EFFECT OF VISCOSITY-MODIFIERS ON THE PICK - UP AND TECHNICAL PROPERTIES OF DIPPED GOODS

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Mr. Mani has worked on this project for about six months. The results embodied in the thesis have not been submitted for the award of any other degree or diploma.

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Mr. Mani has worked on this project from December 1982 to May 1983. The results given in this thesis have not been submitted for the award of any other degree or diploma.

Sadhan De

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PREFACE

Although a few studies have been reported on the various aspects of 'dipping', the effect of various viscosity-modifiers (thickeners) on the pick-up and technical properties of dipped goods still remain largely unexplored. In this thesis five viscosity-modifiers are chosen and they are compared for their pick-up efficiency. The effect of these thickeners on tensile properties are also studied.

The subject matter of the thesis has been presented in three chapters.

The introductory chapter consists of a brief review of earlier works in this field and the scope of the present work.

The experimental techniques are described in Chapter II.

Chapter III consists of viscosity and pick-up measurement studies of five thickeners and the effect of the five thickeners on the physical properties of the vulcanizates.

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GLOSSARY OF TERMS

ASTM : American Society for Testing and Materials
BS : British Standards
cp : Centi Poise
DRC : Dry Rubber Content
EB : Elongation at Break
IS : Indian Standards
Phr : Parts per hundred of rubber
rpm : Revolutions per minute
SP : Styrenated Phenol
TSC : Total Solids Content
TS : Tensile Strength
ZDC : Zinc diethyl dithiocarbamate
ZMBT : Zinc mercapto benzothiazole

CHAPTER I

INTRODUCTION

Natural rubber latex is a milky liquid which consists of extremely small particles of rubber dispersed in an aqueous medium. It is obtained from the bark of Hevea brasiliensis tree. It is collected from the tree by tapping. Shortly after latex is obtained from the rubber tree, bacterial action begins, and in order to preserve latex in fluid condition for more than a few hours after tapping it is necessary that some preservative be added. Ammonia is the best preservative. The concentration of ammonia used for this purpose is 0.7% on concentrated latex. The use of ammonia as a preservative is attended by the advantage of ready elimination when desired, either by aeration of the latex or neutralization which carbon dioxide or formaldehyde.

Hevea latex is a hydrosol in which the dispersed particles are protected by a complex film. The coating imparts colloidal properties to latex particles. Besides rubber particles latex contains Lutoids and Frey Wyssling particles. Lutoids are associated with the process of latex vessel plugging which stops the flow of latex a few hours after tapping.

Each individual latex particle may vary in size between 0.25 to 5 microns. It contains varying proportions of "gel" and "sol" rubber, referring to the insoluble and soluble portions, respectively. Latex particles are either spherical or pear shaped, exhibiting Brownian movement. This Brownian motion overcomes gravitational forces and keeps the colloidal properties to the latex. Important properties of freshly tapped latex is given in the Table below:

Table

Properties of freshly tapped latex

Characteristic	Value
Total solids content (TSC), % by weight	30-35
Dry rubber content (DRC), % by weight	25-40
Particle size, microns	0.25-5.0
Specific gravity	0.96-0.98
pH	6.8
Surface tension, at concentration of 38 to 40%, dynes/cm	38-40

Characteristic	Value
Conductivity, mhos/10^4	40-50
Non-rubber content, % by weight	2-3.5
Viscosity, cP	15-25

The serum in which the rubber particles are suspended has a specific gravity slightly greater than water Viscosity of latex will vary with sources. The presence of ammonia causes some decrease in viscosity as compared with fresh latex. Concentration of rubber greatly increases the viscosity of latex. Time and method of tapping, humidity prior to tapping, age of the tree and of the latex, and the non-rubber content of the latex also influence the viscosity Surface tension value of preserved latex is lower than that of the fresh latex due to the presence of ammonia and that of 60% centrifuged latex is having a surface tension of 40 to 42 dynes per centimeter. The acidity of fresh latex increases somewhat during the first few hours after tapping and eventually it coagulates unless ammonia is added.

Methods used for the manufacture of latex rubber goods are impregnation, spreading, dipping, molding (casting), electrodeposition, extrusion, foaming, and other miscellaneous methods. Preserved field latex is concentrated to a dry rubber content (DRC) of approximately 60% by weight, because of the following reasons:

1. Natural latex is unsuitable for product manufacture.
2. Economy in transportation.
3. To get a pure rubber of more uniform quality.

Important methods for the concentration of field latex are given below:

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

The first method involves the removal of water only. Hence, the ratio of non-rubber constituents to rubber content and the particle size distribution remains unaffected. On the other hand, the three latter methods, all involve partial removal of non-rubber constituents in relation to the rubber content, particle size distribution of concentrate also differ from that of the initial latex, because a proportion of the smaller particles is eliminated at the same time. Only centrifuging and creaming are commercially used now-a-days for the production of latex concentrate.

I. DIPPING PROCESS

The dipping process consists essentially in the immersion of a former into suitably compounded latex or rubber solution, followed by slow withdrawal in such a way as to leave a uniform deposit of latex on the former. The thickness of the deposit may be reinforced with subsequent coatings. The process is completed by drying, leaching and, if necessary, vulcanising the deposit. It is usually desirable to form a rolled bead at the neck of the article, in order to reinforce the thin rubber deposit against tearing[1].

Until comparatively recent times, dipping was carried out using rubber solutions, prepared by masticating dry raw rubber and dissolving it in a suitable organic solvent such as naphtha. Vulcanisation was carried out in a 2% solution of sulphur chloride in carbon disulphide.

I.1 Advantages of latex dipping. Advantages of latex dipping over solution dipping are given below:

1. Deposit has very good ageing characteristics.
2. Natural nerve and quality of the rubber is retained.
3. Elimination of milling cost.
4. Elimination of the cost of solvent for rubber and sulphur chloride.
5. No chance of fire hazards.
6. Elimination of objectionable working conditions of solution dipping.
7. Number of dips required is less when compared to solution dipping.

I.2 Latex dipping methods. Principal latex dipping methods are:

1. Straight dipping:
   - (i) Single dip
   - (ii) Multi-dip
2. Coacervant dipping:
   - (i) Wet-coacervant dipping
     - (a) Initial immersion in coacervant
     - (b) Initial immersion in latex
   - (ii) Dry-coacervant dipping
3. Heat-sensitised dipping

I.2.1 Straight dipping. Straight dipping is dipping without the assistance of any ancillary aids such as coacervants. Deposit forms by virtue of viscosity of the latex and of its tendency to wet out the former. In straight dipping, usually multi-dipping is practised widely. Deposit thickness vary from 0.005 to 0.010 inch per dip depending upon viscosity.

In dipping, the chief disadvantages are that, the latex flows, after the mold is removed from the compound, causing unevenness in thickness and that the thickness obtained by a single dip is very slight. Robertson[2] showed that the first disadvantage could be avoided by regulating the speed of withdrawal of the former from the compound so that the latex film sets by the time the former is completely withdrawn. The second disadvantage can be avoided by the use of thickening agents[3]. Efficiency of dipping can be increased by using a heated former and dipping in a concentrated vulcanized latex compound with alternate dipping and drying of the deposit[4]; also, instead, alternate dipping in latex and in a coagulant can be used[4].

I.2.2 Wet-coacervant dipping. In this method a fluid coacervant such as acetic acid, or formic acid can be used to assist the build-up of the deposit[1]. It can be done in two ways, according as the former is dipped first into the coacervant or first into the latex compound. The thickness of the deposit is determined by the dwell time and the stability of the latex towards the coacervant used[5]. The initial rate of deposition is fast, but slow down until a limiting thickness is attained. The mechanism involves the diffusion of the coacervant out from the former together with the simultaneous consumption of coacervant as deposition proceeds[5,6].

Disadvantages of initial immersion in coacervant method are non-uniformity of deposit and tendency for the deposit to slip off the former during withdrawal. Initial immersion in latex method overcomes the disadvantages of the first; the initial deposit tends to act as a "tiecoat", avoiding slippage of the deposit. The initial deposit also absorbs the coacervant, so that thicker final deposits may be formed[6]. The disadvantage is that it involves two latex dips.

Gorton[6] showed that in wet-coacervant dipping (first immersion in latex) the cross-section of the deposit consists of five regions.

Region I - dry deposit from straight dip,
Region II - dry deposit of coagulant,
Region III - wet coagulum formed by 'straight dip', called 'first deposit',
Region IV - wet coagulum formed by coagulant, called 'second deposit',
Region V - latex compound.

As the coagulum deposit is formed, two effects will hinder its growth[6]:

(i) Release of serum and subsequent dilution of the coagulant,

(ii) Increase in the thickness through which the coagulant will have to permeate to reach the latex compound.

A further controlling effect is the passage of serum towards the former to assist the initial dissolution of coagulant, so that it is not 'starved'.

I.2.3 Dry-coacervant dipping. This is the most popular and widely used method, in which dry coacervants such as calcium chloride, calcium nitrate, cyclohexyl ammonium acetate and other acidic salts are used[8,1]. The former is first immersed in a solution of the dry coacervant in a volatile solvent, e.g., alcohol. After withdrawal from the solution, the solvent is allowed to evaporate leaving either a dry film of coacervant or very viscous and concentrated solution. The former is then immersed in the compounded latex and allowed to dwell for a pre-determined time. The nature of deposit build-up is very similar to that for the wet-coacervant dipping.

I.2.4 Heat-sensitised dipping. This method does not find a great deal of application except in rather specialised processes. The principle here is to employ a heated former and to compound the latex in such a way that it is heat-sensitive. Heat-sensitivity may be induced by several standard methods; the most useful method is by compounding with polyvinyl methyl ether. The thickness of deposit depends on the degree of heat-sensitivity of the latex, the temperature of the former, and the heat capacity of the former.

One importantr problem in latex dipping is web formation, i.e., a continuous film formation of latex between adjacent sections of the formers. Web is not permanent and breaks at some stage during the removal of the former from the latex. Web formation and breaking causes difficulty in achieving a uniform deposit. Gorton and Kuzmany[8] showed that by the incorporation of web breaking agents like milk, casein and trimethyl hexanol this problem could be solved.

II. FACTORS INFLUENCING QUALITY AND PICK-UP DEPOSIT

II.1 Physico-chemical properties. Of the various physico-chemical properties viscosity is the most important which influences quality and pick-up of deposit. Control of viscosity is more important than of concentration. A very much larger variation in deposit weight being obtained if the total solids are kept constant and viscosity varied than if the viscosity is kept constant and the total solids altered[9].

Particles in latex are prevented from coalescing by two factors:

1) their charge,

2) the protective coating.

Both these factors govern the mutual approach of the particles which in turn governs the viscosity of the mixing[9].

The methods by which the viscosity of a mix may be altered by agents, therefore, fall into three groups:

(i) by influencing the charge on the particle,

(ii) by altering the magnitude of the protective envelope,

(iii) by altering the viscosity of the aqueous serum itself.

To control the viscosity, the compound has to be first brought into a desired rheologic state and it has to be kept in that state until desired. The desired rheologic state may be brought about by the addition of thickeners and to control the viscosity the addition of antagonistic salts and change of temperature are useful[9].

II.2 Viscosity-modification. In latex technology, it means modification of bulk flow behaviour. The whole relationship between shear rate and applied stress for the system may be radically modified by the inclusion of viscosity-modifiers (thickeners). Thixotropy and structural viscosity may be imparted by their inclusion.

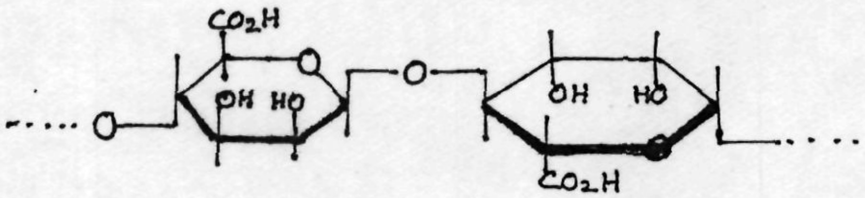
Viscosity modifiers (thickeners) are hydrocolloids, soluble in water to give viscous solutions and show the properties of a typical lyophilic colloid system. They also function as protective colloids (as disperson and emulsion stabilisers). The flow behaviour of a latex-thickener system is not a simple additive function of the flow behaviours of its separate components. Interaction effects are common.

The mechanism of thickening does not involve merely an increase in the viscosity of the continuous phase. One complicating effect is the reversible clustering or flocculating of latex particles. Another is the fact that weak bonds may develop between particles and between molecules, which break down under stress but which reform when the stress is removed. Such bonds give rise to thixotropic effects and to the phenomenon of structural viscosity.

Thickeners can be classified as plant hydrocolloids, proteins, polyvinyl alcohols, cellulose derivatives, starches, polyacrylates and polymethacrylates, carboxylate copolymers, and colloidal clays. Alginates, gum arabic, gum karaya, locust bean gum and Irish moss extract (carrageenan) are the members of the plant hydrocolloids. Casein, glue, gelatin, and haemoglobin are important among proteins. Simple alkyl ethers, hydroxyalkyl ethers and carboxyalkyl ethers of cellulose are cellulose derivatives.

