STUDIES ON HEAT SENSITIZATION OF NATURAL RUBBER LATEX USING POLY VINYL METHYL ETHER AS SENSITIZER

THESIS SUBMITTED
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF

Master of Technology
in
Polymer Technology

By
SHERA MATHEW

DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
COCHIN - 682 022

APRIL 1998

NE : 578311 (7 Lines)

GRAMS: RUBRBOARD
TELEX: 888 265 RRII IN
FAX: 91-481-578317

रबड बोर्ड
(वाणिज्य मन्त्रालय, भारत सरकार)
THE RUBBER BOARD
(Ministry of Commerce, Government of India)
प्रशिक्षण और तकनीकी परामर्श विभाग
DEPARTMENT OF TRAINING & TECHNICAL CONSULTANCY
तकनीकी परामर्श विभाग
TECHNICAL CONSULTANCY DIVISION

ply addressed to the
rector (T & TC)

कोट्टयम - ९, केरल
KOTTAYAM - 686 009
KERALA STATE

ef. No. TC/1/Gen/98

Date 24.4.1998

CERTIFICATE

Certified that the thesis entitled "Studies on Heat Sensitization of Natural Rubber Latex using Poly Vinyl Methyl Ether as Sensitizer" being submitted by Smt. Shera Mathew in partial fulfillment for the award of the degree of MASTER OF TECHNOLOGY in Polymer Technology of Cochin University of Science and Technology, Cochin-22 is a record of bonafide work done by her under the guidance of Smt.G Rajammal, Rubber Technologist, Department of Training & Technical Consultancy, Rubber Board.

KS Gopalakrishnan,
DIRECTOR [T&TC]

Phone : 5-55723

DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY

COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
COCHIN - 682022

No.

Date 24.4.1998

Dr.A.P.Kuriakose
Prof. & Head of the Dept.

CERTIFICATE

This is to certify that the thesis entitled "Studies on Heat Sensitization of Natural Rubber Latex using Poly Vinyl methyl Ether as Sensitizer" submitted by Smt.Shera Mathew for the award of the degree of Master of Technology in Polymer Technology of the Cochin University of Science and Technology is a record of bonafide work carried out by her under the guidance of Mrs.G.Rajammal, Rubber Technologist, Dept.of Training & Technical Consultancy, Rubber Board, Kottayam.

Dr.A.P.Kuriakose,
Prof. & Head of the Dept.

ACKNOWLEDGEMENT

I acknowledge my sincere gratitude to **Mr.K.S.GOPALAKRISHNAN**, Director (T & TC) Rubber Board and to **Dr.A.P. KURIAKOSE**, Professor and Head, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology for arranging my project work in the T & T.C Department, Rubber Board.

I am extremely thankful to **Mr.K.S.GOPALAKRISHNAN**, Director (T & TC), **Dr.N.R.PEETHAMBARAN**, Deputy Director (FM) and to **Smt.G.RAJAMMAL**, Rubber Technologist (T.C) under whose guidance, I could finish the project work successfully in time.

I wish to express my sincere thanks to **Mr.P.VISWANATHA PILLAI**, Dy. Director T.C Division and all other Staff of the Division for their invaluable help and kind Co-operation.

SHERA MATHEW

CONTENTS

EXECUTIVE SUMMARY

REFERENCES

GLOSSARY

NRL - Natural Rubber Latex
PVL - Prevulcanized Latex
HAM Type - High Ammonia Type
UVLC - Unvulcanized latex compound
PVLC - Pre-Vulcanized latex compound
PVME - Polyvinyl Methyl Ether
Zno - Zinc Oxide
ZDBC - Zinc dibutyl dithio Carbamate
VL - Vulkastab VL
TSC - Total Solid Content

EXECUTIVE SUMMARY

CHAPTER I gives an account of the preservation and properties of the natural rubber latex, preparatioin of latex compounds and manufacture of products by dipping methods such as straight dipping, coagulant dipping and heat-sensitized dipping. Heat sensitized dipping involves immersing a hot former in to a suitably heat sensitized latex compound. Heat Sensitization of NR latex can be imparted by Zinc ammine ions and hydrophilic polymers. Poly Vinyl Methyl Ether (PVME) is a hydrophilic polymer with a cloud point in the range of 32-34°C. The literature survey on heat-sensitization of NR latex by PVME reveals that publications giving detailed investigation about the effect of different compounding and processing parameter on heat sensitization are very limited. This work has been undertaken to standardise the effect of a few compound parameters and processing parameters on the heat sensitization of a typical NR latex compound containing PVME.

CHAPTER 2 describes the raw materials and experimental procedure, used in this study. The undermentioned experiments were conducted using typical unvulcanized and prevulcanized latex compounds.

1) The effect of varying the following Compound Characteristics on the heat sensitization of NR latex

   a) Level of Vulca Stab VL (0.25 phr - 1.5 phr)
   b) Level of Zinc oxide (0.5 - 1.5 phr)
   c) Level of PVME (0.5 - 2.5 phr)
   d) pH of the Compound (8.5 - 9.75)

2) Effect of varying Processing Parameters On heat sensitization of NR Latex.

   a) Former temperature (60 - 100°C)
   b) Dwell time (10 - 60 Sec)
   c) Total Solid Content (40 - 50%)

3) Effect of storage on the colloidal stablity of standerdised latex compounds.

4) Study on Technical properties of latex films.

CHAPTER 3 deals with the 'results and discussion' part this project and Chapter 4 - the summary and conclusion. The results are summarised as follows:

a) Degree of heat-sensitization is very much affected by the dosages of Vulcastab VL, Zinc oxide, PVME and pH of latex compound. In the base unvulcanised latex compound studied, the optimum values are found to be 0.75phr of vulcastab VL, 1phr of Zinc oxide, 1phr of PVME and a pH of 9. For prevulcanised latex compound, the optimum values are found to be 1phr of

Vulcastab VL, 1phr of Zinc oxide, 1.5phr of PVME and a pH of 9.

b) The processing parameters such as former temperature, dwell time and TSC of the latex compound affect the thickness of latex deposits by heat sensitized dipping. The optimum dwell time is found to be 40 secs for both unvulcanised and prevulcanised latex compounds. At a total solids content of 50% and former temp of 100°C, a thickness of 3mm is obtained by single dip for the both the latex compounds.

c) The optimum latex compounds are having good storage stability at 15°C and 25°C. But at room temp, the stability is slightly lowered at high shear rate; after one week.

d) The Vulcanised films from the above latex compounds posses good technological properties and ageing resistance.

CHAPTER 1

INTRODUCTION

CHAPTER I

I. INTRODUCTION

1.1 Natural Rubber Latex

Natural rubber latex is mainly obtained from the bark of the tree "Hevea brasiliensis" by the process of tapping. The freshly tapped latex is a Whitish fluid of density between 0.975 and 0.980 gm^{-1}, pH from 6.5[1] to 7.0 and surface free energy from 40 to 45 (ergs cm^{-2}) The rubber content of latex varies between 25 and 40% by weight and this variation is owing to factors such as clone, tapping intensity, soil condition, climatic conditions etc. In addition to the rubber hydrocarbon, a number of non rubber constituents such as proteins, carbohydrates, lipids, inorganic salts etc. are also present in latex.[1] The rubber hydrocarbon in latex is predominantly CIS-1, 4- poly isoprene and it occur as molecular aggregates in the form of discrete particles which are usually spherical with diameter ranging from .02 - 3.0[2] microns.

1.2 Preservation and Concentration of Latex

Natural Rubber latex in vessels of Rubber tree is sterile, but as it comes out, it gets contaminated by bacteria and Yeasts.[3] The micro organisms metabolise the non rubber constitutents of the latex and produce volatile fatty acids such as formic, acetic and propionic acids which lead to coagulation of latex[4]. Therefore, preservatives are added to latex immediately after collection. Among the preservatives, ammonia is still widely used and it inhibits bacterial growth; acts as an alkaline buffer, raises the pH and neutralises free acid formed in latex[5]. But ammonia has the disadvantage that it is punger smelling and prolonged exposure to the gas can cause discomfort to workers. Also high concentration of ammonia leads to processing problems. Therefore, attempts have been made to develop low ammonia preservation systems[6,7,8]. A commonly used low ammonia system is LA-TZ which contains 0.2% Ammonia, 0.013% TMTD, 0.013% Zno and .05% lauric acid[9,10].

Preserved field latex is unsuitable for most latex applications as its rubber content is low. For the manufacture of most of the products, latex of 55-60% rubber content is preferred. The important method for concentration of preserved field latex are evaporation creaming, centrifuging and electrodecantation. In India, only centrifuging and creaming are commercially used for the production of latex concentrate[11]. NR latex concentrate is a highly specified material. The latex properties of significance are dry rubber content (drc) non rubber solids (NRS), Mechanical Stability time, volatile fatty acid number (VFA), potassium hydroxide (KOH) number and alkalinity. The significance of these properties has been discussed by Blackely[12] and Cockbain[13]. Latex concentrate is a non Newtonian fluid and its viscosity decreases with increasing shear rate[14].

1.3 Latex Compounding

Latex products are manufactured from concentrated latex by mixing it with various compounding ingredients. The compounding ingredients are solids or liquids and may be water soluble or water insoluble. They are added to latex as aqueous solutions, if they are water soluble solids or liquids, as dispersions if they are water insoluble solids and as emulsions if they are water unmisable liquids. General principles to be considered while addition of solutions, dispersions and emulsions to[15] latices are

1) particle size of dispersions and the droplet size of emulsions should be comparable to the particle size of the latex.

2) The colloid stability of dispersions and emulsion should be comparable to that of the latex.

3) The pH of solutions, dispersions and emulsions should be similar to that of latex.

4) It is desired that the ionic strength of the aqueous phase of the dispersion should be similar to that of the latex aqueous phase.

Dispersions of solid ingredients are prepared by first making a coarse slurry of the powdered ingredient with water which contains the required amounts of dispersing agents and colloid stabilizer. The slurry is then ground in a suitable mill such as colloid mills, ball mill or attrition mills for an appropriate length of time so as to produce a dispersion of the required small particle size.[15-20]

Emulsions are prepared by first making a coarse suspension of oil droplets in water in the presence of a suitable emulsifying agent using a high speed stirrer and then subjecting this to a refining process.

1.4 Compounding Ingredients

The different ingredients used in latex compound are classified as i) surface active agents (ii) Vulcanising agents (iii) accelerators (iv) activators (v) antioxidants (vi) fillers (vii) Viscosity Modifiers and (viii) special additives.

1.4.1 Surface active agents

These are substances which can bring about marked modifications in the surface properties of the aqueous media, eventhough they are present in small amounts of the order of 1% m/v or less. They have got great importance in latex technology and in this respect latex technology differs significantly from that of dry polymer or polymer solutions.[16] Their principal effect is to reduce significantly the surface free energy of aqueous medium. One part of its molecule is strongly hydrophilic and the other part is strongly hydrophobic. As a result the molecule gets adsorbed at the interphase between the rubber and the aqueous media. Depending on function, they are classified as stabilizing agents, dispersing agents, emulsifiers,wetting agents, viscosity modifiers and protective colloids.

Stabilizers are first added into latex during compounding to maintain the latex in the colloidal condition during compounding and further processing. The dispersing agents prevent the dispersed particles in dispersions from re-aggregating and alkyl sulphonates are used for this. The emulsifieng agents are soaps, usually oleates formed insitu. Wetting agents are used to reduce the interfacial tension between two surfaces. Proteins, alginates, polyvinyl alcohols and cellulose derivatives are used as protective agents and viscosity modifiers in the processing of latex compound.[16,21,22]

Surface active substances are also classified broadly into ionic and nonionic types. The ionic types are subclassified into anionic, cationic and amphoteric according as the surface active part of the molecule is anionic, cationic or amphoteric. According to the nature of the ionic groups the anionic types are subclassified as carboxylates, sulphonates and sulphates. (eg: Potassium Oleate, Sodium naphthalane formaldehyde suphonate etc) Non-ionic surface active substances donot ionise in aqueous media. Important types used in latex technology are ethoxylates. They are less soluble in hot water than in cold water.

1.4.2 Vulcanising agents

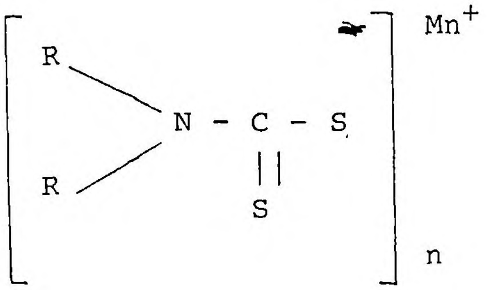
The normal Vulcanising agent for NR latex is sulphur. Depending upon the particular property required for the product, sulphur is added at different levels ranging from 0.3 - 2.5 phr. Thiuram polysylfides (TMTD) along with Thiourea is used as Vulcanising agent for heat resistant products.[23] Dunn[24] reported that butyl Xanthogen disulphide in conjunction with a dithiocarbamate may be used to Vulcanise latex film in the absence of sulfur. It has also been reported that organic peroxide and hydroperoxide may be used to Vulcanise latex films.[16]

1.4.3 Accelerators

Accelerators are chemicals used in the latex compound to reduce the Vulcanization time and also to increase the technological properties of the Vulcanized product. Their dosages vary from 0.5 to 3phr depending on whether the vulcanisation system is high sulphur or low sulphur. Generally fast accelerators are used in latex technology because the vulcanisation temperatures are relatively low. The important classes used in latex compounding are the metallic and amine dialkyl dithiocarbamates[16]. The thiazoles and to a lesser extent, thiurams are of importance as secondary accelerators in conjunction with dithiocarbomates. Limited use has also been made of "Xanthates" for room temperature vulcanization of latex.

1.4.3 a) Dithiocarbamates[16]

The salts of the dialkyl dithiocarbonic acid have the generic structure as shown below.

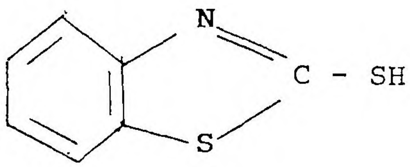


R - alkyl or aryl group

M - Metal

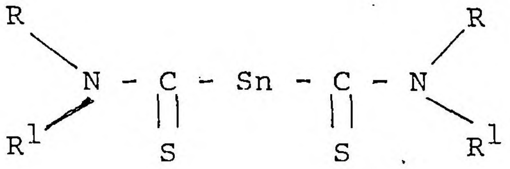
Although a considerable range of accelerators are available under this, Zinc diethyl dithio carbamate (ZDC) and Zinc dibutyl dithio carbamate (ZDBC) are most widely used. They are active in latex mixes in the absence of Zinc oxide and activate thiazole accelerators[25].

1.4.3 b) Thiozoles



Thiozoles are insufficiently active to be used on their own for latex work, but they function as secondary accelerators for the dithiocarbamate giving Vulcanizate of high modules.[16] The most common thiozole in latex compound is Zinc Salt of 2-mercaptobenzothiozole (ZMBT).

1.4.3 c) Thiuram disulphide[16]



As a class thiurams are insufficiently active to accelerate satisfactorily in latex compounding. The most commonly used thiuram in latex compounding as ultra accelerator and Vulcanising agent is tetra methyl thiuram disulphide[16] (TMTD).

1.4.4 Activators[16]

Zinc oxide is used as activator in sulphur Vulcanisation. It boosts up the cure time and also imparts additional heat resistance to latex products.

Its dosage is 0.25 - 0.5 phr for dipped products and 4-5phr for latex foam products.

1.4.5 Antioxidants

The antioxidants protect rubber from deterioration by oxygen, heat, light, ozone etc. Styrenated Phenol and polymerized 1,2 dihydro 2,2,4 trimethyl quinoline are typical antioxidants used in latex compounding. Due to discolouration, aminoderivatives which are powerful antioxidants are not used in latex compounds. Phenolic derivatives, are not much effective, but they have the advantage of non discolouration. BHT, Styrenated phenol and polymerised 1,2-dihydro 2,2,4-trimethyl quinoline is in small dosages (0.25phr) are typical antioxidants used in latex products.

