# EFFECT OF FIXED ALKALI (KOH) ON THE CHEMICAL STABILITY OF NATURAL RUBBER LATEX

PROJECT REPORT SUBMITTED TO
MAHATMA GANDHI UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR
THE DEGREE OF
MASTER OF SCIENCE
IN CHEMISTRY

BY

**SNEHA SUSY**

REG. No. 80510

POST GRADUATE DEPARTMENT OF CHEMISTRY

**ST. DOMINIC'S COLLEGE**
KANJIRAPALLY
KERALA
2006

Phones : 2353311 ( 7 Lines )

Grams : RUBRBOARD
Telex : 888 285 RRII IN
Fax : 91-481-353327
Tele Fax : 91-481-353324
E-ma : rrii@vsnl.com

# THE RUBBER BOARD

(Ministry of Commerce, Government of India)

## DEPARTMENT OF PROCESSING & PRODUCT DEVELOPMENT

Reply to be addressed to
THE DIRECTOR (P&PD)

KOTTAYAM – 686 009
KERALA STATE

Ref.No. P&PD/P&QC/06/PW

22.06.06

## CERTIFICATE

This is to certify that the report ***Effect of fixed alkali (KOH) on the chemical stability of natural rubber latex*** is a bonafide record of the work undertaken by **Kum. Sneha Susy**, IVth semester student, M.Sc. Pure Chemistry, St.Dominic's college, Kanjirappally 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.

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

P & Q C DIVISION
KOTTAYAM - 686 009

**DEPARTMENT OF CHEMISTRY**

**ST. DOMINIC'S COLLEGE, KANJIRAPALLY, KERALA**

# CERTIFICATE

This is to certify that the project report "**Effect of fixed alkali on the chemical stability of NR latex**" submitted by Sneha Susy in partial fulfillment for the award of Degree of Master of Science in Chemistry of Mahatma Gandhi University is a record of bonafide work carried out by her at Rubber Board , Kottayam under the guidance and supervision of Mr. M. Sunny Sebastian , Joint Director, Rubber Processing and Marketing Development Division, Rubber Board, Kottayam.

Roselin Thomas
Teacher-in-charge

Dr. K.P.Sukumaran Nair
Head of the Dept. of Chemistry

# DECLARATION

I do hereby declare that the project work entitled " **Effect of fixed alkali on the chemical stability of NR latex"** is a bonafide record of the work carried out by me under the guidance of Mr. M. Sunny Sebastian , Joint Director , Rubber Processing and Marketing Development Division, Rubber Board, Kottayam for the partial fulfillment of the requirements of the Degree of Master of Science in Chemistry of Mahatma Gandhi University, Kottayam.

Sneha

**Sneha Susy**

# ACKNOWLEDGEMENT

I express my sincere gratitude to all those who helped me throughout the course of this project work.

First of all I express my deep sincere gratitude to God for the blessings during the course of my project work.

I am thankful to **Mr. M.Sunny Sebastian**, Joint director, Rubber Processing and Marketing development division, Rubber Board for assigning this work, for providing literature, encouragement, timely help and valuable advice throughout the course of this project work. It has been a great privilege for me to work under his guidance.

I owe my special thanks to **Prof. Roselin Thomas**, Teacher-in-charge, Department of Chemistry, St.Dominic's College, Kanjirappally for making necessary arrangement, valuable advice and timely help through out the course of this project work.

I express my gratitude to **Dr. K.P. Sukumaran Nair**, The Head of the Dept. and to all my teachers and staff members of Dept. of Chemistry for their help and encouragement.

I express my sincere thanks to my parents and friends for their co-operation during this project work.

**Sneha Susy**

# CONTENTS

## I . INTRODUCTION

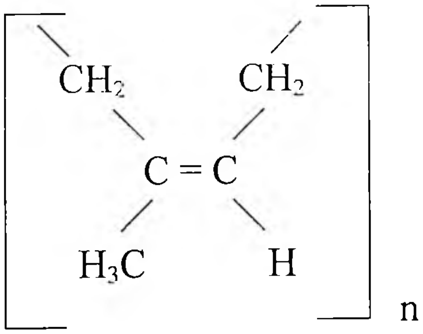
II. MATERIALS & METHODS

# EFFECT OF FIXED ALKALI (KOH) ON THE CHEMICAL STABILITY OF NATURAL RUBBER LATEX

# INTRODUCTION

## Introduction

Raw rubbers are natural or synthetic polymeric materials which are elastic at and around room temperatures. Their high and reversible extensibility and damping properties distinguish them from other materials. At higher temperatures with or without the influence of deforming forces ,raw rubber shows viscous flow, which enables it to undergo shaping processes. Usually from 5 to 20 additives are used to modify the physical properties and processability and/or reduce the compound cost of rubbers. The rubber is shaped and the composite articles built before vulcanization, a process which changes the chemical structure and improves the quality of rubber. Natural rubber latex is also known as Hevea latex. Chemically it is Cis 1,4 polyisoprene which contain one C=C for each isoprene units.



Rubbers have the all round ability to be used in extension, compression, shear, torsion or combination of these methods. Rubbers are resilient. Rubbers are characterized by a high elongation at break. Owing to small atomic masses of atoms and insufficient chain packing rubber densities are low, compared with for eg: metals.

Rubbers dissolve only slowly in appropriate solvents to give solution which have high viscosities even at low concentration. The penetration of small solvent molecules between tangled polymer chains is time and temperature dependent. The resistance to flow, offered by the coiling and tangling of chains, causes a large increase in viscosity of polymer solutions.

Rubber has both a viscous and elastic responses to deformation. The viscous response is proportional to the rate of deformation, while elastic response is proportional to the amount of deformation, ie. the behaviour is viscoelastic.

