FACTORS AFFECTING FATTY ACID SOAP CATALYSED ACID COAGULATION OF FRESH FIELD LATEX

Project work carried out at RRII, Kottayam
in partial fulfilment of the requirements for
the Degree of **Master of Science**
in Chemistry (Polymer Science)

By

LEKHA T. B.

SCHOOL OF CHEMICAL SCIENCES
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Certificate

This is to certify that **Ms. LEKHA T. B.** *has carried out her project work on* **FACTORS AFFECTING FATTY ACID SOAP CATALYSED ACID COAGULATION OF FRESH FIELD LATEX** *at Rubber Research Institute of India, Kottayam, for the partial fulfilment of the Degree of Master of Science in Chemistry (Polymer Science).*

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CERTIFICATE

This is to certify that this project report entitled "FACTORS AFFECTING FATTY ACID SOAP CATALYSED ACID COAGULATION OF FRESH FIELD LATEX" *being submitted by* Ms. LEKHA T.B. *for the partial fulfilment of the requirements for the degree of Master of Science in Polymer Science of Mahatma Gandhi University, Kottayam is an authentic record of the research work done by her in the Rubber Chemistry, Physics and Technology Division of the Rubber Research Institute of India, under my supervision and that no part thereof has been presented for any other degree or diploma.*

Rosamma

Dr. ROSAMMA ALEX,
Rubber Technologist,
RCPT Division,
RRII, Kottayam.

R..R.I.I.,
14/1/1998.

Declaration

I hereby declare that the project work entitled FACTORS AFFECTING FATTY ACID SOAP CATALYSED ACID COAGULATION OF FRESH FIELD LATEX, submitted to the School of Chemical Sciences, Mahatma Gandhi University, Kottayam, for the award of Master of Science Degree in Chemistry is the result of the original research work carried out by me under the guidance of Dr. Rosamma Alex, Rubber Technologist, RCPT Division, RRII, Kottayam. I have not submitted the same in part or in full to this University or to any other University for the award of any degree or diploma.

Lekha T. B.

Kottayam
16..12..1997

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Lekha T. B.

Contents

Chapter 1

INTRODUCTION

Natural rubber latex is a stable colloidal dispersion of cis-1,4 polyisoprene of high molecular mass in an aquous medium. Freshly-tapped natural rubber latex of <u>Hevea Brsiliensis</u> is a whitish liquid having a density in the range 0.975 - 0.980 Mgm^{-3}, pH 6.0 - 7.0, and surface free energy 40 - 45 mJm^{-2}. Its viscosity is variable.

1.1 Composition of natural latex[1,2]

Being a natural product, the composition of fresh latex varies between wide limits. The composition given in Table is typical.

Typical composition of fresh natural rubber latex

Constituent	Proportion/% mm on whole latex
Total solids	36
Dry rubber	33
Proteinaceous substances	1-1.5
Resinous substances	1-2.5
Ash	Upto 1
Sugars	1
Water	ad 100

These substances are distributed between three principal phases; the rubber phase, which account for some 35% of the latex by weight; the aquous phase, which is approximately 55% by weight of the whole; and the lutoid phase, which account for most of the remaining 10%. There are also many other minor phases present in the latex known as Frey-Wyssling particles.

1.1.1 Rubber phase[3,4]

1.1.1.a Size, shape and physical structure

The first important microscope study of natural rubber latex to be reported was that of Hauser (1926). He came to the conclusion that the rubber particles are predominantly pear-shaped rather than spherical consist of a tough, hard elastic shell which encloses a viscous liquid.

The size of the particles varies between wide limits, the range 200 to 20,000 n° being not uncommon. Of special note is the fact that the bulk of the dispersed rubber is in the form of a minority of larger particles, chemical constituion and structure.

A typical composition for the rubber phase of <u>Hevea</u> latex is:

Constituent	Proportion %
Rubber hydrocarbon	86
Water [dispersed in the rubber hydrocarbon]	10
Proteinaceous substances	1
Lipid substances	3

1.1.2 The aquous phase

The aquous phase of fresh natural rubber latex is a dilute aquous solution of density 1.02 g ml^{-1} which contains many chemical species of which the following constitute a partial list.

1.1.2.a Carbohydrates

The principal of these is e-methyl inositol which is known as quebrachitol. It occurs to the extent of about 1% of the whole latex. They have little influence upon the properties of the latex. In the absence of adequate preservation; the carbohydrates become microbiologically oxidised to the so-called 'volatile fatty acids'.

1.1.2.b Proteins and amino acids[5]

The serum contains several proteins of widely separated isoelectic points. The principal ones are known as -globulin and hevein. Especial interest attaches to the proteins of high isoelectric point, since these will be calionic under the conditions of pH which prevail in the serum of the fresh latex.

1.1.2.c Other serum constituents

These include free nitrogenous bases, organic acids, inorganic acids and metallic ions. Fresh latex also contains some 0.25% cyanide. A wide range of enzymes is also present in natural rubber latex.

1.1.3 Lutoids and other particulate phases

Chemically lutoids appear to be mainly in water. They contain, in addition, small quantities of soluble protein, insoluble protein and phospholipid.

1.2 The stability and destabilisation of latices

The subject of latex stability has two quite distinct aspects. The first concerns the tendency or otherwise for an individual particle to undergo changes by interaction with the aquous phase. If more than one particle is present in the system, the possibility now arises that two or more particles may first cohere to give a loose agregate, and may subsequently coalesce to give a single larger particle. Thermodynamically coalescence is favoured; for when coalescence occurs. There is a reduction in the specific surface area of the system, and therefore in the interfacial free energy per unit volume of the dispersed polymer.

1.2.1 Factors which promote latex stability

In the sense that the coalesced or flocculated state is one of lower free energy than the dispersed or deflocculated state, it may be said that all latices are thermodynamically unstable.

At least these important and interrelated factors are responsible for delaying the attainment of the flocculated state. These are respectively, reduction of the free energy associated with the interface which separates the polymer and the aquous phase; the presence upon the particle surfaces of electric charges of similar polarity causing mutual coulombic repulsions between the particles; and the presence around the particles of a layer of tightly bound water molecules which act as a mechanical barrier against the coalescence of two polymer particles.

Of these three factors, the first can do more than mitigate the tendency to thermodynamic instability. Although interfacial free energies may be reduced, they always remain positive, and thus although the free energy change which accompanies coalescence may be reduced, it can never be reversed in sign. Reduction in interfacial free energy does not therefore make coalescence energetically unfavourable; it merely make it less favourable than would otherwise have been the case. It seems that, on balance, there is a net loss in free energy accompanying deflocculation. The cause is probably not so much a negative interfacial free energy as the development of very strong coulombic forces of repulsion, due to the special chemical nature of the polymer, when placed in an alkaline medium.

The second of these three factors, namely the acquisition of electric charges, constitutes a positive deterant to cohesion and coalescence, because of the consequent coulombic repulsions between the particles. The magnitude of the effective electric charge upon a colloid particle is conveniently expressed in terms of the electro-kinetic potential change across the 'diffuse' part of the electrical double layer which occurs at the boundary between the two phases.