1.4.6 **Fillers & Pigments**

Fillers are added to latex compound to modify the mechanical properties, and to cheapen the product. Pigments are used to colour the products. Usually used fillers are Calcium Carbonate, barium sulphate, Titanium dioxide,. Chinaclay, Silica etc. It is seen that no effect analogus to the reinforcement of dry rubber by fillers is observed when the same fillers are added to the latex.

1.4.7 Softners

These are used to reduce the modulus of the product. One example is mineral oil which is used in the manufacture of balloons.

1.5 Preparation of Latex Compound[18]

Preparation of latex compound involves mixing of concentrated natural rubber latex with solutions/ dispersions/emulsion of different compounding ingredients. High Ammonia or Low ammonia preserved latices can be used for compounding. In the case of HA type latex, for mixes containing higher amounts of Zinc oxide, deammoniation is done prior to compounding to avoid Zinc oxide thickening.

After each addition of chemical dispersion to latex, the compound is stirred slowly but thoroughly to get even distribution of the chemical in the latex. It is important to avoid contact between the stirrer and the container since latex may get coagulated by friction.

After the addition of all the compounding ingredients, the compound is allowed to mature for about 24-48 hrs and used for the manufacture of different latex products.

1.6 Coagulants for Latices

Colloidal destabilization of latices can be brought about by the addition of Chemicals. This substances often react chemically with bound Surface groups which confer colloid stability to the latex there by reducing the potential energy barrier conferred by those groups. These substances are mainly classified under three broad heading.

1) direct or contact Coagulants
2) Delayed action Coagulants.
3) Heat sensitizing Coagulants.

1.6.1 **Direct or Contact Coagulants** are substance which are more or less immediately in their effect. Provided that an adequate quantity of the chemical brings colloidal destabilization rapidly. A large number of substances are able to function as direct coacervants for carboxylate stabilized anionic aqueous latices. They are conveniently classified under the headings.

1) Acidic substances eg: acetic acid.
2) Water - soluble electrolyte especially salts of di and trivalent cations eg: Magnesium chloride, Barium Chloride, Salts of Lithium, Sodium, Potassium etc.
3) Hydrophobic Organic liquids.
eg: di-n-butyl phthalate to a polyvinyl acetate latex for sulphur-prevulcanised NR latex chloroform or Cd4 is used as hydrophobic organic liquid.

4) hydrophilic organic liquids eg: ethyl alcohol, acetone to NR latex.

5) Cationic Surface active substances eg: n-hexadecyl trimethyl pyridinium bromide.

6) Water - soluble hydrophilic polymers.

1.6.2 Delayed - action Coagulants

Delayed-action coacervants are substances which have little apparent destabilizative effects when first added to the latex but bring about obvious colloidal destablization after a certain time has elapsed. The most important delayed - action coacervants for carboxylate stabilized latices are the alkali metal salts of hydroflurosilicic acid, H_2SiF_6 commonly known as Silicoflurides eg: Na_2SiF_6, K_2SiF_6. They are added to latex as aqueous dispersions. The usual dosage of addition 0.5pphr to lpphr. Further information concerning the behaviour of Silicofluorides as delayed-action coacervants for Carboxylate stabilized rubber latices, especially for NR latex has been given by Murphy (27), by Twiss and Amphlett (28), by Madge and pounder (29), by Murphy, Madge and pounder (30) and by Madge(31). Other types of delayed action coacervants are salts of other fluroacids eg: Sodium borofluoride ($NaBF_4$), Ammonium peroxodisulphide [$(NH_4)_2S_2O_8$], thiourea $(H_2N)_2CS$ and metal dialkyl dithicarbomaties (R NCSS) M. But none of these alternatives such as $NaBF_4$, $(NH_4)_2S_2O_8$ has achieved the same degree of industrial importance as the Silicofluoride.

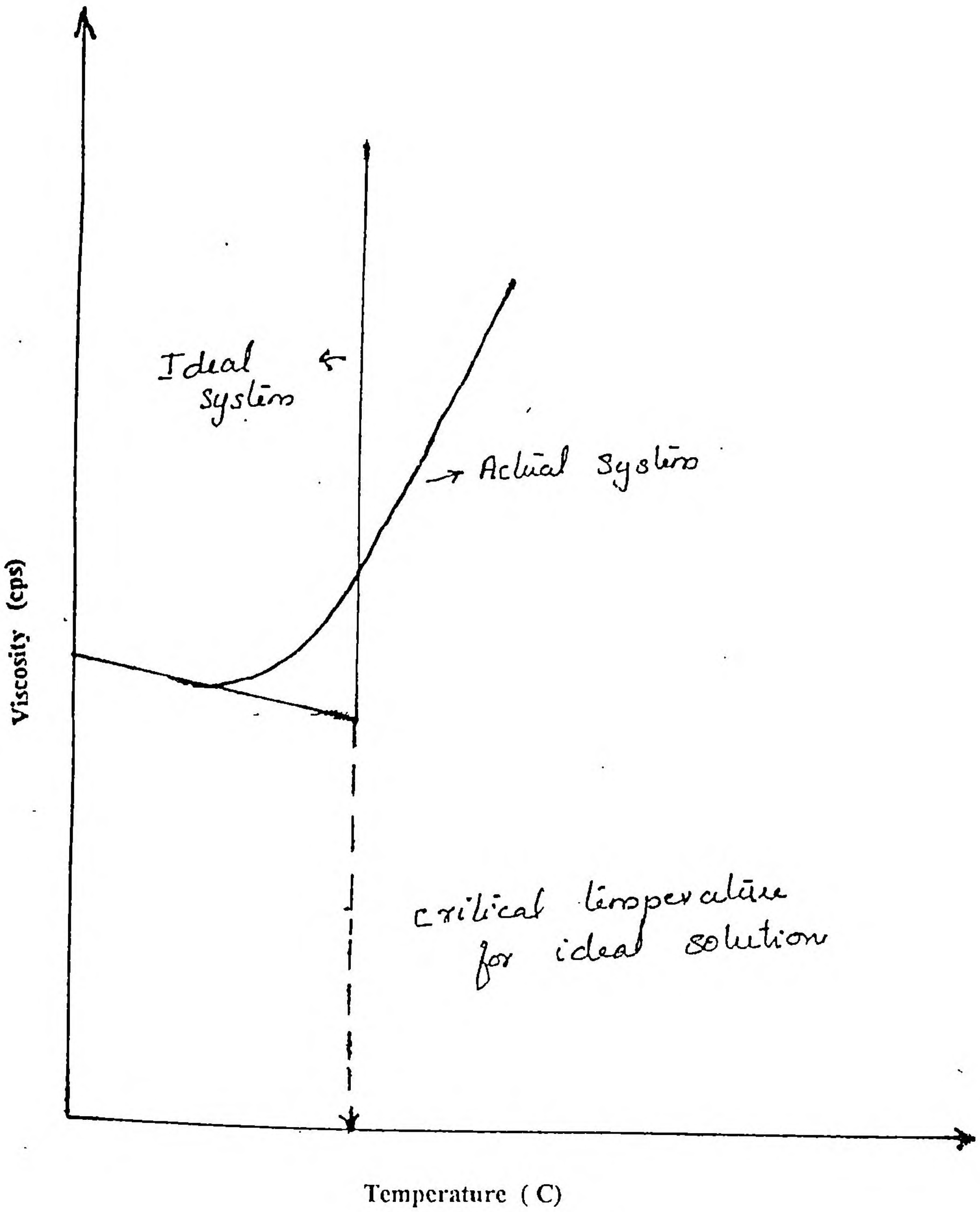
1.6.3 Heat Sensitizing Coagulents

NR Latex can be made heat sensitive by the addition of heat sensitizing coacervants. These are substances which have little apparent destabilizative effect at normal ambient temperature, but bring about rapid colloidal destabilization if the temperature of the latex is raised above some threshold value. Thus a latex is heat-sensitized if it has been modified so that, although it remains moderately stable as a lyophobic sol at normal ambient temperature, its colloidal stability falls rapidly when its temperature is raised.

This colloid destabilization should ultimately cause uniform gelation. The formation of gel is usually preceded by a stage in which the viscosity of the latex increases rapidly, although the latex remains fluid. The gel which eventually forms may subsequently undergo synerisis. The behaviour of an ideal and actual heat sensitizing latices are given in Fig. I

The ideal heat-sensitized latex shows some decrease in fluid viscosity as the temperature is increased, until a certain temperature is attained, when a sudden rapid increase in viscosity is evident as gelation occurs. Actual heat-sensitized latices tend to show a gradual increase in viscosity as the temperature rises, the rate of increase becoming progressively greater.

Fig.1.1
Schematic Illustration of behaviour of ideal and actual heat-sensitized latices



1.7 Latex dipping Process

The latex[32] dipping is a process in which thin walled rubber products are produced by first immersing a former into a latex compound and then slowly with drawing the former from the latex so as to obtain a uniform deposit on the former. The thickness of the deposit is increased by repetition of the process.

The process involves steps such as dipping, leaching drying, beading, Vulcanising dusting and stripping off the deposit from the former. Different types of gloves, condoms, balloonsetc. are produced by dipping technique.

1.8 Principl Dipping Methods

Latex dipping processes are classified according to whether or not any colloid destabilisers are used to assist in the formation of rubber deposit.

1.8.1 Simple dipping or Straight dipping:

In this process, no destablising agency is used. The process consists of immersing the former in latex compound, withdrawing and drying of the deposit adhering to the surface of the former. The deposit formed on the former is by virtue of the viscosity of the latex and of its tendency to wet out the former.

1.8.2 Wet Coagulant Dipping

In this method a 5-10% solution of acetic acid or formic acid in water is used to assist the build up of a deposit. It can be worked in two ways, according as the former is dipped first into the coagulant or first into the latex compound.

1.8.3 Dry Coagulant dipping:

In this, the coagulant is dry such as calcium chloride, calcium nitrate, cyclohexyl ammonium acetate and other salts. The former is first immersed in a solution of the coacervant in a volatile solvent. After withdrawal from the solution the solvent is allowed to evaporate leaving either a dry deposit or one which is in the form of very viscous, concentrated solution. The former with its coacervant deposit is then immersed in the latex and is allowed to dwell for a predetermined time. Again the thickness of the deposit depends largely upon the time of dwell and upon the stability of the latex towards the particular coacervant which is used.

1.8.4 Heat Sensitized dipping:

In this method, the latex is formulated so as to be heat sensitive. A heat sensitive latex is one which is stable at normal room temperature but coagulates when heated to a certain temperature. The principle of this method is that when a hot former is dipped into a heat sensitive latex, a deposit build up around the surface of the former as heat is conducted away into the surrounding latex. Heat sensitivity may be induced by the following chemicals Zinc ammine complex, poly vinyl methyl ether, poly proplylene glycol etc.

The thickness of the deposit obtained depends upon several factors, notably the degree of heat sensitivity of the latex, the temperature of the former and the heat capacity of the former.

1.9 Sequence of latex - dipping operations:

A typical sequence of operations primarily for the production of dipped goods by dry coacervant dipping is discussed below.

1.9.1 Compounding of latex

A suitable latex compound is prepared and allowed to mature for about 24-48 hrs.

1.9.2 Pre-treatment of formers

The formers are cleaned, washed and heated, presence of dirt, grese, oil etc. on the former may lead to uneven thickness of the deposit.

1.9.3 Immersion of formers in latex compound

The hot former is then slowly immersed into the latex compound. The speed of immersion should be sufficiently low to prevent air from being drawn into the latex bath along with the formers, but sufficiently high to maintain the meniscus surrounding the former in a convex to air condition. In manual dipping, the operator may find it advantageous to vary the angle and mode of immersion, as well as the rate of immersion. Sometimes the preffered procedure is a motion in which the former is laid in the latex rather than one in which the former is immersed by a simple downward motion.

1.9.4 Dwell: Dwell time is the period for which the former is kept in the latex compound during dipping. In coacervant dipping, the duration of the dwell period is determined by the thickness of the deposit required in relation to the colloid stability of the latex and the potency and quantity of coacervant held by the former. As dwell time increases, the thickness increases reaches a maximum and thereafter remains the same. The time for getting maximum thickness is known as the optimum dwell time.

1.9.5 Withdrawl of former from latex bath

The former is withdrawn at such a rate so that drainage of the latex doesnot lead to unacceptable variations in the wall thickness of the dried deposit.

1.9.6 Drying, leaching, beading and Vulcanization

The order in which the operation are effected can vary. Drying may be effected by passage through hot air which is heated directly by gas, infra-red rays, electricity or steam etc. Whatever be the method of heating, it is desirable that the film should set as quickly as possible to prevent further flow of ungelled latex. The drying step may be combined with the final Vulcanization or these two stages may be separated. Temperatures are typically within the range 100-140°C in hot air continuous automatic Vulcanization. It is advantageous that the temperature increases progressively as drying proceeds.

The leaching medium is invariably water, which may be hot or cold. The purpose of leaching is to remove as far as possible all the water-soluble substances present in the latex film. It has been noted in recent years that the mechanical properties of dipped films from Sulphur - Prevulcanized natural rubber latex can be significantly improved by leaching with water. This is due to the removal of hydrophilic substances and improved interparticle coalescene.

The process of beading involves rolling down the thin film of rubber, which has been left for this purpose, while the article is still on the former. The beading should be done before Vulcanization to get good adhesion. It can be done manually or automatically.

1.9.7 **Dusting & Stripping** - The article may be dusted to prevent adhesion to itself and to other articles after removal from the former. This adhesion is only seen in the case of unvulcanised products. A wide range of dusting powders are available. Examples include talc, various clays, Zinc Stearate, Starch and various starch derivatives. The removal of article from the former commonly known as stripping. It can be done manually or mechanically with manual assistance. After stripping the products are subjected to visual examinations and tested for physical properties. They are then packed and ready for despatch.

1.10 Vulcanization of NR dipped products

Vulcanization is the process by which the mainly viscous rubber is converted into elastic rubber through the crosslinking of the macromolecule at their reactive sites. It is an intermolecular reaction which increases the retractive force and reduces the amount of permanent deformation remaining after removal of the deforming force. According to the theory of rubber elasticity, the retractive force resulting from a deformation is proportional to the number of network supporting polymer chain per unit volume of elastomer.[34] Vulcanization usually produces network junctures by the insertion of chemical cross links between polymerchains. The cross links may be formed through chain of sulphur atoms, single sulphur atom or Carbon - Carbon bonds. The Vulcanizate properties are affected by the cross link density, type of crosslink nature of polymer type and amount of filler etc. Vulcanization was first discovered by Charles Good year and by Thomas Hancock (1843) by heating rubber with sulphur.[35] The introduction of organic accelerators then enabled to reduce the Vulcanization time and sulphur dose required for optimum physical properties improve the ageing resistance of rubber goods and prevent blooming of Sulphur.[36]

Vulcanization of latex dipped products may be effected by two method.

1) The latex may be Vulcanized before the product is being shaped (pre-Vulcanization)
2. The Vulcanization is carried out after the product has been shaped (post Vulcanization)

The first method involves Vulcanization of latex in the fluid state so that it deposits elastic films of Vulcanized rubber on drying. The second method is carried out by heating the product in the former, in hot air, for optimum cure time to get the balanced technological properties.