## Constitution Of Natural Rubber Latex

Natural rubber latex is a whitish fluid of density between 0.975 \$ 0.980 gml$^{-1}$, pH from 6.5 to 7 and surface free energy from 40 to 45 ergs cm$^{-2}$ . Its viscosity is variable. Progressive dilution of fresh latex with water causes the viscosity to increase at first , reach a maximum and then suddenly decreases. These changes are associated with swelling and bursting of bodies known as 'Lutoids'.

Typical composition of fresh latex are

Total solid content - 36%
Dry rubber content - 33%
Proteinous substances - 1 to 1.5%
Resinous substances - 1 to 2.5 %
Ash - up to 1%
Sugars - 1%
Water - remaining

These substances are distributed between three principal phases the rubber particles (35% of latex by weight), the aqueous phase (approx. 55% by weight of the whole) and the lutoid phase (remaining 10 %). The minor phases present constitute the so called Frey-Whyssling particles. The rubber content of natural latex, excepting the latex which exudes during the initial stages of wound response, varies between the limits of 25 & 35 %.

Of the protein content about one half is dissolved in aq: phase, one quarter adsorbed on the surfaces of the rubber particles and the remaining quarter associated with the larger particulate bodies such as the lutoids.

## The Rubber Phase

### a) Shape, Size, Size Distribution & Physical Structure

The first important microscope study of natural rubber latex was reported by Hauser (1926). He concluded that the rubber particles are pear shaped rather than spherical and consist of a tough, hard elastic shell which encloses a viscous liquid. Later conclusion was based on studies using a micromanipulator. The Hauser two phase model for the latex particle is widely accepted with the view that solid natural rubber comprised two distinct fraction, a sol fraction and a gel fraction. The size of the particle varies between 20 to 20,000 $A^0$, being not uncommon.

## b) Chemical Constitution And Structure

A typical composition for the rubber phase of Hevea latex is

| | |
|---|---|
| Rubber hydrocarbon | - 86% |
| Water ( dispersed in the rubber hydrocarbon) | - 10% |
| Proteinous substances | - 1% |
| Lipid substance | - 3% |

Magnesium , Potassium & Copper are also associated with rubber particles (0.05 %) . Density of rubber particle is $0.92 gml^{-1}$. There is some evidence that the natural rubber molecule contains minor amounts of oxygen in the form of carbonyl group.

The lipids associated with rubber particles comprise sterols and sterol ester, fats and waxes such as eicosyl alcohol and phospholipids. The phospholipids is the effective adhesive which bonds the protein to the rubber. The phospholipids of the Hevea latex particle of the lecithin type in which R groups are hydrocarbon radicles of the hepta decyl ( $C_{17}H_{35}$) or hepta decenyl ($C_{17}H_{33}$) types. Other phospholipids in small quantities include metal phosphotides and cephalin.

## **Aqueous Phase**

1. Carbohydrate

The principal of this is 1-methyl inositol which is also known as quebrachitol (1%).

2. Protein & Amino Acids

The serum contains several proteins of widely separated isoelectric points. The principal ones are known as α globulin and hevein. α globulin may be obtained by precipitation from a solution of freeze dried serum in sodium citrate buffer solution of pH4.5 and ionic strength 0.04. α globulin is a surface active protein which is readily adsorbed at air- water and oil-water interfaces . It is insoluble in distilled water, but is soluble in neutral salt solution , acid solution and alkaline solution. Its isoelectric point pH 4.8 , is close to that of fresh Hevea latex.

Hevein is a crystallized protein of abnormally low molecular weight (10,000) and isoelectric pH4.5 . It contains some 5% of sulphur as cysteine type disulphide linkage. It is soluble in water at all pH. It is not precipitated from water by boiling. A multiplicity of polypeptides and simple amino acids has been observed in latex serum , but whether these are precursors or the degradation products of the latex protein is not clear. The free amino acids comprise 0.1% of the whole weight of the latex.

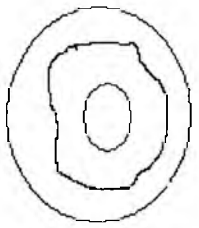
3. Other Serum Constituents

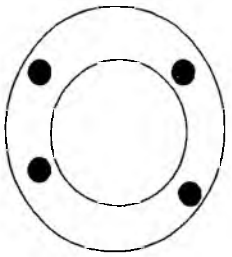
These include free nitrogenous bases such as choline and methylamine, organic acids ,inorganic anions and metallic ions. Fresh latex also contain some 25% of cyanide. A wide range of enzymes also present in fresh natural rubber latex.

## The Crystalline Structure of Rubber

The arrangement of atoms in the rubber crystals can be determined by X-ray examination by the Debye and Scherrer method. Rubber illuminated with a beam of monochromatic X-rays gives a diagram with two concentric halons, which is characteristics of the amorphous state. X-ray diagrams of unfrozen and unstretched rubber show a diffuse halo, which is typical of an amorphous substance. It was a Dutch scientist, Johan Rudolph Katz (1880-1938), who discovered that if rubber is stretched, it gives a diffraction pattern when a beam of X-rays is passed through it, thus disclosing a partial alignment of its long molecules into a crystalline lattice. In the stretched state, rubber gives a fibre diagram which shows marked spots of interference. The segments of the molecular chain in oriented crystallites are aligned more or less along the direction of stretch. The X-ray diagram of elongated rubber is explained by the presence of spatial elements which are not real crystals, but have the characteristics arrangement of crystals in the direction of stretch. These crystallites corresponds to the parallel and uniform arrangement of the isoprene groups which belong to neighbouring molecules. The fibre periodicity of the elementary cell was found to be about 90 nm, each cell actually accommodating an isoprene unit, rather than the whole chain.