The third factor which promotes the colloid stability of latex systems is the presence around the particle of a sheath of tightly bound water molecules. The extent to which hydration occurs is unknown, but it is believed to depend very much upon the nature of the substances which are adsorbed at the particle interface. Likewise the contribution which the hydration layer makes to the colloid stability of the system is far from clear.

1.3 Destabilisation and coacervation of latices

The term coacervation will be applied quite generally to any process which destabilises a latex to such an extent that the particle agglomerate and coalesce in large numbers. It is found that the resultant coacervate may assume one of the three distinct forms: a gel, in which case the process is described as gelation; coagulation, for which the process is described as coagulation; or a mass of floccs, in which event the process is described as flocculation.

Very little is known regarding the details of the mechanism by which coacervation occurs. From general considerations it seems clear that a two stage process is involved. The first stage is the clustering of the particles into coherent aggregates; this is presumably a second order process with respect to the concentration of unclustered particles. The second stage is the coalescence of the particles which constitute an aggregate to form one large particle; this process should be first order with respect to the concentration of aggregates.

Likewise, very little is known regarding the factors which determine the physical nature of the end-product of a coacervation process.

Gelation seems to depend upon the gradual development throughout the latex of a continuous network of aggregated, coalesced particles. Lumps of coagulum seems to be formed under conditions where the coacervating agency is unevenly distributed. Small floccs appear to develop as a result of coacervation processes in which aggregation occurs freely but inter-particle coalescence does not.

We can see that the aggregation of two particles will occur whenever they possess sufficient kinetic energy to overcome the potential energy barrier which separates them. It therefore appears that the process of aggregation may be hastened in atleast two ways: by reducing the height of the potential energy barrier, or by increasing the average kinetic energy of the particles.

1.4 Thermodynamics of particle aggregation

The measure of the driving force tending to ultimate particle aggregation and coalescence in a lyophobic sol is the reduction in Gibbs free energy which accompanies these processes. The Gibbs free energy increase which accompanies the

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1.4 Thermodynamics of particle aggregation

The measure of the driving force tending to ultimate particle aggregation and coalescence in a lyophobic sol is the reduction in Gibbs free energy which accompanies these processes. The Gibbs free energy increase which accompanies the aggregation and coalescence of a single pair of particles is denoted as ΔG and ΔG^* denotes the height of the barrier to aggregation relative to the dispersed state.

The relationship between ΔH^*, ΔH^* and ΔS^* is:

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

ΔH^* quantifies the contribution to ΔG^* from forces which operate between the various parts of the molecular system which confers stability upon the Sol. $-T\Delta S^*$ quantifies the contribution to ΔG^* from any increase in the order within the various parts of that molecular system as the two particles approach each other.

The requirement for a stable lyophobic sol is that ΔG^* should be positive. There are three types of combination of ΔH^* and ΔS^* which give rise to $\Delta G^*>0$. They are as follows:

1. ΔH^* and ΔS^* are both positive and $\Delta H^*>T\Delta S^*$
2. ΔH^* and ΔS^* are both negative and $/T\Delta S^*/>/\Delta H^*/$ and
3. ΔH^* is positive and ΔS^* is negative.

1.5 Destabilising agencies

The agencies which can reduce the colloid stability of a latex fall into types, chemical and physical.

1.5.1 Chemical coacervants

1.5.1.1 Possible modes of action

Chemical coacervants function mainly by reducing electrokinetic potential which is associated with the electrical double layer surrounding the latex particle. This reduction may be brought about in atleast three distinct ways:

(i) Direct interaction may occur between the added coacervant and one of the adsorbed components of the double layer, causing neutralisation of the electrical charge which has responsible for the existence of the double layer. Loss of one associated hydration layer may also occur. The most usual form which such interaction takes may be conveniently described as the "insolubilisation" of the adsorbed stabiliser which was responsible for the electrical double layer in the first place.

(ii) Alternatively, direct interaction of a more "physical" kind may occur between the added coacervant and the electrical double layer. Such indirect interaction usually takes the form of a swamping or "compression" of the double layer by ions of opposite polarity to that of the particle side of the double layer.

(iii) A third possibility may be described as an indirect interaction between the added coacervant and the surface phase which separates the polymer and the aquous phases. Such indirect interaction may occur when the coacervants occurs a fine precipitate of high specific surface area to form in the aquous phase of the latex. The precipitate may then successfully compete with the polymer particles for the colloid stabilisers which are present in the system. In such cases, agglomeration of the particles occurs because they have been robbed of the stabilisers which formerly prevented them from coming together.

In practice, it is often impossible to dissociate each of these modes of action from the other two and it is always difficult to predict what type of coacervate a given coacervant will produce.

It is convenient to subdivide chemical coacervants into three groups: direct coacervants, heat sensitising coacervants and delayed action coacervants.

1.5.1.2 Direct coacervants

This group includes those substances which bring about an immediate and evident destabilisation as soon as they are added to the latex. A large number of substances function as direct chemical coacervants for carboxylate stabilised anionic latices. It is convenient to classify them under five sub-headings:

Strong acids
Metallic ions
Water-miscible organic solvents
Polymer-miscible organic solvents
Cationic surface-active substances

1.5.1.2.a Strong acids

Any substance which generates hydrogen ions will bring about an immediate destabilisation of most latices. This effect is due principally to interaction between the added hydrogen ions and the carboxylate ions which stabilise the latex.

$$\mathrm{RCOO^{-} + H^{*} \longrightarrow RCOOH}$$

The result is the formation around the particle of a layer of free fatty acid which is insoluble, unionised and unhydrated. The electrokinetic potential falls to virtually zero, and the electric double layer surrounding the particle collapses. Any hydration sheath becomes dispersed as the insoluble fatty acid.

The usual effect of strong acids upon the latices of rubbery polymers is to cause the rapid formation of lumps of coagulum. Small quantities of acid may some times be incorporated without any immediate apparent change, although a slow gelation may subsequently occur.

Coacervation by acids is a feature of several technological processes, not the least important of which is the production of dry natural rubber from natural rubber latex. Formic acid and acetic acid are mainly used for this purpose. Good use is made of the fact that dilute acids may be added to fresh latex without the immediate formation of coagulum. Instead gelation gradually occurs over a period of time.

1.5.1.2.bMetallic ions

Two types of reaction may occur when a solution containing heavy metal ions is added to a latex which has an alkaline aquous phase. In the first place, direct interaction with the stabilising carboxylate ions may occur with the formation of insoluble, unhydrated, un-ionised metallic soaps:

$$M^{n+} + nRCO^{-}\ 2 \text{ -------> } (RCO_2)_nM$$

Alternatively, an insolubile heavy metal hydroxide may be precipitated in the aquous phase.

$$M^{n+} + nOH^{-} \text{ --------> } M(OH)_n$$

Both these reactions can cause destabilisation of the latex, the first through collapse of the electrical double layer which surrounds the particle and also through loss of any hydration layer, and the second through the adsorption of latex stabilisers on to the precipitated hydroxide. In this latter case there may also some mechanical entanglement or co-precipitation of the polymer particles with the insoluble hydroxide.

The univalent etallic ions, such as those of sodium and potassium, have a relatively small effect upon the stability of anionic lattices. Some destabilisation does occur if they are added in large quantity. But bivalent metallic ions, such as Ca, Mg, strontium, barium, etc. tend to cause rapid and intense coacervation. Trivallent metallic ions, such as those of Al and of ferric ion, tend to cause latex particles to flocculate.

