TITLE .... PROCESSING BEHAVIOUR OF NR LATEX
WITH SPECIAL REFERENCE TO
DIPPING

AUTHOR .... Bholan Ruby Arora, ...

DEGREE ....

AWARDING BODY
DATE .... The Polytechnic of North London, CNAA 1990

THESIS
NUMBER ....

PROCESSING BEHAVIOUR OF NR LATEX WITH SPECIAL REFERENCE TO DIPPING

A thesis submitted to the
Council for National Academic Awards
for the degree of
Doctor of Philosophy

by

Bholan Ruby Arora, B.Sc. (Hons.), M.Sc.

Sponsoring establishment:

The Polytechnic of North London,
London School of Polymer Technology,
Holloway Road,
London N7 8DB.

Collaborating establishment:

London International Group plc.
Reasearch and Development,
Unit 205,
Cambridge Science Park,
Milton Road,
Cambridge CB4 4GZ.

August, 1990

ABSTRACT

Processing behaviour of NR latex with special reference to dipping

by

B. R. Arora

A detailed study of the effect of added ingredients upon processing behaviour of NR latex with reference to dipping has been conducted in an endeavour to further understanding of the fundamental science underlying latex dipping processes.

A preliminary investigation of the effect of heating on the properties of uncompounded and compounded NR latex has shown that properties such as TSC, DRC and VFA No. are unaffected by heating the latex. Properties such as MST and KOH No. increase, whilst alkalinity and pH decrease by heating the latex. These changes are thought to be attributable to the hydrolysis of lipids and proteins, which may have been accelerated by heating the latex.

The new test methods, namely, a microgel test, a calcium stability test, a set-time test and a test for the curtaining effect, have been developed to investigate the factors responsible for the stability of NR latex and hence the quality of the finished product. All these tests have proved to be useful.

The effects of selected latex variables upon the processing behaviour of NR latex with reference to the formation of films by straight- and coagulant-dipping have been assessed. A straight-dipped film produced from prevulcanised NR latex has been found to form a coherent film on the surface at an early stage of drying. This was thought to be mainly a consequence of gelation caused by local drop in pH resulting from loss of ammonia at the surface. An initial sharp drop in ammonia content in less than 30s has been observed. The main feature of this stage of drying is that the water passes through the surface by diffusion at rate which is equal to that at which it is removed from the surface by evaporation. A linear relationship has been found between the coefficients of diffusion and evaporation, The values for diffusion coefficient and activation energy have been found to be 10^{-6} cm^{2}s^{-1} and 1.4kJ mol^{-1} respectively. However, the early stages of the drying of wet latex gels formed by coagulant dipping can be divided into two regions. In Region I, which is an initial region of constant rate, the loss of water is principally by syneresis. The Region II begins when the rate of drying drops off rapidly to a value 15-25 times smaller than that in Region I. The main feature of this stage drying is thought to be that the water passes through a capillary network formed by partial coalescence of the latex particles by diffusion, at a rate equal to at which it is removed from the surface by evaporation. A complex relationship has been found between the diffusion coefficient and the evaporation coefficient.

Finally, an investigation of the effect of certain added ingredients upon certain of the properties of latex has been carried out. Principally, it has been found that the non-rubber substances which interfere with the colloid stabilisation of the latex also cause changes in the process properties, and to a lesser extent, the physical properties of films from prevulcanised latex.

ACKNOWLEDGEMENTS

I wish to express my deep appreciation and gratitude to Dr. D. C. Blackley (Reader in Polymer Science and Technology) and Dr. W. F. H. Burgar (Director of Studies) for their excellent joint supervision, interest and encouragement throughout the duration of this investigation. I am also very grateful to Dr. W. D. Potter (External supervisor) for his useful discussions and suggestions during the tenure of this work.

I wish to thank the technicians of the London School of Polymer Technology for their co-operation in the experimental work. The assistance extended to me by the library staff of London School of Polymer Technology and of Malaysian Rubber Producers' Research Association is gratefully acknowledged.

I am especially grateful to London International Group plc. for the award of Research Studentship during the tenure of this work.

Last, but not least, very special thanks are due to my parents, who have made my higher education possible.