A short description of the five thickeners used for the study is given in the following paragraphs.

II.2.1 Ammonium alginate. It is a plant hydrocolloid and used as a creaming agent, thickener, and stabiliser for latices and as a stabiliser for dispersions. The use of this water-soluble alginate is confined to systems which are alkaline and free from heavy metal ions. The structure of alginic acid is shown below:



Alginic acid is a high molecular weight linear poly 1,4'-β-D-anhydromannuronic acid. The degree of polymerisation may range from about 200 to 1000.

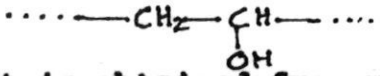
II.2.2 Cyclohexanol. The structure of cyclohexanol is shown below:

$CH_2(CH_2)_4CHOH$

It is a colourless, rather viscous liquid with a camphoraceous odor. It was first prepared by Baeyer in 1894. Its melting point is 25.15°C, boiling point 161.1°C and viscosity at 25°C is 4.6 cP. It shows most of the typical reactions of secondary alcohols. It is used as a latex thickener, stabilizer and homogenizer for soaps and synthetic detergent emulsions.

II.2.3 Polyvinyl alcohol. It is the first of the completely synthetic water-soluble resins to attain commercial importance, and was first prepared by Willie Hermann, a German Chemist. It is a water-soluble resin, the aqueous solutions are not viscous at concentrations below 5-10%. Polyvinyl alcohol is a surface active agent and its solutions have a tendency to foam, but it tends to be rather unstable. They are quite temperature stable and show no permanent viscosity loss even after boiling for several days. Although this polymer is non-ionic, it may be salted out of solution by small amounts of some salts. Water solutions of polyvinyl alcohol should be stabilized against bacterial attack. It imparts good solvent resistance, high dielectric constants, low gas permeability (except for water and ammonia), and low elongation. It is quite hygroscopic and can absorb 25-50% water at 100% relative humidity.

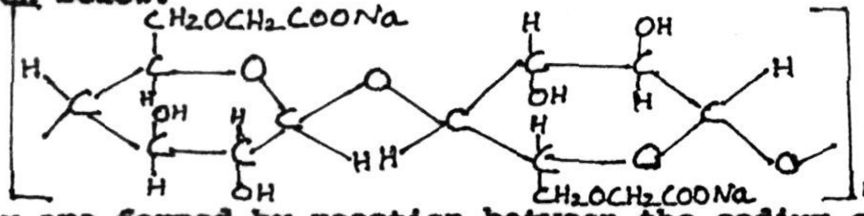
The structure of polyvinyl alcohol is shown below:



$$\cdots\cdots - CH_2 - \underset{OH}{\underset{|}{CH}} - \cdots\cdots$$

It is obtained from polyvinyl acetate by acidic or alkaline hydrolysis. It has a comparatively regular 1,3("head-to-tail") structure. Degree of hydrolysis vary between 40 and 100% and several viscosity grades are available.

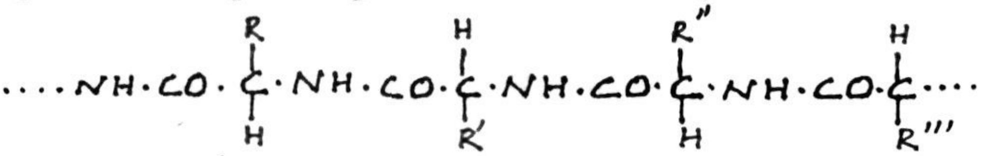
II.2.4 Sodium carboxymethyl cellulose. It is the most widely known of the water-soluble cellulose derivatives. Cellulose is a linear poly 1,4'-β-D-anhydroglucopyranose of molecular weight between 200,000 and 800,000, depending upon its source. Each cellulose molecule may therefore contain between about 1300 and 5000 glucose units. The general formula of sodium carboxymethol cellulose is given below:



They are formed by reaction between the sodium salt of chloro-acetic acid and sodium cellulose.

It is an anionic type resin soluble in both hot and cold water. Solution viscosities are dependent on the method of preparation, with high shear mixing resulting in viscosity reduction. The solutions are pseudoplastic and sometimes thixotropic; their viscosity is relatively uniform throughout the pH range of 3-10. It is capable of substantially increasing the viscosity of water at relatively low polymer concentrations. A range of chain lengths and degrees of substitution is available commercially. All the cellulose ethers are very stable and may be stored for long periods without change. They are somewhat hygroscopic in damp atmospheres. Their aqueous solutions are very much less prone to attack by micro-organisms. However, it is wise to include a preservative if maintenance of viscosity is desired over long periods[11].

II.2.5 Casein. Casein is a phosphoprotein which is obtained from caseinogen, the raw protein of milk. Proteins are essentially linear high molecular weight polyamides derived from D-α-amino acids, which may also have various prosthetic groups incorporated in the molecule. They are represented by the general structure given below:



$$\cdots\cdot NH\cdot CO\cdot \underset{H}{\overset{R}{C}}\cdot NH\cdot CO\cdot \underset{R'}{\overset{H}{C}}\cdot NH\cdot CO\cdot \underset{H}{\overset{R''}{C}}\cdot NH\cdot CO\cdot \underset{R'''}{\overset{H}{C}}\cdots\cdot$$

The substituents R, R', R'', R''', etc form a quite definite sequence which is characteristic of the particular protein.

Acid casein has a molecular weight of the order of 40,000 and there is some evidence that it is a single molecular species. Casein is very sparingly soluble in water, but is readily soluble in acids and alkalies. To enhance the keeping quality of the solutions, preservatives such as sodium pentachlorophenate are added in amounts of 0.1 to 0.5% on a solution basis.

Many of the various uses of casein require adjustment and control of the viscosity of its solutions. It is having the highest viscosity at pH of about 9.2. The isoelectric point of acid casein is in the region of pH 4.6. Casein is used as a thickener, protective colloid and dispersion stabilizer.

II.3 <u>Concentration for incorporation in latex.</u> Most thickeners must be diluted below a characteristic concentration before mixing with latex. More concentrated solutions may cause local precipitation due to dehydration or salt effects, or may be difficult to mix to give a homogeneous combination. Other things being equal, the thickener which may be incorporated at the highest concentration is preferable[12].

III.1 Comparative thickening efficiency. Since viscosity does not have a linear dependence upon the concentration of the thickener, a comparison of viscosities at equal concentrations give a different and misleading index of efficiency[12]. Under the conditions of use, the relative thickening efficiencies of different viscosity modifiers should be judged by the amounts of the thickeners needed to achieve the desired viscosity or pick-up.

Schroeder and Brown[12] made studies on the comparative thickening efficiency of sodium polyacrylate ("acrysol GS"), methyl cellulose and sodium carboxymethyl cellulose.

It was found that with "acrysol GS" viscosity increases much less sharply with concentration than for the two cellulose derivatives. And, with "acrysol GS", at relatively low temperatures, viscosity depends sharply on temperatures, but a much less pronounced dependence at normal use temperatures. In the alkaline region, the viscosity of a 5% solution of "acrysol GS" was affected only slightly by changes in pH. In the acid region, viscosity drops fairly sharply with decreasing pH.

III.2 Relation between dwell time, latex compound viscosity and deposit thickness. Despite the long established practice of latex dipping, surprisingly little has been published on this subject till 1967, apart from patents and general descriptions of the process. In 1967 Gorton[6] had made studies in the field of latex dipping, and established relationship between dwell time, latex compound viscosity and deposit thickness for straight and coagulant dipping by variation in dwell time and compound viscosity.

In the case of straight dipping, Gorton established the relationship:

$t = a_1 + K_1 \log (\eta 60)$, where

t = straight dip deposit thickness,

a_1 and K_1 are constants,

$\eta 60$ = apparent viscosity (Brookfield) at 60 rev/min.

Such relationship holds at other rates of shear (and therefore viscosity).

And, in the case of coagulant dip, total dip deposit is dependent on two factors: dwell time and latex compound viscosity. Gorton established the relationship:

$tc = K_5 \sqrt{D} \log_{10} \eta$, for the true coagulant deposit thickness (tc),

where, D = dwell time

η = apparent viscosity (Brookfield)

K_5 = constant

And, for the total thickness of deposit (Tn) following a straight dip with 'n' further coagulant dips he has established the relationship:

$$Tn = 2a_1 + \log_{10} \eta \, [(n+1)K_1 + K_5 \sqrt{D}].$$

where, a_1, K_1 and K_5 are constants.

It is thus possible to predict deposit thickness from a knowledge of dwell time and latex compound viscosity.

Gorton and Iyer[7] examined the above relationship, established for coagulant dipping, between the thickness of rubber deposited under the influence of coagulants with variation in dwell time and compound viscosity, over a wider range of latex compounds. The effect of the concentration and type of coagulant on the thickness of deposit had been studied. A method of predicting deposit thickness, which may be useful for industrial processes, is proposed from prior knowledge of coagulant, latex compound viscosity and dwell time. The amount of rubber deposited by coagulant dipping depends on the ionic diffusion of the coagulant and the pore size of the coagulum.

IV. SCOPE OF THE PRESENT WORK

A large variety of dipped goods are manufactured from natural rubber latex. These include thin surgical goods (for eg., gloves), household gloves, nipples, bathing caps, bathing shoes, bathing rubbers, fitted overshoes, rubber toys, balloons, rubber bands, rubber threads, etc. Natural rubber consumption in India during 1981-'82 was 186,920 metric tonnes, out of which about 3.1% of latex rubber has been consumed for dipped goods production only. Dipped goods manufacturing has a good future, and in the coming years consumption of latex would be more than the present figure.

But, this sector faces a number of problems. A major problem is that compounds of low viscosity give too thin a film per dip so that a number of dips are required to attain sufficient thickness. This reduces the overall production tremendously and the labour cost per kilogram of product increases. Also it is difficult to maintain compounds of low viscosity in uniform condition and the compounding ingredients tend to separate, thereby affecting the quality of the product.

Attempts to increase viscosity of latex compounds are justified in this context. In order to improve the quality, to reduce the labour cost and to increase production, some attempts have been made by the incorporation of five thickeners into a latex compound and comparative efficiencies have been determined. From these studies, the best thickener having maximum efficiency could be chosen.

Incorporation of thickeners may be accompanied by changes in technical properties. Hence it has become important to investigate whether the thickeners have got some adverse effect on technical properties of the compound.

The review outlined above indicates that studies on the effect of thickener addition on pick-up are not many. Schroeder and Brown[12] observed that sodium polyacrylate ("acrysol GS") is a better thickener when compared to methyl cellulose and sodium carboxymethyl cellulose. No other study on comparative evaluation of thickeners have been reported yet. Also, no work has been reported yet on the effect of viscosity-modifiers on the technical properties of the vulcanizates. Hence it would be interesting to study comparative thickening efficiency of various thickeners and their effect on physical properties. In the present thesis, which attempts to give a clear picture on these facts, the following studies have been made.

(a) Five thickeners, viz. casein, ammonium alginate, polyvinyl alcohol, cyclohexanol and sodium carboxymethyl cellulose were incorporated into a latex compound; each thickener has added in varying concentration of 0 to 1.5 and the effects on viscosity have been studied.

(b) Each thickener, in varying concentrations, has been subjected to pick-up measurement by straight dipping and coacervant dipping with dwell times of ½ minute and 1 minute.

(c) Comparative pick-up efficiency of the thickeners for straight and coacervant dipping have been determined.

(d) Tensile and tear properties of the vulcanizate after addition of the thickeners have been studied. Ageing study also has been conducted. These results are compared with the control (without thickener) and the effect of the thickeners on technical properties have been noted.

CHAPTER II

EXPERIMENTAL TECHNIQUES

The materials used and the experimental procedures adopted in the present investigations are given in this chapter. As far as possible, materials conforming to Indian Standard Specifications have been used. Experimental procedures for latex compounding, dipping, etc., which are very well known are only briefly described. However, the procedures for viscosity measurement, the preparation of tensile test slab from latex compound, etc. have been described in detail.

I. MATERIALS USED

I.1 Natural rubber latex. The natural rubber latex used was high ammonia centrifuged latex of 60% dry rubber content. The Indian Standards Specifications (IS:5430-1981) for this grade of concentrated latex are given below:

Characteristic	Requirement
Dry rubber content, % by mass, minimum	60.0
Non-rubber solids, % by mass, maximum	2.0
Coagulum content, % by mass of latex, maximum	0.05
Sludge content, % by mass, maximum	0.10
Alkalinity as ammonia, % by mass of latex, minimum	0.6
KOH number, maximum	1.0
Mechanical stability, seconds, minimum	475
Volatile fatty acid number, maximum	0.15
Copper content, ppm of total solids, maximum	8.0
Manganese content, ppm of total solids, maximum	8.0

Five batches of centrifuged latex were used for the study.

1.2 Rubber chemicals.

1.2.1 Vulcanising agent. Sulphur used as the cross linking agent was conforming to the Indian Standards Specifications (IS:8851-1978).

1.2.2 Accelerators. Zinc diethyl dithio carbamate (ZDC), and zinc salt of mercaptobenzothiazole (ZMBT) used were obtained from M/s. Alkali & Chemicals Corporation of India (ACCI Ltd), Rishra, and conforming to the manufacturers specifications.

