mm either by hand roller or other devices such as mechanical roller. Washed the coagulum with running water with atleast 6 changes of water. Dried the coagulum at a temperature of approximately 70±2°C Cooled in a desiccator and weighed. Determination must be duplicated.

Calculations:

$$\text{DRY RUBBER CONTENT} = \frac{w_1}{w_2} \times 100$$

w_1 - Wt. of dried film.

w_2 - Wt in gm of latex sample taken.

2.4 Determination of Total Alkalinity (NH_3)

Reagents

1) 0.1N H_2SO_4 or HCl
2) Methyl Red solution

Took about 20ml well mixed sample in a stoppered conical flask. Weighed to the nearest 0.01gm. Took about 150ml distilled water in a 250ml beaker, added 5 to 6 drops of methyl red indicator. Poured about 2gm of latex into the water from the flask and weighed to obtain the weight of latex taken by difference. Contents are titrated with 0.1N H_2SO_4 or HCl, till the yellow colour change to pink. Noted the volume of acid . The acid used is standardised with 0.1N Na_2CO_3 using methyl orange as indicator.

0.1N HCl - 1ml conc. HCl dilute to 100ml.

0.1N Na_2CO_3 - 0.53gm dried Na_2CO_3 (100°C) in 100ml.

Calculations

$$\text{Ammonia Concentration (\%)} = \frac{1.7 \times N \times V}{W}$$

N - Normality of acid

V - Volume of acid

W - Wt. of latex taken

2.5 *Determination of KOH number.*

Prepared an approximately 0.5N KOH and stadardised it with standard potassium hydrogen phthalate.

Weighed a portion of latex of known solid contents and alkalinity containing 50gm of solids accurately to a 250ml beaker. Adjusted the ammonia content to 0.5% calculated on the water phase by adding 5% HCHO solution while stirring. (1ml of 5% HCHO = 0.0189 NH_3). Added enough distilled water to dilute the latex to about 30% total solids. Inserted the electrodes and added slowly 5ml of 0.5N KOH with gentle stirring using a glass rod. Recorded the P^H using a P^H meter. Continued additions of 1ml increments of 0.5N KOH solution with stirring at the same time. Recorded the P^H after each addition. The end - point is obtained from the inflection point of the KOH titration curve. At this point the slope of the curve that is the 1st differential reaches a maximum and 2nd differential changes from a positive to negative value. The end-point may be calculated with reasonable accuracy from the second differential assuming that the change from a positive value bear a linear relation to the addition of 0.5N KOH during the 1 ml interval involved.

Calculations

$$\text{KOH number} = \frac{V \times N \times 561}{TS \times M.}$$

V - Volume in ml of std. KOH.

N - Normality in ml of std. KOH

TS - % of Total Soild Content

M - Wt. in gm of sample.

2.6 Determination of volatile fatty acid number.

Weighed about 50gm of latex of known DRC and TS into a beaker. Added 50ml, 30% $(NH_4)_2 SO_4$ solution and stirred the mixture warming over a waterbath until the latex thickened and coagulated. Pressed the serum out of the coagulum. 25ml of the filtered serum was taken and acidified with 5ml dilute sulphuric acid. Pipetted out 10ml of the acidified serum into the inner tube of the Markham still (steam outlet open) and added 5 drops of silicon antifoaming agent. Washed with distilled water and closed.

Placed a 250ml conical flask under the tip of the condensor to receive the distillate. Closed the steam outlet partially to divert the steam into the innertube. Passed the steam gently at first, then closed the steam outlet fully. Continued distillation until 100ml distillate was collected. Titrated the distillate with carbonate free 0.02N Barium hydroxide using phenophthalein as indicator till pink colour was obtained. A blank test was conducted by substituting 20ml of water from the 50gm of concentrated latex. Titrated the distillate against std. 0.02N Barium hydroxide using phenolphthalein as indicator. VFA number is calculated using the equation,

$$\text{VFA Number} = \frac{561\,NV\,[50 + ((100\text{-}DRC) \times 50/102)]}{50 \times 10 \times TS}$$

DRC - Dry rubber content

N - Normality of Barium hydroxide

V - Volume of Barium hydroxide

TS - Total solid content.