1.5.1.2.c **Water-miscible organic liquids**

Water-miscible organic liquids, such as ethyl alcohol and acetone, tend to cause immediate destabilisation of litices. Two distinct mechanisms are operative. The first involves the dehydration of the layer surrounding the particles by the successful completion of the added hydrophilic molecules for the available water molecules. Secondly, the reduction in the dielectric constant of the aquous phase promotes the tendency to ion-pair formation at the particle surfaces. It also promotes a general compression of the double layer. The electrokinetic potential is reduced as a consequence, and so the stability is also reduced.

1.5.1.2.d **Polymer miscible organic liquids**

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1.5.1.2.d Polymer miscible organic liquids

The addition to a latex of a liquid such as benzene or carbon tetrachloride, which is immiscible with the aquous phase but miscible with the polymer, causes a gradual thickening with the formation of an apparently uniform coacervate. The mechanism of these effects undoubtedly involves the gradual inhibition of the solvent by the polymer with consequent swelling of the particles. Eventually the particles touch one another and begin to calesce with an invision of phase. The eventual coacervate is probably a dispersion of latex serum in a continuous matrix of swollen polymer.

1.5.1.2.e Cationic surface active substances

The addition of cationic soaps such as cetyl trimethylammonium bromide, to a negatively charged latex causes a progressive thickening which eventually results in coacervation. Surface-active cations are readily adsorbed by the negatively charged particles, but the effective charge on the particles is thereby reduced.

1.5.1.3 Heat sensitizing coacervants

The second group of chemical coacervants include a number of substances which have relatively little effect upon the stability of a latex at room temperature. When a latex which contains one of these substances is heated coacervation occurs rapidly, once some threshold temperature has been exceeded. In these circumstances coacervation usually occurs as gelation. These include; the zinc-ammine system, polyvinyl methyl ethers and polypropylene glycols.

1.5.1.4 Delayed action coacervants

The third group of chemical coacervants include substances which have little effect when initially added but bring about a gradual coacervation, usually with the formation of a gel, after the lapse of a certain tiem. The ideal delayed action system would show no change of viscosity until after the lapse of a certain critical time, when instantaneous gelation would suddenly occur. Actual systems are characterised by a more or less gradual increase in viscosity, with the ultimate formation of a uniform gel. Delayed action coacervants may be classified into (i) Salts of hydrofluoro silicic acids, (ii) Salts of other fluoro acids and (iii) Other delayed action coacervants.

1.5.2 Physical destabilizing agents

Roughly speaking, physical agencies are able to bring about a destabilisation of a latex system if they increase either the frequency or the violence of the collisions between particles or both. Thus raising the temperature of a latex brings about both of these effects, although the increase of violence, rather than the increase of frequency, is the more important factor here.

Lowering of temperature also enhances the destabilisation of latex. A third physical agency which tends to destabilise latices is mechanical agitation. The particles are thereby caused to collide more frequently and more violently.

1.6 Scope of the present work

When acid is added to latex there is a time delay before coagulation occurs. Also coagulum must be kept for a further 2 hours before it is sufficiently hard to allow for handling. Latex has been coagulated by chemical agents. If latex can be coagulated rapidly with the formation of a coagulum of sufficient strength, then the use of coagulation tanks in the production of crumb rubber from latex can be avoided. Another advantage of rapid coagulation is that the volume of coagulant required for coagulation can be known immediately. Then it could be possible to relate the volume of acid required for coagulation. With the rubber content or total solids of the latex, as it is the rubber and non-rubber solids which get coagulated by the addition of acid. Metrolac method is a quick method for determination of DRC. But the accuracy is not good as there is a variation of ± 5%[6].

No systematic work on rapid coagulation of latex is carried out. Hence an attempt is made to study the rapid coagulation of latex, the factors affecting the rapid coagulation and to get a correlation of the dry rubber content of the latex with the volume of acid required for coagulation.

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When acid is added to latex there is a time delay before coagulation occurs. Also coagulum must be kept for a further 2 hours before it is sufficiently hard to allow for handling. Latex has been coagulated by chemical agents, if latex can be coagulated rapidly[9,10] with the formation of a coagulum of sufficient strength, then the use of coagulation tanks in the production of crum rubber from latex can be avoided. Another advantage of rapid coagulation is that the volume of coagulant required for coagulation can be known immediately. Then it could be possible to relate the volume of acid required for coagulation. With the rubber content or total solids of the latex, as it is the rubber and non-rubber solids which get coagulated by the addition of acid. Metrolac method is a quick method for determination of DRC. But the accuracy is not good as there is a variation of ±5%.[11] Microwave technique is also used for the determination of DRC.[12]

No systematic work on rapid coagulation of latex is carried out. Hence an attempt is made to study the rapid coagulation of latex, the factors affecting the rapid coagulation and to get a correlation of the dry rubber content of the latex with the volume of acid required for coagulation.

Chapter 2

MATERIALS AND METHODS

2.1 Materials

Fresh natural rubber latex of different clones obtained from Rubber Research Institute of India, Kottayam was used for this study. Sulphuric acid (0.05N), fatty acid soaps (15%) and standard sodium carbonate solution (0.1 N) were of laboratory reagent grade. Phenolphthalein used was also of reagent grade. Toluene used was of HPLC grade.

2.2. Methods

2.2.1 Determination of total solid content[13]

Procedure

Take 5 to 10 g. of well mixed sample in a stoppered conical flask. Weigh to the nearest 0.1 g. Pour about 5 g. of sample into precisely weighed petridish of about 60 mm diameter and weigh to obtain the weight of latex added by difference. Dry the test portion in a vented air oven at a temperature of 70°C. Cool in a dessicator and weigh as quickly as possible. Repeat the drying operation until the loss in weight is less than 1 mg, during a period of 30 minutes for temperature between 70°C and 85°C.

Calculation

Total solid percentage by weight = $(W_1/W_2) \times 100$

where W_1 is the weight in gram of dry coagulum and

W_2 is the weight in gram of sample latex.

2.2.2 Determination of dry rubber content[14]

Reagents

2% solution of acetic acid.

Procedure

Weigh about 10 g. of the well mixed sample accurately to a 250 ml beaker from stoppered conical flask. Add water until total solids content of the latex is 20%. Add about 2-4 ml of acetic acid/g of the sample with gentle stirring. Keep the solution undisturbed for about 10 minutes in a water bath. If the serum remains milky add about 0.5 ml of rectified spirit/g of the sample and gently stir. When the serum is clear, filter the serum through Whatman No. 1 filter paper. Collect any small particles of coagulum. Thickness of the coagulum is reduced to about 2 mm. Wash the coagulum with running water. Dry the coagulum at a temperature of approximately 70±2°C. Cool in a dessicator and weigh. Repeat drying, until the loss in weight is less than 1 mg.

Calculation

Dry rubber content percentage by weight = $(W_1 / W_2) \times 100$

where W_1 is the weight in gram of dry coagulum and

W_2 is the weight in gram of sample latex.

2.2.3 Determination of percentage of acetone extract[15]

Instrumental

The extraction apparatus should be of the reflux type with the condenser placed immediately above the cup which holds the sample. The cup must be situated in the vapour of the boiling solvent for enough away from the sides of the extraction flask or condenser jacket to ensure that it will be maintained at the temperature of the boiling solvent.