On freezing rubber, Debye-Sherrer rings typical of random crystallites, become superimposed on the amorphous background. Thermal crystallization of natural rubber is spherulitic and initiated at a number of independent nucleation sites.(eg. naturally occurring impurities like non-rubbers). Natural rubber, both raw and vulcanized can be frozen from the rubbery state to a state of partial micro-crystallinity. The interference points obtained with elongated rubber can be super-imposed exactly on the rings in the diagram of frozen rubber. This indicates the existence of a definite spatial network.





| Amorphous halo | Fibre pattern halo |
|---|---|
| No crystallization | Dense regions show crystallities |
| Either unstrained rubber | |
| or strained. | Eg: Strained rubber, |
| SBR,BR,EPDM,NBR, | NR,IR,CR,IIR,PU |
| ECO,etc. (most other synthetic) | NR-Natural Rubber |
| SBR- Styrene Butadiene Rubber | IR-Isoprene Rubber |
| BR- Butadiene Rubber | CR-Chloroprene Rubber |
| EPDM-Ethylene Propylene Diene Co polymer | IIR-Isobutylene Isoprene Rubber |
| NBR-Acrylonitrile Butadiene Rubber | PU-Poly Urethane |
| ECO-Epichlorodrin & Ethylene Oxide Co polymer | |

## The Preservation Of Natural Rubber Latex .

When natural rubber latex is kept for a long time without preservation putrefaction sets in with the development of bad odour. In order to prevent this process we have to preserve the natural rubber latex.

Coagulation of rubber depends on ambient temperature and upon the stability of the latex itself . But always the result is a separation into clots of rubber and clear serum. There are long term and short term preservations. Short term preservations are commonly known as anticoagulants.

## The Ideal Preservative

An ideal preservative should have efficiency and ancillary requirements. An ideal preservative should have following characteristic properties.

1. It should destroy micro organism or suppress their activity & growth .
2. It should contribute positively to the colloid stability of the latex by increasing the charge on the particle and the $\zeta$ potential at the rubber-water interface.
3. It should deactivate trace metal , especially heavy metal ions, either by sequestration in solution or by precipitation as insoluble salts.
4. It should obviously harmless to both people & rubber.
5. It should not impart an offensive odour.

## Ammonia As A Preservative

Ammonia is used for both long term and short term preservations. 0.2 % ammonia on the whole latex is sufficient for short term preservation, about 0.7% is requires for permanent preservation.

Ammonia matches upto the exacting requirements for the ideal preservative , it appears that it is very effective as a bactericide if the level present exceeds 0.3% on the whole latex.

Ammonia imparts an alkaline reaction to the serum of latex and there by enhances the magnitude of the negative $\zeta$ Potential at the rubber serum interfaces in consequences it includes the stability of the latex. The lower pH of latex at any given level of ammoniation is due to the partial interaction between the added ammonia and protein which are present in the latex.

Ammonia is able to sequester some metallic ions by amine formation, magnesium ion, in particular, precipitate as the very sparingly soluble magnesium ammonium phosphate.

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

Ammonia does not cause any changes in some of the non-rubber constituents of the latex. It imparts no colour to the latex but it does impart a strong odour. Ammonia preserved latex undergoes a marked thickening when compounded with ZnO. The precise mechanism of this thickening is related to heat sensitising reaction associated with the presence of ZnO, ammonia & ammonium ions. Ammonia interfaces with the gelation of the latex by sodium silico fluoride and therefore has to be reduced to a low level prior to the production of latex foam rubber by this process.

## Low Ammonia Preservation Systems.

Some low ammonia preservation systems are also used .

1) Penta chlorophenate latex combination of 0.2% of ammonia +0.2% of sodium penta chloro phenate on the weight of the whole latex.

2) Zinc Dialkyl Dithio Carbamate Latices

A typical combination would comprise 0.2 % of ammonia +0.1% of to 0.2% of zinc dialkyl dithio carbamate +0.2% lauric acid latices which are preserved in this way give deposits which tend to discolour badly on ageing.

## Concentration Of Natural Rubber Latex

The rubber globule is surrounded by a protective layer of proteins and phospholipids which imparts the colloidal nature to latex. Also, it contains a variety of non rubber constituents both organic and inorganic. In order to remove these non rubber constituents concentration is necessary. There are three methods mainly used for concentration; evaporation, creaming, centrifuging. Centrifuging is the practically useful method.

## Concentration By Centrifuging

This is the most important of the methods which are presently available for the concentration of natural rubber latex. Centrifuging may be regarded as a type of accelerated creaming process, in which separation is affected by means of a centrifugal field rather than a gravitational one.

## Theory Of Centrifuging

To a first approximation the motion of a centrifuging latex particle relative to it's serum is confined to the radial direction. For most practical purposes the coriolis motion ie. the lateral movement relative to the serum, may be neglected. The equilibrium radial velocity of the particle is determined by the balance between two forces, namely, the centrifugal buoyancy, which tends to accelerate the particle and viscous drag which tends to retard it. As in the case of creaming the later force is, for a spherical particle given approximately by Stoke's law for a spherical particle of diameter X and density $\rho$ moving in a circular path of radius R with angular velocity $\omega$ in a medium of density ($\sigma > \rho$) this equality leads to the relationship.

$$4/3\ \pi(1/2X)^3\ (\sigma-\rho)\omega^2R = 6\ \pi\eta\ 1/2\ X\,(-dR/dT)$$

$$(-dR/dT) = \frac{X^2(\sigma-\rho)\omega^2R}{18\eta}$$

where $\eta$ is the viscosity of the aqueous phase of the latex. Thus it appears that the rate of centrifuging increases with squares of the both the particle diameter and the angular velocity and increases linearly with inverse viscosity of the serum. The density difference determines both the direction of centrifuging as well as the rate; for dR/dt is $\overset{<}{\geq}$ 0 and as $\sigma \overset{>}{\leq} \rho$

Furthermore the radial velocity of the particle increases linearly with the radius of it's path, so that the particle is subject to a continuous radial acceleration, even in the equilibrium condition.