3. Physical Tests Done.

3.2.1 Viscosity

The viscosity of a latex is very much dependent upon concentration of polymer which it contains. At low concentration the effect is slight, but becomes increasingly pronounced as the concentration rises. The viscosity - concentration relationship for centrifuged concentrate can be represented using an equation,

$$\log_{10}(\eta + 0.0309) = 0.143 + (1.014\,r) / (1 - R)$$

Where, R = Weight fraction of dispersed phase

r = Weight ratio of polymer to serum

η = Coefficient of viscosity.

Viscosity will become infinite when volume fraction in dispersed phase $= a^{-1}$ where 'a' is a constant.

Increase in fluidity is due to the increase in particle size and it effects the viscosity. Also variation in stabilizer content is an important factor. The effect of temperature upon viscosity of ammonia preserved natural rubber latex is irreversible, due presumably to denaturation of proteins and loss of ammonia. But effect is however slight.

3.1. 2. Viscosity Measurement Apparatus

Viscosity of latex is usually determined using a Brookfield viscometer.

This instrument is a technical viscometer which is widely used for the measurement of latex viscosity. It consist of a rotating chamber, which is usually a cylinder driven by a synchronous motor through a Beryllium - Copper torque spring. The viscous drag on the cylinder causes an angular deflection on the torque spring, which is proportional to the viscosity of the fluid in which the disc is rotating. The torque and therefore the viscosity are indicated by means of a pointer and scale. The pointer is attached to the cylinder spindle and the scale to the drive spring, so that both pointer and scale rotate. To obtain a reading, they must be clamped together and the rotation stopped when the pointer is opposite a window which is cut out of the caring. For this reason, it is not always possible to follow continuously the course of viscosity changes due to temperature or associated with non-Newtonian behaviour. The calibration is normally based upon immersing in fluid contained in a 600ml beaker. A range of speed and of discs and cylinder is available so that a wide range of viscosity may be covered. This 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 viscometer is some what similar to a concentric cylinder instrument with a very wide annular space. In general to such instrument, the distribution of shear rate depend 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 extent, by the angle of immersion of the spindle.

3. 1. 3. Method Adopted to Test Viscosity

Took 220g of well mixed and seived latex sample in a beaker. Found the viscosity at 25^{0}C using the Brookfield viscometer. Usually viscosity of latex is determined at 60 rpm with spindle No. 2.

3.1 Stability Tests

3.1.1. Mechanical stability (MST)

By the term mechanical stability of a latex is meant its resistance towards those mechanical influences which tend to increase the number and violence of collisions between particles and so tend to coacervate the latex. It is a difficult property to define and assess quantitatively. Mechanical stability tests contrast with several other tests which are routinely carried out on latices such as total solid content, P^H, alkalinity etc.

Two distinct types of MST are currently in common use for rubber latices, the one being used for natural rubber latex concentrate and the other for synthetic rubber latex. These two types are developed because both the latices behave differently when subjected to mechanical destabilization. The objective of MST test is to determine time, known mechanical stability time which elapses before signs of incipient gross colloidal destabilization appear, the latter being usually taken us the first visible signs of flocculation. It is expressed in either sec or min. Obviously, the greater is the number which is reported for the test, the more mechanically stable is the latex. For natural rubber latex , the test is a direct measure of mechanical stability.