I.2.3 Activator. Zinc oxide ($\rho = 5.5$) was used as the activator and conforming to the IS Specifications (IS:3399-1973).

I.2.4 Antioxidant. Nonox SP (a phenolic anti-oxidant) obtained from ACCI Ltd., Rishra was used as the antioxidant and conforming to the IS Specifications (IS:7351-1974).

I.2.5 Stabilisers. An ethylene oxide condensate preparation (vulcastab VL) from ACCI Ltd., Rishra, meeting the manufacturers specifications, and a chemically pure grade of potassium hydroxide were used as stabilisers.

I.2.6 Dispersing agent. Sodium salt of naphthalene sulphonic acid (Dispersol F) of ACCI Ltd., Rishra, meeting the manufacturers specifications, was used as dispersing agent.

I.2.7 Emulsifying agent. Chemically pure grades of oleic acid, triethanolamine, and ammonia were used for emulsification of the antioxidant and cyclohexanol (thickener).

I.2.8 Coagulant. Commercial grade of formic acid was used as coagulant.

I.2.9 Thickeners. The thickeners casein, polyvinyl alcohol, and sodium carboxymethyl cellulose (low viscosity grade) used were obtained from M/s. BDH (chemically pure grade). Cyclohexanol was obtained from M/s. E. Merck (chemically pure grade), and ammonium alginate was obtained as free sample from M/s. Cellulose Products of India Ltd., Ahmedabad.

II. PREPARATION OF DISPERSION/EMULSION

II.1 Preparation of dispersions. The general method for preparing dispersions for latex work is first to make a coarse slurry of the powder with water which contains small amounts of dispersing agent and stabiliser, and then to grind the slurry in a suitable mill to produce a disperson of small particle size. In the present study, a ball mill had been used for preparing dispersions. The quantity of the dispersing agent to be used for preparing the dispersons depends on the nature of the material to be dispersed.

II.1.1 Formulations for dispersons. The proportion by weight of active ingredient in a disperson should always be a simple integral sub-multiple, eg., 2/3, 1/2, 1/3, 1/4, so that the conversion of active ingredient weight to requisite disperson weight can be effected as simply as possible.

Sulphur is difficult to disperse and it flocculates and sediments easily after disperson. Rather higher proportions of dispersing agents are needed (2 to 4 parts per 100 parts of sulphur); it is preferable to add a stabilizer, as well. Disperson formulations used for the present work is given below:

(i) Sulphur disperson, 50%
Sulphur : 100 parts by weight
Dispersol F conc. : 4 "
Distilled water : 96 "
(Ball milled for 48 hours)

(ii) ZDC disperson, 50%
ZDC : 100 parts by weight
Dispersol F conc. : 2 "
Distilled water : 98 "
(Ball milled for 24 hours)

(iii) ZMBT disperson, 40%
ZMBT : 100 parts by weight
Dispersol F conc. : 3 "
Distilled water : 147 "
(Ball milled for 24 hours)

(iv) Zinc oxide disperson, 40%

Zinc oxide : 100 parts by weight
Dispersol F conc. : 3 "
Distilled water : 147 "
(Ball milled for 24 hours)

II.1.2 Ball milling. Ball mills consist essentially of cylindrical containers in which the slurry is placed together with a charge of balls. The presence of an air space is essential for satisfactory grinding. The mill is operated by causing the cylindrical container to revolve slowly about its longitudinal axis, which is horizontal. When the mill is working properly, the balls are carried round with the container a short way and then cascade. It is this process of cascading which causes the particles of the slurry to be comminuted. The container must not be rotated too quickly, otherwise the balls tend to centrifuge to the sides of the container and fail to cascade.

Frothing of the disperson can be troublesome; the air-space then becomes filled with foam, and this prevents proper grinding.

Of the various parameters which affect the efficiency of a ball mill, the more important ones are mill speed, size of balls, distribution of ball sizes, ball material, charge volumes of balls and slurry, mill diameter, and viscosity of slurry.

The slurry of the solid for dispersion, water, wetting and dispersing agent as per the disperson formulation were charged to the ball mill. Grinding charge should be half or 2/3 of the container; charge should just cover the balls, that is, the volume of paste is equal to the intersticial space of grinding balls, which is equal to 50% of the volume occupied. Ball milling was continued for the required time. Then the contents were discharged with the help of a metal gauge. Total solid content of the dispersion was determined and then the dispersion was diluted, if needed, appropriately to the required concentration.

The dispersions prepared were evaluated by allowing a drop of the dispersion to fall on the surface of water in a tall glass cylinder. The drop must not fall to the bottom, but should disperse well in the water phase, leaving a cloudy trail.

II.2 Preparation of emulsion. Nonox SP and cyclohexanol were incorporated in the latex as emulsions.

Two techniques are available for the preparation of coarse emulsions. The first one is by dissolving the dispersing aids, stabiliser, etc., in water and then adding the liquid under high speed stirring. The second technique, and the more effective one, is the soap-insitu method. This method was adopted for the present work.

In this method, a soap is used as the principal dispersion aid. The fatty acid component of the soap is dissolved in the liquid, and the alkali component in water together with the stabiliser. The liquid is then poured into the aqueous phase with rapid stirring, when emulsification takes place spontaneously. The method derives its effectiveness from the fact that soap forms spontaneously wherever a new oil-water interface is created.

II.2.1 Emulsion formulation.

Nonox SP emulsion, 50%

Nonox SP	: 50	parts by weight	Part A
Oleic acid	: 2	"	
Tri-ethanol amine	: 1.5	"	Part B
Distilled water	: 46.5	"	

Part A was heated to about 60°C and added under high speed stirring to Part B also at the same temperature. Stirring continued till emulsion attains room temperature.

Cyclohexanol emulsion, 10%

Cyclohexanol	: 50	parts by weight	Part A
Oleic acid	: 2	"	
Ammonia (25%)	: 6	"	Part B
Distilled water	: 42	"	

Part A and Part B were heated to 60°C; Part A was added to Part B under high speed stirring and stirring continued till the emulsion attained room temperature.

III. COMPOUNDING

Most of the solid ingredients of the latex compounds are insoluble in water and hence the particle size of the ingredients has to be reduced to that of the rubber particle in the latex for getting uniform distribution of the ingredients[13]. This was achieved by preparing dispersions of the solid ingredients and emulsion of the liquid ingredients. As far as possible, the stability of dispersions and emulsions should be comparable with that of the latex, and the pH of dispersions, solutions, and emulsions should be adjusted to that of the latex to which they are to be added[13].

III.1 Deammoniation of latex. Ammonia is the common preservative used for natural rubber latex, at a concentration of 0.7 to 1.0%. But a high concentration of ammonia in latex causes problems in product manufacturing. Thickening caused by zinc oxide in ammonia-preserved latex and the subsequent loss in stability of latex are well known[14]. A number of dipping problems emanate from the amount of zinc oxide that becomes soluble in the ammonia used as preservative. Skinning, instability, crinkling, and the icicle surface result from an excess use of zinc oxide are the most important ones; ammonia content should be kept to the minimum and the smallest quantity of zinc oxide should be used to produce the desired results[1]. Also, high ammonia content in dipping compounds leads to the formation of webs between adjacent protruding parts[8].

Due to these reasons, high ammonia centrifuged latex was deammoniated as follows: A current of moist air was blown over the surface of the latex while it was stirred at about 50 rpm. A small quantity of vulcastab VL was added before deammoniation to minimise the risk of destabilization.

III.2 Mixing. Total solid contents of the solutions, dispersions and emulsions prepared were determined, and diluted to the required concentrations, with distilled water, before mixing with deammoniated centrifuged latex. A few drops of ammonia were added to the sulphur dispersion, as it was slightly acidic. The total solids of the dispersions and emulsions were adjusted in such a way that the total solid content of the latex compound should not fall below 55%. Too dilute a latex compound may result in more number of dips. Order of mixing was in the following sequence: Vulcastab VL solution, potassium hydroxide solution, Nonox SP emulsion, ZDC dispersion, ZMBT dispersion, sulphur dispersion, zinc oxide dispersion.

The latex compound thus prepared was allowed to mature for 24 hours before adding thickener, and after addition of thickener it was again allowed to stand for 24 hours at 21.0±0.5°C (the temperature of viscosity measurement and dipping). After maturation care was taken to see that no air was drawn into the compound. Total solid content of the compound before thickener addition was determined.

III.3 Representation of formulation. Latex formulations are normally expressed in parts by weight. Two sets of parts by weight designation are used here, viz. parts by weight dry, and parts by weight wet. The first one is the weight of active ingredient and the second one is the weight of dispersion/emulsion in which it is contained.

III.4 Addition of thickeners. After the determination of the total solids of the latex compounds, 10% thickener solutions were added to the compound in the concentrations of 0.25, 0.50, 0.75, 1.00, 1.25 and 1.50 parts per hundred rubber of the active ingredient. A control compound was also run, without the addition of the thickener. Calculated quantity of distilled water containing 1.0% ammonia was pipetted out into each latex compound in order to keep the total solids constant, that is, to avoid the dilution effect. As thickener concentration increases from 0 to 1.50 phr there would be a slight increase in the total solid concentration; it was assumed throughout these studies that the total solids were constant for all the batches, for each thickener.

These compounds were conditioned for 24 hours at $21.0 \pm 0.5^{\circ}C$ before viscosity measurement and dipping. The total solids of each batch was determined to ensure that the total solids concentration was constant.

IV. DIPPING AND PICK-UP MEASUREMENT

In the present investigation, straight dipping and wet-coacervant dipping (initial immersion in latex compound) were used with dwell times of ½ minute and 1 minute. Coacervant used was 10% formic acid. Formers used were boiling tubes of 32 mm diameter and dipping height was 12 cm. 600 ml tall beakers having lids were used as dipping tanks.

IV.1 Straight dipping.

IV.1.1 Pre-treatment of former. Formers were first cleaned by scrubbing with a mild alkaline detergent solution, followed by a water rinse. Detergent cleaning is better for glass formers. After washing, formers were dried in an air oven at 105°C.

IV.1.2 Dipping tanks. When not in use dipping tank was covered with lid. Temperature of the latex compound was maintained constant at 21.0±0.5°C throughout the course of the study. Control of the temperature would help in getting greater uniformity of the product, rate of prevulcanisation would be retarded, and constant viscosity and stability would be maintained.

IV.1.3 Immersion of former. The immersion rate should be sufficiently slow to prevent air being drawn into the batch with the former, but sufficiently fast to maintain the meniscus surrounding the former in a convex-to-air condition. If it was allowed to revert to the normal concave-to-air condition, then it could be found that the deposit which formed was defaced by transverse striations and undulations. The speed of immersion was also kept uniform. A dipping speed of 90 cm per minute (approx) was used.

IV.1.4 Dwell. It is believed that in straight dipping, the pick-up is independent of dwell time. In the present study, dwell times of ½ minute and 1 minute were given, in order to see whether, in the presence of thickener, dwell time had any effect on pick-up.

IV.1.5 Withdrawal. Withdrawal should take place slowly, slower than the dipping speed. Withdrawal speed of 60 cm per minute was given.

IV.1.6 Inversion and drying. It is desirable to invert the withdrawn former through 180°C in order to ensure dispersal of the drops which inevitably form at the lower extremities of the deposit. Rotation was continued through a full revolution. It was then dried at 85°C to constant weight.

IV.2 Coacervant dipping. Pre-treatment of the formers was as given in the section IV.1. Dipping tank was 600 ml tall beaker with lids.

IV.2.1 Immersion, dwell, withdrawal and drying. In the case of coacervant dipping, a straight dip was given first with a dipping speed of 90 cm per minute, withdrawal speed of 60 cm per minute with dwell times of ½ minute and 1 minute. After the straight dip, the former with the latex deposit was coagulant dipped in the coagulant with a dipping speed of 130 cm per minute and withdrawal speed of 130 cm per minute. After withdrawal from the coagulant the former was inverted for 1 minute. Then it was again dipped in the latex compound with the immersion speed of 130 cm per minute and withdrawal speed of 60 cm per minute giving dwell times of ½ minute and 1 minute.

After withdrawal, inversion and rotation were carried out as described above and then dried to constant weight in an air oven at 85°C.

IV.3 Pick-up measurement. Pick-up was measured as the dry weight of the deposit formed on the former. Knowing the dip-height, diameter of the former, and the dry deposit weight, weight of the dry deposit per square cm could be calculated. Thus, in the present study, pick-up is expressed as grams of dry deposit per square cm.

V. TEST PROCEDURES

V.1 Total solids content, TSC. The total solids determined as per BS-1672:1972. About 2.0 gm of well-mixed sample was weighed into a dried and weighed petri-dish (about 60 cm diameter). The sample was dried at 100±2°C in an air oven until the sample lost its whiteness. After cooling in a desiccator, the petri-dish was weighed. Drying, cooling and weighing was repeated for periods of 15 minutes until loss in mass between successive weighings was less than 1 mgm.

$$\text{Total solids content, TSC} = \frac{M_2}{M_1} \times 100\%$$

Where, M_1 = mass of test portion (gm)

M_2 = mass of dried sheet (gm)

Duplicate determinations were conducted.