To my beloved brother,
Shri Rama

CONTENTS

CHAPTER 1 : INTRODUCTION

CHAPTER 2 : LITERATURE SURVEY

CHAPTER 3 : MATERIALS, EQUIPMENT AND EXPERIMENTAL PROCEDURES

CHAPTER 4 : CALCIUM STABILITY TEST

CHAPTER 5 : EFFECT OF HEATING UPON PROPERTIES OF NR LATEX

CHAPTER 6 : EFFECT OF SELECTED LATEX VARIABLES UPON THE PROCESSING BEHAVIOUR OF NR LATEX WITH REFERENCE TO STRAIGHT DIPPING

CHAPTER 7 : EFFECT OF SELECTED PROCESS VARIABLES UPON THE DRYING BEHAVIOUR OF COAGULANT-DIPPED FILMS

CHAPTER 8 : EFFECT OF ADDED INGREDIENTS UPON THE PROCESSING PROPERTIES OF PREVULCANISED NR LATEX

CHAPTER 9 : CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

CHAPTER 1 : INTRODUCTION

1.1 Definition of NR latex

NR latex may be defined as a polydispersed colloidal system of natural rubber hydrocarbon particles dispersed in an aqueous medium, which originates from the Hevea brasiliensis tree. It is therefore essentially a two-phase system, consisting of a disperse phase and a dispersion medium.

The disperse phase consists of latex particles, made up of cis-1,4-polyisoprene with a molecular weight in the region of one million. The shape of particles is spherical and size ranges from 0.1 to 4 μm. The particles exhibit a strong Brownian movement and are stable due to an exterior natural protective layer of soaps and proteins. These particles carry negative electric charges, thereby giving rise to electrostatic repulsions.

The dispersion medium is a dilute aqueous solution of non-rubber materials. The chemical composition of the solution may vary from one latex to another. Nevertheless, the major constituents are known to be proteins and their decomposition products, fatty-acid soaps, and a range of organic and inorganic salts.

1.2 Utilisation of NR latex

NR latex is obtained from the botanical source Hevea brasiliensis. On tapping the Hevea brasiliensis tree, natural rubber latex exudes. The latex has on average a rubber content of 30 per cent by weight. This latex is usually termed 'field' latex, and is not utilised in its original form due to its high water content and susceptibility to bacterial attack. A few hours after the latex is obtained from the tree, bacteria act on sugars and other latex components resulting in the formation of acids and the subsequent coagulation of the latex. It is therefore necessary both to preserve and concentrate the latex, thus producing stable products that contain 60 per cent or more of rubber.

Until 1920, practically all NR latex was converted on the plantation into crude rubber, and was sold for the manufacture of rubber articles by dry rubber technology. After this date, methods of preserving, concentrating and shipping NR latex were introduced. Since then, these methods have been improved. As a consequence, NR latex is now available anywhere for use in the manufacture of rubber goods directly from latex.

A large number of materials have been used as preservatives, of which alkalis are particularly important, especially ammonia.

1.3 Properties and composition of NR latex

1.3.1 Introduction

A great deal is known about the composition and properties of NR latex, but the relationships between the two are still only vaguely understood. This is especially true of the relationship between the natures and amounts of non-rubber materials, and the batch-to-batch variations in processing behaviour. Recent work (1,2) has indicated that changes in the amounts and natures of the serum anions are not sufficient to explain the observed variation in processibility. It appears that part of the reason for these variations is variability associated with the particle-serum interface. However, the composition of NR latex is exceedingly complex, thus rendering investigation of these matters difficult.

1.3.2 Fresh NR latex

The solids content of fresh latex may vary from 25 per cent to 45 per cent by weight. This variation is due to the factors such as the type of tree, the tapping method, the soil conditions, and the season.

The latex contains small quantities of non-rubber substances, the amount approaching 10 per cent of the rubber solids content. The pH ranges from 6.5 to 7.0, and the density ranges from 975 to 980kg m^{-3}. The colloid stability of fresh latex is thought to be primarily a consequence of the presence of an adsorbed layer of protein-lipid complex on the particle surface.