3.2.2. Chemical Stability

By the term chemical stability, to a polymer latex is meant the ability of the latex to withstand chemical colloid - destabilizative influences. The behaviour of a given latex to one type may provide little indication of likely behaviour towards another type. Thus tests for chemical stability are of limited usefulness. In effect, the mechanical stability tests are intended to provide an indication of the magnitude of the interparticle potential - energy - barrier in the latex as received where as chemical stability tests are intended to provide an indication of the ease or otherwise with which the height of that barrier is susceptible to reduction by specified chemical influences. Chemical stability is important for rubber latices because overt chemical destabilization is a crucial step in many important manufacturing processes which use these latices. Tests which have been proposed for assessing chemical stability of rubber latices are classified as follows;

1. Various **zinc - stability time (ZST)** tests, including one developed in the UK

and a variant developed in Germany ;

2. Various **zinc-oxide viscosity (ZOV)** tests, also known as **zinc - oxide thickening (ZOT)** tests;
3. Other **zinc - oxide stability tests**;
4. Tests which are **zinc - ammine acetate** as the destabilizative reagents;
5. Various tests using other **destabilizative reagents,** such as calcium chloride, magnesium chloride, barium chloride or sodium silicofluoride.

All these tests are applied to ammonia - preserved natural rubber latex concentrate.

It may be noted that when the soap additions are less than that required for optimum stability the end - point of the test is similar to that for standard untreated concentrate, but when the optimum quantity is exceeded it is found that the end-point is sharpened and that as the soap addition is increased, so the coacervation becomes more rapid and complete. Synthetic latices show high stability to zinc oxide than natural latices when the ZST test is conducted.

3. 2. 3. Apparatus for stability measurements. - Klaxon MST tester.

The apparatus used is shown as in fig. 3 (a). The cup and stirrer are shown in fig 3(b) and reference in table. Both BS & ASTM requires the stirrer to rotate at 14000 ± 200 rpm throughout the duration of test. The speed is controlled by means of a rheostatic control which is used in series with the motor which drives the stirrer. Ideally, the centre reed should vibrate violently the whole time. The stirrer shaft is to be vertical and test cup must be flat bottomed, cylindrical and of smooth inner surface. The cup must be concentric with the shaft.

TABLE A

Details of BS and ASTM procedure for the mechanical stability of natural rubber latex.

Detail / parameter	**British Standard Procedure**	**ASTM procedure**
Latex concentration	55 ± 0.2% TSC	55 ± 0.2% TSC
Dilution fluid	1.6% Ammonia solution	1.6% ammonia solution for HA type and distilled water for LA type.
Sample weight	80 ± 1 gm	80 ± 1 gm
Latex temperature	35 ±1°C	35 ±1°C
Stirrer speed	14000 ± 200 rpm	14000 ± 200 rpm
Dimension of cup And stirrer (see fig3b)		
A	0.5 ± 0.1 in	0.5 ± 0.1 in
B	0.820 ± 0.001 in	0.820 ± 0.001 in
C	0.062 ± 0.002 in	0.062 ± 0.002 in
D	0.25 in	c 0.25 in
E	c 6 in	any convenient length
F	2.25 ± 0.05 in	2.28 ± 0.04 in
G	43.5 in	c 0.5 in
H	c 3 / 16 in	c 0.09 in
Material of cup	Polymethyl methacrylate or polystyrene	glass
Material of stirrer	Stainless steel	disc to be of stainless steel
Indication of end point	85- mesh coagulum content of whole test latex sample to exceed 0.5gm when washed and dried	dip glass rod into and draw once lightly the palm, first appearance of coagulated rubber in the film
Maximum allowable discrepancy between duplicates	5%	5%