V.2 Viscosity measurement. Many methods are available for determining the viscosity of a fluid. Most of the methods have been used with polymer latices, and some have been found to be more suitable than others. Both absolute viscometers and technical viscometers are available. The function of technical viscometer is to provide a rapid check on viscosity for the purpose of quality control or compounding development.

V.3 The Brookfield viscometer. This instrument is a technical viscometer which is widely used for the measurement of latex viscosity. In the present study Brookfield Viscometer LVT model was used for viscosity measurement at 6 and 60 rev/min at $21.0 \pm 0.5^{\circ}C$ using spindle numbers 2, 3 and 4.

It consists of a rotating member, which is usually a cylinder driven by a synchronous motor through a beryllium-copper torque spring. The viscous drag on the cylinder causes an angular deflection 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 obtain a reading, they must be clamped together and the rotation stopped when the pointer is opposite a window which is out of the casing. For this reason it is not always possible to follow continuously the course of viscosity changes due to temperature or associated with non-Newtonian behaviour.

A range of speeds and of discs and cylinders is available, so that a wide range of viscosity may be covered. Brookfield viscometer readings are affected by turbulence and by the angle of immersion of the spindle.

In the present studies, all viscosity measurements were done just prior to dipping. And, also, precautions were taken to eliminate any thixotropic tendency of the compounds by subjecting them to high shear stirring, 60 rev/min, for 4 minutes before measuring the viscosity.

V.4 <u>Physical properties</u>. In the present study, it is to be tested that incorporation of viscosity-modifiers into the latex compound to enhance pick-up, has got any adverse effect on the technical properties of the products manufactured from them. For this, tensile and tear properties are to be determined for each batch of the various thickener compounds. Ageing characteristics were also assessed. For these tests, it needed to prepare thin sheets having uniform thickness, not less than 1.0 mm thickness. The following method had been adopted for the tensile sheets preparation.

V.4.1 Preparation of sheets. Latex compound sheets had been prepared according to the method described by Flint and Nawston[15]. The method is as follows:

Rectangular pieces of stout window glass, 9 x 5¾" were cleaned. Gummed strips of cellophane sheets were folded along their length and then stuck on to the edges of the glass plates to convert them into shallow trays. Required quantity (60-80 ml) of the mixes under test were poured on to such plates which were tilted slowly to distribute the latex uniformly. The plates were then placed on a level table consisting of a good piece of plate glass supported on three screws of adjustable height. The trays were kept in a dust-free atmosphere. After 24 hours of drying, sheets were vulcanized in a thermostatically controlled air oven at 100±0.5°C upto the cure time. Cure time was determined as follows:

V.4.2 Cure time determination. As for the dry rubber compound the cure time cannot be determined instrumentally. Cure time had been determined by 500% modulus and tensile strength determination. A series of sheets prepared by the above method from the same batch of compound were vulcanized at 100±0.5°C for 20, 25, 30, 35, 40, 45, 50, 55, 60, etc. minutes and the tensile properties of each sample were determined by the ASTM method D-412:75.

The sample which was having the maximum modulus and tensile strength was noted and the corresponding cure time was selected as the cure time for the study of the compounds.

V.4.3 Physical test methods. At least three specimens per sample were tested for each property and the mean values are reported.

V.4.3.1 Modulus, tensile strength and elongation at break. In the present work, these tests were carried out according to ASTM Designation D:412-75 using dumb-bell specimens. All the above tests were carried out at 21.0±0.5°C. Samples were punched from vulcanized sheets using the small dumb-bell die (D-type). The thickness of the narrow portion was measured by bench thickness gauge. Two marks were made, 1.25 cm apart, in the middle of the narrow portion. The sample was held tight by the two grips in a 'Scott' tensile testing machine (sensitivity 0.5 kg), the upper grip of which being fixed. The rate of separation of the power actuated grip was 50 cm per minute. The load at 300% elongation and at break were read from the dial (and also from the graph, recorded automatically); elongation at break was noted from the graph (and was also measured using a scale). From the recorded loads, the stress was calculated on the basis of the original cross-sectional area.

The tensile strength and modulus are reported in MPa (Conversion factor : 1 kgf/cm^2 = 0.098 MPa).

V.4.3.2 Tear resistance. The test was carried out as per ASTM method D:624-73; unnicked, 90° angle test pieces were used. The samples were cut from the vulcanised sheets. The test was carried out on a 'Scott' tensile testing machine. The speed of extension was 50 cm per minute and the temperature 21.0±0.5°C.

Tear resistance has been reported in kN/m. (Conversion factor : 1 kg/cm = 0.98 kN/m).

V.4.3.3 Ageing. Ageing was carried out as per ASTM Designation D:1870-68 using a tubular ageing oven at a temperature of 70.0±0.5°C for 96 hours. On completion of the ageing period the tensile properties of the aged samples were determined as described in the section V.4.3.1.

Effect of ageing is expressed as percentage of the original property retained after ageing.

Change, % = $[(O-A)/O] \times 100$
Where, O = original value
A = value after ageing.

CHAPTER III. RESULTS AND DISCUSSION

EFFECT OF VISCOSITY-MODIFIERS ON:

1. VISCOSITY
2. PICK-UP OF DIPPED GOODS
3. TECHNICAL PROPERTIES OF DIPPED GOODS

III.1 EFFECT OF VISCOSITY-MODIFIERS ON VISCOSITY

Viscosity of a fluid is the ratio of the shear stress to the shear rate during its flow. Natural rubber latex is a non-Newtonian fluid, the viscosity of which changes with shear rate; as shear rate increases viscosity falls. Viscosity-polymer concentration relationships depend on the viscosity of the dispersion medium, the particle shape, size, and size distribution. Viscosity of a latex is virtually independent of the molecular weight of the polymer which it contains. A narrow distribution of size favours a higher viscosity at any given polymer concentration.

Viscosity measurements have been made at two speeds, viz., 6 rpm and 60 rpm, taking into account the thixotropic nature of high viscosity latex compounds. The results, as given in Tables III.2 to III.6, show that among the five thickeners studied, the maximum thickening is caused by ammonium alginate and the minimum by cyclohexanol. The order in which the thickeners increase viscosity of latex is as:

Cyclohexanol < Casein < Polyvinyl alcohol < Sodium carboxymethyl cellulose < Ammonium alginate.

This gradation is valid at all the concentration of the thickeners studied and at both speeds of the spindle.

The mechanism of thickening of latex compound by viscosity-modifiers was described by Madge[9]. According to him, thickeners reduce the mutual repulsion between the latex particles thereby increasing the viscosity. Mutual repulsion of latex particles can be reduced by reducing the electric charge on the particle, altering the magnitude of the protective envelope, increasing the extent of hydration, and by altering the viscosity of the aqueous serum itself. The thickeners studied in the present work are expected to act in more than one way. However, it is very difficult to identify the exact mechanism by which thickening of latex is brought about.

III.2 EFFECT OF VISCOSITY-MODIFIERS ON PICK-UP OF DIPPED GOODS

Gorton[6] established that for straight dipping, pick-up is dependent on apparent viscosity at 60 revolutions per minute, and for coacervant dipping it is dependent on dwell time and apparent viscosity at 60 revolutions per minute. In the present study viscosity of latex was increased by addition of thickeners and their effect was examined for straight and coacervant dippings at dwell times of ½ minute and 1 minute. Pick-up efficiency of each thickener under varying conditions of dwell time and method of dipping was assessed from the observations.

III.2.1 Cyclohexanol. From Table III.2 and Figure III.1 it can be seen that for straight dipping pick-up is independent of dwell time. For coacervant dipping, pick-up depends on dwell time. In both methods of dipping, pick-up increases linearly with increase in concentration of cyclohexanol. The rate of increase in pick-up with concentration of thickener is more in the case of straight dipping. Comparing both dipping techniques with respect to pick-up at any concentration of thickener and at a particular dwell time, coacervant dipping has got a higher pick-up. The increased pick-up is more due to the action of the coacervant.

III.2.2 Casein. It is evident from Table III.3 and Figure III.2 that pick-up is practically independent of dwell time in straight dipping; in coacervant dipping it is more dependent on dwell time. In both techniques of dipping, pick-up is linearly increasing with increase in concentration of casein. Unlike in the case of cyclohexanol, the rate of increase is more in coacervant dipping, at both dwell times. As in the case of cyclohexanol, coacervant dipping has got more effect on pick-up than straight dipping.

III.2.3 Polyvinyl alcohol. From Table III.4 and Figure III.3 it is evident that pick, up is only slightly enhanced by dwell time in straight dipping; dwell time has got only less effect on pick-up in coacervant dipping, when compared with cyclohexanol and casein. In both dipping techniques, pick-up is increasing with concentration of polyvinyl alcohol; a linear increase is seen with straight dipping and for coacervant dipping. As in the case of cyclohexanol, the rate of increase of pick-up with concentration of the thickener is more in straight dipping than in coacervant dipping. In the latter technique, the rate of increase is negligible up to a concentration of 0.5 phr of the thickener and afterwards pick-up increases slowly. Coacervant dipping has got more effect at lower concentrations of the thickener, when pick-up at both techniques is compared.

III.2.4 Sodium carboxymethyl cellulose. Table III.5 and Figure III.4 depict that in straight dipping, pick-up is independent of dwell time, and dwell time has got more effect on pick-up in coacervant dipping. In both techniques of dipping, pick-up increases with concentration of the thickener; but the relationship is non-linear. As in the case of polyvinyl alcohol and cyclonexanol, the rate of increase of pick-up is more in straight dipping, upto a concentration of 1 phr, than in coacervant dipping.

Beyond this concentration, the pick-up is more for coacervant dipping as in the case of casein. When the dwell time is ½ minute the coacervant dip gives lower pick-up compared to straight dipping. However, when the dwell time is raised to one minute, the coacervant dipping gives higher pick-up irrespective of the concentration of the thickener. It is to be assumed that sodium carboxymethyl cellulose retards the diffusion of the coacervant from the former surface to the latex compound.

III.2.5 Ammonium alginate. In the case of ammonium alginate, pick-up is independent of dwell time in straight dipping but dependent of dwell time in coacervant dipping, as evident from Table III.6 and Figure III.5. In both dipping methods, pick-up increases with increase in concentration of ammonium alginate; but the increase is not linear. The rate of increase is more in coacervant dipping, as in the case of casein. For straight dipping, rate of increase of pick-up decreases at higher concentrations of ammonium alginate. Comparing both methods of dipping, it is seen that a higher pick-up is observed for coacervant dipping; pick-up increases with increase in dwell time.

Gorton and Iyer[7] found out the following relationships with respect to deposit thickness (pick-up) and viscosity at 60 revolutions per minute for straight dipping and that between deposit thickness (pick-up) and dwell time and latex compound viscosity at 60 revolutions per minute.

$$t = a_1 + K_1 \log_{10} (\eta_{60}) \qquad \text{(i)}$$

Where, t = straight dip deposit thickness
a_1 and K_1 are constants,
η_{60} = apparent viscosity (Brookfield) at 60 rev/min.

$$tc = K_5 \sqrt{D} \log_{10} \eta_{60} \qquad \text{(ii)}$$

Where, D = dwell time,
η = apparent viscosity (Brookfield)
K_5 = constant
tc = true coagulant deposit thickness.

$$Tn = 2a_1 + \log_{10} \eta_{60} \left[(n+1)K_1 + K_5 \sqrt{D} \right] \qquad \text{(iii)}$$

Where, Tn = total thickness of deposit following a straight dip with 'n' further coagulant dips,
a_1, K_1 and K_5 are constants,
D = dwell time.

The results obtained from the present study are generally in agreement with the above relationships.

III.2.6 Comparative evaluation of the thickeners.

III.2.6.1 Straight dipping. Dwell time has got only a very little effect on the nature of the relation between pick-up and concentration of thickener, as seen from Figures III.6 and III.7. The effect of the thickeners on pick-up at both dwell times is in the order given below:

Cyclohexanol ∠ Casein ∠ Polyvinyl alcohol ∠ Sodium carboxymethyl cellulose ∠ Ammonium alginate.

In all the cases pick-up increases with increase in the concentration of the thickener; a linear increase in pick-up is observed for casein, cyclohexanol and polyvinyl alcohol. The rate of increase of pick-up with concentration at both dwell times is in the following order:

Ammonium alginate > Sodium carboxymethyl > cellulose > Polyvinyl alcohol > Cyclohexanol > Casein.

For ammonium alginate and sodium carboxymethyl cellulose, the rate of increase of pick-up is more at lower concentrations than at higher ones.

From Figures III.6 and III.7 the pick-up efficiency at any concentration can be predicted for each thickener. At ½ minute dwell, the concentration of each thickener needed to attain a pick-up value of 20×10^{-3} g.cm^{-2} is given below:

Casein : 3.68 phr
Cyclohexanol : 2.73 phr
Polyvinyl alcohol : 1.15 phr
Sodium carboxymethyl cellulose : 0.35 phr
Ammonium alginate : 0.10 phr

The pick-up efficiency of each thickener at a concentration of 0.5 phr and dwell time of ½ minute is given below:

Cyclohexanol : 7.75×10^{-3} g.cm^{-2}
Casein : 9.25×10^{-3} "
Polyvinyl alcohol : 12.00×10^{-3} "
Sodium carboxymethyl cellulose : 24.25×10^{-3} "
Ammonium alginate : 39.00×10^{-3} "

There is only a very slight increase for the corresponding values at 1 minute dwell.