Field latex is collected from the tapping cups and bulked. Preliminary ammoniation to about 0.05-0.20% is carried out to protect the latex from bacterial attack prior to delivery to the factory at which concentrate is produced. To facilitate the transportation of fresh latex, and because many manufactured articles require a high concentration of rubber in the latex, the rubber content of latex is increased to 60-66% by concentration.

1.3.3 Ammonia-preserved NR latex concentrate

The ammoniation of NR latex causes the hydrolysis of proteins and phospholipids. The former are hydrolysed to polypeptides and amino acids and the latter are hydrolysed to various substances such as glycerol, fatty-acid anions, phosphate anions and organic bases. The adsorption of the liberated fatty-acid anions at the particle surfaces is thought to account for the spontaneous increase in mechanical stability when ammoniated latex is stored (3).

The hydrolysis of lipids is often assumed to be complete in mature latex, but some indirect evidence suggests that natural lipids may still be present (3). Also, a high proportion of the phosphorus detected in latex cannot be identified in the serum and may possibly be present at the particle surface as phospholipids (1,2).

However, little is known directly about the materials adsorbed at the surface of the latex particles. The surface proteins have never been isolated as such, and they are often presumed to be similar to those which have been identified in the serum (4), but they may be different.

Altman (5) determined the composition of fresh field latex as received and after preservation and storage for several weeks. The results are shown in Table 1.1. As can be seen from Table 1.1, there is a marked increase in the acid value of the acetone extract within a short time. It is probable that the ammonia has brought about the hydrolysis of lipids to fatty-acid soaps. This interpretation is consistent with the decrease in surface tension. These soaps partially displace the proteins of the protective layer, surrounding the particles, thereby bringing about an increase in colloid stability during the first few months of storage.

The ammonia further increases the stability directly by increasing the degree of ionisation of adsorbed fatty-acids, thereby increasing the charge on the particles. It also deactivates the peroxidase and coagulase enzymes present in the fresh latex.

Table 1.1 Differences between fresh field latex and ammonia-preserved latex stored for several weeks, as found by Altman (5)

property	fresh latex	ammoniated and stored latex	
		10 days	50 days
TSC (%)	40.12	40.10	—
DRC (%)	37.65	36.17	—
non-rubbers (%)	2.47	2.97	—
acetone extract (%)	3.41	3.84	3.91
acid value of acetone extract (mg KOH/100g TSC)	139	256	299
surface tension (mN m^{-1})	44.7	38.6	37.8
viscosity (cP)	15.3	5.6	5.8

1.3.4 Latex properties

The following are the more important properties of NR latex: TSC, DRC, MST, VFA No., KOH No. and alkalinity.

Standard methods for determining these properties have been established for many years. The TSC gives a measure of the solids content of the latex. Essentially, the technique consists of evaporating a known weight of latex to dryness under standard conditions and then weighing the residue. The DRC gives a measure of the fraction of the latex which can be coagulated under controlled conditions. The method involves the coagulation of a known weight of latex under standard conditions, and then separating, drying and weighing the coagulum.

The DRC taken in conjunction with the TSC provides information regarding the fraction of non-volatile non-rubber constituents in the latex which remain soluble in the serum after coagulation.

The VFA No. of an ammonia-preserved latex gives a measure of the extent of micro-organic activity which has occurred during the time since the latex exuded from the tree. The VFA No. is defined as the number of grammes of potassium hydroxide equivalent to the volatile fatty-acids in latex containing 100g total solids. The volatile fatty-acids present in rubber latex are determined by steam-distilling rubber-free latex serum, and estimating by acidimetric titration the total amount of volatile fatty-acids distilled.

The KOH No. gives an indication of the ageing and general condition of the latex. It measures the extent of the hydrolytic degradation of proteins and lipids. The KOH No. of ammonia-preserved latex is defined as the number of grammes of KOH equivalent to the acids which are combined with ammonia in latex containing 100g total solids. The method is to titrate a known weight of latex with standard carbonate-free potassium hydroxide solution, the pH of the latex being followed by means of a pH meter as the titration proceeds. The KOH No. is inferred from the inflection point of the titration curve.