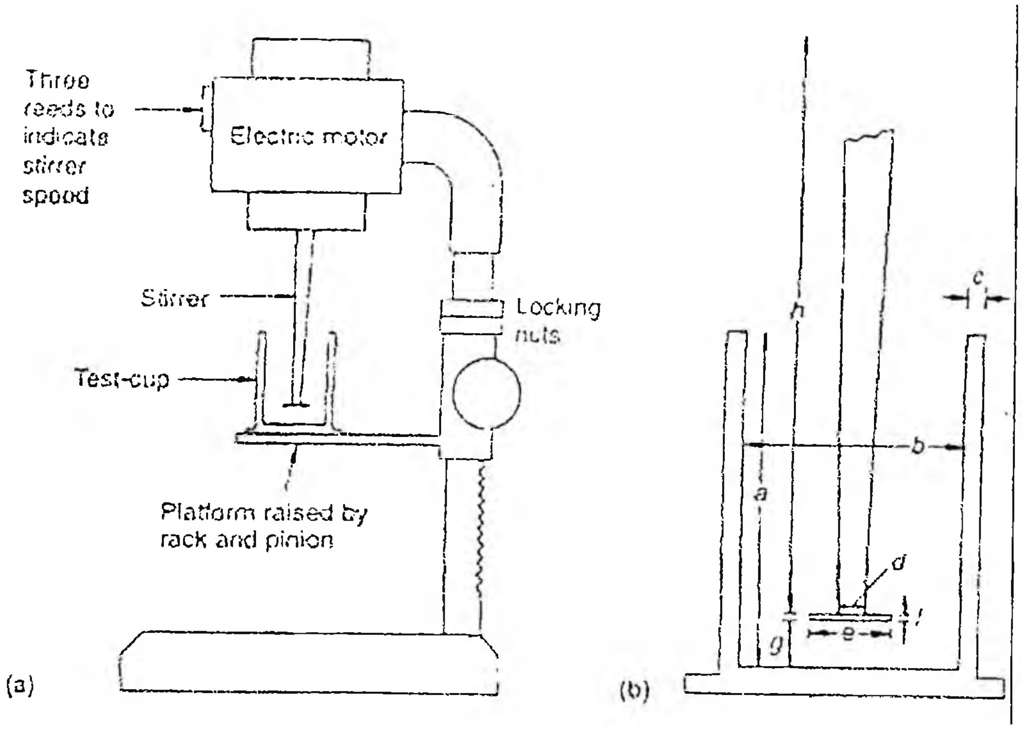


Fig.3 Klaxon MST Tester

3.2.4. Method adopted - Test for Mechanical stability

Reagents used - ammonia solution (1.6% or 0.6% w / v)

Diluted 100gm of well mixed sample to 55.0 ± 0.2 total solid content with appropriate ammonia solution depending on whether the latex is HA or LATZ. Warmed the contents to 37°C in a waterbath. Transferred 80ml of this into the MST container. Placed the container in position and stirred the latex with Klaxon MST tester at a speed of 14000 ±200rpm, until the end point is reached. The end - point is the appearance of the coagulation with a drop of latex gently spread over the palm. Noted the time taken for coagulation.

3.2.5 Test for chemical stability - Zinc oxide stability (ZST)

Took 100gm of the latex and added approximately 1.5 - 1.6gm of 40% zinc oxide. Mixed the sample well and after 1 hour took 80gm of the above sample and mechanical stability is tested.