Procedure

Place 2 to 5 g sample in a paper extraction-thimble which has previously been extracted with acetone. Insert the wrapped sample in the extraction cup and pour sufficient freshly distilled acetone into the extraction flask. Subject the sample to continuous extraction for 20 hrs. After distilling off the acetone from the extract, dry the flask and contents in a current of air for 1 hour at 65-70°C, cool in air and weigh. Dry for a half hour and reweigh. The dried residue is the 'acetone extract'.

Calculation

Acetone extract percentage = $(W_1/W_2) \times 100$

where W_1 is the weight in gram of dry coagulum and

W_2 is the weight in gram of sample latex.

2.2.4 Preparation of fatty acid soaps[16]

2.2.4.a Potassium Oleate soap (15%)

Reagents

	Parts by weight	
Oleic acid	100	A
Water	400	
Potassium hydroxide	19.85	B
Water	236.64	

Procedure

A is warmed to 75°C and B is added to A with efficient stirring.

2.2.4.b Castor oil soap (20%)

Reagents

	Parts by weight	
Castor oil	100	A
Water	400	
Potassium hydroxide	25	B
Water	50	

Procedure

A is warmed to 75°C and B is added to A with efficient stirring.

2.2.5 Determination of molecular weight[17,18]

Instrumental

Molecular weight determination is carried out by a waters 510 gel permeation chromatography instrument attached with a 410 diffraction refractometer. HPLC grade toluene was used as the solvent with flow rate set to 1 ml min^{-1}. The GPC columns were calibrated with polystyrene standards.

Procedure

0.1% solution of rubber in HPLC toluene is prepared. About 1 ml of the solution is injected into the GPC columns. The flow rate is kept at 1 ml/min. The refractive index of the solution is compared with the solvent (HPLC toluene) and monitored. The change in refractive index with time gives a measure of the fhange in concentration of the rubber in the solution with time. The election time of the rubber solution is about 30 minutes. The high molecular weight fractions are eluted first followed by the low molecular weight fractions.

2.2.6 Determintion of K, Na, Mg and Ca

Instrumental

a) Flame photometer[19]

The concentration of potassium and sodium in the dry ashed extract is determined with a flame photometer. The principle of operation of a flame photometer is based upon the quantitative measuremnt of the characteristic

2.2.5 Determination of molecular weight[17,18]

Instrumental

Molecular weight determination is carried out by a waters 510 gel permeation chromatography instrument attached with a 410 diffraction refractometer. HPLC grade toluene was used as the solvent with flow rate set to 1 ml min^{-1}. The GPC columns were calibrated with polystyrene standards.

Procedure

0.1% solution of rubber in HPLC toluene is prepared. About 1 ml of the solution is injected into the GPC columns. The flow rate is kept at 1 ml/min. The refractive index of the solution is compared with the solvent (HPLC toluene) and monitored. The change in refractive index with time gives a measure of the fhange in concentration of the rubber in the solution with time. The election time of the rubber solution is about 30 minutes. The high molecular weight fractions are eluted first followed by the low molecular weight fractions.

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light emitted when a solution of the element being determined is atomised as a mist into the gas flame. In the gas flame the liquid sample is transformed into the optically radiating vapour.

b) Atomic absorption spectrophotometer[20,21]

The concentration of calcium and magnesium in the sample solution is determined with an atomic absorption spectrophotometer.

Principle

In atomic absorption analysis the element being determined must be reduced to the elemental state, vapourized and imposed on the beam of radiation from the source. This process is most frequently accomplished by drawing a solution of the sample as a fine mist into a suitable flame. The flame thus serves a function analogous to that of cell and solution in conventional absorption spectroscopy. Atomic absorption spectrum of an element in its gaseous, atomic form consists of a series of well defined narrow lines arising from the electronic transition of the outermost electrons.

Procedure

About 5 g. sample is mixed with 1 ml conc. HNO_3 and kept for ashing at 550°C. Ashed sample is digested with 2 ml 1:1 HNO_3 on a waterbath and make upto 100 ml. Filter the solution if necessary. This is the stock solution.

a) Na (Flame photometry)

Stock solution as such is used for Na determination.

K (Flame photometry)

10 ml. stock solution, diluted to 100 ml is used.

Mg (Atomic absorption spectrophotometry)

Pipette out 1 ml stock solution into 100 ml standard flask. Add 5 ml. $SrCl_2$ solution and make up to the volume strontium chloride solution is prepared by dissolving 91.16 g $SrCl_2.6H_2O$ in water and diluting it to 2 litres.

Ca (Atomic absorption spectrophotometry)

25 ml stock solution, diluted to 50 ml after the addition of 2.5 ml $SrCl_2$ solution is used.

Calculation[22]

Percentage of K = R / (10 x Wt)

Percentage of Na = R / (Wt x 100)

Percentage of Ca = R/ (10 x Wt)

Percentage of Mg = R / Wt

2.2.7 Determination of volume of acid required for coagulation

Reagents

0.05N H_2SO_4, fatty acid soap 15%, phenolphthalein, std. sodium carbonate solution.

Procedure

Take 100 ml fresh field latex in a 100 ml conical flask and mix with 13.33 ml of 15% fatty acid soap solution. Pipette out exactly 5 ml of the latex into a

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0.05N H_2SO_4, fatty acid soap 15%, phenolphthalein, std. sodium carbonate solution.

Procedure

Take 100 ml fresh field latex in a 100 ml conical flask and mix with 13.33 ml of 15% fatty acid soap solution. Pipette out exactly 5 ml of the latex into a

500 ml beaker. Transfer the contents of the pipette completely by repeated washing. Make up the solution to 50 ml with distilled water. Add a drop of phenolphthalein and titrate the diluted latex with standard sulphuric acid. Note the reading when the pink colour disappears and also when the diluted latex coagulates.

Calculation

Actual volume of acid required to coagulation = $V_2 - V_1$.

where V_1 is the volume of acid required for neutralisation and V_2 is the total volume of acid required for coagulation.

2.2.8 Determination of Mg. content in latex

Reagents

EDTA	:	0.005 M (1.86 g/litre of water)
$MgSO_4$	:	0.308 g/250 ml
Buffer solution	:	Ammonium chloride 67.5 g+ 570 ml Ammonia in 1 litre of water
Eriochrome black indicator	:	0.3 g with 100 ml NaCl or 0.06% in alcohol

Procedure

<u>Standardisation of EDTA with standard $MgSO_4$ solution</u>

10 ml of the standard $MgSO_4$ solution is taken, 2 ml buffer and a few drops of the indicator are added and titrated with EDTA to a faint blue colour.

Estimation of magnesium on latex

About 5 g. of latex is accurately weighed into a volumetric flask and made up to 100 ml. 10 ml of the solution is taken, 2 ml buffer and a few drops of the indicator are added and titrated with EDTA to a faint blue colour.

Calculation

Standardisation of EDTA

$$\text{Strength of Mg solution} = \frac{\text{Wt. of } MgSO_4 \times 24.32 \times 1000}{\text{Volume of } MgSO_4 \text{ made up} \times 246.5}$$

$$= \frac{0.308 \times 24.32 \times 1000}{10 \times 246.5}$$

= 3.04 mg of mg/ml.