The maximum radial displacement of a particle of diameter which has been subjected to centrifuging for a time 't' will be obtained by the integration of the equation.

$$dR/R = \frac{-x^2(\sigma - \rho)\omega^2\, dt}{18\eta}$$

The lower limits of the integral will be $R=R_0$ & $t=t_0$ respectively where $R_0$ is the radius of the path in which the particle was moving initially. The upper limit are arbitrary. The result is

$$R = R_0 e^{\frac{-x^2(\sigma-\rho)\omega^2 t}{18\eta}}$$

Hence the radial displacement is given by

$$\Delta R = R_0 - R = R_0\left\{1 - e^{\frac{-x^2(\sigma-\rho)\omega^2 t}{18\eta}}\right\}$$

The effect of centrifuging upon particle size distribution is evident from the above equation. Consider a particle which initially moves in a path of radius $R_0$, but after a time t now moves in the path of radius R. To meet this requirement, its diameter, $x_R$ must obviously be given by

$$x_R = \sqrt{18\eta/(\sigma - \rho)\omega^2 t \,.\log R_0/R}$$

## Centrifuging In Practice

Of the various centrifuges which may be used for the concentration of natural rubber latex, the type most commonly used is the de Laval. The rotating mass of latex is broken up into a number of thin conical shells, within a bowl which rotates at high speed. The maximum distance which a particle has to traverse in order to pass from the skim into the cream is very small.

## Latex Products

Rubber in fibre form originated in the 1920s as a result of research by US Rubber Company. The early fibres were obtained by extruding rubber latex as the core with cotton, rayon or nylon fibres wrapped around it. Latex is compounded and vulcanized and the technique which is used in covering the rubber core with fibre, controls the degree of elongation and elasticity of the final yarn. Rubber yarn are used in underwear, swimwear, surgical bandages, shoe fibres and elastic tape. Where as the elasticity, strength, impermeability to water and air and low density are advantages. Rubber yarns are susceptible to deterioration by sunlight, damage from body oils or petroleum solvents, the garments must be washed with soap or detergents and are dried.

There are several advantages in using a latex for producing rubber articles.

1. It can be shaped and worked easily and thus find certain applications where dry rubber or a rubber solution cannot be used.
2. It does not require any heavy or expensive machinery.
3. Power requirement is less.
4. The physical properties of latex articles are usually good.
5. Latex is safe to handle .

The disadvantages are:

1. Latex process require strict controls and batch to batch adjustments due to variability in latex properties.
2. Latex processes are not suitable for making rubber goods of heavy or bulky nature.
3. Fillers do not reinforce latex, they act as diluents reducing the product properties.
4. Latex is usually more expensive than dry rubber of comparable rubber contents.

## Characteristic Properties Of Rubber

Rubber have the all round ability to be used in extension, shear, torsion or combination of these methods. Rubbers are resilient. Rubbers are characterized by a high elongation at break. Rubbers dissolve only slowly in appropriate solvents to give solutions which have high viscosities even at low concentrations. The penetration of small solvent molecules between tangled polymer chains is time and temperature dependent. The resistance to flow, offered by the cooling and tangling of chains, causes a large increase in viscosity of polymer solutions.

When rubber is stretched, then heated, it tries to contract. Its modulus of elasticity, ability to carry load, increases with rise in temperature. Rubber also absorbs heat when allowed to contract rapidly. Rubbers are generally insulators ie. poor conductors of electricity, since the bonding is covalent and there is no charge carriers . A large application of rubber is in insulation application where it's flexibility required combined with high resistance to the passage of an electric current. Rubber, when dry, has a remarkable high coefficient of friction, but this is greatly reduced when the rubber is wetted with water.

The properties of rubber can be considerably varied by compounding with fillers and by adjusting the condition of vulcanization. During mixing, the finely divided particles of filler are well dispersed in the rubber, and this produces improved physical properties in the vulcanized product ie. greater resistance to abrasion, tear, higher modulus of elasticity, hardness and tensile strength when new samples of gum and carbon filled rubber vulcanizates are stretched and then allowed to retract, subsequent extensions to the same strain require a lower force. Most of this softening occurs during the first deformation, and, after a few stretching cycles, a steady state is reached. This phenomenon has been termed as the "Mullins Effect". The dynamic properties of rubber are important in such diverse applications as tyres, conveyor belts, high pressure hoses, antivibration mounting and bridge bearings.

In the raw state, rubber should be easy to mix and has sufficient stiffness for conventional processing. Most rubbers contain some form of additive, introduced for some specific purposes such as fillers, plasticizers, colourants, stabilizers against heat and oxidation, flame retardants, processing aids etc. The viscosity of the rubber should be such that initial mastication is not required or is done with minimum energy expenditure.

The process of working rubber on a mixing mill or in an internal mixer until it becomes soft and plastic is known as mastication . The inventor of the first masticator was Thomas Hancok. The breakdown of rubber in air occurs much more rapidly at either high or moderately low temperatures that it does at temperatures around $100^{\circ}$C. Mastication in nitrogen, however, results in a small increase in viscosity or no appreciable change in molecular mass.

The natural rubber molecule may be chemically modified by molecular rearrangement, eg: cyclization, depolymerization, by adding new groups to the molecules or by grafting chemical claims to the molecule. Such modification help to upgrade certain properties such as air permeability, solvent and flame resistance, vulcanization efficiency and processability. Economic factors are obviously important and commercially important modifications have included cyclization, depolymerization, isomerization, chlorination, epoxidation, and grafting with methacrylates.

The rubber goods industry is mainly divided into tyre and non tyre sector. The tyre sector manufactures tyres for aircraft, heavy vehicles, light motor vehicles, two wheelers and off the road tyres also. The non-tyre sector, making use of natural, and synthetic reclaimed rubbers produces cycle tyres, tubes, camel back , foot wear, belts, hoses and extruded goods.