III.2.6.2 Coacervant dipping. Based on pick-up the thickeners fall under the following order:

Polyvinyl alcohol ∠ Cyclohexanol ∠ Casein ∠
Sodium carboxymethyl cellulose ∠ SAmmonium alginate.

At lower concentrations, pick-up efficiency of sodium carboxymethyl cellulose decreases and below 0.5 phr at ½ minute dwell, it is having the least pick-up efficiency among the five thickeners; but at 1 minute dwell this drawback gets reduced. A linear increase in pick-up with concentration of thickener is seen for cyclohexanol, casein and polyvinyl alcohol at ½ minute and 1 minute dwell times. Increase in pick-up with concentration of thickener is non-linear for sodium carboxymethyl cellulose and ammonium alginate. The rate of increase in pick-up with concentration for both dwell times is in the order as given below:

Ammonium alginate > Sodium carboxymethyl-cellulose > Casein > Polyvinyl alcohol > Cyclohexanol.

Pick-up efficiency at a particular concentration can be predicted from Figures III.8 and III.9, for each of the thickeners. At a dwell time of ½ minute, the dosage of each thickener needed to get a pick-up value of 35 x 10^{-3} g.cm^{-2} is given below:

Cyclohexanol : 4.50 phr
Polyvinyl alcohol : 3.20 phr
Casein : 1.75 phr
Sodium carboxymethyl cellulose : 1.15 phr
Ammonium alginate : 0.05 phr

The pick-up efficiency of each thickener at a concentration of 0.5 phr and 1 minute dwell is as follows:

Polyvinyl alcohol : 22.25×10^{-3} g.cm^{-2}

Cyclohexanol : 26.25×10^{-3} "

Casein : 27.50×10^{-3} "

Sodium carboxymethyl cellulose : 28.50×10^{-3} "

Ammonium alginate : 71.75×10^{-3} "

In a similar manner the pick-up efficiency at any other concentration and dwell time can be predicted.

III.3 EFFECT OF VISCOSITY-MODIFIERS ON TECHNICAL PROPERTIES OF DIPPED GOODS

The present study will be more meaningful if the effect of these viscosity-modifiers on physical properties is examined. A thickener with good pick-up efficiency is useful for practical application, only if the physical properties are not adversely affected by its incorporation in the latex compound. Tensile properties are the best criteria for this purpose.

III.3.1 Cyclohexanol. Addition of cyclohexanol in the latex compound has no effect on modulus, tensile strength and elongation at break as evident from Table III.7. Tear resistance has increased slightly.

Percent retention of tensile strength and elongation at break, on ageing at 70°C for 96 hours, is very high. Modulus slightly decreased which may be due to cross-link break down and chain scission. It may be noted here that the latex compound used in this study contains only a mild antioxidant.

III.3.2 Casein. From Table III.8, it is evident that, as in the case of cyclohexanol, tensile properties have not been affected by the incorporation of casein in the latex compound. But tear resistance has increased slightly. Accelerated ageing causes a slight decrease in the modulus, which may be due to break down in cross-links/main chain. A slight increase in tensile strength values is observed. This may be due to post curing reactions.

III.3.3 Polyvinyl alcohol. As in the case of casein and cyclohexanol, it is seen from Table III.9 that, tensile properties are not affected by the addition of polyvinyl alcohol. Tear resistance has been slightly enhanced by its addition. Accelerated ageing study shows no change in modulus; a slight decrease in T.S. and E.B. values are observed.

III.3.4 Sodium carboxymethyl cellulose. From Table III.10 it is seen that the tensile properties are not adversely affected by the thickener. Here again, an increase in tear resistance is observed. The presence of sodium carboxymethyl cellulose in the vulcanizate, perhaps, causes to deflect/arrest the growing cracks and thereby enhancing the overall tear resistance of the vulcanizates. Accelerated ageing study shows a slight decrease in modulus and T.S. values. E.B. values are not affected by ageing.

III.3.5 Ammonium alginate. Effect of ammonium alginate on physical properties of the vulcanizates is summarised in Table III.11. Modulus, tensile strength and elongation at break values are unaffected by ammonium alginate. Here also an increase in tear resistance is noted. Ageing studies show a slight increase in T.S.

In general, the five thickeners do not show any adverse effect on the physical properties of the vulcanizates. All the five thickeners increase tear resistance slightly. The ageing resistance of the vulcanizates is also not affected by the presence of the thickeners in them.

TABLE III.1

FORMULATION OF BASE LATEX COMPOUND*

INGREDIENT	PARTS BY WEIGHT DRY (Phr)	PARTS BY WEIGHT WET (Phr)
NR Latex (as 60% HA concentrate)	100.00	167.00
Vulcastab VL, 20% solution	0.25	1.25
Potassium hydroxide, 20% solution	0.30	1.50
Sulphur, 50% dispersion	1.00	2.00
Zinc oxide, 40% dispersion	0.25	0.63
ZDC, 50% dispersion	0.75	1.50
ZMBT, 40% dispersion	0.20	0.50
Nonox SP, 50% emulsion	1.00	2.00

* Cure time at 100±0.5°C = 50 minutes

TABLE III.2

EFFECT OF CYCLOHEXANOL ON VISCOSITY AND PICK-UP

CONCENTRATION OF THICKENER (Phr)	TOTAL SOLIDS CONTENT (%)	VISCOSITY, BROOKFIELD			PICK-UP x 10^3 ($g.cm^{-2}$)			
					STRAIGHT DIPPING		COACERVANT DIPPING	
		6 RPM (cp)	60 RPM (cp)	SPINDLE No.	½ MIN DWELL	1 MIN DWELL	½ MIN DWELL	1 MIN DWELL
0.00	55.4	100	57.5	2	5.1	5.1	22.0	25.0
0.25	55.6	115	60.0	2	6.6	6.6	22.5	25.6
0.50	55.7	120	62.5	2	8.0	8.3	23.0	26.3
0.75	55.8	130	70.0	2	8.8	9.0	23.8	27.0
1.00	55.9	150	75.0	2	9.8	11.1	24.6	27.6
1.25	56.1	175	90.0	2	11.8	11.9	25.4	28.2
1.50	56.2	240	108.5	2	13.3	13.6	26.2	28.4

TABLE III.3

EFFECT OF CASEIN ON VISCOSITY AND PICK-UP

CONCENTRATION OF THICKENER (Phr)	TOTAL SOLIDS CONTENT (%)	VISCOSITY, BROOKFIELD			PICK-UP x 10^3 (g.cm^{-2})			
					STRAIGHT DIPPING		COACERVANT DIPPING	
		6 RPM (cp)	60 RPM (cp)	SPINDLE No.	½ MIN DWELL	1 MIN DWELL	½ MIN DWELL	1 MIN DWELL
0.00	55.4	240	120.0	2	7.6	8.0	19.3	22.0
0.25	55.6	265	127.5	2	7.8	8.3	22.5	25.0
0.50	55.7	290	147.5	2	9.2	9.8	25.2	28.4
0.75	55.8	330	167.5	2	10.0	10.8	26.7	30.4
1.00	55.9	375	186.5	2	10.9	11.6	27.9	32.8
1.25	56.1	450	215.0	2	11.8	12.7	30.7	35.7

TABLE III.4

EFFECT OF POLYVINYL ALCOHOL ON VISCOSITY AND PICK-UP

CONCENTRATION OF THICKENER (Phr)	TOTAL SOLIDS CONTENT (%)	VISCOSITY, BROOKFIELD			PICK-UP x 10^3 ($g.cm^{-2}$)			
					STRAIGHT DIPPING		COACERVANT DIPPING	
		6 RPM (cp)	60 RPM (cp)	SPINDLE No.	½ MIN DWELL	1 MIN DWELL	½ MIN DWELL	1 MIN DWELL
0.00	55.4	250	115.0	2	6.4	7.4	20.6	22.3
0.25	55.6	600	202.5	2	8.7	10.1	20.9	21.8
0.50	55.7	1250	312.5	2	11.8	12.2	21.5	22.6
0.75	55.8	2050	445.0	2	14.7	15.5	22.5	23.7
1.00	55.9	3400	650.0	3	19.2	19.7	24.0	25.6
1.25	56.1	4900	880.0	3	21.6	21.6	25.3	26.7
1.50	56.2	6000	1050.0	3	23.4	23.6	26.8	28.5

TABLE III.5

EFFECT OF SODIUM CARBOXYMETHYL CELLULOSE ON VISCOSITY AND PICK-UP

CONCENTRATION OF THICKENER (Phr)	TOTAL SOLIDS CONTENT (%)	VISCOSITY, BROOKFIELD			PICK-UP x 10^3 (g.cm^{-2})			
					STRAIGHT DIPPING		COACERVANT DIPPING	
		6 RPM (cp)	60 RPM (cp)	SPINDLE No.	½ MIN DWELL	1 MIN DWELL	½ MIN DWELL	1 MIN DWELL
0.00	55.4	150	70	3	6.1	7.3	18.7	19.7
0.25	55.6	3400	640	3	17.0	18.1	20.3	23.9
0.50	55.7	5900	1030	3	24.0	24.6	23.4	30.1
0.75	55.8	9000	1490	3	29.9	29.9	25.9	31.8
1.00	55.9	18000	2950	4	31.1	31.3	30.5	41.9
1.25	56.1	22500	3700	4	35.3	35.9	38.0	43.6
1.50	56.2	35000	5750	4	38.0	39.0	57.7	59.9

TABLE III.6

EFFECT OF AMMONIUM ALGINATE ON VISCOSITY AND PICK-UP

CONCENTRATION OF THICKENER (Phr)	TOTAL SOLIDS CONTENT (%)	VISCOSITY, BROOKFIELD			PICK-UP x 10^3 ($g.cm^{-2}$)			
					STRAIGHT DIPPING		COACERVANT DIPPING	
		6 RPM (cp)	60 RPM (cp)	SPINDLE No.	½ MIN DWELL	1 MIN DWELL	½ MIN DWELL	1 MIN DWELL
0.00	55.5	350	152.5	2	9.6	10.5	32.9	38.2
0.25	55.6	5600	940.0	3	35.5	35.0	43.5	58.9
0.50	55.7	8500	1360.0	3	39.0	38.7	58.0	70.9
0.75	55.8	11900	1800.0	3	45.6	46.0	71.0	81.3
1.00	55.9	20000	3000.0	4	50.8	49.8	75.4	92.7
1.25	56.1	32000	4750.0	4	53.9	55.1	91.6	92.5
1.50	56.2	43500	6150.0	4	63.5	62.5	89.3	100.9

TABLE III.7

EFFECT OF CYCLOHEXANOL ON PHYSICAL PROPERTIES

CONCENTRATION OF THICKENER (Phr)	BEFORE AGEING				PERCENT RETENTION AFTER AGEING (70°C, 96 Hrs)		
	500% MODULUS (MPa)	TENSILE STRENGTH (MPa)	ELONGATION AT BREAK (%)	Tear RESISTANCE kN/m	500% MODULUS	TENSILE STRENGTH	ELONGATION AT BREAK
0.00	1.0	25.1	1038	56	80.1	100.0	100.0
0.25	0.9	25.6	1050	58	82.0	99.2	95.9
0.50	1.1	25.0	983	64	79.3	99.5	98.0
0.75	1.1	25.2	916	60	82.0	98.7	100.0
1.00	1.0	25.8	958	60	80.0	100.0	98.0
1.25	1.0	24.0	1028	61	80.1	98.5	97.9
1.50	1.0	23.7	937	61	79.0	99.0	98.9

TABLE III.8

EFFECT OF CASEIN ON PHYSICAL PROPERTIES

CONCENTRATION OF THICKENER (Phr)	BEFORE AGEING				PERCENT RETENTION AFTER AGEING (70°C, 96 Hrs)		
	500% MODULUS (MPa)	TENSILE STRENGTH (MPa)	ELONGATION AT BREAK (%)	TEAR RESISTANCE kN/m	500% MODULUS	TENSILE STRENGTH	ELONGATION AT BREAK
0.00	1.1	21.8	858	61	90.9	120.2	104.3
0.25	1.1	21.7	857	67	90.9	123.0	105.6
0.50	1.1	22.1	798	64	90.9	113.1	113.4
0.75	1.1	23.7	853	63	90.9	110.6	105.3
1.00	1.2	22.8	867	64	86.7	115.8	105.3
1.25	1.1	22.7	860	65	90.9	105.3	102.3