Estimation of Mg.

$$\%\ \text{Mg on latex} = \frac{\text{Volume of EDTA} \times \text{Strength of EDTA} \times 10 \times 100}{\text{Wt. of latex taken} \times 1000}$$

Chapter 3

RESULTS AND DISCUSSION

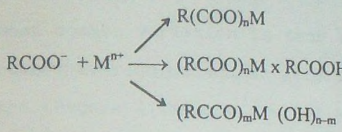
3.1 Effect of the type of fatty acid soap required for the coagulation of fresh field latex

Volume of acid required for fatty acid soap sensitised coagulation of fresh field latex for two different clones PB235 and RRIM600 using three soaps are shown in Table 1(a) and Table 1(b). The soaps used were 15% solution of castor oil soap, 15% solution of potassium oleate soap and 15% solution of rubber seed oil soap. Addition of soap brings about immediate coagulation of 2 clones studied. Cartor oil soap is found more effective as it brings about immediate coagulation at a concentration of 0.12 grams per 100 ml of latex. In the case of rubber seed oil soap and castor oil soap a higher concentration is required for immediate coagulation with the formation of a clear serum. The volume of acid required for coagulation increases with concentration of soap, above a critical value of soap concentration. Critical value of COS is 0.12% w/v, for POS and RSO soap it is 0.24% w/v on latex. In the case of potassium oleate soap minimum volume of acid required for coagulation is at a concentrtion of 0.24 parts per 100 ml latex and in the case of rubber seed oil soap it is at a concentration of 0.5 parts per 100 ml. latex.

Preserved field latex stored for 2 days has been shown to coagulate immediately in presence of agents such as dioctyl sodium sulphosuccinate or ammonium ricinoleate by the addition of acids.[23,24,25] acid. When fatty acid soap is added to latex it is possible that part of the proteins which attached to the latex particles is displaced by them. These soap carboxylates are characterised by sensitivity to acids and dissolved heavy metal ions, both which destroy their surface activity. This loss of activity is accompanied by precipitation of either the free carboxylic acid or the corresponding heavy metal soap.

^ the

$$2RCOO^- + H^+ \longrightarrow RCOOH + RCOO^- \xrightarrow{H^+} 2RCOOH$$



$$RCOO^- + M^{n+} \longrightarrow \begin{cases} R(COO)_nM \\ (RCOO)_nM \times RCOOH \\ (RCCO)_mM\ (OH)_{n-m} \end{cases}$$

So the fatty acid anions of soaps of oleic acid, castor oil and rubber seed oil which stabilise latex, get precipitated on addition of acid thereby depriving the latex stabilizers leading to coagulationof latex.

There are important differences in the solubility behaviour of various straigth cham aliphatic carboxylates. As far as the nature of R is concerned, increasing the length of hydrocarbon chain decreases the solubility, whereas the introduction of unsaturation and substitutiton of hydroxyl groups increases the solubility of the common straight cham carboxylates containing 18 carbon atoms in all, the stearates are the least soluble and ricinoleates are the most soluble; the oleates are intermediates. The sodium soaps are least soluble and the ammonium soaps are intermediate.

Castor oil soap contains 86% riccinoleic acid, rubber seed oil soap contains about 69% of unsaturated fatty acids like oleic acid, linoleic acid and linolenic acid.

3.2 Effect of molecular weight on the volume of acid required for soap sensitised coagulation of fresh fieLd latex

Molecular weight of natural rubber varies from 3.75 x 10^3 to 10^7 (samples 1 and 3 in Table 3, Figure 1). And the most common variation is from 45 x 10^4 to 6.9 x 10^7. The number average molecular weight varies from 60,000 to 7 lakhs (Figure 2).Weight average molecular weight varies from 1-25 lakhs (Figure 3).

There are basically two patterns for molecular weight distribution curves. One in which there is a single curve and the others in which a single peak and a shoulder. When there is a single peak and a shoulder the polydispersity is higher. But in some cases molecular weight distribution curve of single peak shows higher polydispersity (Figure 4).

Generally as molecular weight increases, the volume of acid required increases and then decreases after the molecular weight exceeds 2 lakhs. This is seen from Table 2 and from Figure 7. But there is no direct correlation of volume of acid required for coagulation with the molecular weight of latex. Molecular weight distribution follows a similar pattern for different clones (Figure 5 and 6). The size of the rubber particles is entirely without significance in coagulation process depending upon the addition of chemical reagents.

3.4 Effect of bivalent and monovalent metal ions

As seen from the Table 3 volume of acid required for coagulation is not proportional to DRC of the latex. The magnesisum ions present in the latex does not seem to enhance fatty acid soap sensitised acid coagulation of fresh field latex. A sample of low DRC and higher amount of bivalent metal ions requires a high volume of acid for coagulation compared to another sample of latex having a higher DRC and a lower concentration of metal ions[23] (samples 5 and 7). Latex samples of similar DRC but containing varying amount of bivalent metal ions required the same volume of acid for coagulation (sample 7 and 14). The quantity of metal ions do not vary much from latex to latex and it is found to be comparatively very low. From the observations which have noted it is clear that bivalent metal ions do not have much influence on the soap sensitised coagulation of fresh field latex. The Na and K ions also does not affect the soap sensitised coagulation of latex.

3.5 Effect of non-rubber solids

The non-rubber solids present in latex do not influence the soap catalysed coagulation of fresh field latex. This is seen from Table 4. Acetone extract follows a similar pattern for different clones (Figure 5 and 6). The size of the rubber particles is entirely without significance in coagulation process depending upon the addition of chemical reagents.

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3.5 Effect of non-rubber solids

The non-rubber solids present in latex do not influence the soap catalysed coagulation of fresh field latex. This is seen from Table 4. Acetone extract contains long chain fatty acids like oleic acid, linoleic acid and stearic acid along with small quantities of sterol and sterol esters. Non rubber solids account for the total amount of proteins, sugars and ash. It has shown earlier that resins play no role in the coagulation of latex by acetic acid. In fatty acid soap catalysed coagulation of fresh field latex, the influence of dry rubber content predominates the influence of non rubber solids.

3.6 Effect of DRC

As a general trend, volume of acid required for coagulation increases with the DRC, reaches a maximum and then decreases with the further increase of DRC. At extremely low dilutions volume of acid required for coagulation varies directly with concentration of DRC (for lattices containing less than 8%) (Table 6). At very low concentrations, the volume increases with DRC because as DRC increases more quantity of soap is adsorbed on the surface and hence a larger quantity of acid is required to neutralise these anions. As the concentration of dry rubber content is increasing the number of rubber particles are also increasing and it is probable that there is a reduction in the brownian movement and coagulation takes place with some types of mechanical entrapment of the rubber particles. Coagulation of rubber particles in suspension is a matter in which physicochemical forces between the particles and the stabilising properties of the envelope coating the rubber particles are both of importance.