1.11 Pre-Vulcanization of latex

NR dipped products may also be prepared from prevulcanized latex. The term prevulcanized latex refers to a chemically modified latex which on drying gives a Vulcanised film.[37] This type of latex is prepared from field latex or concentrated latex either in the rubber plantation factory or in the consumers factory. It is especially useful for the small to medium sized dipping factory since compounding of the latex is either unnecessary or is limited to the incorporation of the desired pigments. The manufacture of medical dipped items, feeding teats and toyballoons are usually based on prevulcanised latex. The cross linking of rubber in latex can be effected by reaction with sulphur, sulphur doners,[28] peroxide[39] orirradiation.[40] Commercially, prevulcanised latex is prepared by reacting latex with ingredients such as sulphur and accelerator (dithiocarbomate type, usually ZDC, ZDBC) and heating in a water jacketted vessel at 60-70°C.[41]

1.12 Heat Sensitizing coacervants of NR Latex

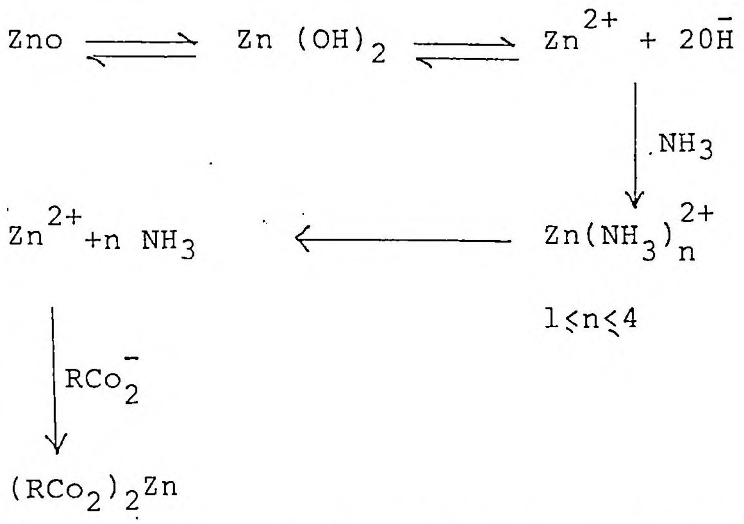
Heat sensitizing Coacervant of NR latex are (1) Zinc ammine ions (2) various hydrophilic polymers such as polyvinyl methyl ether, poly propylene glycols etc.

1.12.1 Heat-Sensitization of NR Latex by Zinc-ammine ion[42,43]

Ammonia paeserved natural rubber latex can be heat sensitized by the Zinc ammine system by addition of excess of aqueous ammonia solution or an ammonium salt. The prerequesite for latex heat sensitization by Zinc ammine ions are that

1) there should be present in the latex a sparingly soluble source of Zinc ions, free ammonia and ammonium ions.
2) the latex should be stabilized with surface bound anions capable of forming an insoluble Zinc compound with un-amminated Zinc ions or with Zinc-ammene ions of low degree of ammination.

The gelation rate increases as the temperature is raised, and becomes very marked at temperatures above 50°C. The chemistry of the system is believed to conform the following scheme



Insoluble Zinc Carboxylate (eg: Soap or proteinate) precipitated in the Surface of the latex particle, with consequent colloidal destabilization.

pronounced heat-sensitivity imparted by the Zinc-ammine system to ammonia preserved natural rubber latex arises from the conjunction of two effects as the temperature increases.

a) acceleration of loss of ammonia from the inital interaction products between Zinc-ammine ions and colloid stabilizers.

b) Reduction of the pH.

1.12.2 Heat Sensitization of latices by various hydrophilic polymeric Substances like PVME, polyglycols etc.

PVME and polypropylene glycols are soluble in cold water but become insoluble on heating. The solution changes in appearance from clear to cloudy as the temperature changes. The temperature at which transition occurs is known as cloud point temperature. According to Cockbain (44) the heat sensitivity of latices which contain polypropylene glycols has effect on pH on the range over 9.0 - 10.8. Poly alkoxy acetals, poly alkoxy alkanols and polyacetals are closely related to PVME. As a class they are said to be soluble in cold water and show cloud point transition. Other examples of this are polysiloxanes, surface active ethoxylates, organic nitro compounds etc.

1.12.2.1 Possible Mechanisom for Heat Sensitization Of Latices By Water Soluble polymers

Mechanisms which depend upon the presence of water soluble polymer dissolves in the aqueous phase of the Latex.

According to these mechanisms, Heat Sensitization is a consequence of reduction of the solubility of the polymer in the aqueousphase as the temperature is raised. These mechanisms are of two types.

1. Those in which heat-sensitization is a consequence of the precipitation of hydrophilic polymer within the aqueous phase. They subdivide further into a mechanism in which the latex particles become entrapped in a gel of precipitated polymer, and one in which the precipitated polymer adsorbs the colloid stabilizers from the latex particles and so reduces colloid stability.
2. Those in which heat sensitization is a consequence of adsorption of the dissolved polymer at the particle surface as the temperature of the latex is raised, gelation then occuring by one or other of the processes out lined in section below.

1.12.2.ii Mechanisms which depend upon the presence of water Soluble polymer adsorbed at the particle surface

According to these mechanisms, heat-sensitization is a consequence of changes in the nature of the hydrophilic polymer which is initially adsorbed at the surface of the latex particles. The polymer remains adsorbed as the temperature of the latex is raised, but the condition of the adsorbed macromolecules changes as a consequence of Variations such as loss of hydration. These mechanisms are of three types.

1. Those in which heat-sensitization is a consequence of reduction in the colloid stability of the latex because adsorbed polymer is no longer able to function as a steric stabilizer.
2. Those in which heat-sensitization is a consequence of inter particle bridging by the adsorbed polymer molecules.
3. Those in which heat-sensitization is a consequence of interaction between the adsorbed macromolecule and other latex colloid stabilizers.

The overall conclusion drawn from the observation summarised above concerning the mechanism of the heat sensitization of ammonia - preserved natural rubber latex by poly vinyl methyl ether is that the phenomenon is a consequence of adsorption of PVME macromolecule at the surface of the rubber particles. The effects of several types of additivesupon heat-sensitization are consistent with these additives affecting the availability of adsorption sites at the particle surface, and also possibly the facility with which adsorption can occur. These effects are not generally consistent with the alternative hypothesis that heat sensitization is a consequence of precipitation of the polymer in the aqueous phase of the latex as the temperature is raised. Whilst the occurence of interparticle bridging by adsorbed poly vinyl methyl ether macromolecules as the temperature is raised is not demonstrated fully.

1.13 Heat-Sensitization of Latices by PVME

Polyvinyl methyl ether is a polymer which is non-ionogenic at normal latex pH values. It is soluble in cold water, but become insoluble as the temperature is raised. When a cold aqueous solution is gradually heated the solution changes in appearance from clear to cloudy at a temperature of 33°C. The ability of PVME to heat sensitize ammonia preserved natural rubber latex is almost certainly a consequence of this behaviour. Only a few publication are available giving information concerning its effect upon other types of latex. Sinn (45) writing in 1974 states that PVME has heat-sensitizing effect in synthetic latices as well as in natural rubber latex. However, he also states that for most of the synthetic latices now available PVME is unsuitable as a heat-sensitizing agent because their colloidal chemical behaviour gives them excessive stability. Abramova, Chenaya and Gorelik[46] have stated PVME can be used in Synthetic polychloroprene rubber latices but the results shows that the degree of heat-sensitivity imparted to these latices is less than that imparted to NR latex. Blackely, Gorton& Siva gurunathan[47] have reported about their work on polystyrene latices stabilized respectively by potassium myristate, ammonium myristate, sodium n-do decyl sulphate etc. Electro micrographs of polystyrene latices containing PVME indicated that some aggregation depends on pH, polymer content of the latex, presence of Zno etc. It has observed that in these synthetic polystyrene latices and in ammonia NR latex have similar origins.

The earliest report of the heat-sensitization of polymer latices by polyvinyl methyl ether appears to be a German patent granted to Rother and Sinn in 1949 (48). This described the heat-sensitization of various synthetic latices (of glassy as well as of rubbery polymers) by this additive, as well as of natural rubber latex is said to gel at 30°C if de-ammoniated with formaldehyde and compounded with a 20% m/m aqueous solution of polyvinyl methyl ether in the ratio 12:100. The gelation temperature of various synthetic latices containing polyvinyl methyl ether are said to range from 45°C to 80°C. Other publications on this subject include those by Cockbain (44,49,50) by Abramova, Chernaya and Gorelik (46), by Sandomirskii etal (51-52) by Sinn (45) by Gorton (53) by Gorton and pendle (54) and by Blackely, Gorton and Siva Gurunathan (47,55,56).

54

A.D.T. Gorton & T.D. Pendle N.R. Technology Vol II page I, 1980 presents a comparison of existing heat sensitive systems with noval ones based on selected nonionic surfactants, alkyl phenol ethylene oxide adducts and fatty alcohol ethylene oxide adducts with cloud point in the range 45-60°C are found to be useful for this purpose.

.14 **Aim of the project** - It has been reported that heat-sensitized NR latex by PVME can be used for the manufacture of a variety of latex products such as foamed carpet backing extruded latex tubing, dipped products like teats & soothers, foamed products, meterological balloons etc. The advantage of heat sensitized dipping compared to concervant dipping is higher thickness in a single dip. (by reducing labour and eliminating the problem of delamination). In heat-sensitized dipping the latex compound is formulated so as to be heat-sensitive and a deposit is allowed to form around the former by dipping a hot former into the latex compound. The degree of heat sensitization can be estimated by measuring the gelling time or the thickness of the deposit in heat-sensitized dipping. The thickness of the dry deposit formed will depend on a number of compound characteristics[42] such as pH of the latex compound, concentration of Zno, concentration of PVME, nature and level of surfactants, molecular mass of PVME, ionic strength of latex aqueous phase etc. The thickness of the dry deposit also depends upon the number of processing parameters such as rate of immersion, dwell time, temperature of the former, heat capacity of the former etc.

Eventhough there are many reports on the heat sensitization of NR latex by PVME, publications giving detailed investigation of the above factors are very limited. For manufacturing the products with various thicknesses, a detailed knowledge of how the above factors would affect the gelling characteristics is highly essential.

It is also mentioned in the literature that Industrial utilization of the heat sensitive system has not become wide spread due to the limited low temp stability of existing formulation which can cause difficulties in large scale manufacture. Therefore, the initial temperature of the former be closely controlled and the tanks which contain the latex for heat sensitized dipping must be cooled otherwise the stability of the latex will gradually decreases. This is the principal difficulty reported for heat sensitized dipping process as compared with coagulant dipping processes.

The stability of heat-sensitized latex compound thus depend on the compound formulation as well as the temperature of storage. The compounding variables include pH of the latex compound, level of Zno, level of PVME, level of stabilizer etc. There is no much detailed information available in the literature, how these factors affect the stability of the latex compound except for a study on heat sensitization of NR latex by PVME using different surface active agents by A.D.T Gorton & T.D. pendle.

This work has been undertaken with a view to standardising the effect of the following compounding parameters and processing parameters on the heat sensitization of a typical NR latex compound using PVME.

Compounding Variables

1) Dosage of Non ionogenic stabilizer-Vulkastab VL.
2) Dosage of Zno
3) Dosage of PVME
4) PH of latex compound

Processing Parameters

1) Temperature of the mould
2) Dwell time
3) TS of the latex compound.

It is also envisaged to study the stability characteristics of the Optimum latex compound by measuring the viscosity at different temperatures at different shear rates and at different periods of storage.

Studies on Pre-Vulcanised latex

Pre-Vulcanised latex is now a days used for the manufacture of dipped products. It is prepared by heating the latex compound at a higher temperature (60°C) in a water jacketted vessel. In this project, it is also planned to include prevulcanised latex for the studies on heat sensitization. The effect of compound characteristics and the processing parameters on the thickness of the latex deposit is also proposed to be studied. Storage stability of the latex compound would be investigated as in the case of unvulcanised latex compound.

Studies on technological properties

It is also proposed to study the technological properties of the latex film vulcanisates prepared from the optimum latex compounds by heat sensitized dipping, both from unvulcanised and prevulcanised latex.

CHAPTER 2

EXPERIMENTAL

CHAPTER 2

2. EXPERIMENTAL TECHNIQUES

2.1 Raw Materials

The raw materials used are

2.1.1 60% Centrifuged Natural Rubber Latex (High Ammonia)

60% centrifuged Natural Rubber Latex HA type, collected from the Pilot Latex Pocessing Centre, Chethackal Rubber Board was used for this study. Properties of the latex, given in Table 2.1 conformed to BIS specification 5430-1981.

Table 2.1

Properties of 60% Centrifuged NR Latex (HA Type)

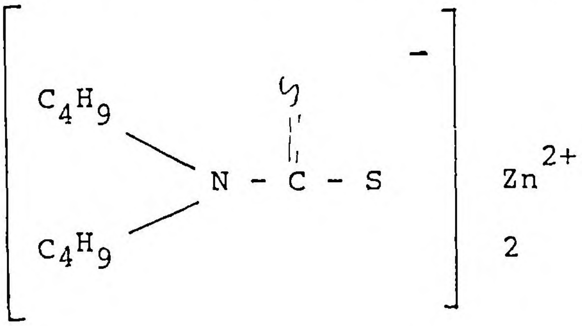
	Properties	Value	Requirements (BIS 5430-1981)
1.	Dry Rubber Content %	60.2	60 (min)
2.	Non Rubber Solids % by mass	1.5	2 (Max)
3.	Sludge content % by mass	0.05	0.10(max)
4.	NHz content % by mass	0.7	0.16 (min)
5.	KOH No	0.5	1 (max)
6.	MST (Secs)	1300	475 (min)
7.	VFA No	0.05	0.15 (max)
8.	Coagulum Content % by mass	0.03	0.05 (max)
9.	Cu ppm	1	8 (max)
10.	Mn ppm	Trace	8 (max)

2.1.2 Vulkastab VL

A nonionogenic stabilizer, manufactured by M/s.Alkali & Chemical Corporation of India Ltd., Calcutta. It is ethylene oxide condensate type, conformed to the general formula $R[CH_2CH_2O)_nH]_m$ In which RHm is the active hydrogen compound from which the ethoxylate is prepared.

2.1.3 Zinc Di Butyl Zymate (ZDBC) 16

An ultra accelerator manufactured by M/s. R.T. Vanderbilt Company Inc, U.S.A. The chemical name is Zinc dibutyl dithio carbamate. Structure of the chemical is



It is a white to yellowish powder, specific gravity 1.24 (20/20°C), melting range 104-108°C. Pleasant odour, soluble in CS2, benzene, chloroform insoluble in water and dialkalies.

2.1.4 Sulphur (Rhombic type) 59

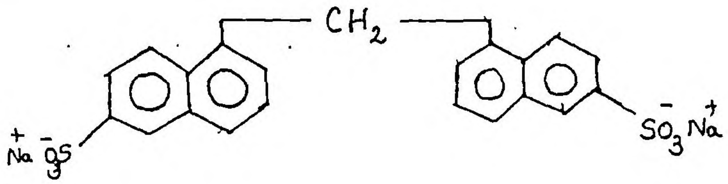
Laboratory grade manufactured by EMERK Ltd., Bombay was used in this study. Yellow crystals stable at room temperature, specific gravity 2.06.

2.1.5 Zinc Oxide 59

Laaboratory grade manufactured by EMerk Ltd., Bombay was used in this study. It is a coarse white powder, specific gravity 5.47.