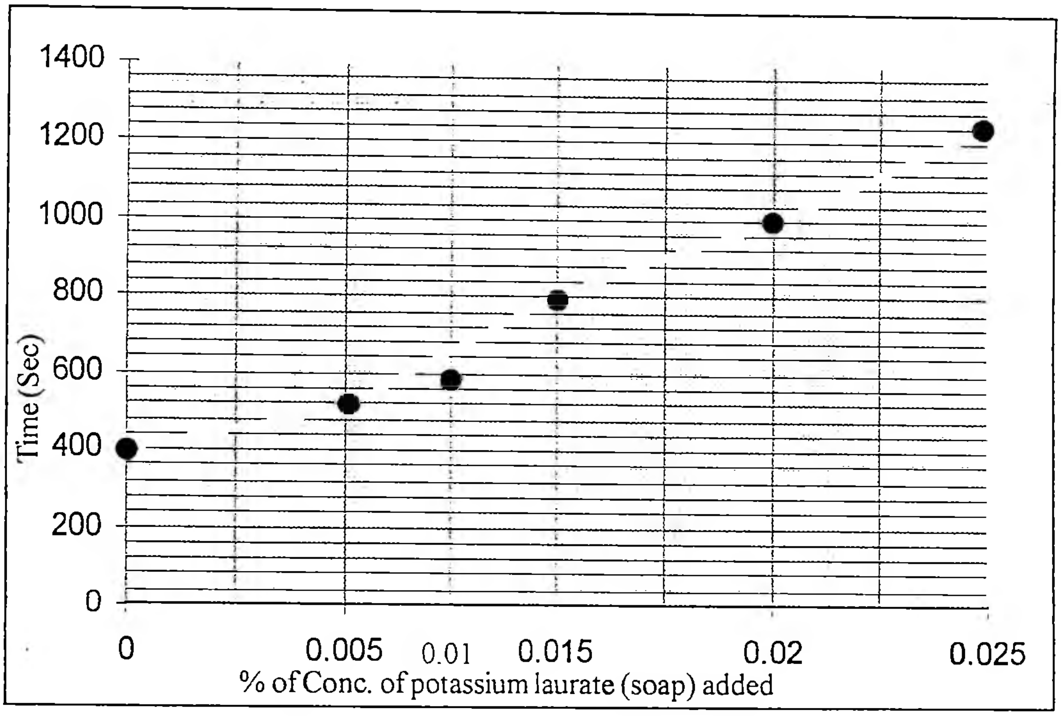
CHAPTER - III

RESULTS & DISCUSSION

Table. 1. Variation in MST of Latex against soap content

% of potassium laurate in 250gm of Centrifuged Latex	MST(Sec)
0	347
.005	512
.01	600
.015	750
.02	954
.025	1274

MST Graph



1400
1200
1000
800
600
400
200
0
Time (Sec)
0
0.005
0.01
0.015
0.02
0.025
% of Conc. of potassium laurate (soap) added

Mechanical stability of a latex is its resistance towards those mechanical influences which tend to increase the number and violence of collision between particles and so tend to coacervate the latex. The mechanical stability test involves the increasing of the translational energy of the particle. The Mechanical stability of latex is very sensitive to small quantities of an anionic soap, potassium laurate, ie, additions of 0.3% caused a 12 fold increase in MST, while addition of 0.3% of cationic soap or surface active substance cetyl, trimethyl ammonium bromide caused a two third reduction.

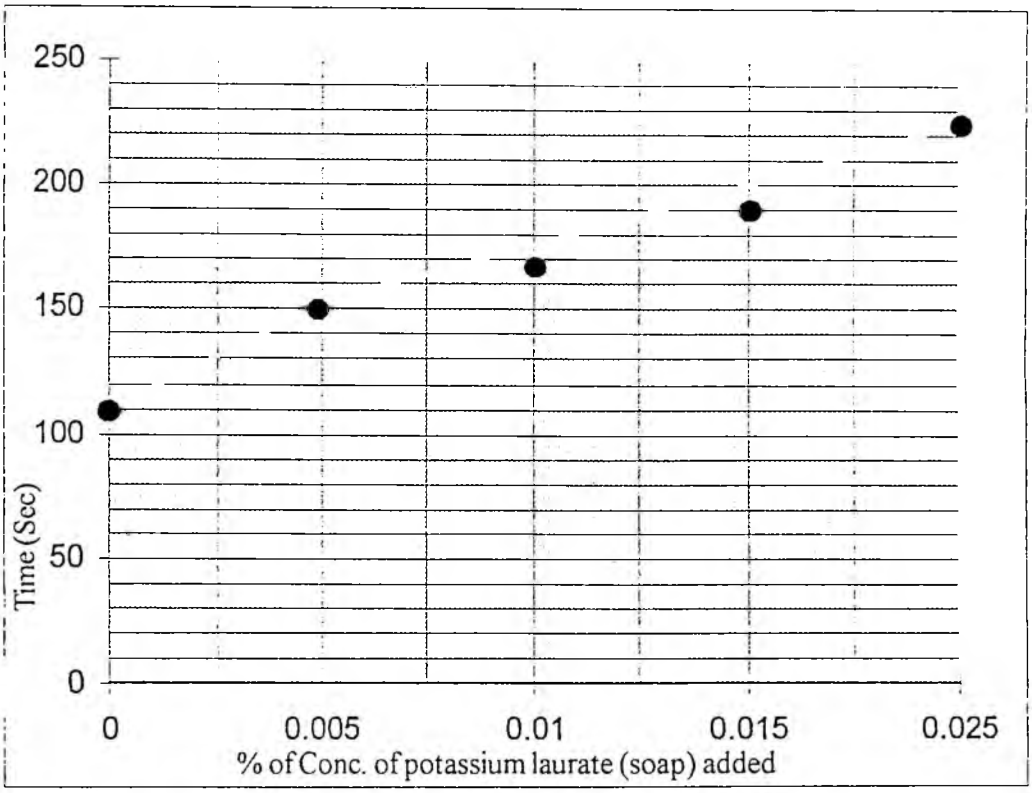
Hence in MST studies, the stability of the latex increases with increase in percentage of cationic soap added. As the chain length of fatty acid soap is increased, their effect upon mechanical stability (judged on a weight-weight basis) passes through a maximum in the C_{10} to C_{12} region. As the percentage of potassium laurate added increases with the increse in the charge density on latex particles and the increased hydration effect predominates over the adverse effect of zeta-potential of the rubber serum . Then the surface active effect of anionic potassiun laurate enhances mechanical stability of the latex sample together with the effect of the free alkali which is produced by its partial hydrolysis.