Table 1. Effect of the type of fatty acid soap on the volume of acid required for the coagulation of fresh field latex

Type of soap	Volume of soap (ml)	Concentration of soap (g/100 ml latex)	Volume of latex (ml)*	Volume of 0.0669 N H_2SO_4 (ml)	Remarks
–	–	–	5	10	Does not coagulate
Castor oil soap 15%	0.04	0.12	5	2.4	Clear end point
	0.08	0.24	5	2.8	Clear end point
	0.165	0.50	5	3.45	Clear end point
	0.33	1.00	5	4.90	Clear end point
Potassium oleate Soap 15%	0.04	0.12	5	3.5	Not clear serum
	0.08	0.24	5	2.5	Clear serum
	0.165	0.50	5	3.2	Clear serum
	0.33	1.0	5	3.9	Clear serum
Rubber seed oil soap 15%	0.04	0.12	5	3.5	Not clear serum
	0.08	0.24	5	3.2	Clear serum
	0.165	0.50	5	3.05	Clear serum
	0.33	1.0	5	3.9	Not clear

* NR latex

DRC% = 21.98

TSC% = 25.81

Mg% w/v = 0.0255

Table 2. Effect of molecular weight on the volume of acid

Sl. No.	Mn	DRC %	Volume of acid (ml)
1	60,338	29.69	5.15
2	83,675	29.00	5.12
3	1,54,884	29.90	5.20
4	2,89,771	30.37	5.65

Table 3. Molecular weight variation in natural rubber latex

Sl. No.	Mn	Mw	Mp	Polydispersity	DRC %
1	436810	1563192	1065259	3.578653	26.64
2	755426	2927329	2654686	3.345829	26386
3	38862	110540	84620	2.844389	27.76
4	83075	413171	198067	4.973469	29.05
5	60338	137310	98109	2.275691	29.61
6	229847	695446	563333	3.025692	29.69
7	44584	102201	77149	2.292339	33.26
8	419787	2138990	2014462	5.095411	34.30
9	235301	1808869	1787592	7.687478	38.82
10	136692	489832	314440	2.954439	39.76
11	106858	360020	247265	3.369138	41.45

Table 4. Effect of bivalent and monovalent metal ions on the volume of acid required for fatty acid soap sensitised acid coagulation of latex

Sl. No.	DRC %	Mg %	Ca %	K %	Na %	Volume of 0.0669 N H_2SO_4 (ml)
1	28.7	0.26635	0.00601	1.9707	0.00995	5.54
2	28.9	0.32423	0.00400	1.99406	0.0196	6.04
3	31.9	0.19682	0.009711	1.9304	0.00796	4.86
4	32.5	0.15028	0.02803	1.92915	0.0096	5.3
5	33.2	0.24288	0.01437	1.75197	0.0139	5.64
6	33.8	0.19650	0.00687	1.70876	0.00813	5.64
7	35.3	0.17285	0.01821	1.52980	0.0099	5.47

Table 5 Effect of non rubber solid percentage on the volume of acid

Sl. No.	TSC %	DRC %	Non rubber solids	Acetone extract %	Vol. of acid (ml)
1	33.36	29.24	4.12	2.44319	5.6
2	32.189	29.92	2.269	2.30897	5.0
3	32.949	30.37	2.579	2.51749	5.6
4	36.130	31.964	4.166	1.58733	4.9
5	35.35	32.58	2.77	3.26161	5.2
6	35.67	32.96	2.71	1.87975	5.0
7	38.24	33.88	4.36	2.46592	5.6
8	39.723	34.01	2.713	2.073	5.15

Table 6. Effect of DRC on the volume of acid required

Sl. No.	DRC %	Volume of 0.0669 N H_2SO_4 (ml)
1	3.6	0.75
2	4.3	0.8
3	6.6	1.15
4	9.0	1.95
5	11.0	2.05
6	14.0	2.50
7	15.7	3.7
8	17.9	4.15
9	22.8	4.75
10	28.9	5.55
11	30.4	5.65
12	31.0	5.55
13	31.25	5.85
14	32.6	5.3
15	35.15	5.45
16	41.05	5.15