Many latex processes involve the agitation of latex over prolonged periods of time. Under such conditions the increased number and frequency of collisions between particles may lead to premature agglomeration or flocculation. The MST test provides some indication of the stability of latex under such conditions. It also provides an indication of the general colloid stability of the latex. The test is basically concerned with stirring the latex at high speed under closely-controlled conditions and measuring the time taken to produce visible traces of flocculation. In the flocculation process induced by such mechanical agitation, the larger particles having greater kinetic energy will probably flocculate first (6,7).

The final colloid stability of ammonia-preserved natural rubber latex is governed by the balance between the effects of the products of volatile fatty acids formation, which tend to reduce colloid stability, and the effects of the products of hydrolysis of lipids and proteins, which tend to enhance colloid stability.

1.3.5 Mechanical properties of latex products

The mechanical properties of the latex deposits in both the wet and dry states are of great importance. It is well-known that the tensile properties of dried products are far superior to those of wet gels. Furthermore, the tensile properties of wet gels may improve with age. This is because once a gel has formed it may, depending upon ambient conditions, begin to undergo a process known as 'syneresis'. 'Syneresis' is a process whereby the aqueous phase is exuded spontaneously, thus causing the shrinkage of the gel. The occurrence of syneresis increases the strength of the gel because the area of contact between latex particles is increased, and because coalescence of the particles is induced by interfacial forces.

In most industrial applications of NR latex, the initial contact between particles is achieved by gelation. Gelation is a uniform destabilisation of the latex which results in three dimensional aggregate of rubber particles termed the 'gel'. The aqueous phase of the latex is retained in the interstices of the gel. The wet gel formed must be able to sustain a certain amount of mechanical handling without being damaged or distorted. Thus, an important aspect of the investigation of the processing behaviour of NR latex is the determination of the wet-gel strength of deposits formed from the latex. The wet-gel strength may be defined as the tensile strength of the freshly-set latex film.

Although some workers (8,9) have made attempts to determine wet-gel strength, no adequate method so far is available. One reason for this is that the freshly-set latex deposit is difficult to remove from the surface against which it was formed.

1.4 Compounding of NR latex

1.4.1 Introduction

In nearly all applications of latex, it is normal that the latex be compounded with a variety of substances. This may be necessary both for economic reasons and in order to enhance the mechanical properties of the resulting rubber article. The essential compounding ingredients include:

(a) latex stabilisers to ensure adequate but not excessive, colloid stability during processing;
(b) vulcanising agents to effect subsequent crosslinking of the rubber molecules; and
(c) antioxidants to ensure adequate service life.

In addition, depending on the nature of the process or the end product, some latex compounds may require the addition of gelling agents, foaming agents, thickners, flame proofing agents, pigments, fillers, extenders and tackifying resins.

A typical basic formulation for a pre-vulcanisable or post-vulcanisable NR latex is shown in Table 1.2. The compounding ingredients are usually added in the form of aqueous dispersions or solutions.

Table 1.2 A typical formulation used for vulcanisation of NR latex (16)

ingredient	function	parts by weight	
		dry	wet
NR latex (60% DRC)	—	100.0	167.0
sulphur (33%)	crosslinking agent	1.0	3.0
ZDEC (33%)	accelerator	0.75	2.25
zinc oxide (33%)	activator	1.0	3.0
anti-oxidant	prevents ageing	1.0	3.0

1.4.2 Latex stabilisers

The colloid stabilisers are regarded as very important additives for latex compounds. If the compound has insufficient stability to withstand the processing conditions, no products can be made. However, the excessive colloid stability can also be a problem. NR latex contains its own indigenous colloid stabilisers, namely, proteins and soaps. In a few cases, these may provide sufficient colloid stability, but in most cases, the further addition of stabilisers is required to increase the colloid stability of the compound.

In latex dipping, where the compounded latex must be continually agitated to inhibit surface skin formation, extra stabilisation is necessary to produce sufficient mechanical stability to withstand the agitation. However, this increased stability should not be obtained at the expense of the ability subsequently to form a coherent gel. In this respect, the widely-used fatty-acid soaps are ideally suited as they give significant increases in mechanical stability without inhibiting the subsequent gelation.