## Chemical Stability Of Latices

The ability of the polymer latices to withstand the destabilizing effects of added substances such as acids, metallic salts and water miscible organic liquids is known as chemical stability .A latex should be normally stable towards certain chemicals added in the compounding stage where as it should form a coherent dry polymer at a later stage in the manufacture of latex goods .Chemical stability tests aim to determine the ease with which particles pass over the energy barrier (which is reduced by chemical means),by measurement of gelation time or viscosity. Several procedures have been proposed for the assessment of the ability of a latex to resist the effects of chemical destabilising agencies. Some of which are discussed below.

## I. Zinc Oxide Thickening (ZOT) Test

The principle of this is to determine the change in viscosity which occurs when a latex is compounded with zinc oxide under standard conditions. The condition are 55% TSC, 3% zinc oxide on the rubber content, pH 9.0, and a very low ammonia content(0.05%). The smaller the change of viscosity, the more stable is the latex. This test gives a qualitative indication of chemical stability, it is of little use as a quantitative measure. This is due to the fact that the coefficient of viscosity becomes markedly dependent upon the shear rate when appreciable thickening occurs.

A variant of this procedure is to determine the zinc oxide thickening in the presence of an added soap. It appears that as the amount of soap is increased, the thickening increases sharply with further soap addition. One interpretation of these observations it is found that the effect of soap is two fold; it stabilizes and also sensitizes towards zinc ions. The former effect predominates at low soap additions and the latter at high additions.

Other tests have been described in which a known amount of sodium silicofluoride is stirred into the latex and the time required for gelling to occur is measured or alternatively the pH at which gelation starts is determined. It may also be more relevant to carry out this test in the presence of zinc oxide. Interpretation of the results gives the fundamental properties of the system is not easy; but at least such results have the virtue of being closely related to certain practical processes.

Still other chemical stability tests aim at determining the amount of dilute solution of a salt, such as calcium, magnesium or barium chloride, which can be run into a well-stirred, suitably diluted latex before coagulation occurs.

The present procedure is to prefer a test procedure in which the mechanical stability of the latex is determined after it has been compounded with zinc oxide and added soap. Such methods are known as ZST tests. Madge, Collier and Newham have published curves which show the effects of increasing addition of various surface active substances upon the mechanical stability of latex containing 3% zinc oxide. As castor oil soap is added, the stability increases at first , passes through a maximum, and then falls sharply. A minimum, followed by a second increases, is observed if the test is carried out shortly after the addition of zinc oxide, but this flattens out and almost disappears if the latex is left to stand for one hour. The simplest explanation of these effects parallels that given for the analogous effects observed in connection with ZOT test, namely that the soap anions first stabilize the particles and then sensitize them towards the action of Zn ions. The flattening out of the second minimum upon standing is associated with gradual dissolution of further quantities of zinc ions. The definite procedures for the Zinc Oxide Stability Testing of natural and synthetic latices have been described by Newham and Simcox. A similar procedure has become the basis of a recent British Standard methods for zinc oxide stability. An amount of latex containing 100 g of total solids is weighed out 1% of potassium oleate is added on a 15% solution of pHvalue between 10 and 10.5. Concentrated formaldehyde solution is added drop wise in order to reduce the pH to 9.80. The total solids content is then reduced to 55%. The latex is placed on a water bath at $30 \pm 1^{0}$ c and left for 10 to 15 minutes, after which time 5g of dry zinc oxide is added with stirring over the course of about 15minutes.The compounded latex is left to stand for 45 minutes at 30°C.It is then strained through an 85-mesh stainless steel gauz. The mechanical stability is then determined at 14,000 rpm and 30°C , using 80g test portion. The averaged result is expressed in seconds.

Newham and Simcox interpret the results of their test for natural rubber latex as follows. A ZST of less than 150 second is regarded as indicative of low stability towards zinc oxide; extra stabilizer may be required. A ZST between 150 and 300seconds is characteristic of medium stability latices which are suitable for latex foam production. Between 300 and 500 seconds implies high zinc oxide stability. ZST greater than 500 seconds is taken to mean great storage stability in the presence of zinc oxide.

The Zinc Stability Time (ZST) test involve adding definite amounts of potassium oleate and zinc oxide to the latex, allowing the mixture to stand at a certain temperature and then performing a mechanical stability test on the sample .The mechanical stability time of the matured mixture is taken as a measure of the chemical stability of the latex. This test is normally performed on natural rubber latex and blends of natural and synthetic rubber latices.