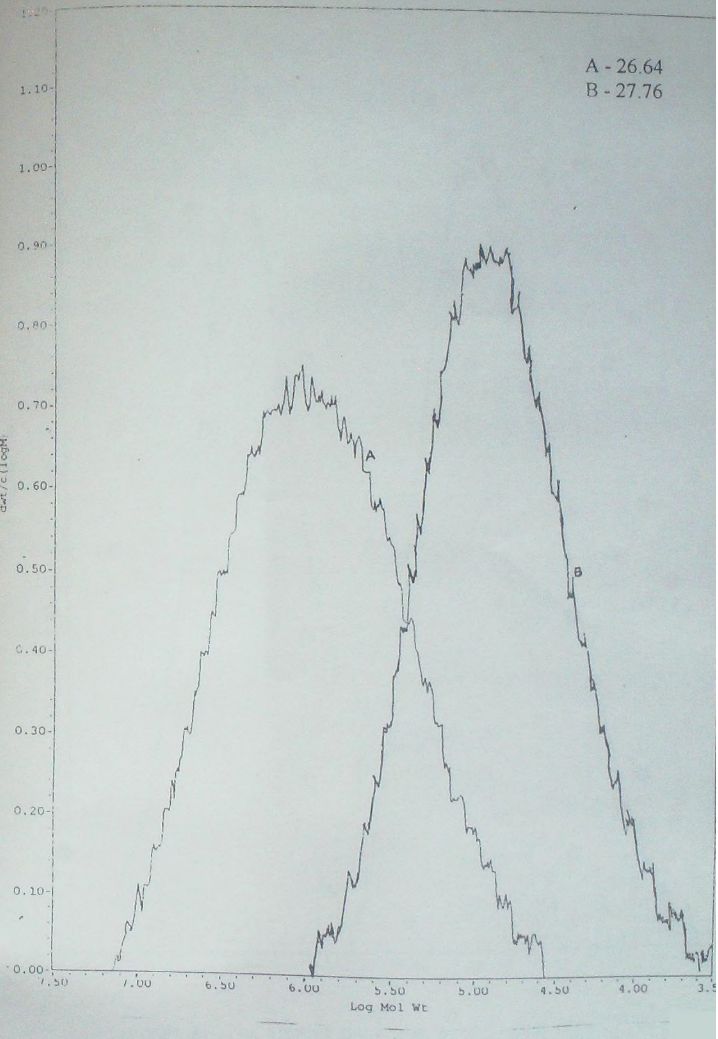


Figure 1. Molecular weight of N. R. varies from 3.75×10^3 to 10^7

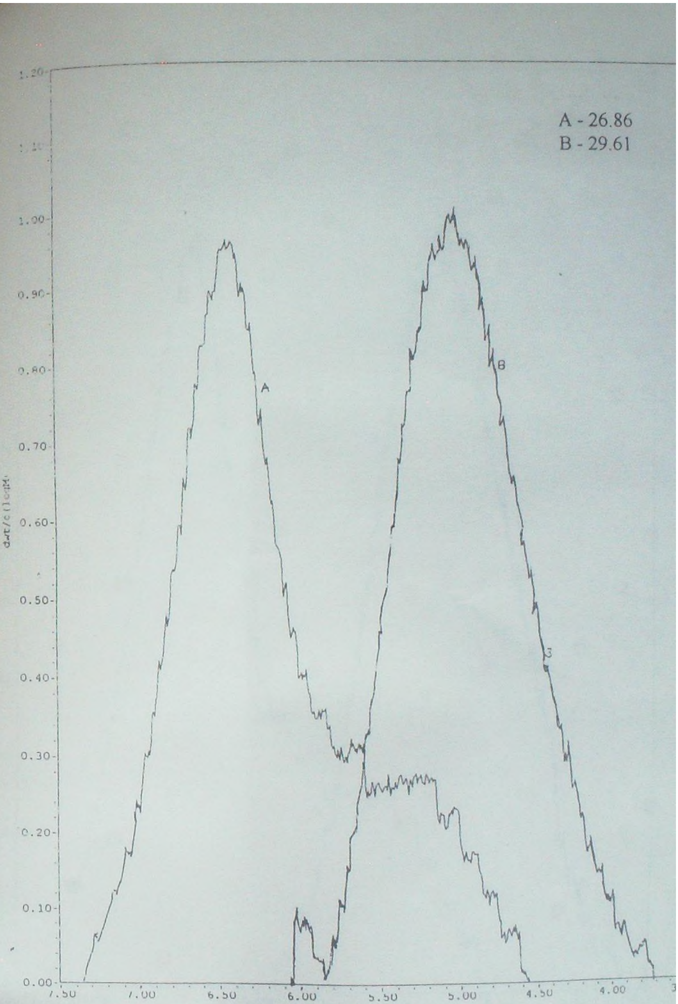


Figure 2. No. average molecular weight varies from 60,000 to 7 lakhs

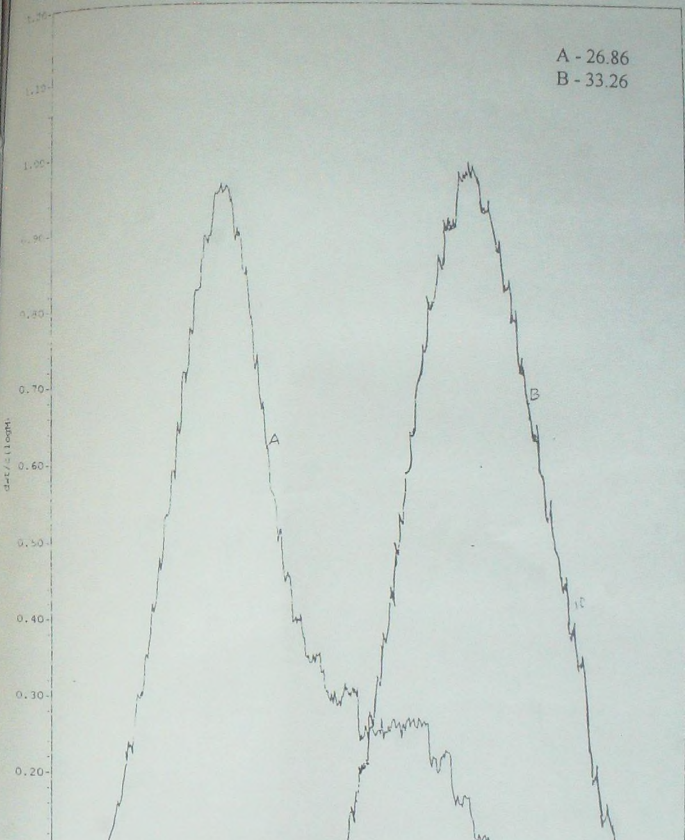


Figure 3. Weight average molecular weight varies from 1-25 lakhs

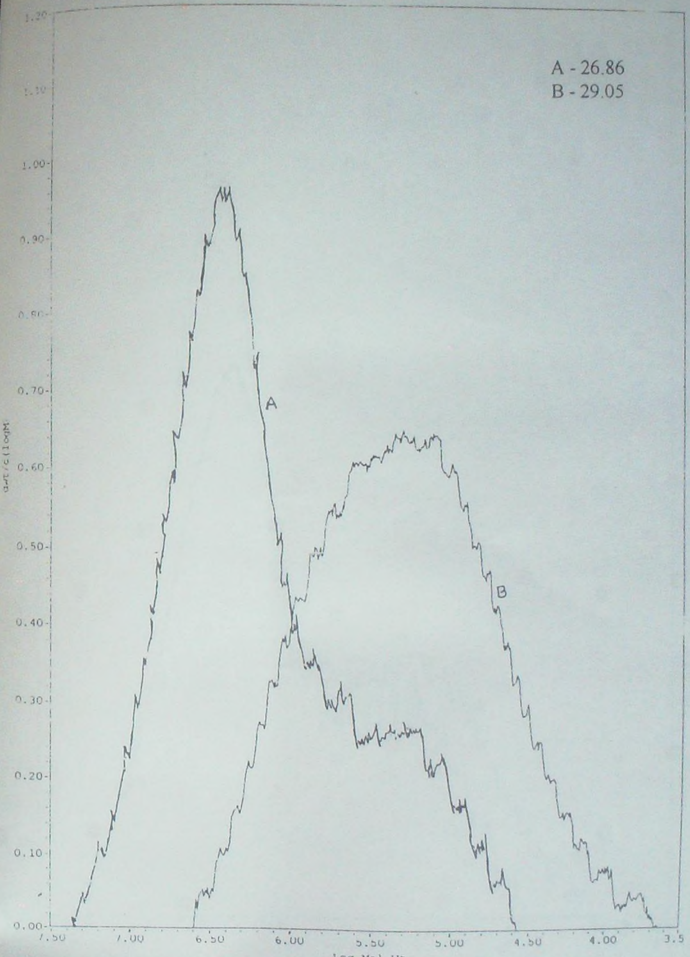


Figure 4. Sample with a molecular weight distribution curve of single peak but higher polydispersity