TABLE III.9

EFFECT OF POLYVINYL ALCOHOL ON PHYSICAL PROPERTIES

CONCENTRATION OF THICKENER (Phr)	BEFORE AGEING				PERCENT RETENTION AFTER AGEING (70°C, 96 Hrs)		
	500% MODULUS (MPa)	TENSILE STRENGTH (MPa)	ELONGATION AT BREAK (%)	TEAR RESISTANCE kN/m	500% MODULUS	TENSILE STRENGTH	ELONGATION AT BREAK
0.00	0.8	27.6	945	56	100.0	70.9	99.8
0.25	0.8	28.0	945	65	100.0	74.3	97.0
0.50	0.8	27.2	962	63	100.0	73.2	94.6
0.75	0.8	26.9	927	66	100.0	69.9	96.3
1.00	0.8	27.6	902	68	100.0	68.8	92.2
1.25	0.8	27.1	933	69	100.0	72.0	92.4
1.50	0.8	27.7	887	63	100.0	71.1	98.9

TABLE III.10

EFFECT OF SODIUM CARBOXYMETHYL CELLULOSE ON PHYSICAL PROPERTIES

CONCENTRATION OF THICKENER (Phr)	BEFORE AGEING				PERCENT RETENTION AFTER AGEING (70°C, 96 Hrs)		
	500% MODULUS (MPa)	TENSILE STRENGTH (MPa)	ELONGATION AT BREAK (%)	TEAR RESISTANCE kN/m	500% MODULUS	TENSILE STRENGTH	ELONGATION AT BREAK
0.00	0.8	22.5	883	56	87.5	95.2	99.1
0.25	0.8	21.8	920	74	100.0	100.0	100.0
0.50	0.9	23.3	908	73	88.9	96.9	100.0
0.75	0.9	20.2	875	78	100.0	99.0	100.0
1.00	0.9	22.4	923	74	88.9	96.2	99.7
1.25	0.9	22.0	910	76	88.9	97.5	100.0

TABLE III.11

EFFECT OF AMMONIUM ALGINATE ON PHYSICAL PROPERTIES

CONCENTRATION OF THICKENER (Phr)	BEFORE AGEING				PERCENT RETENTION AFTER AGEING (70^{o}C, 96 Hrs)		
	500% MODULUS (MPa)	TENSILE STRENGTH (MPa)	ELONGATION AT BREAK (%)	TEAR RESISTANCE kN/m	500% MODULUS	TENSILE STRENGTH	ELONGATION AT BREAK
0.00	1.0	23.5	912	61	98.0	105.2	103.4
0.25	1.0	21.3	917	64	100.0	106.6	103.6
0.50	1.0	20.2	858	74	101.0	105.5	103.7
0.75	1.0	24.3	913	71	95.4	101.7	103.2
1.00	1.0	18.3	840	68	100.0	108.2	106.6
1.25	1.2	18.3	790	64	100.0	107.9	106.6

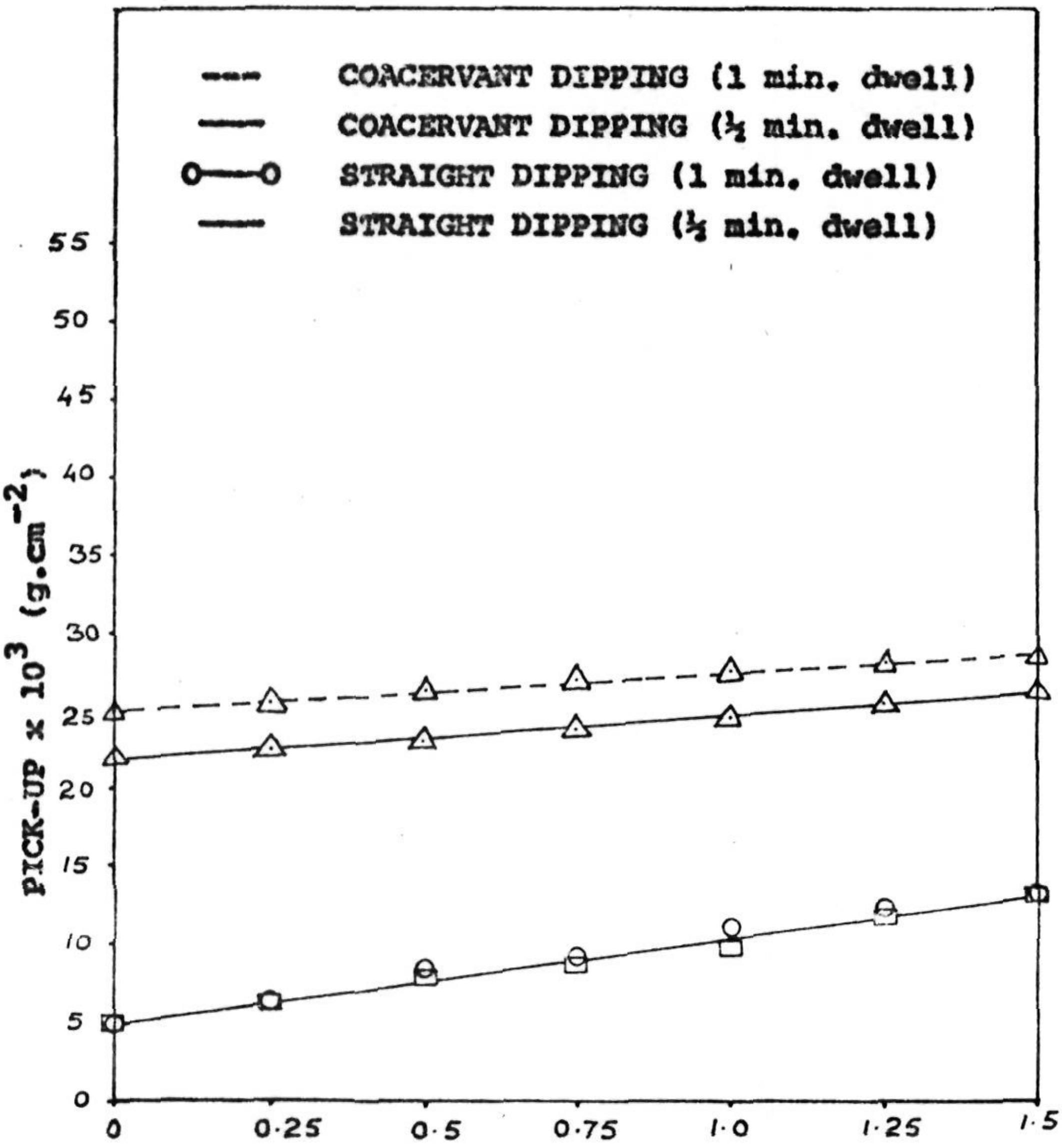


Fig.III.1: Effect of cyclohexanol on pick-up.

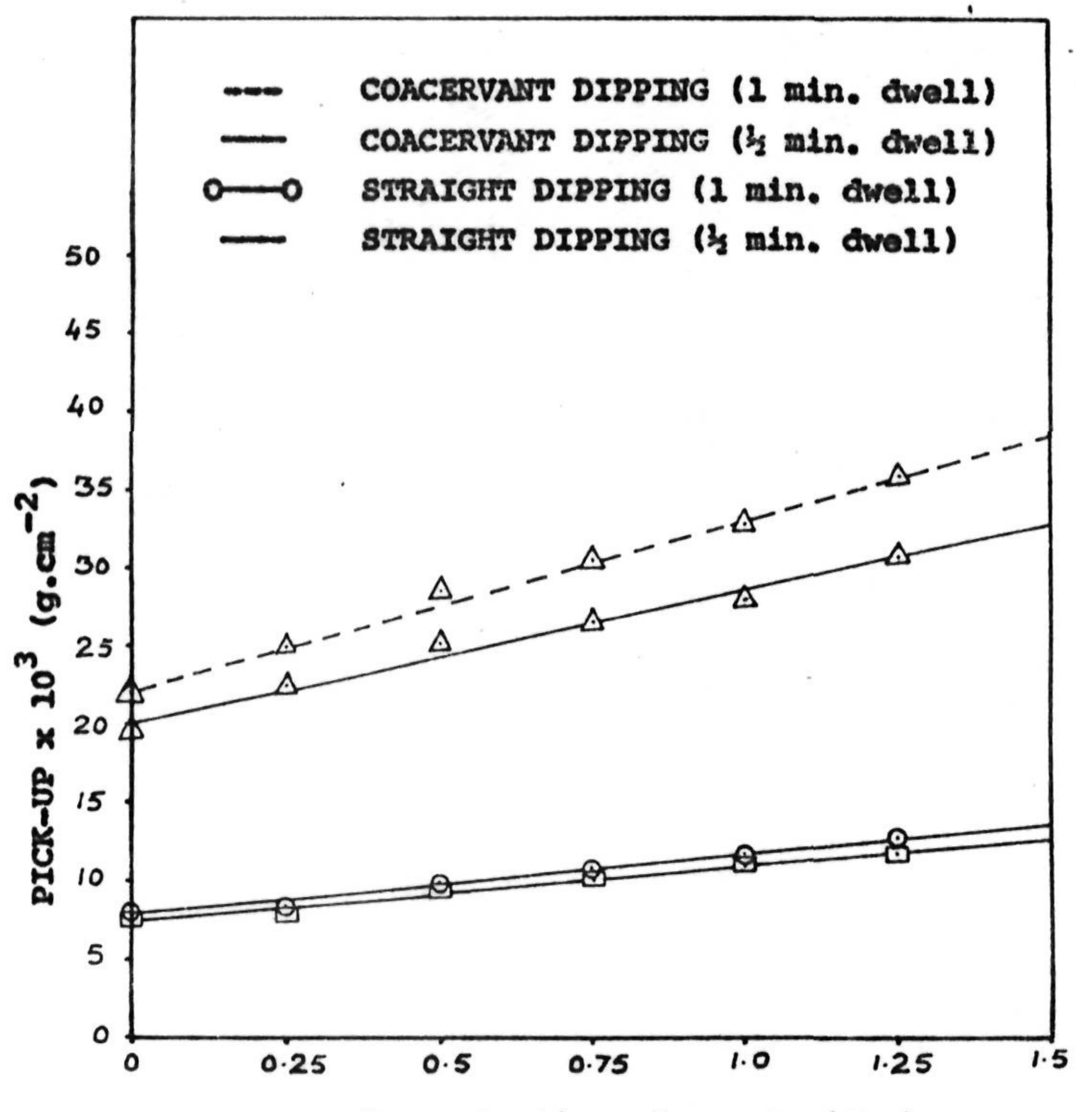


Fig.III.2: Effect of casein on pick-up.