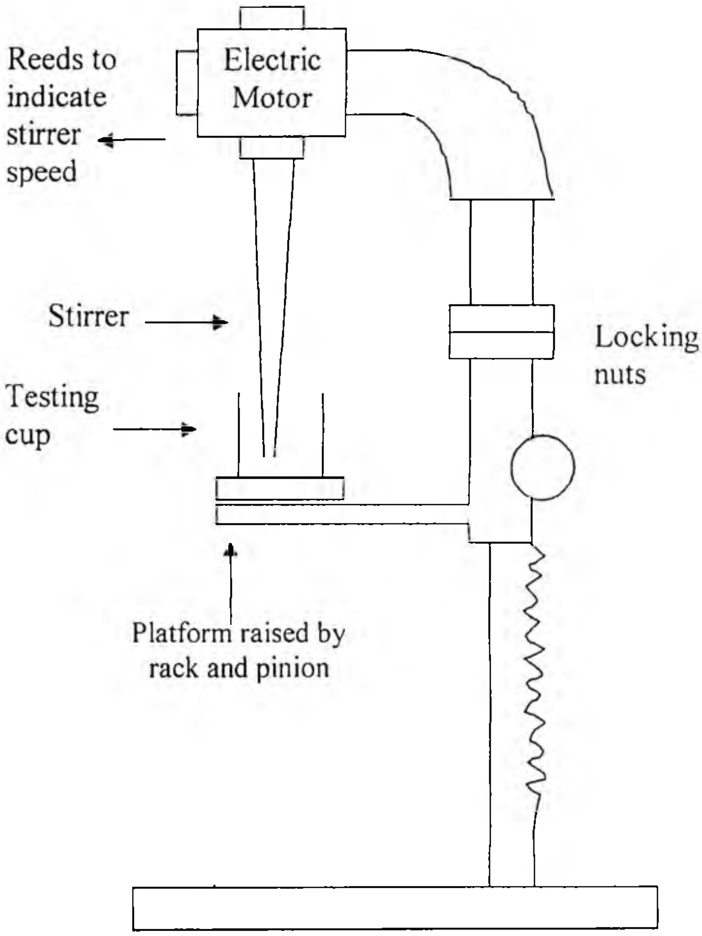
**Procedure**

Chemical stability of natural rubber latex is measured with the same instrument that used to measure the mechanical stability. The chemical stability for natural rubber latex is the time taken for visible aggregation of latex particles under high speed agitation with a specified rot and container. It rises from 100seconds in freshly prepared concentrate to over 700seconds in 4-5 weeks .The coagulum content is defined as the quantity of material remaining on a 180 micron sieve when a sample of latex is strained through it. The 'sludge content' is the quantity of material expressed as a percentage of the latex weight, which may be removed from the latex by centrifuging under specified condition.

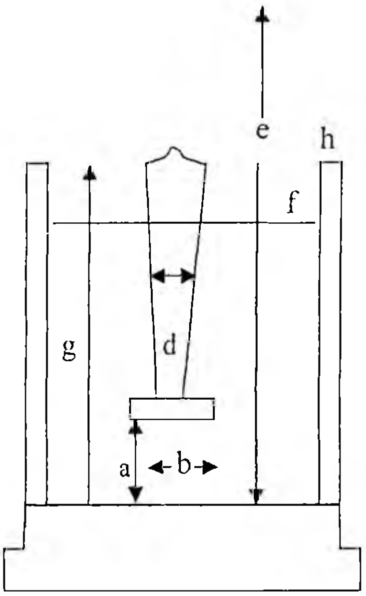
The general procedure for chemical stability determination is to stir definite amount of latex under given conditions of dilution, temperature and speed of stirring and to measure the time which elapses before signs of incipient coacervation appear. The chemical stability is expressed in seconds.

We add ZnO to the natural rubber latex. Therefore the obtained result is Zinc Stability Time (ZST).

## Illustration Of Apparatus For ZST Testing Of Latex.



(a)



(b)

In order to conduct the mechanical stability test for natural rubber latex.

1 The stirrer shaft is to be vertical .

2 The test cup is to be flat – bottomed cylindrical and of smooth inner surface.

3 The cup must be concentric with the shaft.

4 A convenient method for ensuring that the disc and the floor of the cup (dimension“a”in the figure) shall be within specification limits, makes use of a cylindrical slipguage and the two locking rings indicated in figure.

5 The weight X of water, or the ammonia solution, which is required to reduce the fractional solid content of a weight W of latex from its initial value. So to some other value S may be readily calculated from the observation that we must have

$$S = WS_0 / W+X$$

$$X = W\{ S_0/S-1\}$$

In this case it is required that S = 0.55, and hence with the sufficient accuracy may be calculated from the formula,

$$X= W(1.82S_0-1)$$

Both BS & ASTM require the stirrer to rotate at 14,000 ± 200 rpm throughout the duration of the test .The speed is usually adjusted by means of a rheostatic control which is wired in series with the motor which drives the stirrer. The speed is estimated by means of the three reeds indicated in figure. These reeds are tuned to vibrate violently when the shaft speeds are respectively 138000, 14000 and 14200 rpm. Ideally, the centre reed should vibrated violently the whole time; but so long on it is known that the first reed has already vibrated, but the third has get to do so, then the requirements for the procedure in this respect is satisfied.

The details of the BS and ASTM procedures are summarized in the table below :-

| **Details** | **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 11 A type ,distilled water for LA type. |
| Sample weight | 80± 1g | 80± 1g |
| Latex temp: | 35± 1°C | 35 ±1°C |
| Stirred speed | 14,000 ± 200 rpm | 14,000 ± 200 rpm |
| Dimension of cup& stirrer(figure) | | |
| 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 | k 3.5 in | c 0.5 in |
| h | c 3/16 in | c 0.09 in |
| Material cup | Poly methyl methacrylate or Polystyrene | Glass |
| Material of stirrer | Stainless steel | Disc to be of stainless steel |
| Indicator of end point | 85- mesh coagulum content of whole test sample to exceed 0.5 g when washed & dried | Dip glass rod into latex & draw once slightly over the palm; first appearance of small pieces of coagulated rubber in the film so deposited is the end point; may be verified by determining the 80- mesh coagulam, which should be c 0.1% of the total solids |
| Maximum allowable discrepancy between duplicate | 5% | 5% |

in - inch

rpm - rotation per minute

## II. Total Solid Content Test

Total solid content of latex is defined as the percentage by weight of the whole which is non-volatile at a definite temperature in an open atmosphere. The general procedure is to weigh a known quantity of latex (2g)in to a flat bottomed dish and evaporated to constant weight at a definite temp($70^{\circ}C$ ).If $W_0$is the initial weight of latex sample and W is the weight of the dry film,then the total solid content is given by

$$T.S.C = \frac{W}{W_0} \times 100$$

## Scope and Objectives

Aim of my work was to study the effect of fixed alkali (KOH) on the chemical stability of natural rubber latex. For this purpose different concentrations of KOH were prepared and for each concentration ZST and pH were noted. The latex initially contain ammonia then ZnO was also added to the latex to conduct stability studies.