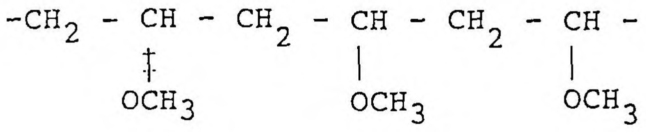
2.1.6 Dispersol F 59 - Dispersing agent manufactured by M/s.ICI Ltd., Calcutta. Chemical name is Sodium naphthaline formaldehyde sulphonate, also described as Sodium methyline bis-(naphthaline Sulphonate)

<u>Structure</u>



2.1.7 Poly Vinyl Methyl Ether 60 (PVME)

Poly Vinyl Methyl Ether manufactured by M/s.BASF Ltd. Cheadle, UK was used in this study. It is a water soluble synthetic polymer of the composition.



$$-CH_2 - \underset{\substack{| \\ OCH_3}}{CH} - CH_2 - \underset{\substack{| \\ OCH_3}}{CH} - CH_2 - \underset{\substack{| \\ OCH_3}}{CH} -$$

2.1.8 Formaldehyde - (35%) (HCHO)

Laboratory grade manufactured by M/s.Emerk Ltd., Bombay.

2.1.9 Water - Distilled water was used for all the experiments.

2.2 Preparation of Dispersions

Fifty percent dispersion of Sulphur, Zno and ZDBC were prepared seperately by grinding in a ball mill using Dispersol F as the dispersing agent. The recipes used for making dispersions are given in Table 2.2.

Table 2.2

Ingredients	Parts by weight (Pbw)	
A. 50% Sulphur dispersion		
Sulphur	100	Ball milled
Dispersol F	3	for 72 hrs.
Water	97	
B. 50% ZDBC dispersion		
ZDBC	100	Ball milled
Dispersol F	2	for 48 hrs.
Water	98	
C 50% Zno dispersion		
Zno	100	Ball milled
Dispersol F	2	48 hrs.
Water	98	

2.3 Preparation of Latex Compounds

For studying the effect of various compounding parameter on heat-Sensitization of natural rubber latex, a base latex compound was first prepared. Formulation of this compound is given in Table 2.3.

Table 2.3

Formulations

Ingredients	Parts by weight	
	Dry	Wet
60% Centrifuged NR latex(HA type)	100	167
20% Vulcastab VL Solution	0.5	2.5
50% Sulphur Dispersion	1	2
50% Zno Dispersion	1	2
50% ZDBC dispersion	0.5	1
5% Formaldehyde Solution	to PH9	to PH9
10% PVME Solution	1	10

NR latex was mixed with stabilizer dispersions of sulphur, Zno and ZDBC under constant stirring at a speed of 50-60rpm. The pH of the latex compound was adjusted to 9 by the addition of small amounts of 5% formaldehyde solution. 10% PVME was then added. After that the total solid content of the latex compound was adjusted to 50% m/m by the addition of distilled water. It was then kept for maturation for 24 hrs.

2.4 Preparation of Pre-Vulcanised Latex Compound

Pre-Vulcanized latex compound was prepared by mixing stages. The recipes are given in Table IV A & IV B. Of

In the first stage compounding, NR latex was fi mixed with dispersion of Sulphur, Zno and ZDBC as given Table IV A. It was then prevulcanised to the extent chloroform No.3 by heating in a water jacketted vessel. T extent of prevulcanisation was tested by the chlorofo coagulation test. In this test, one part of latex was mixe with one part of chloroform and the nature of the coagul was observed to be in the form of non tacky agglomerates conforming to chloroform No.3 state. Pre-Vulcanised late was then cooled and treated with Vulkastab VL.

Table 2.4

	Ingredients	Parts by Weight(Wetwt)
IV A	<u>First Stage Compounding</u>	
	60% Centrifuged NT latex HA Type	167
	20% Vulkastab VL Solution	2.5
	50% Sulphur dispersion	2
	50% Zinc Oxide dispersion	0.4
	50% ZDBC dispersion	1
IV B	<u>Second Stage Compounding</u>	
	50% Zinc oxide dispersion	1.6
	5% HCHO solution	to PH9
	10% PVME Solution	10

2.5 Procedures for Determining the different properties of the latex compound

Brokefield viscosity, pH and Total solids content of the latex compounds were determined.

2.5.1 Brookefield Viscosity using LVT Model Brookefield Viscometer (ASTM D 2526-29)

Viscosity of the latex compound was measured using Brookefield Viscometer. which is widely used for the measurement of latex Viscosity. It consists of a rotating member, which is usually a cylinder driven by a synchronous motor through a berryllium - Copper torque spring. The viscous drag on the cylinder causes an angular deflection of the torque spring which is proportional to the viscosity of the fluid in which the disc is rotating. The torque and therefore the viscosity is indicated by means of a pointer and scale. The pointer is attached to the cylinder spindle and the scale to the drive spindle above the spring so that both pointer and scale rotate.

To measure the viscosity of the compound 200ml latex compound was taken and placed it below the viscometer by fitting the spindle No.2 in correct position and is in such a position as to dip in the compound upto the cut mark of the spindle. Then allowed the spindle to rotate at a particular speed (viz 6 & 60 rpm) to obtain a reading. The pointer and scale are clamped together and the reading is noted and which is multiplied by correction factor and the result is expressed in cps.

2.5.2 Determination of Total Solid Content.

The total solid content of a latex is defined as the percentage by weight of the whole is non volatile at a definite temperature in an open atmosphere. The amount in grams of total solid present in 100grams of latex.

Weighed correctly a clean petridish (W1gm) added about 2 gms of latex into the petridish and again weiged correctly (W2 gms). Gently swirl the dish so that the latex is distributed over the bottom of the dish and dry the specimen in an oven at 70± 2°C for 16 hrs or 2 hrs at 100 ± 2°C. Cool the sample to room temperature and weiged again (W3). The total solids content is calculated as follows.

$$\text{Total solid \%} = \frac{W_3 - W_1}{W_2 - W_1} \times 100$$

Where W_1 = Wt of petridish

W_2 = Wt of petridish + Sample

W_3 = Wt of petridish + dried sample.

2.5.3 Determination of PH

The most convenient method which is used for the determination of the pH of aqueous media, that using a glass electrode in conjunction with a saturated calomel electrode and an electronic amplifier.

According to BS procedure, the pH meter is first standardised by adjusting the instrument to read pH 9.18 when the electrodes are immersed in .05 M sodium tetraborate in carbondioxide free water at 25 ± 1°C. The linearity of the glass electrode is then checked by measuring the pH of .01M trisodium phosphate in carbon dioxide free water at 25 ± 1°C. The reading should be between 11.67 and 11.77. The electrodes are then washed with water and wiped dry with soft absorbed paper. They are then immersed in the latex and the pH is determined at 25±1°C. A duplicate is also carried out and the average is taken.

2.6 Heat-Sensitized dipping process

Unvulcanized latex compound and pre-vulcanised latex compound prepared as described in 2.3 & 2.4 respectively were subjected to heat-sensitized dipping. Steel formers of diameter 1.5mm were used for dipping. The formers were washed dried and heated to 100°C in an oven. It was then uniformly and slowly immersed into the latex compound by keeping the meniscus surrounding the former in a convex to air condition. The former was allowed to dwell for a period of 30 seconds and slowly with drawn. After withdrawl the former was inverted through 180° and rotated. This was to ensure uniform distribution of the deposit. Then the product with the former was dried partially at the tempeature of 60°C and the deposit was stripped off from the former. The latex tubes were then subjected to Vulcanization by heating in hot air at 100°C for one hour. After vulcanization the thickn ess of the products was measured by using Verneir Calipers.

Thickness = Main scale reading + (Vernier Scale reading x least count)

The unit is in millimeters.

2.7 Determnation of Physical Properties Using Tensile Tester

For determining the tensile properties of the film, the latex film vulcanization of size (10cml x 10cm wx (0.5-1mm) thick) were prepared by heat-sensitized dipping using glass plates in unvulcanized and prevulcanized latex compounds as described in 2.6. Tensile properties such as modulus, Tensile strength and elongation at break are tested using tensile tester (Instron model 4411) as per ASTM D-3188. The machine consists of a load frame an electronic control unit and a monitor, load measuring device is a load cell fixed at the top of the load frame. Below the load cell is a moving plat form driven by a continuously variable speed motor. Grips suitable for the dum bell specimens are fixed on to the load and the moving plat form.

During testing the specimen is subjected to stretching at constant speed. Force and elongation are continuously monitored by the electronic circuit. As soon as the test specimens breaks, test results are displayed in the electronic circuit and printed as a table.

All the tests were carried out at ambient temperature (30°C). Dumb bell specimens were cut from the dipped film for measuring tensile properties. The thickness was measured by bench thickness gauge. The moving cross head is adjusted by operating the switch. The velocity of the moving cross head is adjusted to 500mm/min. The specimen was elongated and the values corresponding to ultimate tensile strength, elongation, modulus 100%, 300% are are measured.

2.8 Experiments

2.8.1 The Effect of varying compound Characteristics on the Heat Sensitization of NR Latex

To study the effect of compound characteristics on the heat-sensitization of NR latex using PVME as sensitizer the following parameters were varied in unvulcanised and pre-vulcanized latex compounds prepared as described in 2.3 and 2.4 respectively.

1) Level of Vulcastab VL (0.25phr - 1.5phr) Keeping others const.
2) Level of Zinc oxide (0.5 - 1.5phr) "
3) Level of poly vinyl methyl ether (0.5-2.5 phr) "
4) pH of the compound (8.5 - 9.75) "

Heat-sensitized dipping was carried out using steel formers at 100°C giving a dwell time of 30 secs as described in. Thickness of the latex vulcanizates were measured. The results of pre-vulcanized and unvulcanized latex compounds are in figures 3.1, 3.4, 3.7, 3.10.

Viscosity of the latex compounds were also measured at intervals for a period of two weeks by keeping the compounds at a temperature of 25°C. The results are given in figures 3.2, 3.3, 3.5, 3.6, 3.8, 3.9, 3.11, 3.12.

2.8.2 Effect of Processing parameters on Heat-Sensitization of NR Latex

From the previous study optimum compound formulation giving maximum heat-sensitization and storage stability was standardized. And the effect of processing variables on heat-sensitization were studied with this standardized compound.

The parameters studied were.

1) Former temperature (60 - 100°C)
2) Dwell time (10 sec - 60 sec)
3) Total solids content of the latex compound (40-50%)

The mould temperature were varied from (60°C to 100°C), bykeeping the dwell time at 30 secs and Total solid content at 50%. The thickness of the latex films were measured and the results are given graphically in figure 3.13.

The experiment was repeated by varying the dwell time from (10 sec to 60 sec) keeping the mould temperature at 100°C and the total solid content at 50%. The results are shown graphically in figures 3.14.

To study the effect of varying the total solid content the standardised latex compounds were diluted to various TS from 40% to 50%. Films were prepared by heat-sensitized dipping using steel moulds at a temperature of 100°C giving a dwell time of 30 secs. The thickness of the films are given in the fig. 3.15.

2.8.3 Storage-Stability of the Standardised Compound

Storage-Stability of the optimum latex compounds giving maximum heat-sensitization were studied by measuring its viscosityat different shear rates (6, 60 rpm). The compounds were kept at different temperatures 15, 25°,32°C and the viscosity were measured for a period of 7 days. Results are given in Table 3.3.

2.8.4 Technological Properties

For determining the technological properties latex film Vulcanizates were prepared from optimum formulation (given in Table 3.1 & Table 3.2) as per procedure described in 2.3 and the tensile properties such as elongation at break, modulus at 100%, 300% and Tensile strength were determined using Instron Tensile Tester model 4411 as described in 2.7. The films are subjected to ageing at 100°C for 22 hrs in a multicellular ageing oven and the tensile properties were determined. Tensile properties before and after ageing are given in Table 3.4 & 3.5.

CHAPTER 3

RESULTS AND DISCUSSIONS

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 Effect of Compound Characteristics on Heat Sensitization

3.1.1 Level of Vulcastab VL

The effect of varying the level of Vulcastab VL on the heat sensitization (as measured by thickness of dipped films) using unvulcanised latex compound (UVLC) and pre-vulcanised latex compounds (PVLC) is given in Fig.3I. It is seen that for both the latex compounds the concentration of VL has got remarkable effect. As the dosage of VL increases, thickness increases initially, reaches a maximum and, thereafter, decreases. Maximum thickness is obtained at a level of 0.75 phr for UVLC and 1phr for PVLC.

Vulcastab VL is a non-ionogenic stabilizer and they are less soluble in hot water than in cold water. Aqueous Solutions of Non-ionogenic stabilizer become turbid on heating and the temperature at which it occurs is known as the cloud point. The surface activity of these substances and their ability to confer colloid stability is fugitive as the temperature is increased and reappears on cooling. The effect of VL on heat-sensitization is due to the above property.

In natural rubber latex, any added surface active agent has to compete for the available surface with the naturally occuring surface active agent such as soaps & proteins.

Only when sufficient quantity of VL is adsorbed on to the surface of the rubber particle, the heat-sensitivity imparted by it become significant. The initial increase in heat-sensitization as the level of VL increases may be due to this.

One mechanism suggested for heat sensitization is that it is due to the adsorption of PVME in the latex particle surface. Very few adsorption sites may be required to anchor the PVME macromolecules to the surface of the rubber particles in sufficient numbers and to a sufficient extent to impart heat-sensitivity. Thus when sufficient VL is present to block these sites the heat-sensitivity is reduced and reaches a minimum.

The viscosity of the UVLC and PVLC each containing different amounts of VL at different periods of storage at 25°C are given in Fig 3.2&3 respectively. It is seen than latex compounds with lower dosages of VL show marked changes in viscosity compared to latex compounds with higher amounts of VL. The stability of UVLC with 0.75 phr vulcastab VL and PVLC with 1phr Vulcastab VL remained comparatively constant. The slight increase in viscosity during the initial stages may be due to the time required for displacing the already presents soaps in the latex by VL. Once it is sufficiently adsorbed on rubber particle the stability of the latex doesnot change much with storage.

3.1.2 Level of Zno - The effect of varying the level of Zno on thickness of heat sensitized dipped film for UVLC and PVLC is given in Fig. 3.4. It is seen that as Zno increases thickness also increases. The thickness of film of pre-vulcanised latex compound is found to be higher than from the UVLC.

The result shows that the heat sensitivity of NR latex by PVME is very sensitive to the addition of Zno present in a compound. Zinc oxide react with ammonia to form Zinc ammine ions and the effect of Zinc oxide may be due to the fact that these zinc ammine ion interact with surface bound carboxylate ions, there by creating additional sites for the adsorption of PVME at the particle surface.

During pre-vulcanization the individual rubber particles in latex get crosslinked seperately without interaction with each other. This cross linked particles are dispersed in the aqueous phase as in the unvulcanised latex. Due to crosslinking the rubber is converted from a soft plastic material to a hard elastic material. The high heat sensitization of pre-vulcanized latex may be due to the hard surface nature of the cross linked rubber leading to different adsorption characteristics.

In UVLC the viscosity increases in the first two days (Fig 3.5) then decreases and remain almost stable for a period of up to ten days. In the case of PVLC Viscosity increase gradually. day by day and stability decreases

(Fig 3.6). These results show that the stability of pre-vulcanized latex compounds. This can be attribute to the hard surface nature of the rubber particles in PVL.

3.1.3 Level of Poly Vinyl Methyl Ether (PVME)

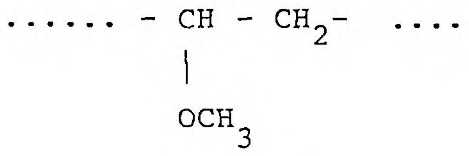
From the figure (3.7) we see that as the dosage of PVME increases thickness increases reaches a maximum and thereafter decreases. The maximum thickness of 2.94mm obtained at 1phr PVME in the case of UVLC and thickness of 3.03 is obtainedat a dosage of 2phr PVME for PVLC.

The result show that only small amounts of PVME (1-2 phr) required to impart significant heat-sensitivity to ammonia preserved natural rubber latex. The initial increase in thickness may be due to the fact that as the level of PVME increases, more PVME is adsorbed on the surface of the rubber particle but when sufficient amount capable of producing heat sensitivity has been adsorbed, further increase in PVME has no effect. The higher amount of PVME required for PVLC in getting maximum heat sensitization is may be due to the different adsorption characteristics of the hard rubber particles.