Table 2.

Variations in Chemical Stability of Latex (measured as Zinc - Stability Time) against soap content

% of potassium laurate in 250gm of Centrifuged Latex	ZST(Sec)
0	109
.005	149
.01	158
.015	175
.02	167
.025	223

ZST Graph


250
200
150
100
50
0
Time (Sec)
0
0.005
0.01
0.015
0.025
% of Conc. of potassium laurate (soap) added

The stability measurements by zinc oxide is based on the differences between cationic and anionic soaps. The reaction between cationic soap and centrifuged ammonia preserved latex having zinc oxide is as follows:-

$$ZnO + 2NH_3 + 2NH_4^{+} \rightleftharpoons Zn(NH_3)_4^{+2} + H_2O$$

$$\downarrow$$

$$Zn^{2+} + 4NH_3$$

$$\Big\downarrow \; RCOO^{-}$$

$$Zn\,(OCOR)_2$$

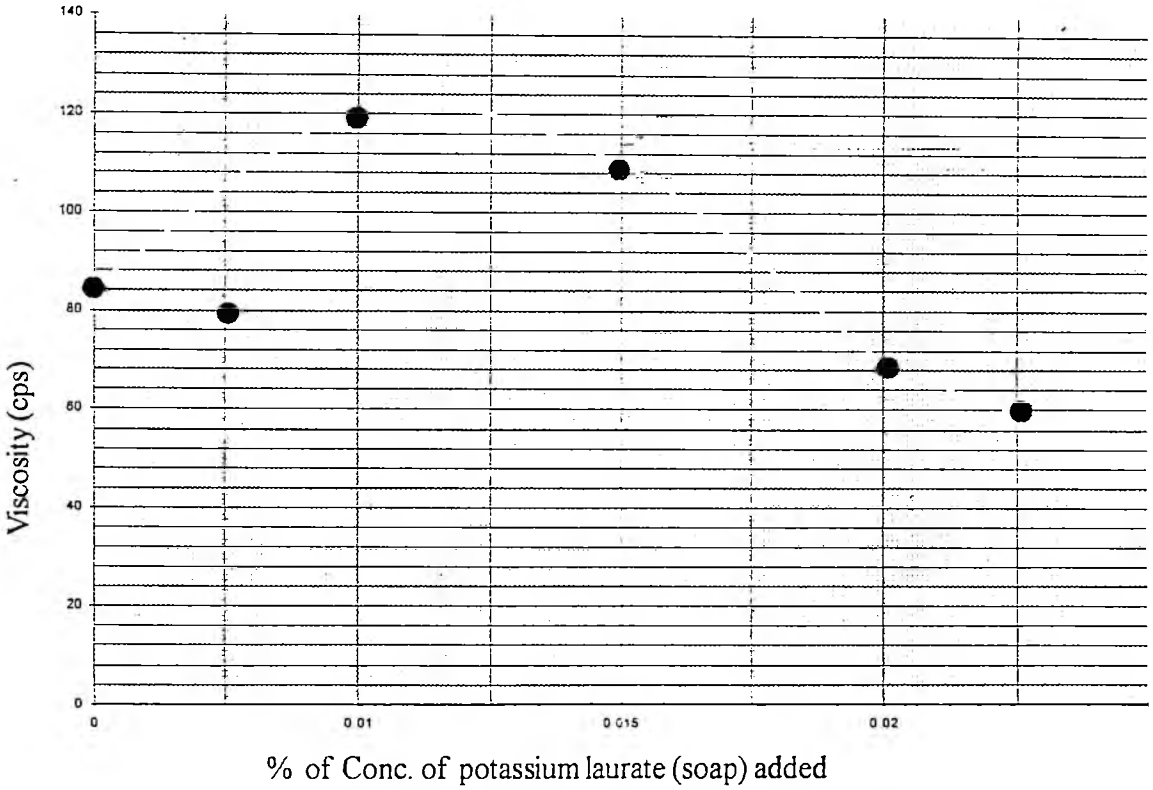
If cationic soap with $(NH_4)^+$ is added to latex, the excess ammonia formed destabilizes the latex according to the above reaction. The zinc oxide added forms a complexation product with ammonia present in the centrifuged latex. This zinc ions then react with $RCOO^-$ group to form $Zn(OCOR)_2$, which decreases the chemical stability of the centrifuged latex. The increase in ZST with anionic soap is due to the fact that, if the soap anions stabilize the particles and then sensitize them towards the action of zinc ions. Since mechanical stability test does not involve any zinc oxide addition, it has no effect on MST values. Therefore if cationic soap is added, ZST values decrease with every addition of soap but MST values increases.

But as we are using an anionic potassium laurate soap, in centrifuged latex the formation of the complex $Zn(OCOR)_2$ is prohibited, ie, the latter latex is more stabilized by the addition of soap. This ZST tests provide an indication of the interparticle potential energy barrier after the latex has been colloidally destabilized by such zinc ions as are available to the latex aqueous phase from solid zinc oxide. Small additions of soap anions increase the colloidal stability of latex particles but cationic soaps sensitize them towards the destabilizative effect of zinc ions ,ie. The ZST values decrease for cationic soaps and increase for anionic soaps. But for MST values soap additions increase MST values.