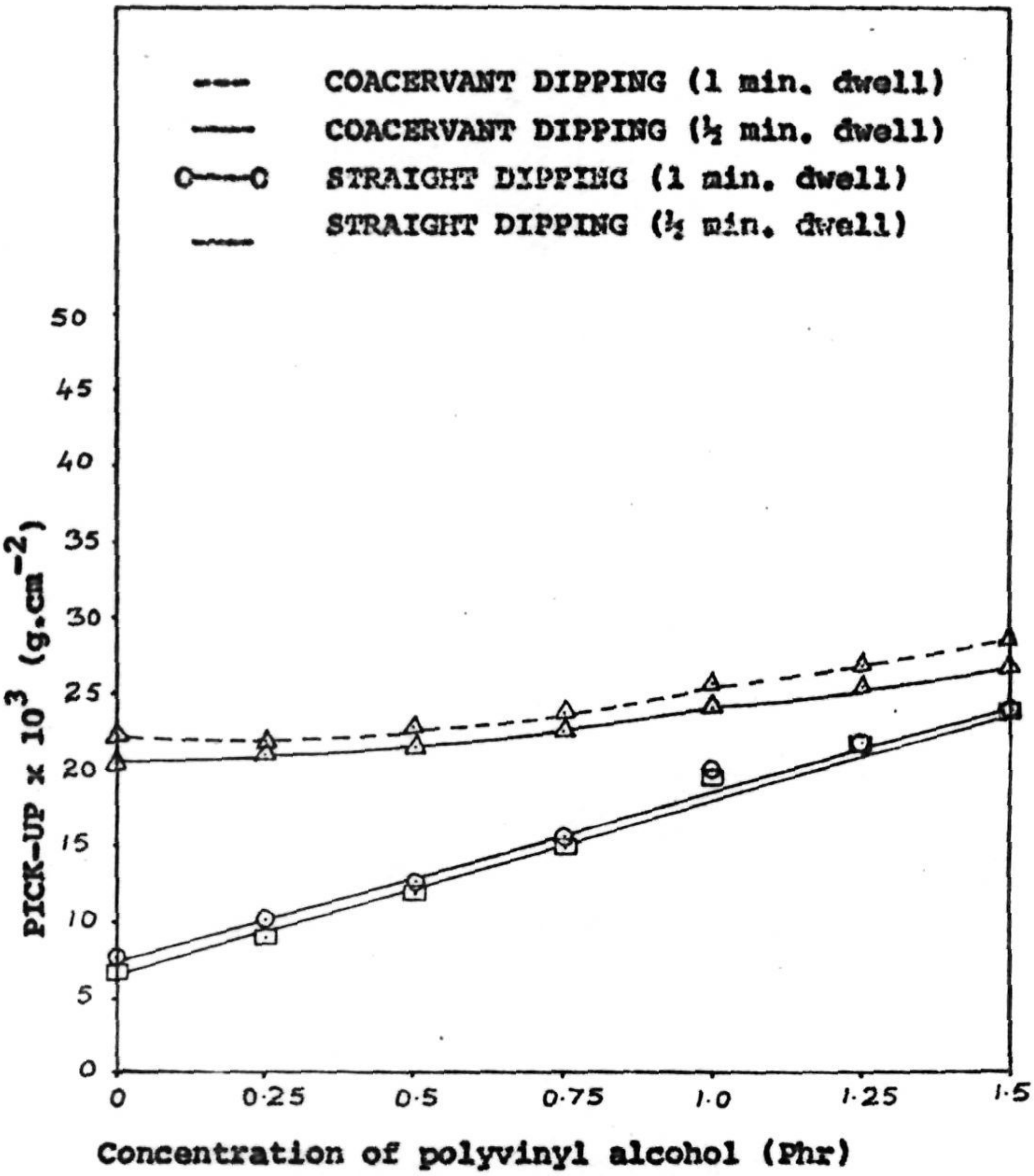
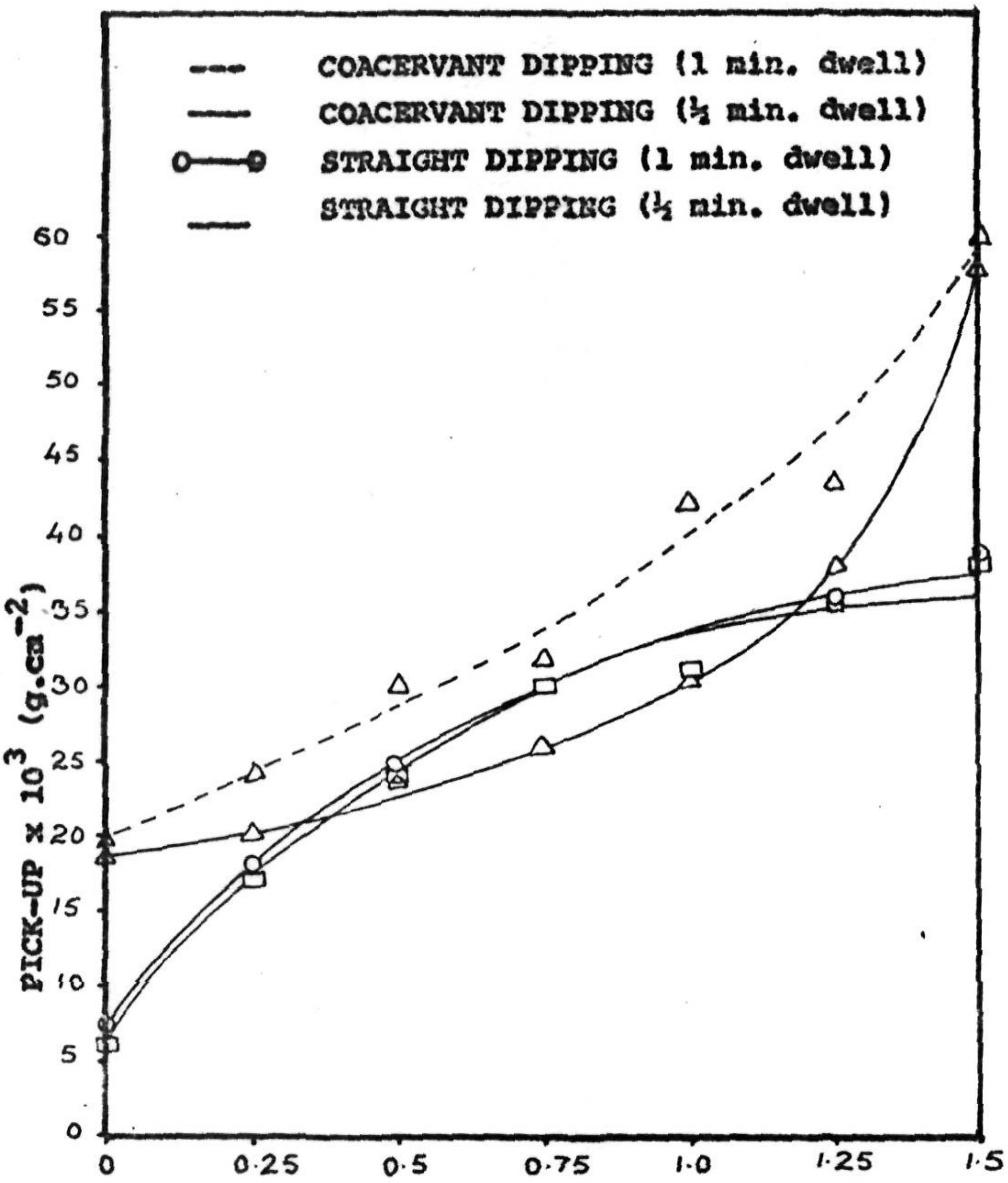


Fig.III.3: Effect of polyvinyl alcohol on pick-up.



Concentration of sodium carboxymethyl cellulose (Phr)

Fig.III.4: Effect of sodium carboxymethyl cellulose on pick-up.

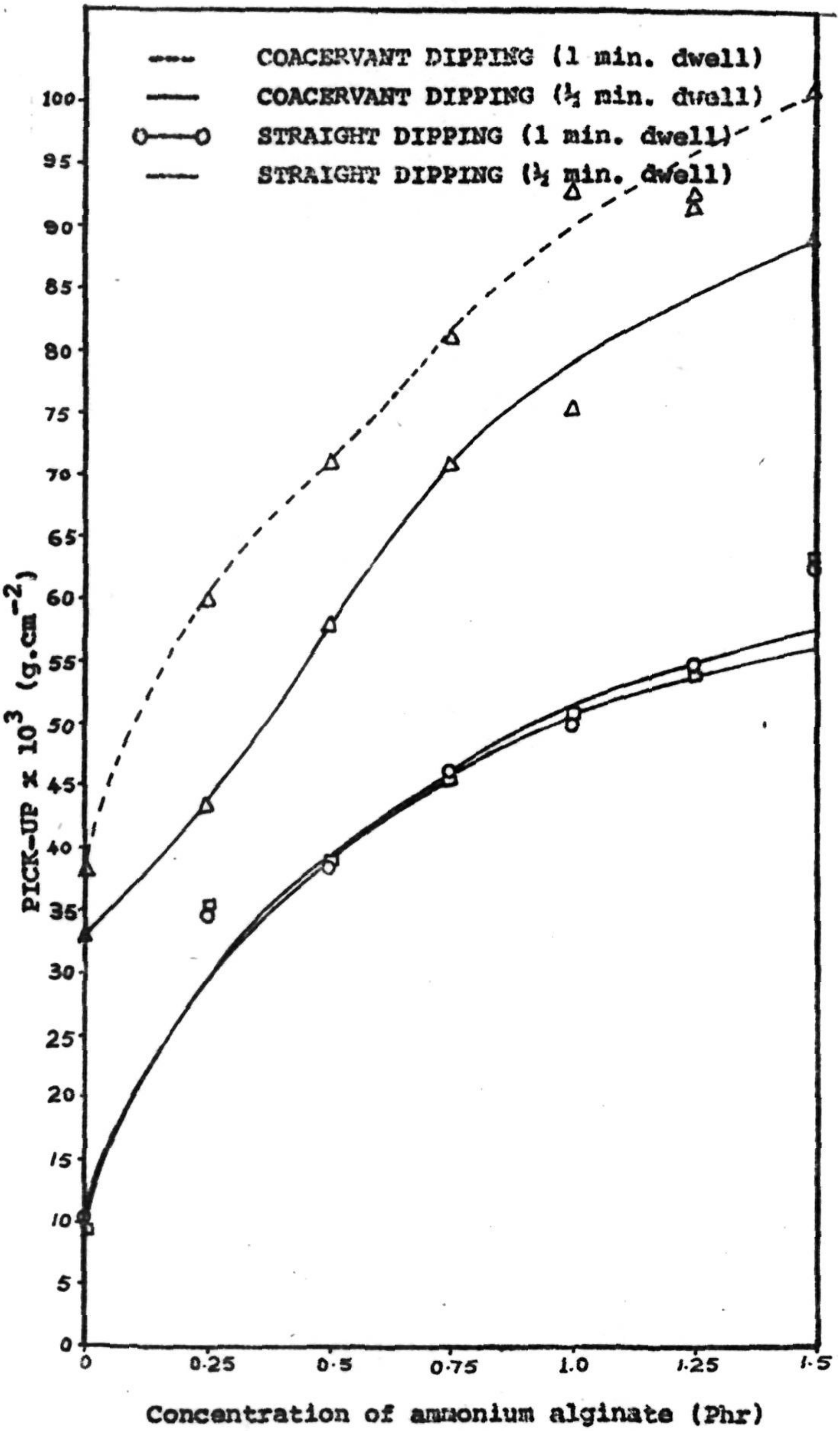


Fig.III.5: Effect of ammonium alginate on pick-up.

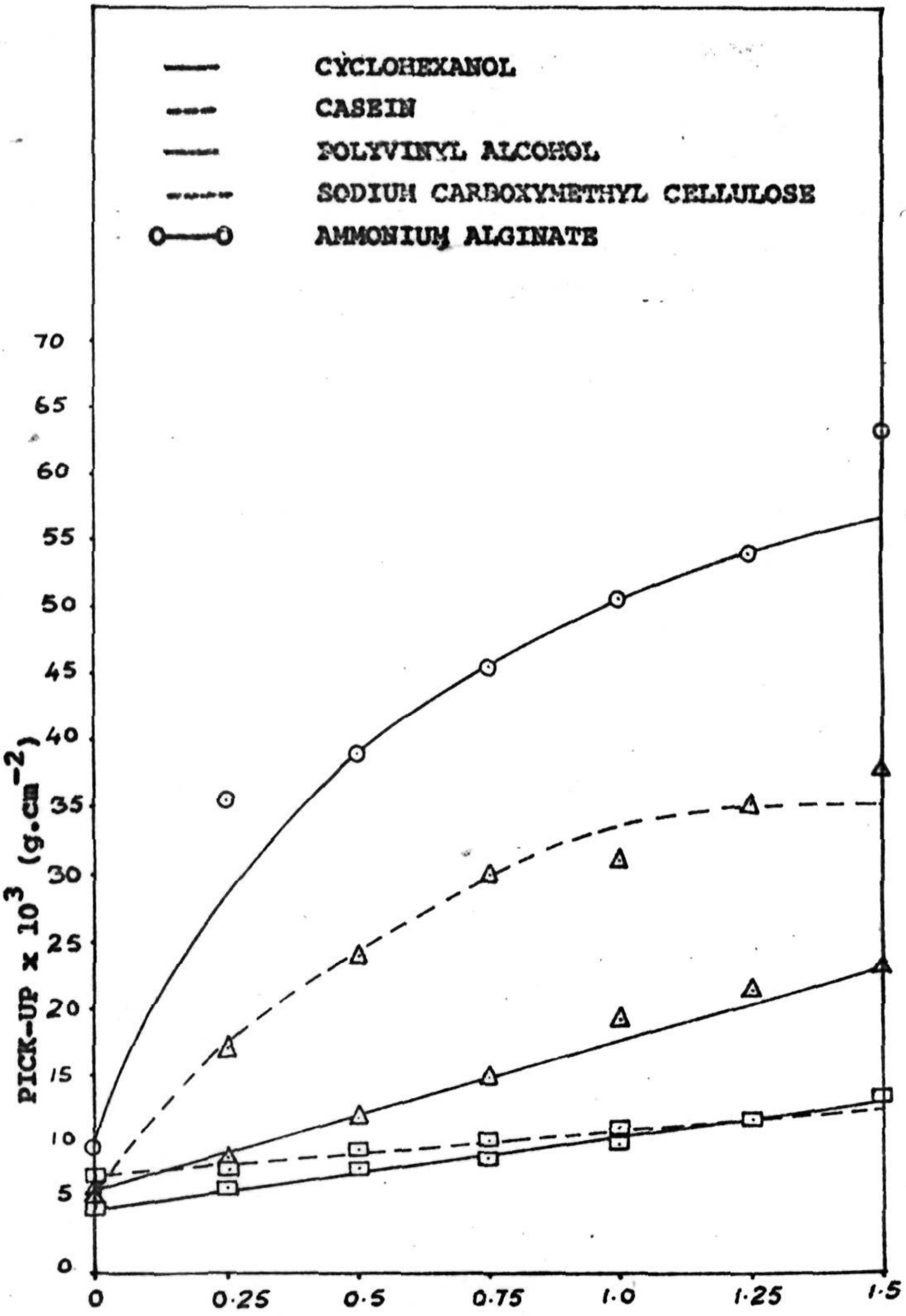


Fig.III.6: Comparative evaluation of thickeners by straight dipping (½ min. dwell)