Viscosity of UVLC and PVLC containing different amounts of PVME are plotted in Figures (3.8) & (3.9). It is seen that as the level of PVME increases viscosity increases. As the period of storage increases viscosity increases initially and after a period of one or two days get reduced slowly and becomes stabilized. The UVLC remains stable for a period of 20 days.

In the case of PVLC remained stable for a period of one week. PVME is a hydrophilic polymer is soluble in cold water but becomes insoluble in hot water hence it can act as a heat-sensitizer for NRL. It can also act as a colloid stabilizer due to steric/hydration effect at normal temperatures.

The increase in viscosity as the dosage of PVME is raised may be due to the fact that PVME interacts with the colloid stabilizers already present in the latex. Due to this interaction the initial viscosity increases on storage. But PVME being a hydrophilic polymer can act as a stabilizer due to the steric/hydration effect.



$$\ldots\ldots - \underset{\displaystyle OCH_3}{\underset{|}{CH}} - CH_2 - \quad \ldots$$

The decrease in viscosity on prolonged storage may be due to this effect.

3.1.4 pH of Latex Compound

Effect of varying the pH on heat-sensitization of UVLC & PVLC containing 1phr of Zno is given in Fig (3.10). As the pH is reduced, thickness of the latex deposit increased for both the compounds. The results show that pH has got profound effect for both PVLC & UVLC. But when the pH is reduced below 8.5 and 8.75 for UVLC & PVLC respectively, the colloidal stability was lost. There fore a pH of 9 was selected for the standard compound while studying the processing parameters and technological properties.

One of the mechanisms proposed for heat-sensitization is that it is due to the precipitation of PVME within the aqueous phase, but heat-sensitization of PVME solutions, ie the cloud point is independent of pH. The above result show that the heat-sensitization by PVME depends on pH. A second mechanism suggested for heat-sensitization is that it is a consequenceof adsorption of the dissolved polymer in the particle surface as the temperature is raised. This mechanism is more plausible. The effect of pH may then be explained as due to the ionization of adsorbed carboxylate groups present at the particle surface as the pH is reduced. This probably facilitates adsorption of PVME on the particle leading to more heat-sensitization .

The stability of latex compounds as measured by viscosity, pH is plotted against pH of the latex and period of storage. In figures 3.11 & 3.12. It is seen that for UVLC the viscosity is highly sensitive to pH below a value of 8.5. A moderate stable viscosity is obtained at a pH of 9. In PVLC the viscosity increase with decrease of pH. A comparatively stable viscosity is obtained for one week for PVLC

From the results of the above study of compound characteristics formulations of the standardised compounds for UVLC & PVLC are given in Table 3.1 & 3.2. The effect of processing variables on heat sensitization and their result are discussed below.

3.2 Effect of processing Parameter

3.2.1 Former Temperature

From the figure (3.13) we can see that as the mould temperature increases the thickness of the deposit also increases. This is because higher the mould temperature higher the opportunity for heat transfer occure from the former to the latex. Gelation of the latex initially occurs in the region where the temperature has just reached approximately that of the cloud point transition in aqueous solution. As heat continuous to transfer from former to latex, so this region moves out wards from the former and the thickness of the gelled deposit increases.

3.2.2 Dwell time

Figure (3.14) illustrates that as the dwell time increases the thickness of the deposit increases to a particular level and remains constant during dwell period the heat is transfered from the hot former to the latex compound and consequently gelation occurs.

3.2.3 Total solid content (TS)

It can be seen from the Figure (3.15) as the TS is reduced thickness also decreases for both PVLC & UVLC. Maximum thickness of 3.2mm is obtained at a TS of 50% in PVLC and 2.94mm in the case of UVLC.

Storage-stability of the Standardised Compounds

From the results given in Table 3.3 it is seen that on storage at all temperatures namely 15°C, 25°C & room temperature (32°C), the viscosity first increases and after one or two days decreases and reaches a stable value. The viscosities at 60 rpm were less than the viscosity at 6 rpm for all the samples at temperatures 15° & 25°C. It shows that the latex behaves like a pseudoplastic fluid of those temperatures. After storage time of four or five days at room temperature (32°C) viscosity increases at high shear rates. This may be due to the fact that colloidal stability of the latex might have reduced at 32°C, which is near the cloud point temperature of polyvin yl methyl ether.

Technological properties

The tensile properties (before and after ageing) of latex films prepared from unvulcanized and pre vulcanized compounds are given is Table 3.4 & 3.5 respectively. It is seen that the films have good tensile properties and ageing resistance.

Table 3.1

Formulation for UVLC System

Ingredients	Parts by weight	
	Dry	Wet
60% Centrifuged latex	100	167
20% Vulcastab VL solution	0.75	3.75
50% Sulphur dispersion	1	2
50% Zno dispersion	1	2
50% ZDBC dispersion	0.5	1
5% Formaldehyde solution	to PH 9	to PH 9
10% PVME Solution	1	10

Table 3.2

Formulation for PVLC System

Ingredients	Parts by Weight	
	Dry	Wet
60% Centrifuged latex	100	167
20% Vulcastab VL Solution	1	5
50% Sulphur dispersion	1	2
50% Zno dispersion	1	2
50% ZDBC dispersion	0.5	1
5% Formaldehyde	to PH 9	to PH9
10% PVME solution	1.5	15

Table 3.3

STABILITY STUDY

	HEAT SENSITISED SYSTEM						PRE VULCANISED HEAT SENSITISED SYSTEM						
	Viscosity in days - Cps							Viscosity in days - Cps					
Viscosity	RPM	Ist	IInd	IIIrd	IVth	VIIth day		RPM	Ist	IInd	IIIrd	IVth	VIIth day
At 15°C	6rpm	200	175	125	125	125	At 15°C	6rpm	2.00	150	175	175	175
	60rpm	32.5	32.5	35	30	35		60rpm	72.5	62.5	70	72.5	72.5
At 25°C	6rpm	175	160	125	125	150	At 25°C	6rpm	250	150	175	175	175
	60rpm	25	27.5	27.5	30	30		60rpm	62.5	77.5	75	75	175
Room Temp. (32°C)	6rpm	200	175	150	150	150	Room Temp.at 32°C	6rpm	350	200	150	175	175
	60rpm	35	60	177.5	200	200		60rpm	67.5	75	75	80	170

Table 3.4

Technological Properties of UVLC

Property	Before Ageing	After Ageing
Stress Mod 100%	0.63 (Mpa)	0.73 (Mpa)
Stress Mod 300%	0.97 (Mpa)	1.38 (Mpa)
Tensile Strength	18.95 (Mpa)	16.4 (Mpa)
Elongation at break	1200 (%)	830.5 (%)

Table 3.5

Technological Properties of PVLC

Property	Before Ageing	After Ageing
Stress Mod 100%	1.02 (Mpa)	0.71 (Mpa)
Stress Mod 300%	2.18 (Mpa)	1.58 (Mpa)
Tensile Strength	21.11 (Mpa)	16.37 (Mpa)
Elongation at break	1050 (%)	659 (%)

Fig.3.1 Effect of Vulcastab VL on thickness in UVLC and PVLC systems

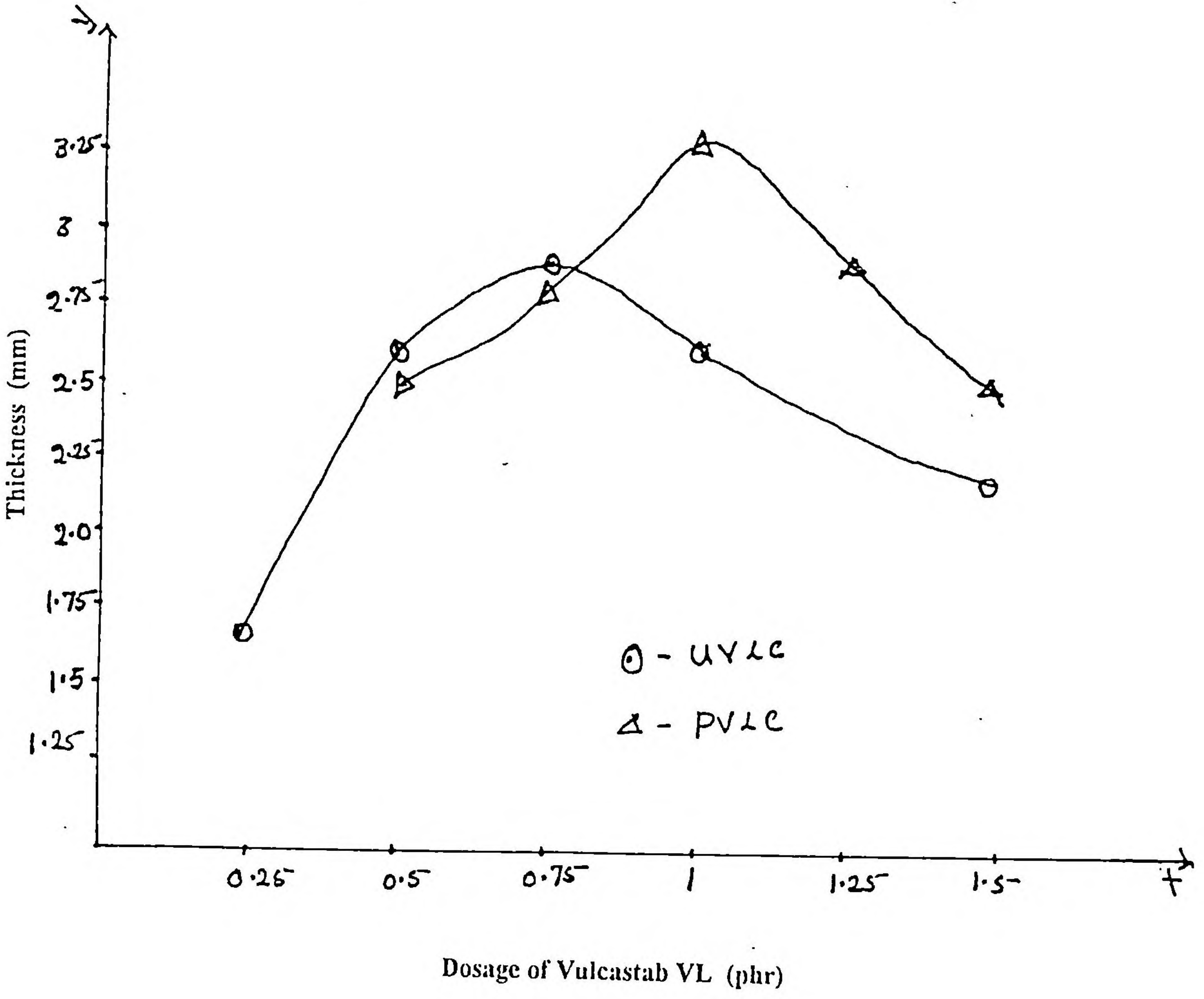


Fig.3.2 Effect of viscosity on storage at different levels of Vulcastab VL in UVLC system

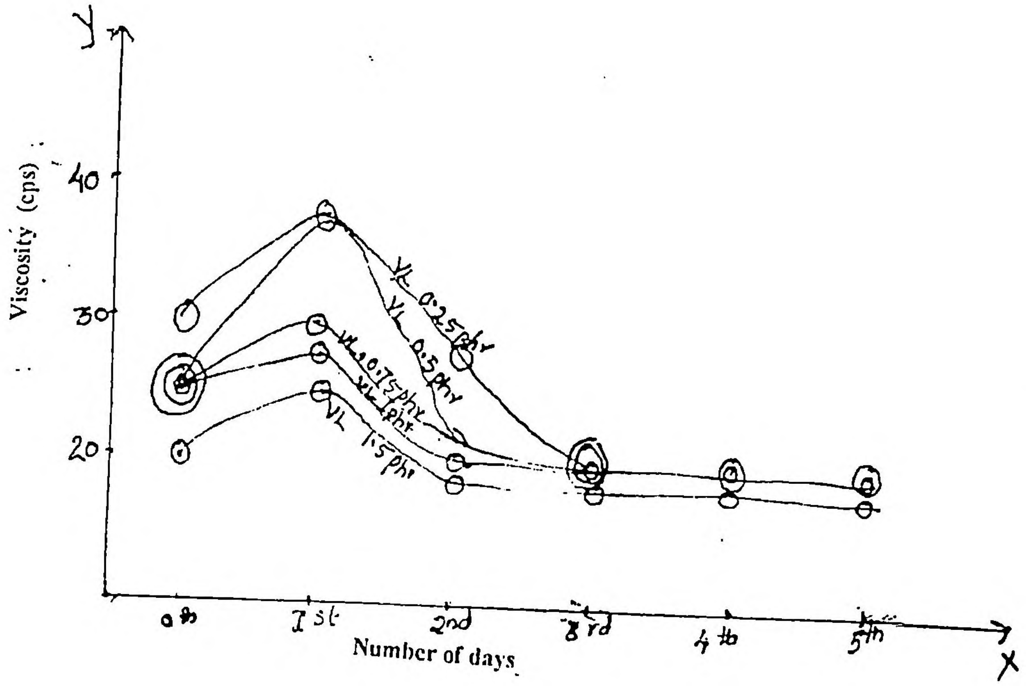


Fig.3.3 Effect of viscosity on storage at different levels of Vulcastab VL in PVLC systems