Table 3. Viscosity Studies of Centrifuged latex by adding soap

% of potassium laurate in 250gm of Centrifuged Latex	Viscosity(cps)
0	84
.005	81.5
.01	116
.015	108.5
.02	68.5
.025	66

Viscosity Graph



Viscosity studies are conducted on centrifuged latex while studying the effect of mechanical stability values on adding anionic soap on centrifuged latex. Viscosity studies shows that on adding an anionic soap potassium laurate on centrifuged high ammonia preserved latex first increases to maximum for 0.0125 % of soap addition and then decreases. The initial increase in viscosity is believed to be due to the increase in ionic concentration in the aqueous phase. However, by subsequent addition repulsive force between the particles increase, leading an increase in average free path and subsequent increase in latex stability and reduction in viscosity.

CONCLUSION

From the stability studies conducted, we can infer that the mechanical stability of the centrifuged latex having (TS-60%) increases with increase in percentage of anionic soap, ie, potassium laurate, added. However, if the soap added may be a cationic one the effect is the same, since it has no zinc oxide in it. Also the chemical stabilities based on zinc oxide tests, ie, ZST of centrifuged latex shows that it increases in the case of anionic soap but decreases with cationic soap. The reverse effect in ZST is due to the destabilizative effect of zinc oxide with cationic soap present in centrifuged latex. Viscosity studies conducted simultaneously show that it first increases to a maximum for certain addition of soap but decreases further for every increase in percentage of soap.

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