## Materials And Methods

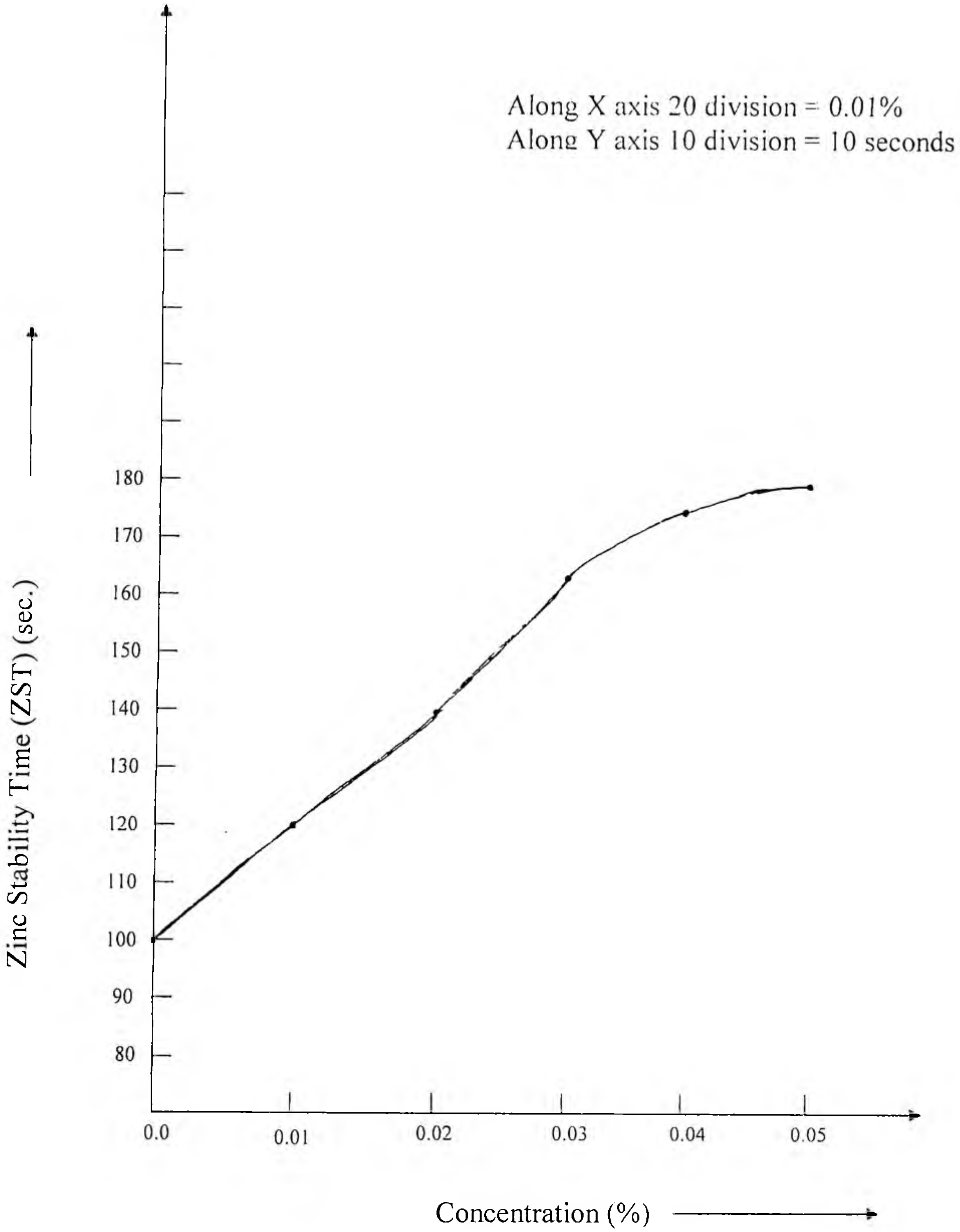
**a. Requirements :** KOH ( 0.01, 0.02, 0.03, 0.04, 0.05)
ZnO ( 1.5g for each)
Ammoniated Latex ( 80g for each)