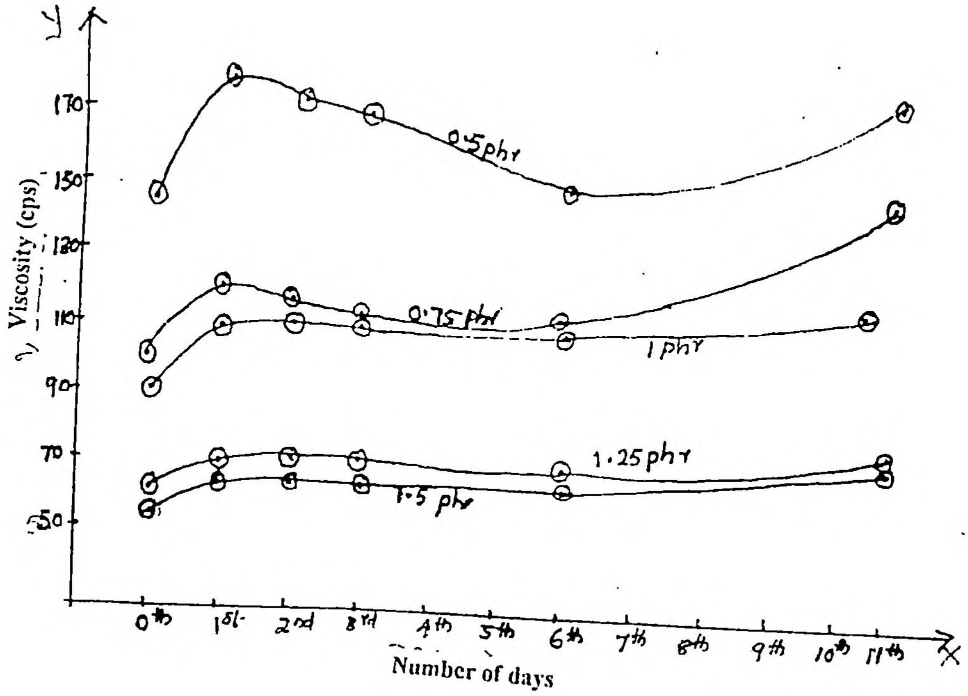


Fig.3.4 Effect of ZnO on thickness in UVLC and PVLC

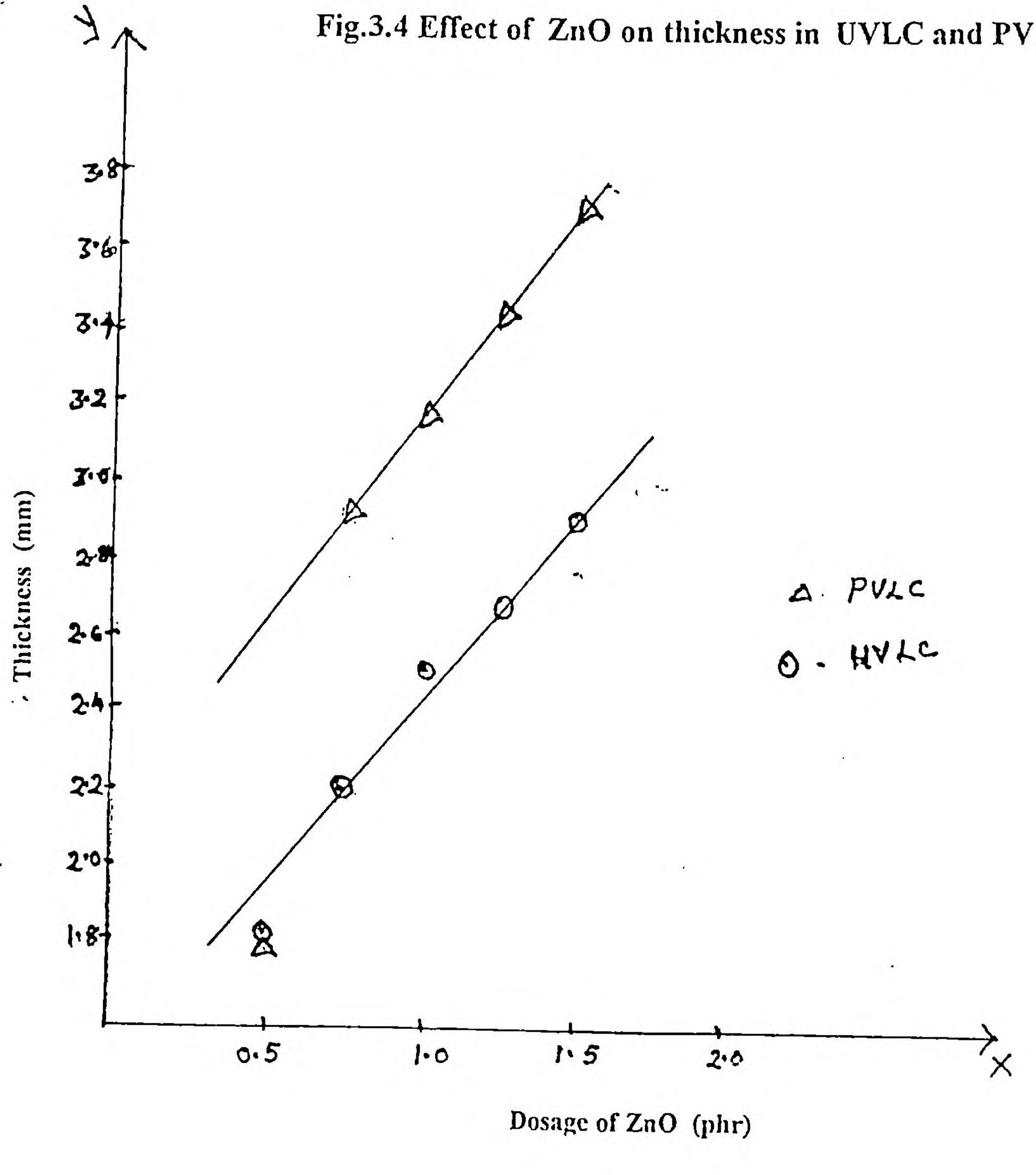


Fig.3.5 Effect of viscosity on storage at different levels of ZnO in UVLC system

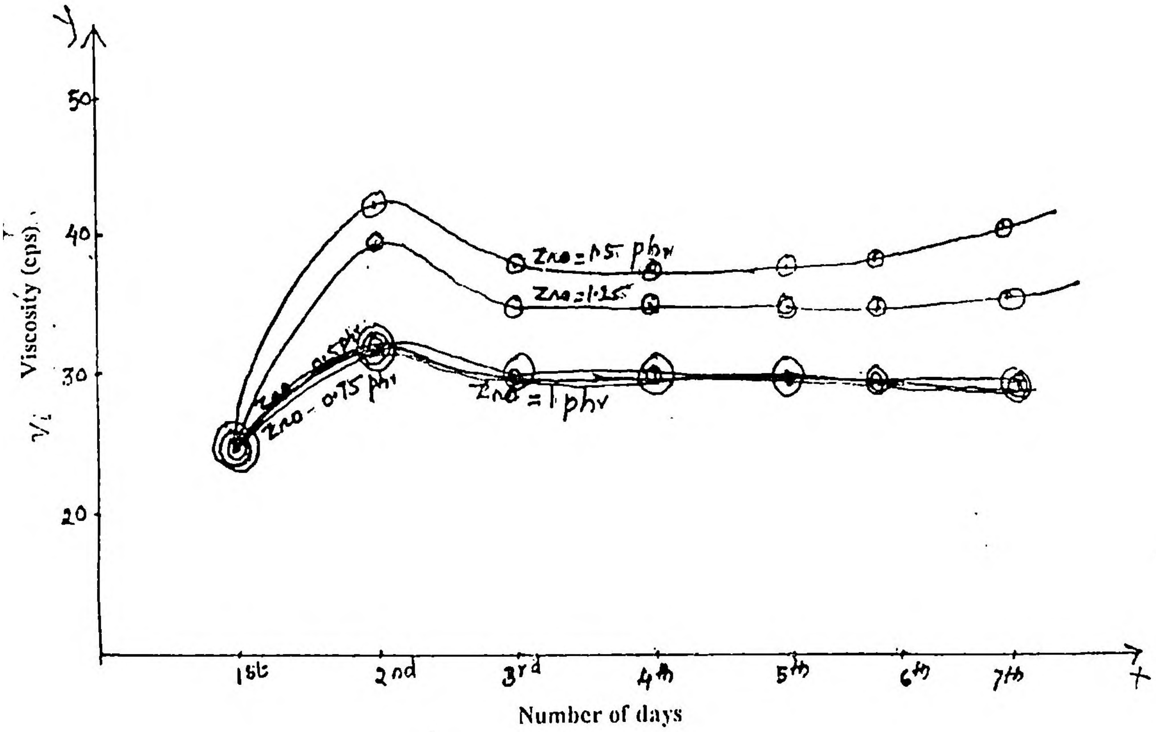


Fig.3.6 Effect of viscosity on storage at different levels of ZnO in PVLC system

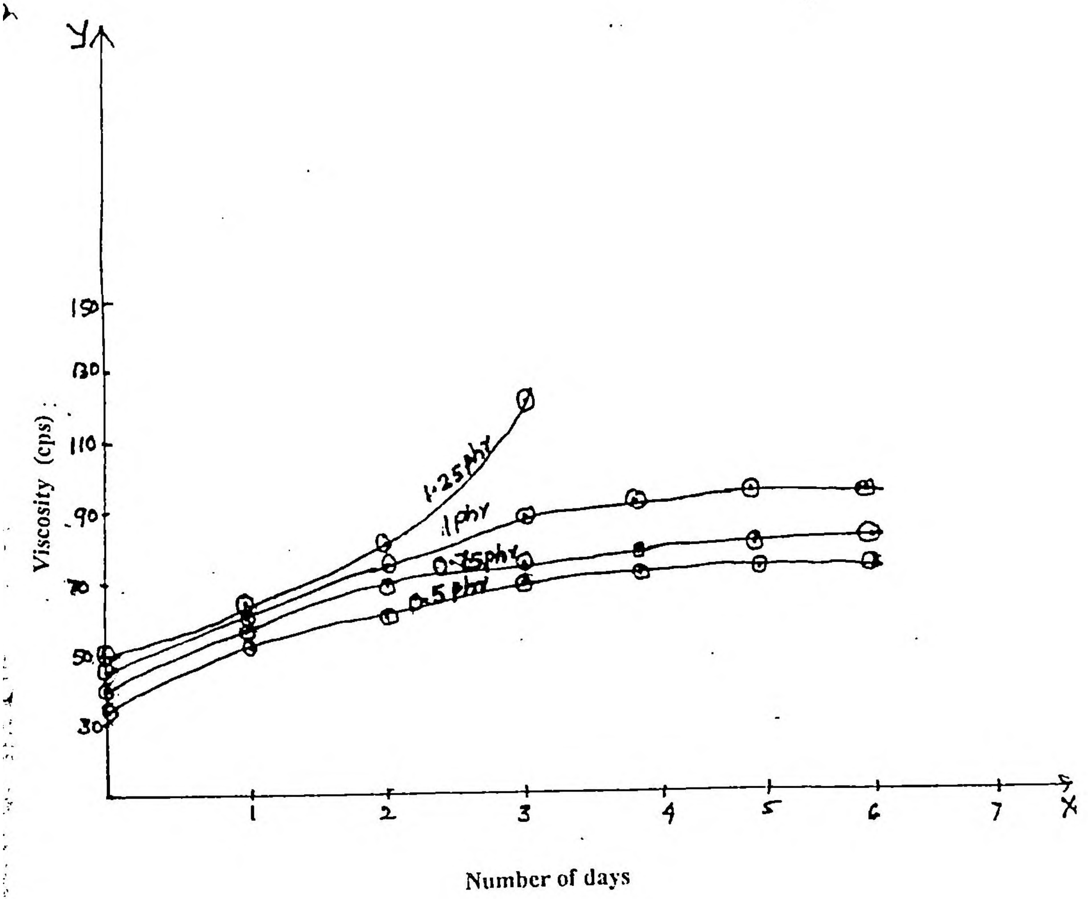
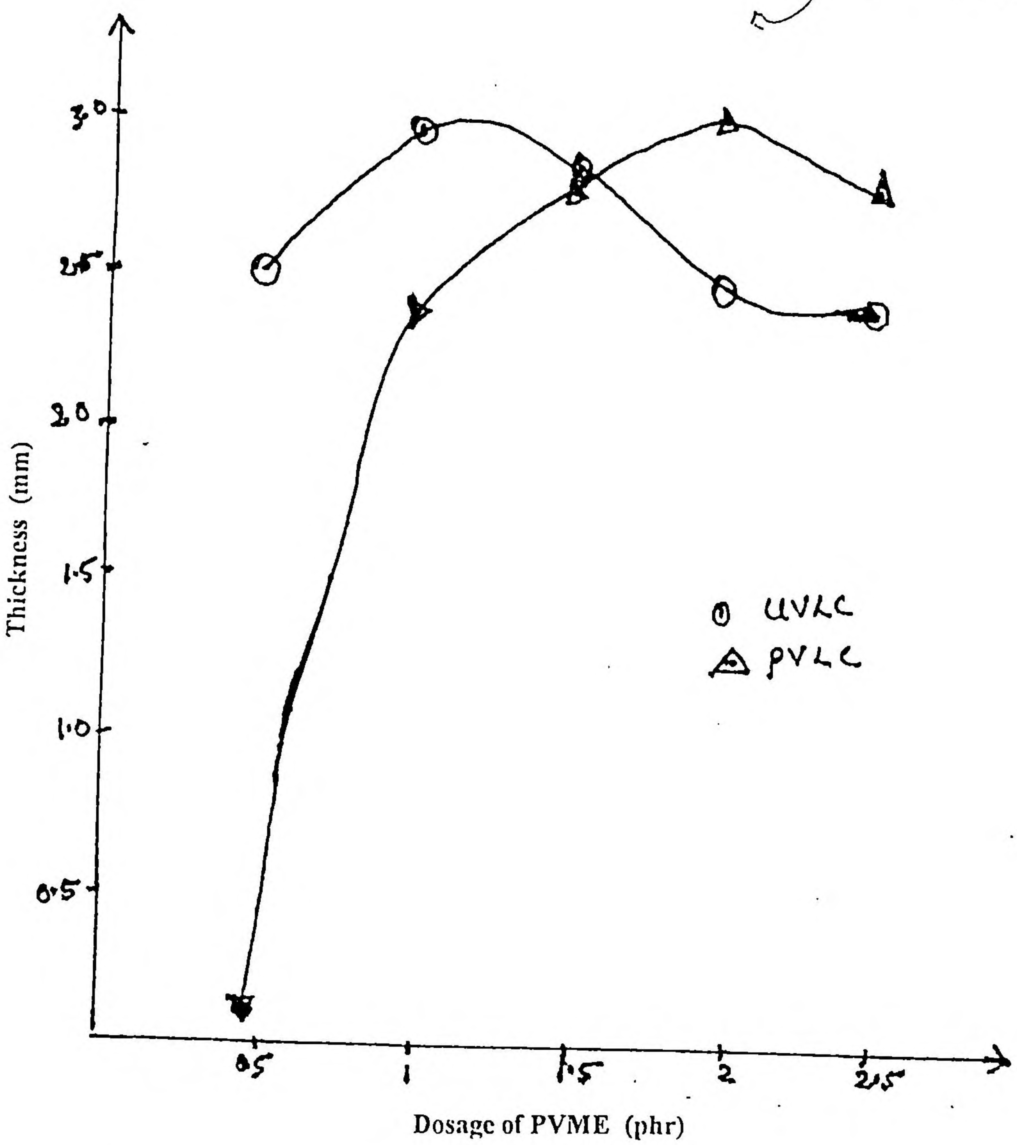


Fig.3.7 Effect of PVME on thickness in UVLC and PVLC



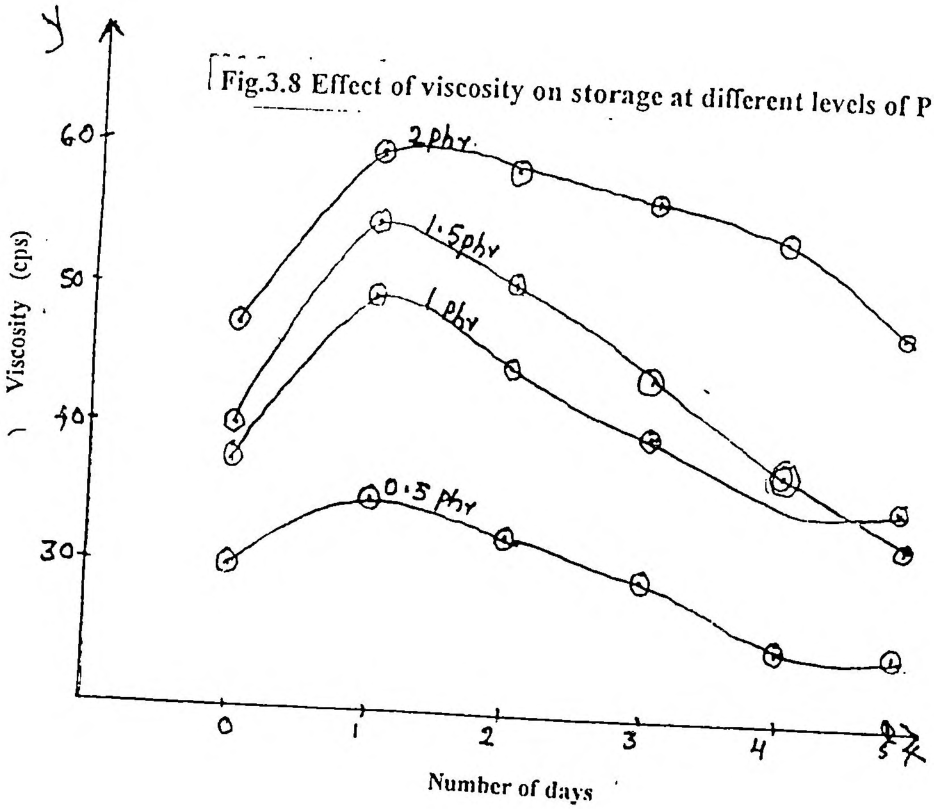


Fig.3.8 Effect of viscosity on storage at different levels of PVME in UVLC system