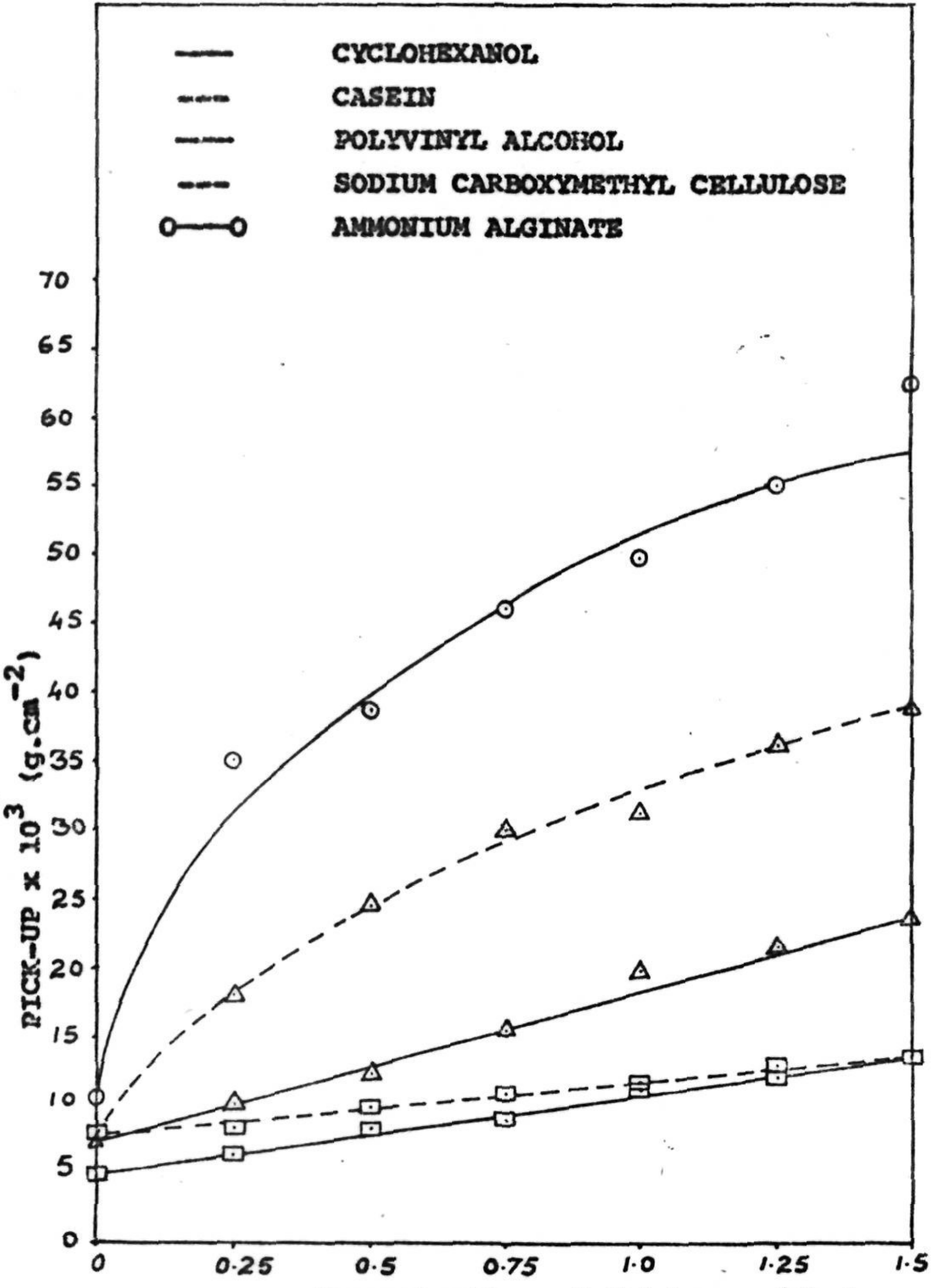


Fig.III.7: Comparative evaluation of thickeners by straight dipping (1 min. dwell)

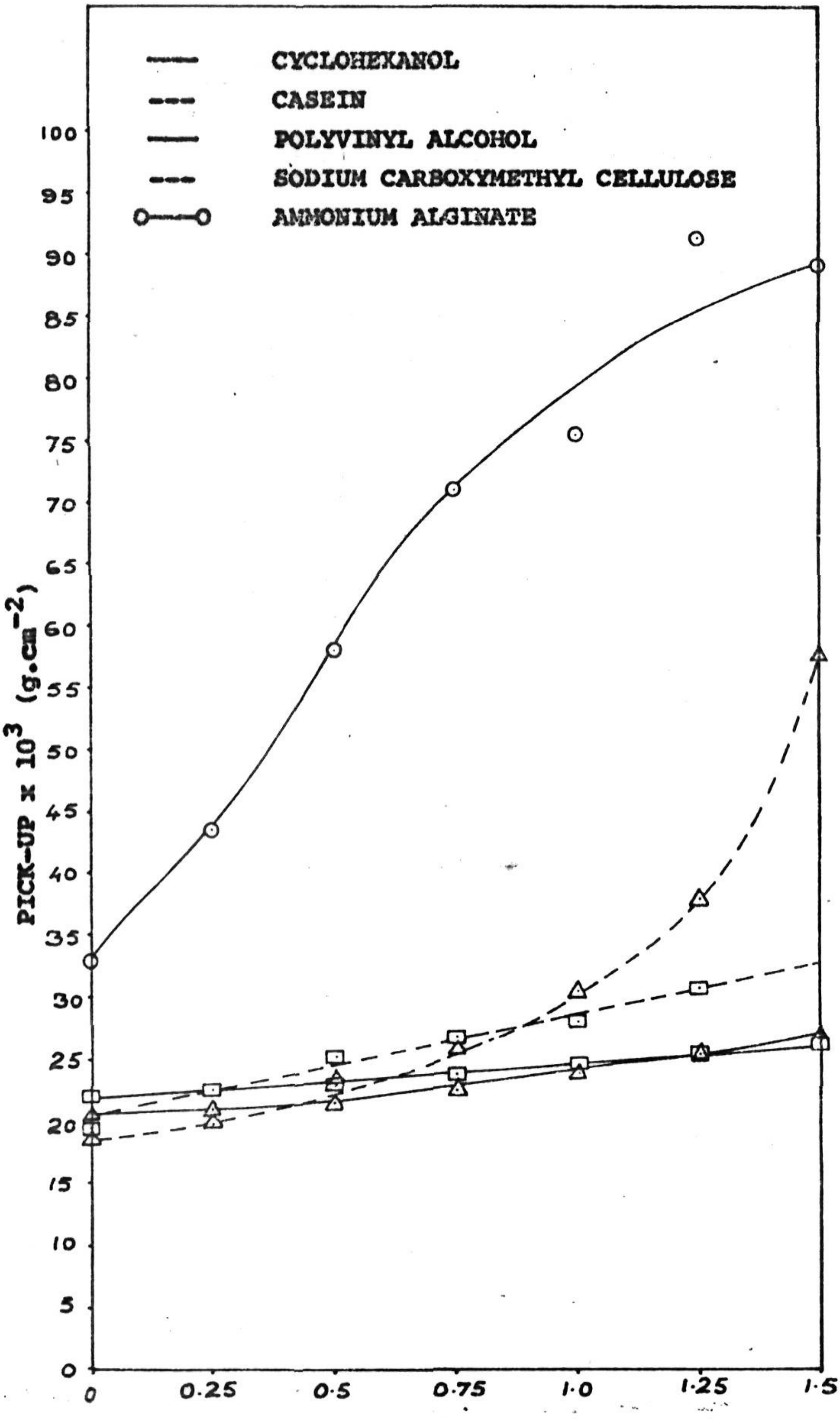


Fig. III.8: Comparative evaluation of thickeners by coacervant dipping (½ min. dwell)

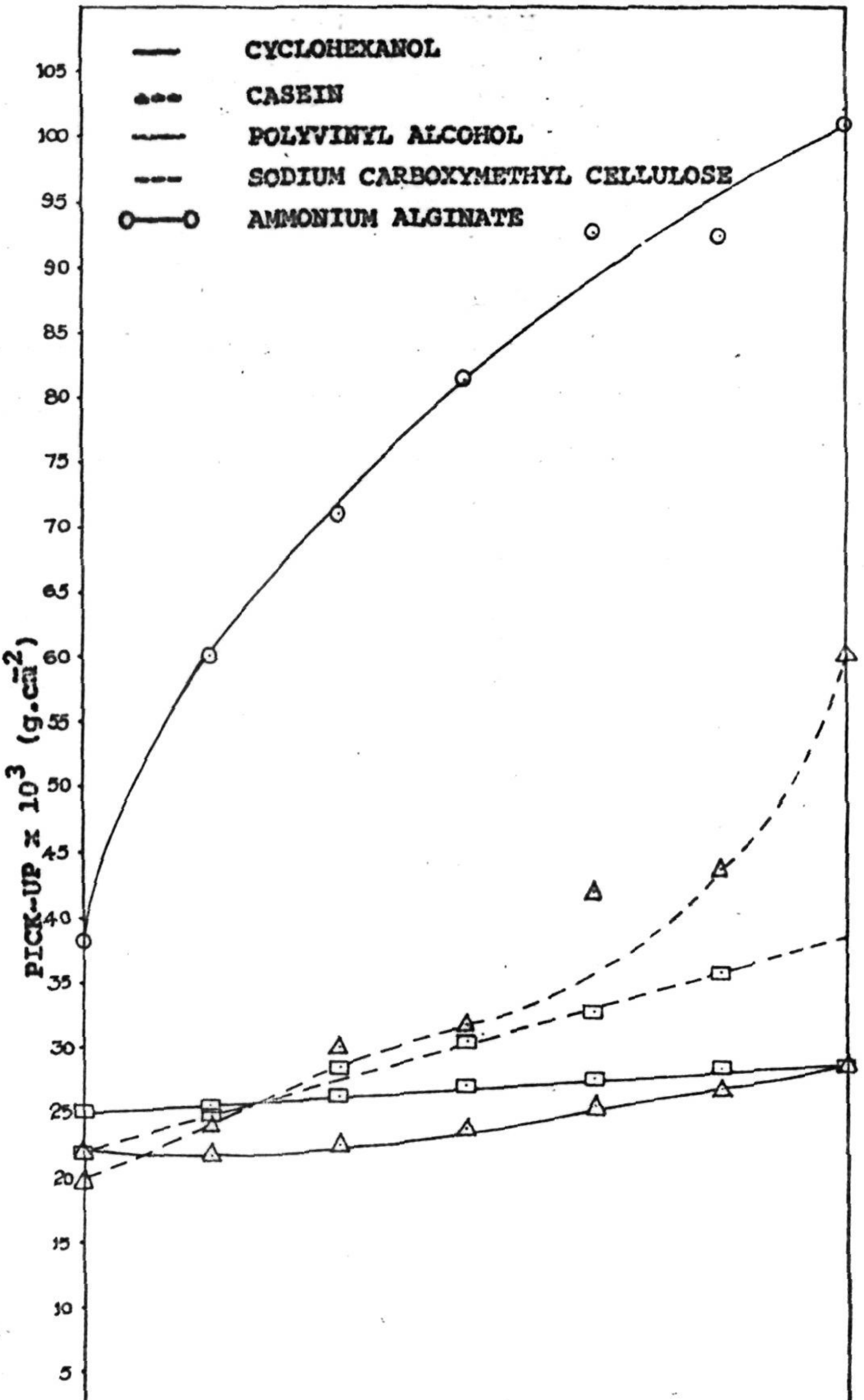


Fig.III.9: Comparative evaluation of thickeners by coacervant dipping (1 min. dwell)

SUMMARY AND CONCLUSIONS

From the present study, it is concluded that the addition of thickeners increase the viscosity of the latex compounds and their effect is in the order given below:

Ammonium alginate > Sodium carboxymethyl cellulose > Polyvinyl alcohol > Casein > Cyclohexanol.

Dwell time has comparatively no effect on pick-up in straight dipping; but in coacervant dipping, pick-up is dependent on dwell time. As is expected, at a constant thickener concentration and dwell time, coacervant dipping has got a much higher pick-up compared to straight dipping.

In the case of straight dipping, the thickeners modify the pick-up efficiency in the same order as they influence viscosity. Dwell time has no effect on this order. In coacervant dipping, efficiency of pick-up at a dwell time of 1 minute is in the following order:

Polyvinyl alcohol < Cyclohexanol < Casein < Sodium carboxymethyl cellulose < Ammonium alginate.

The rate of increase of pick-up with concentration of thickener in the case of straight dipping is in the order given below:

Casein < Cyclohexanol < Polyvinyl alcohol < Sodium carboxymethyl cellulose < Ammonium alginate.

For coacervant dipping, it is in the order of:

Cyclohexanol < Polyvinyl alcohol < Casein < Sodium carboxymethyl cellulose < Ammonium alginate.

Dwell time has no effect on the above order of rates for both straight and coacervant dippings.

The rate of increase of pick-up is linear for casein, cyclohexanol, and polyvinyl alcohol in both straight and coacervant dippings.

From the present study it is possible to predict pick-up efficiency of a particular thickener at any concentration, dwell time, or mode of dipping.

Also, the extent of the increase in viscosity by the addition of any of these thickeners into a latex compound at any concentration can be predicted.

The five thickeners do not show any adverse effect on physical properties of the vulcanizates. An increase in tear resistance of the vulcanizates is observed by all of the five thickeners studied. The ageing resistance of the vulcanizates is also not affected by the presence of the thickeners in them.

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