All fatty-acid soaps stabilise not only the rubber-water interface but also the air-water interface, and therefore tend to promote foaming. Thus, the amount of soap used for stabilisation must be limited. In latex dipping compounds, for example, soap additions should not exceed 0.4 pphr. A further feature of fatty-acid soaps is that all of those having 12 or more carbon atoms, whether saturated or unsaturated form insoluble zinc ammine salts and therefore promote colloid destabilisation in the presence of zinc compounds such as zinc oxide.

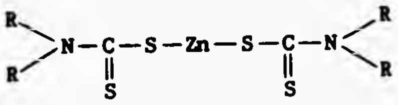
Additional contributors to the colloid stability of latex compounds can be made by non-surfactant substances. For example, the fixed alkalis like sodium and potassium hydroxide will raise the stability of latex compounds (11) by minimising the solubilisation of zinc.

1.4.3 Vulcanising agents

Essentially, sulphur-vulcanising systems for natural rubber often consist of three components, namely, sulphur, accelerator and zinc oxide. However, the use of sulphur donors

(10) instead of sulphur or the use of two accelerators to give modified vulcanisation behaviour may be desirable in some cases. The amount of sulphur varies with the nature of the article being manufactured, but is usually between 0.3 and 2.5 pphr. The modulus and hardness of the vulcanisate increase with increasing sulphur content, assuming that the added sulphur is utilised in forming crosslinks.

The accelerators used in latex technology are mainly of the zinc dialkyldithiocarbamate type:



This class of accelerators gives fast post-vulcanisation rates with sulphur at 100°C, and some types are very active at much lower temperatures. Zinc oxide is not essential for latex vulcanisation if zinc-containing accelerators are employed, but it is commonly used in latex compounds to provide further activation of vulcanisation and to contribute towards the gelation process.

Before being added to the latex, the vulcanising additives are normally made into aqueous dispersions by a grinding technique. Grinding is usually continued until the largest particles in the dispersion are roughly commensurate with the larger rubber particles in the latex. This means achieving a maximum size of about 5 μm.

1.4.4 Antioxidants

The protective agents such as antioxidants may be required in latex formulations. The addition of such agents will depend on the nature of the product and the service conditions envisaged. The most commonly used antioxidants are phenolic derivatives.

1.5 Prevulcanisation of NR latex

Generally, sulphur vulcanisation is achieved by a chemical reaction which involves the formation of chemical crosslinking of the long, linear and flexible rubber molecules to produce a three-dimensional network. NR latex may be either prevulcanised or postvulcanised. Postvulcanisation is a process which involves the vulcanisation of the film after it has been cast. By contrast, prevulcanisation is a process whereby the rubber within the latex particles is chemically crosslinked without the latex being colloidally destabilised. Thus on drying the prevulcanised latex, a vulcanised film can be obtained without further heating.

Prevulcanisation of latex was first discovered by Schidrowitz in the 1920s (12-15). He described a 'hot' vulcanisation process whereby the latex containing sulphur and zinc oxide was heated in an autoclave under pressure. The introduction of accelerators soon rendered high temperatures unnecessary, and modern work is based on the use of ultra-fast accelerators which enable vulcanisation to be carried out at 40-60°C.

At present, all commercially-produced prevulcanised latex is prepared by reacting latex with ingredients including sulphur and one or more accelerators of the carbamate type, usually zinc diethyldithiocarbamate. The latex is contained in a stirred jacketed mixing vessel, and the compounding ingredients added. The vessel is heated by passing hot water through the jacket. After heating for typically 3-5 hours at 50-60°C, the latex is cooled to room temperature. It is filtered and sometimes clarified centrifugally before use.

1.6 Latex dipping

1.6.1 Introduction

NR latex is employed predominantly in those applications which require good film-forming ability, high wet-gel strength and final product strength. A distinctive characteristic of latex technology is that the conversion of the latex into a product involves minimal energy consumption in mixing, shaping, and vulcanising operations, but high energy consumption in drying. The difficulty and expense of drying restricts latex technology to the manufacture of products generally less than 3mm in thickness.