Fig.3.9 Effect of viscosity on storage at different levels of PVME on PVLC system

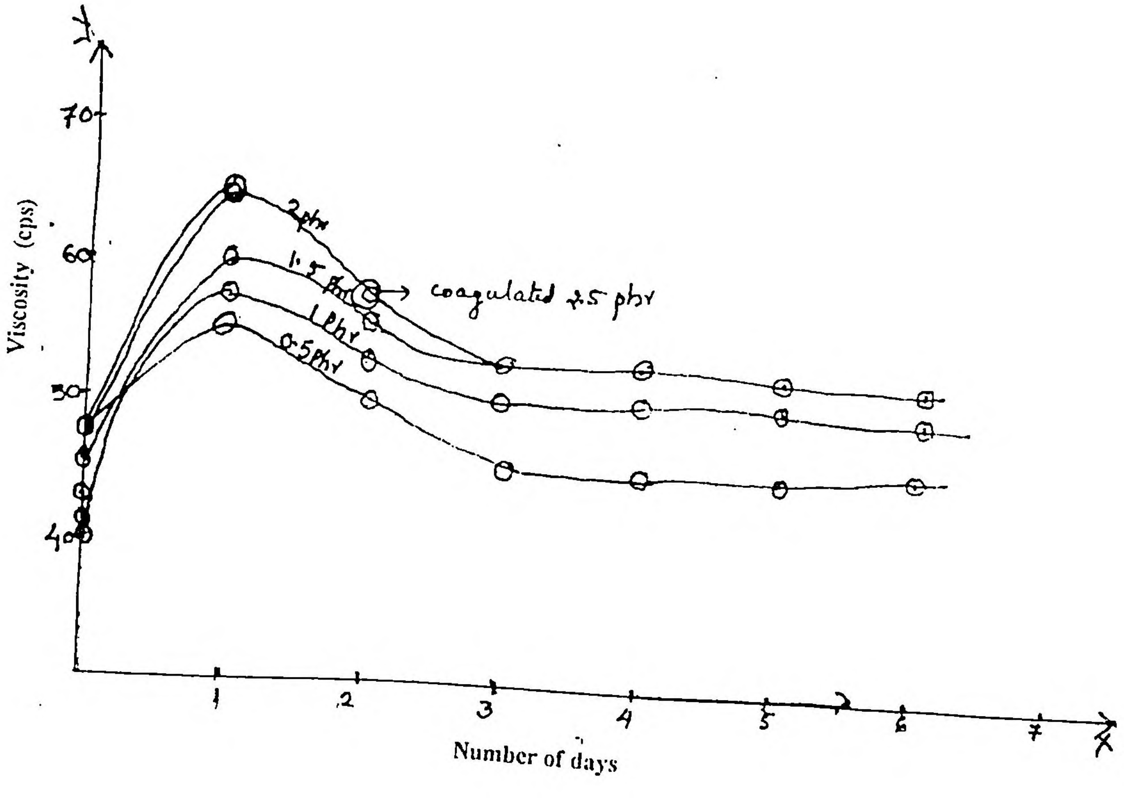


Fig.3.10 Effect of pH on thickness in UVLC and PVLC

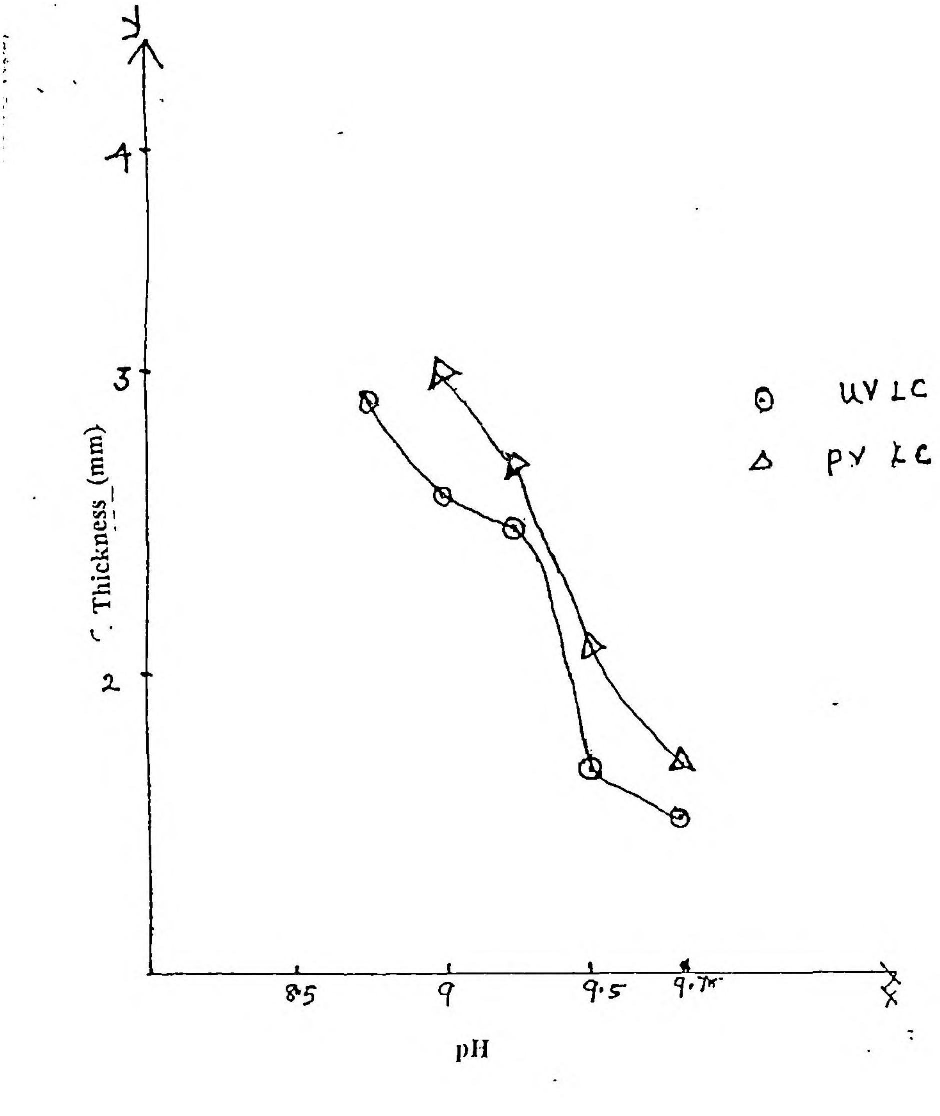


Fig.3.11Effect of viscosity on storage at different pH in UVLC system

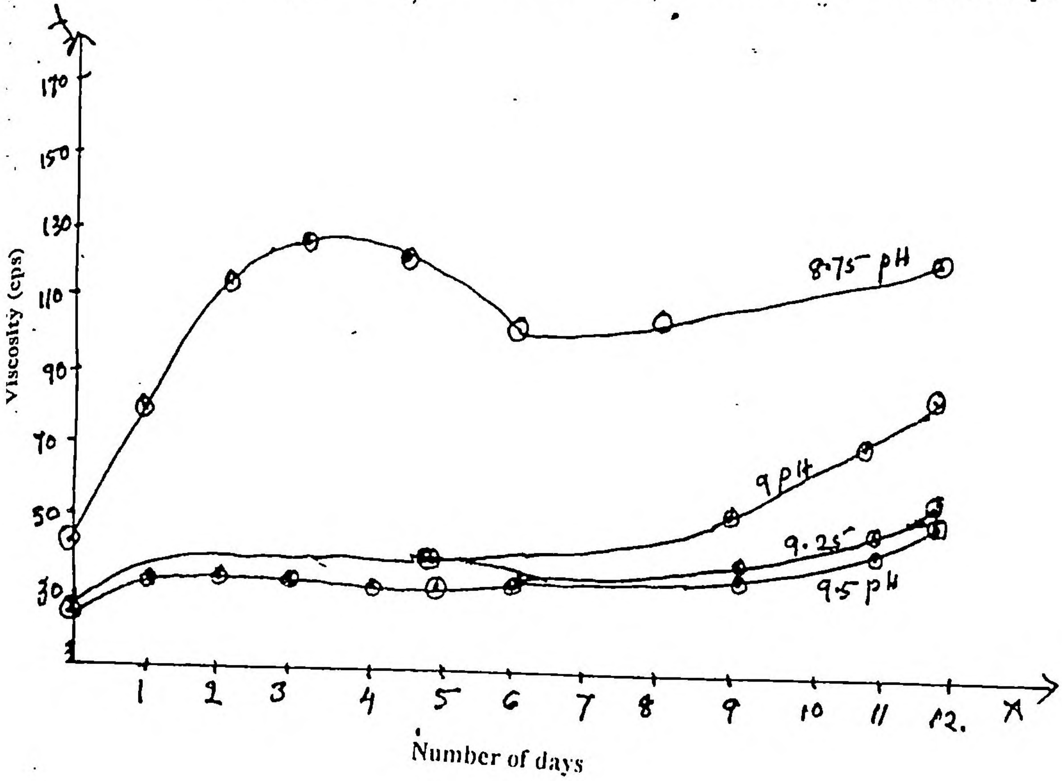
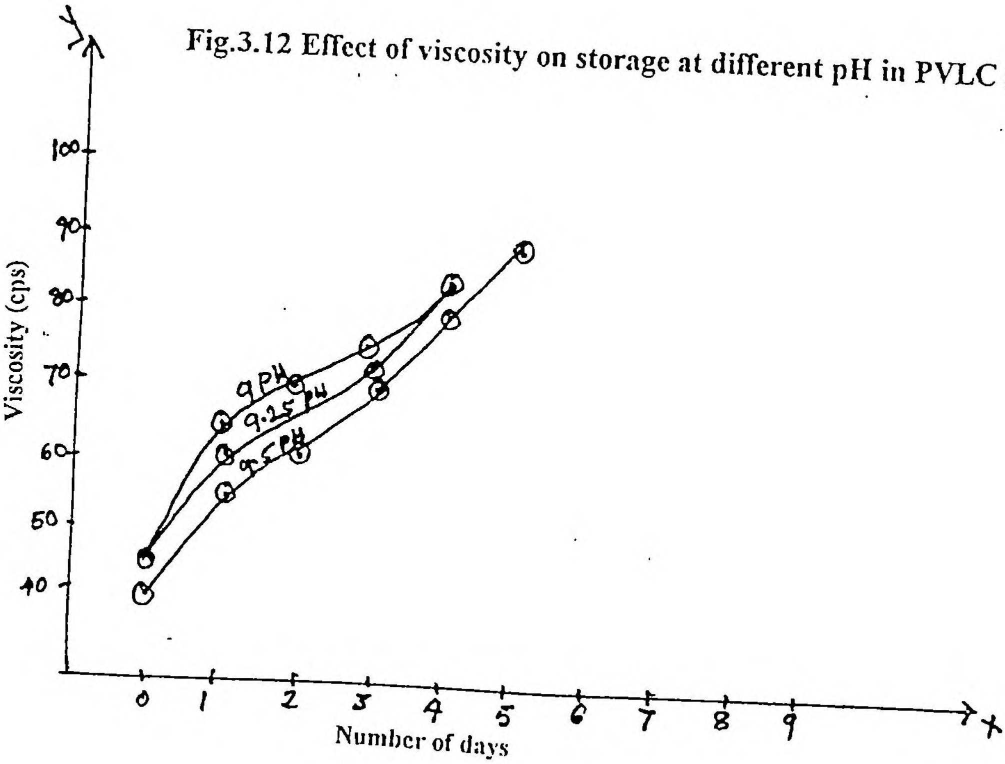