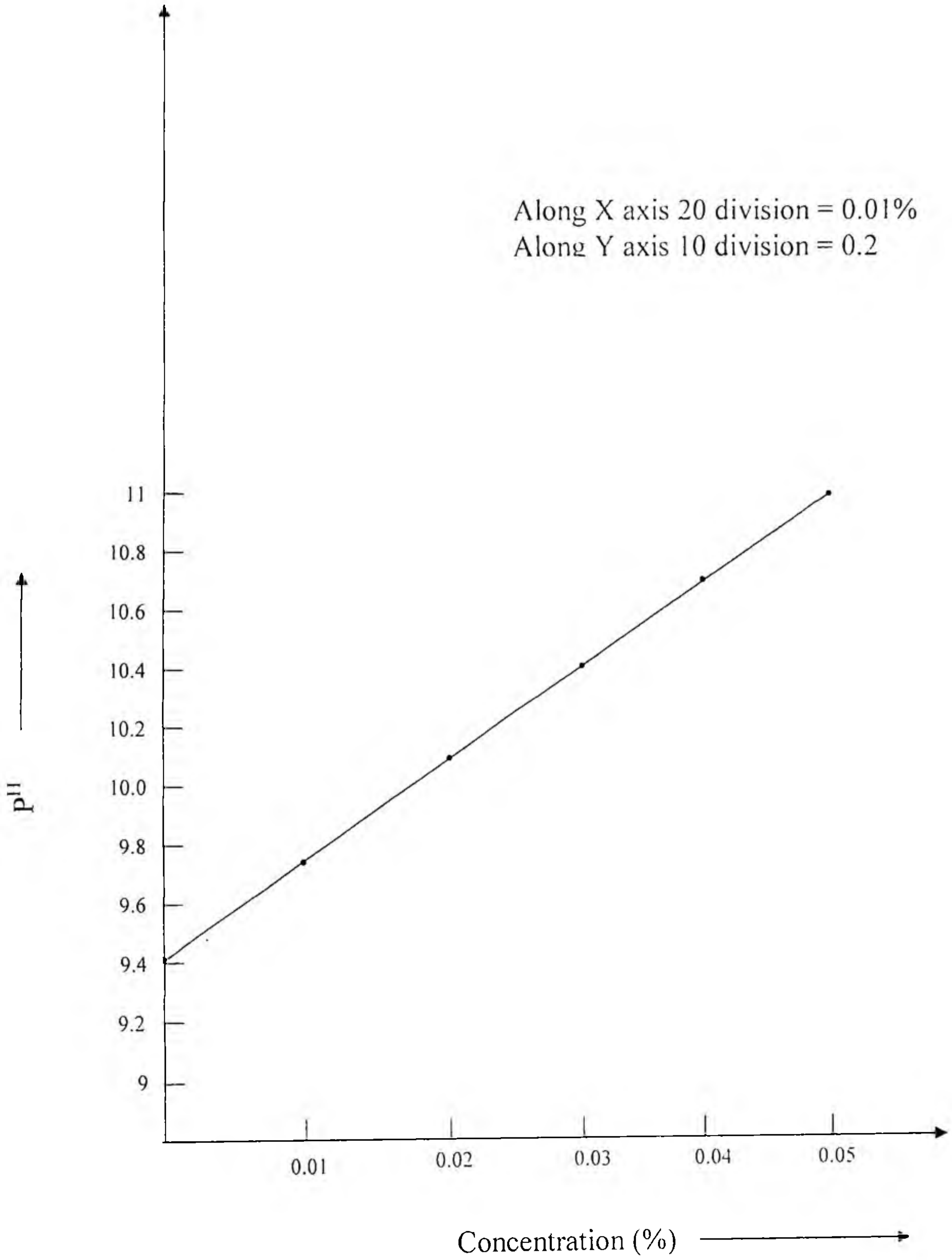
## b. Procedure

100g: of natural rubber latex was accurately weighed and transferred in to a 250 ml beaker. Five such samples were taken. 100ml 5N KOH was prepared. Then 0.2, 0.4, 0.6, 0.8 and 1 ml KOH added to it. A sixth sample was also taken without adding KOH. The six beakers were covered and kept for 24 hours .After 24 hours 1.5g : of ZnO added to each sample, shaken well and kept for one hour . 80g of latex from the first beaker was taken in the mechanical stability instrument .Time for the coagulation of the latex was noted. The same test was repeated with all the concentration of KOH. Now a small amount of the latex was taken in the pH meter and pH was also determined for all the concentration

| Concentration of KOH (%) | pH | ZST (sec) |
|---|---|---|
| 0 | 9.41 | 100 |
| 0.01 | 9.72 | 120 |
| 0.02 | 10.06 | 140 |
| 0.03 | 10.38 | 164 |
| 0.04 | 10.7 | 175 |
| 0.05 | 11.02 | 180 |

A graph can be plotted by taking concentration along X axis and time along Y axis. Another graph can be plotted by taking concentration along X axis and $P^H$ along Y axis. They are shown below.


Along X axis 20 division = 0.01%
Along Y axis 10 division = 10 seconds
Zinc Stability Time (ZST) (sec.)
180
170
160
150
140
130
120
110
100
90
80
0.0
0.01
0.02
0.03
0.04
0.05
Concentration (%)



Along X axis 20 division = 0.01%
Along Y axis 10 division = 0.2

## Result And Discussion

Ammonia reacts with water to form ammonium hyroxide which on decomposition give $NH_4^+$ & $OH^-$. Now ZnO is added to the latex which reacts with ammonia & ammonium ions in the latex to form tetramine zinc salt. This is thermally unstable. Therefore forward reaction is most favourable. This undergoing decomposition to give $Zn^{2+}$ & $NH_3$ .This $Zn^{2+}$ reacts with soap present the latex to form insoluble zinc soap .This determines the stability of the latex.

Now KOH is added which is a strong base. It undergoes complete dissociation to give $K^+$ & $OH^-$ . The $OH^-$ concentration increases and it reverses the first reaction at a faster rate. It also reduces the availability of $NH_3$ .As a result $RCOO^-$ simply left in the latex and thus the chemical stability increases by the addition of KOH. Similarly increasing $OH^-$ concentration increases the pH.

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

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

$$Zn(NH_3)_4^{+2} \rightleftharpoons Zn^{+2} + 4NH_3$$

$$Zn^{+2} + 2RCOO^- \longrightarrow Zn(OCOR)_2$$

Insoluble Zinc soap.

$$KOH \longrightarrow K^+ + OH^-$$

# CONCLUSION

My work was to add different concentrations of KOH (0.01, 0.02, 0.03, 0.04, 0.05) to natural rubber latex, then to determine the chemical stability and pH. By observing the results and graph , it is concluded that when a fixed alkali like KOH is added to the natural rubber latex it's stability increases . The stability can be increases upto the concentration 0.15% of KOH. As more and more KOH added to the latex it become more alkaline, and this cause an increase in pH to a very high value.

# REFERENCES

1. Rubbery materials & their compounds, J.A.Brysdon.
2. High Polymer Latices, D.C.Blackley
   Applide Science publishers; London, 1966.
3. Polymer Latices: Science & Technology, D.C.Blackley
4. Polymer Latices, Chapmann & HALL London, 1997.
5. Polymer Latices & their applications , K.O.Calvert
   Applied Science Publishers, London 1983.
6. Rubber Engineering; Indian Institute; Tata Mc Graw Hill Publishing Company Ltd, New Delhi.
7. Hand book of Rubber Technology; Steven Blow, Galgotia Publicatons Pvt. Ltd, New Delhi.
8. Polymer Science :V.R. Gowariker ; N.V. Viswanathen, Jayadev Sreedhar.
9. Text book of polymer Science: Billmeyer.
10. T.D.Pendle and ADT Gorton(1988) Processability Testing of Natural Rubber Latex Concentrate.
11. ADT Gorton(1988) Pre-vulcanised Natural Rubber Latex for Dipping Proceedings of International Rubber Technology conference .