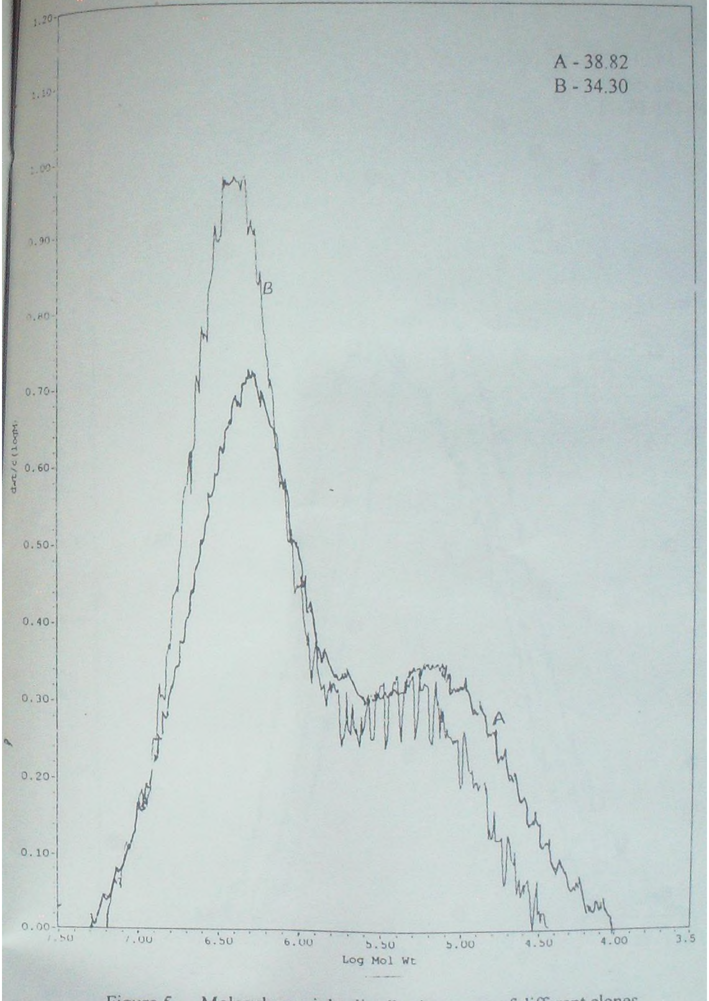


Figure 5. Molecular weight distribution curve of different clones

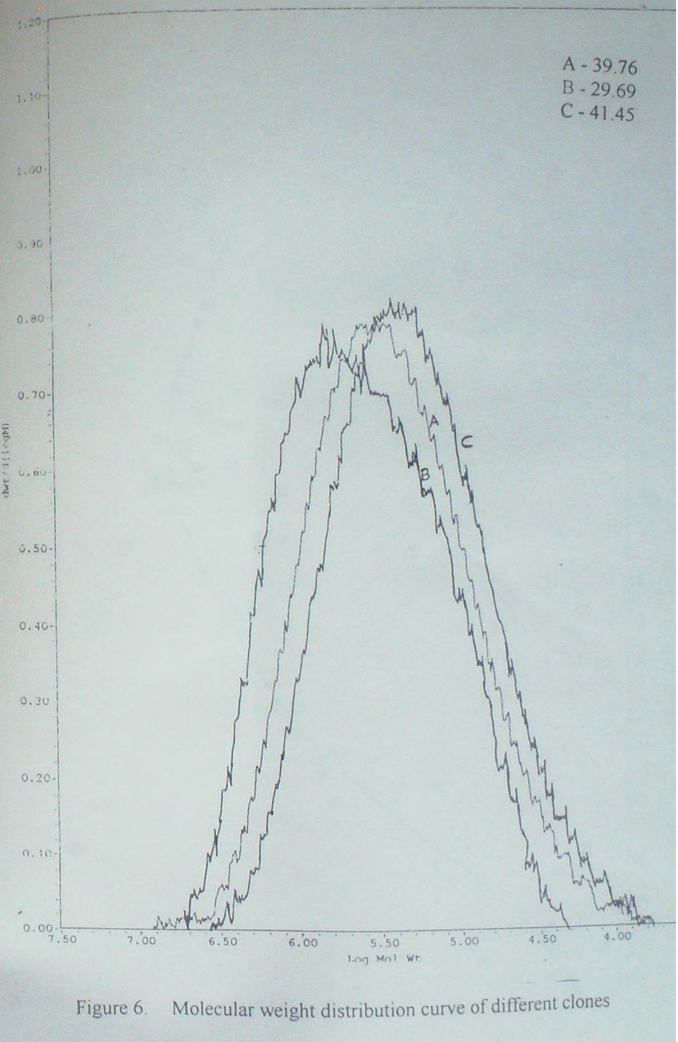
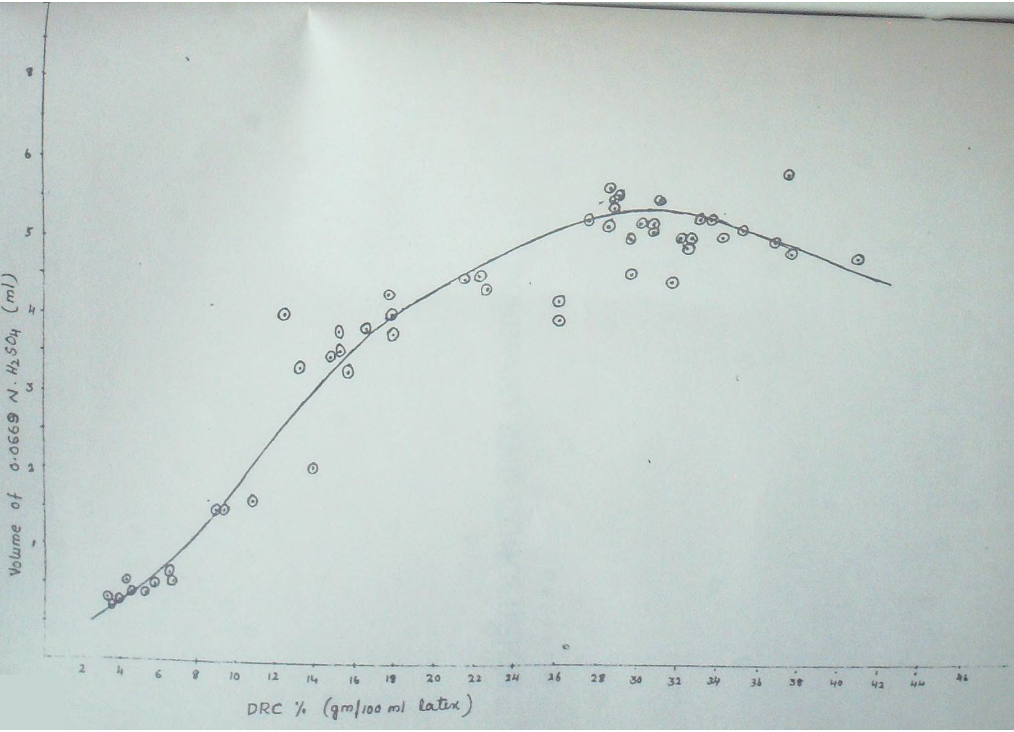


Figure 6. Molecular weight distribution curve of different clones


Volume of 0.0669 N. H2SO4 (ml)
1
2
3
4
5
6
8
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
DRC % (gm/100 ml latex)

Chapter 4

SUMMARY AND CONCLUSION

Fatty acid soap catalysed acid coagulation of fresh field latex was studied. The rapid coagulation of fresh field latex which is sensitised with fatty acid soap avoids the use of coagulation tanks in the production of crumb rubber. In addition this provides a method to determine the volume of acid required for coagulation.

Fatty acid soaps catalysed acid coagulation of fresh field latex used 15% solutions of castor oil soap, potassium oleate soap and rubber seed oil soap. Castor oil soap was found more effective as it brought about immediate coagulation. Higher concentrations of RSO, soap and PO soap were required for immediate coagulation. The volume of acid required for coagulation increases with concentration of soap above a critical value of soap concentration.

Generally as molecular weight of the rubber increased the volume of acid increased and then decreased after the molecular weight exceeded 2 lakhs. When low molecular weight fractions were more, the volume of acid required was more.

The monovalent and bivalent metal ions have little effect on the soap catalysed acid coagulation. In fatty acid soap catalysed coagulation the influences of dry rubber content predominates the influence of non rubber solids. It was shown earlier that resins played no role in the coagulation of latex by acetic acid. As a general trend, the volume of acid required for coagulation increased with DRC, reached a maximum and then decreased with further increase of DRC. A linear correlation of volume of acid with DRG was possible only at extremely low concentrations. The natural rubber latices at a DRC content varies from 3%-8% showed a direct relationship for the volume of acid required for coagulation and the dry rubber content.

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