Fig.3.12 Effect of viscosity on storage at different pH in PVLC system



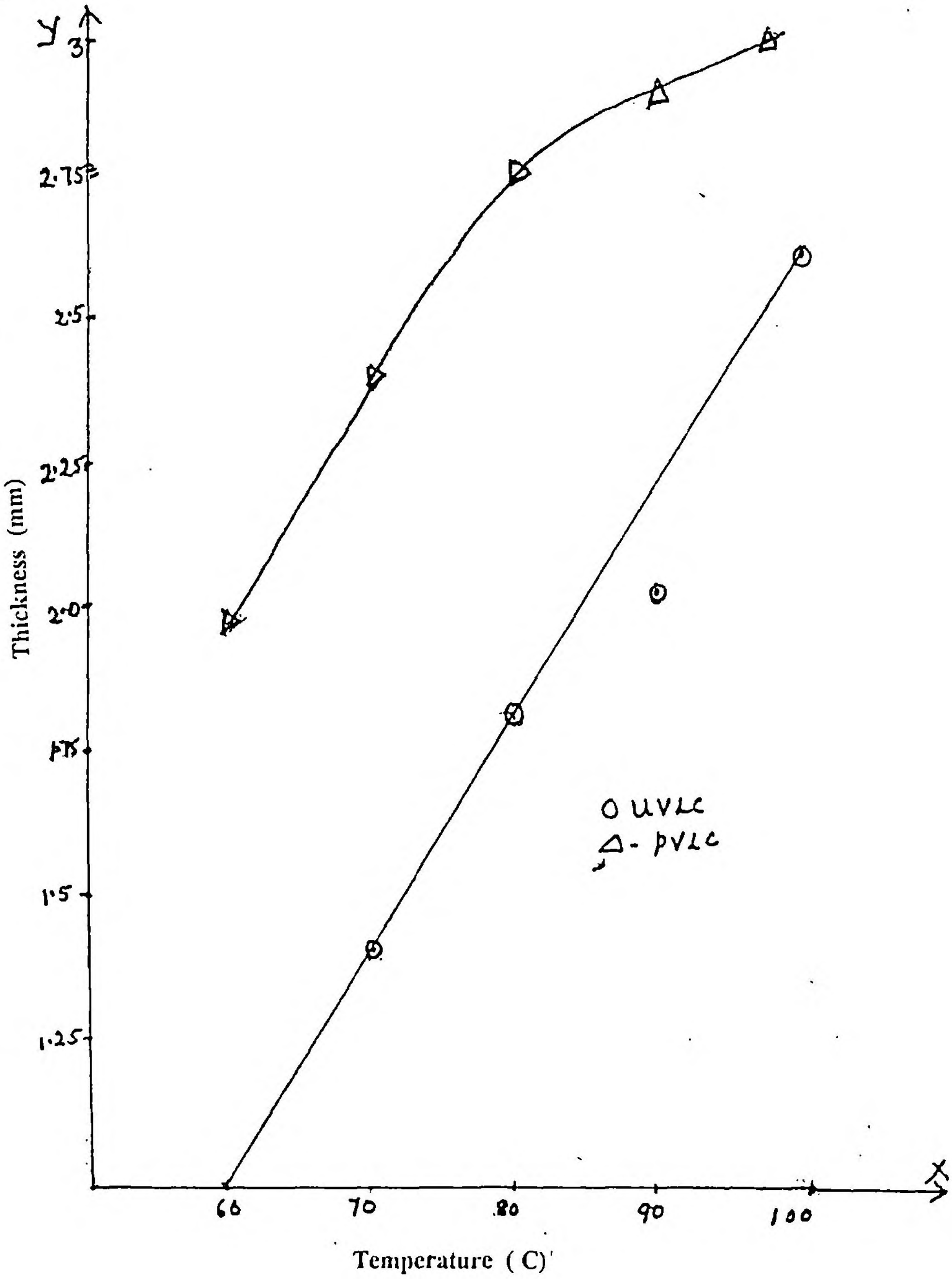


Fig.3.13 Effect of former temperature on thickness in UVLC and PVLC

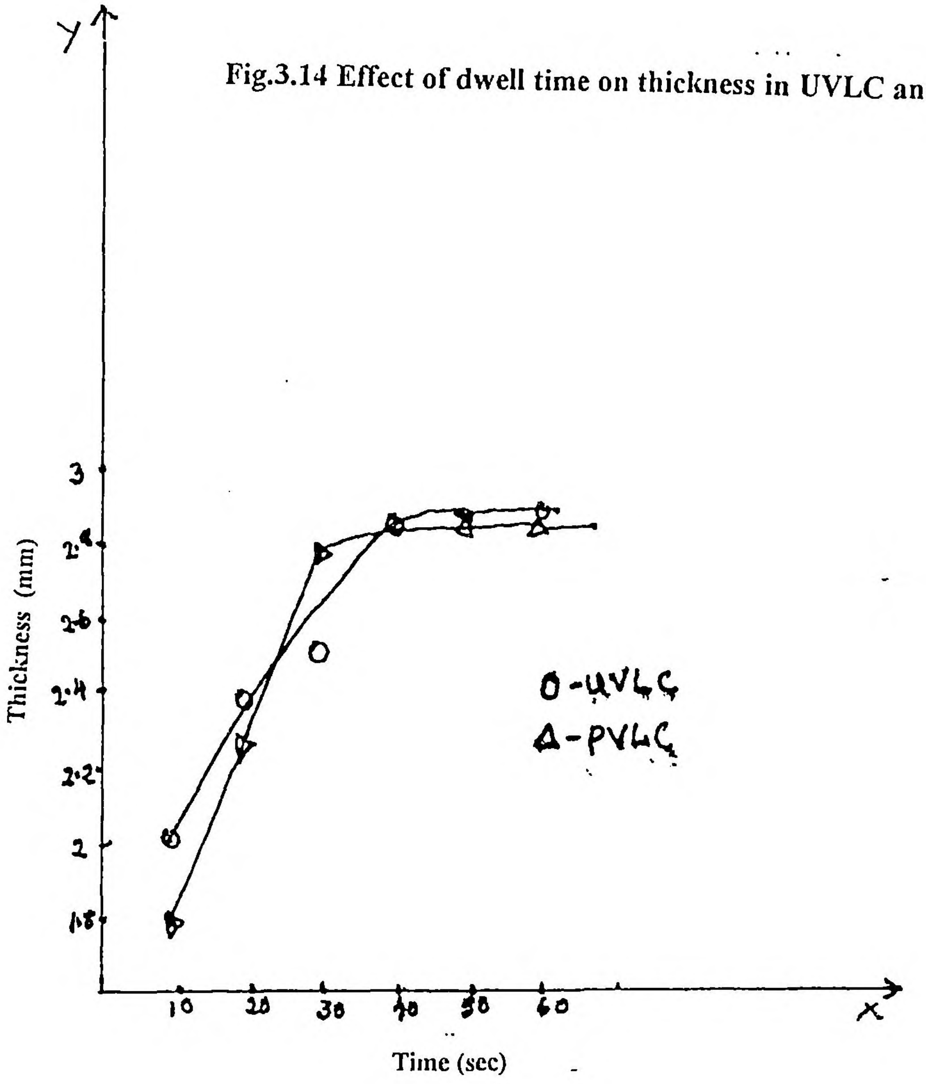


Fig.3.14 Effect of dwell time on thickness in UVLC and PVLC

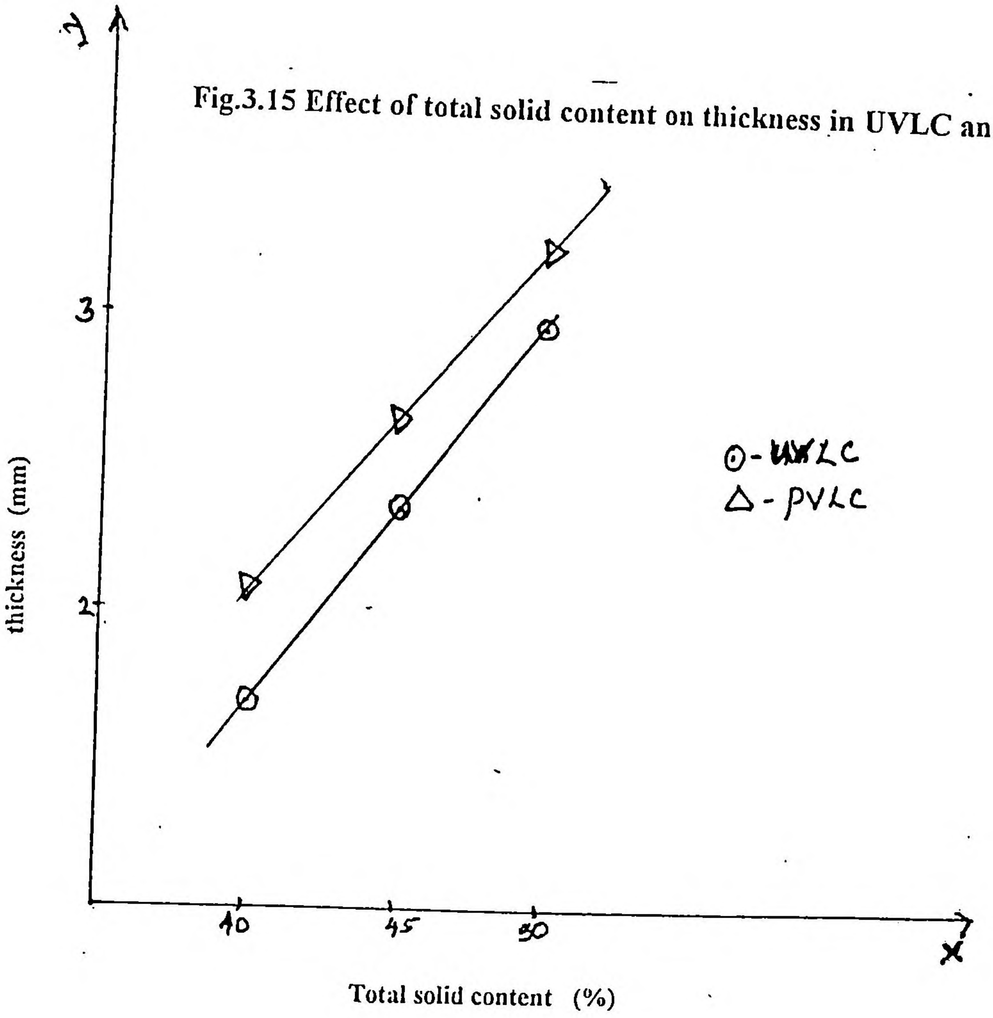


Fig.3.15 Effect of total solid content on thickness in UVLC and PVLC

CHAPTER 4

SUMMARY AND CONCLUSIONS

CHAPTER 4

SUMMARY & CONCLUSION

4.1 Summary

In the present work heat sensitization of Natural Rubber Latex by poly vinyl methyl ether has been investigated. The effects of varying different compound and processing parameters have been evaluated in unvulcanised and prevulcanised latex systems. Optimum compound formulation for both the systems have been standerdized and their stability characteristics have been studied. The technological properties of the latex film have also been determined.

From the results obtained, following conclusions are drawn.

1) Degree of Heat-Sensitization is affected by the dosages of Vulcastab VL, Zinc oxide, poly vinyl methyl ether and pH of latex compounds. In the base latex compound studies, the optimum values obtained are given below.

Compound Parameter	Optimum UVLC System	Values PVLC System
1) Level of Vulcastab-VL (phr)	0.75	1
2) Level of Zinc oxide(phr)	1	1
3) Level of PVME (phr)	1	1.5
4) pH	9	9

2) Thickness of the latex deposits depends on processing parameters such as former temperature, Dwell time and Total solid content of the latex compound. The optimum dwell time is found to be 40secs for both the system. When the mould temperature is 100°C, and the total solid content is 50% a thickness of 3.0mm is obtained by a single dip for both the systems.

3) The above latex compounds are having good storage stability at 15°C and 25°C.

4) The vulcanised film from the above latex compounds posses good technological properties and ageing resistance.

4.2 CONCLUSION:

Heat sensitized dipping by PVME can be used for the manufacture of a numberof thick products like medical tubings, teats, soothers, meterological balloons etc. It is felt that the results of this study would be helpful in designing compound formulation and processing parameters for the manufacture of the above products from unvulcanised and prevulcanised latex compounds. The results can also be used for designing compound formulations for the manufacture of extruded latex tubings.

Recently radiation Vulcanised natural rubber latex has been developed for the manufacture of dipped medical products. This study can also be extended using radiation Vulcanised natural Rubber latex.

REFERENCES

1. D.C. Blackely, High Polymer Latices Vol.I Maclares and Sons Ltd., London (1966) 214-240.

2. B.L.Archer, D.Barnard, E.G.Cockbain, P.I.Dickens and M.I. McMuller, The Chemistry and Physics of Rubber like substances L Bateman Ed, Macleres and Sons Ltd., London (1963) 41-94.

3. D.C. Blackely, High Polymer Latices, Vol II, Chapmann & Hall Ltd, London (1997) 24-42.

4. J.S.Lowe Tran Instn. Rubb Ind, 36 (1960) 225.

5. S.N.Angore, Tran Instn, Rubb Ind 40 (1964) 251-261.

6. E.Rhodes J. Rubb Res Inst, Malaya 8(3) 324-30

7. C.K.John, M.Nadarajah, P.S.Ramarao, C.M.Lam & C.S.Ng proc Int. Rubb Conf. 4 (1975) 339-357.

8. P.S.Ramarao, C.K.John, C.S Ng, M.G. Smith and C.F.Robert, RRIM Planters Conference (1976) 324-333.

9. C.K.John, N.P.Wing, A.C.Chin and Abdul Latif, proc. Int. Rubb Conf 2 (1985) 451-467.

10. A.D.T. Gorton and T.D.Pendle Proc Int. Rubb Conf Kulalumpur, Vol II (1985) 468.

11. D.C.Blackely, High Polymer Latices, Vol II Chammann & Hall, London (1997) 42-77.

12. D.C.Blackely, high Polymer Latices, Vol I, Chapmann & Hall Ltd, London (1997) 416-447.

13. E.G.Cockbain and M.W.Philpott, the Chemistry and Physics of Rubber Like Substances, L Bateman, Ed. Maclaven and Sons Ltd., London (1963) Chapter one.

14. J.R.Vanwazer, J.W.Lyons, K.U.Kin and R.E.Colwell, Viscosity and flow measurement, Inter Sciences, New York (1966) 6.

15. K.F.Gazeley, A.D.T. Gorten and T.D. Pendle Natural Rubber Science & Technology, A.D.Roberts, Ed. MRPRA, Oxford University Press, London (1988) 100-140.

16. D.C.Blackely, polymer Latices, Vol III, Chapman & Hall (1997) 34-99.

17. A.D.T.Gorton and T.D.Pendle, NR Technol 12 (1981) 21

18. A.D.T. Gorton and T.D.Pendle, NR Technol 12 (1981) 1

19. B.S 3900, part of determination of fineness of grind (1983).

20. A.D.T. Gorton and T.D.Pendle Proc Eml polym Conf. PRI London (1982) June.

21. G.L.Brown and B.S.Garret, J.Appl. Polym Sci. I (1959) 283

22. W.D.Schroader and G.L.Brown, Rubb Age 69 (1951) 433.

23. M.W.Philpott, proc, Rubb. Tech Conf. ITI London (1962) 470.

24. J.R.Dunn Trans. Inst. Rubb Ind 34 (1958) 249.

25. C.A.Blokh, Organic accelerators in the vulcanizate of rubber, IPST, Jerusalem (1968) 16-68.

26. D.C.Blackely polymer Latices Vol I, Chapman & Hall London (1997) 240-363.

27. Murphy. E.A (1938) proceedings of the Rubber Technology Conference, London 1938 p 151.

28. Twiss, D.F and Amphlett, P.H (1940) Journal of Society of Chemical Industry, 59, 202.

29. Madge E.W. and Pounder D.W (1947) Transactors of the institution of the Rubber Industry.

30. Marphy. E.A, Madge.E.W and Pounder D.W (1948) proceedings of the Second Rubber Technology Conference, London p.303

31. Madge C.W (1952) Transactions of the Institution of the Rubber Industry, 28, 207.

32. D.C.Blackely polymer Latices Vol III Chapman & Hall London (1997) page 159-171.

33. D.C.Blackely Polymer Latices Vol III Chapman & Hall London (1997) page 187-193.

34. A.Y.Coran, Science and Technology of Rubber, Frederick, R.Erich, Ed, Rubber Frederick, R. Erich, Ed, Rubber Division of ACs (1978) 291-335

35. B.A Dogadkin, ZN Tara Sova and Golberg, Proc 4th Rubb Technol conf. London IRJ (1962) 65.

36. L.Bateman, C.G Moor, M.Porter and B.Saville, The Chemistry and Physics of Rubber like substance, L.Bateman Ed, Maclarsen and Sons Ltd., London (1963) 451-561.

37. A.D.Roberts, Natural Rubber Science and Technology, Oxford Science Publisher Ltd., London 91988) 83-85.

38. Philpott.M.W, (1962) Activation of Sulphur bearing Vulcanisation accelerators and curing agents proc 4th Rubb Technol Conf, London p-470. Malaysian Rubber produces Research Association, Bricendonburg.

39. Bloonfield, G.F, (1952) The modification of natural rubber by synthetic polymers, Rubb Developments, 5,2,34.

40. K.Makuuchi, progress in Radiation Vulcanization of Natural Rubber Latex through International Co-operation proc. Int. Sym on RVNRL. Japan Atomic Energy Research Institute (1990) 91-96.

41. Pounder D.W. curing of rubber latex and the production of articles there from B.S.Patent 853, 926 (1956).

42. D.C.Blackely polymer Latices Vol I Champmann & Hall London (1997) page 306-345.

43. Heat Sensitization of Natural Latex, Recent Developments by E.G.Cock Bain Transactions, IRI 97-101.

44. Cock Bain E.G (1956) Transaction of the Institute of the Rubber Industry, 32,97.

45. Sinn. G(1974) paper presentes at polymer paint and colour Journal Latices and Dispersions Symposium, Hastings, UK.

46. Abramova E.N. Chernaya, V.V and Gorelik, E.A (1960) Soviet rubber Technology, 19, 8

47. Blackley D.C. Gorton A.D.T and Sivagurunathan. L(1990) Journal of Dispersion Science and Technology, 11,279.

48. Rother K. and Sinn, G/Farbenfabricken bayer Aktiengesel// Schaft, German patent No.869, 861, 8 July 1949.

49. Cockbain E.G (1951) Journal of the Rubber Research Institute of Malaya 13, 157.

50. Cockbain E.G (1954) Rubber Developments 7,66.

51. Sandomirskii D.M and Pilmenshteen I.D (1962) Kolloidn Zhurnal 24, 314.

52. Sandomirskii D.M Pil'menshtein I.D and lebednskaya, M.L (1963) Kolloidn Zhurnal 25, 679.

53. Gorton A.D.T (1976) Plastics and Rubber, processing 1,3

54. Gorton, A.D.T and Pendle T.D (1980) NR Technology, 11,1

55. Blackely, D.C Gorton, A.D.T and Sivagurunathan L (1990) Journal of Dispersion Science & Technology 11,215

56. Blalckely, D.!C Gorton, A.D.T and Sivagurunathan L (1990) Journal of Dispersion Science and Technology.

57. Bis specification for centrifuged Natural Rubber Latex HA type 5430-1981.

58. D.C.Blackely polymer Latices Vol III Chapman & Hall London (1997) page 99-119.

59. GIRRAJ MAL Dictionary of Rubber Chemicals page 10-50

60. COCKBAIN E.G Heat Sensitization of Latex and synthetic Emulsions by poly vinyl methyl ether British Rubber producers Association paper No.27.

61. Determination of Viscosity using Brookefield Viscometer ASTM D 2526-29.