The conversion of NR latex into products is accomplished in many different ways. In all these processes, a stable colloidal system is maintained until, at the desired time, it is made unstable and converted to a solid product. Preserving the balance between too much and too little stability constitutes a major challenge in latex processing technology. The destabilisation of NR latex can be brought about in a variety of ways, such as acidification, addition of salts of polyvalent metal ions or high concentrations of salts, dehydration and mechanical agitation or freezing. In latex dipping, the destabilisation of NR latex is often brought about by the use of salts of polyvalent metal ions. However, very thin-walled products are produced without the aid of a coagulant.

1.6.2 Destabilisation of latex by salts

Industrially, the most important salts used for the destabilisation of latex are those of calcium and zinc. Calcium salts, in particular, calcium nitrate are widely used in the dipping industry to produce gels on 'formers'. This is because calcium forms insoluble soaps with all fatty-acid soaps, and with proteins, such as lactic casein. It seems probable, therefore, that calcium destabilises latex principally by means of its reaction with adsorbed anions and consequent destruction of surface charge. However, recent investigations (17) of the coagulant-dipping process have shown that the formation of the gel does not appear to be directly related to the equivalence of soap and calcium ion concentration. It seems, therefore, that the industrial process also utilises the effect of high ionic concentrations. High concentrations of ions reduce colloid stability by compressing the electrical double layer around the particle and thus reducing the net repulsive potential between pairs of particles.

Zinc salts destabilise latex in similar ways to calcium ions, but there are some significant differences. The principal difference is that zinc ions in ammonia-preserved natural rubber latex react with ammonia to give complex zinc ammine cations:

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

These cations form insoluble salts with all fatty-acid soaps having 12 or more carbon atoms, but do not appear to react in the same way with proteins (20).

1.6.3 Types of dipping processes

Basically, there are three different methods of obtaining a deposit on a former by latex dipping. These are:

(a) straight dipping
(b) coagulant dipping
(c) heat-sensitive dipping

Only methods (a) and (b) are employed in the present work, and so only these two methods will be described.

(a) straight dipping

A clean, dry former is immersed into the latex and then slowly withdrawn. The former is then normally inverted to redistribute excess latex and the deposit dried. This process gives rise to very thin articles (~ 0.05mm in thickness), e.g., condoms.

(b) coagulant dipping

A clean, dry former is immersed into a coagulant solution, e.g., calcium nitrate in methylated spirit, withdrawn and dried to produce a substantially dry layer of calcium nitrate on the former. It can then be immersed in the latex compound. After a suitable dwell time (1-5 minutes), the former is slowly withdrawn, inverted and dried. This process gives articles of medium thickness (~ 0.5mm), e.g., rubber gloves, balloons and catheters.

1.6.4 Leaching

This is a process whereby the dipped articles are washed in water to remove water-soluble materials. The efficiency of this process may have a significant effect upon characteristics such as clarity, blooming, discoloration and the tensile strength of an article. Leaching is of particular importance in medical goods and in electricians' gloves (18) where the presence of hydrophilic materials would absorb atmospheric moisture and lower electrical resistance.

Leaching may be carried out on the wet gel before vulcanisation using hot (60-80°C) water. At this stage, a few minutes' washing is sufficient to extract a high proportion of the water-soluble substances. However, complete removal of these materials requires much longer times, which is only practicable after vulcanisation and removal of the product from the former.

1.6.5 Drying and vulcanisation

Dipped articles are usually dried and vulcanised in hot-air ovens. Intermediate drying, as between dips in a multiple dipping operation, is performed at relatively low temperatures (60-80°C), but final drying and vulcanisation is performed at higher temperatures (100-140°C).

1.7 Factors affecting deposit thickness

1.7.1 Straight dipping

In straight dipping, the main requirement is the control of the thickness of the deposit. If the former is of non-porous material such as glass the rubber deposition is controlled by the rheological properties of the latex compound. It has been shown (19) that the straight dip deposit thickness, t, is related linearly to the logarithm of the latex viscosity. Thus,

$$t = A + K \log_{10} (\text{viscosity}) \qquad (1.1)$$

where A and K are constants. Since the viscosity is related to the TSC of the latex, it is apparent that there is also a relationship between the deposit thickness and the TSC of the latex.

1.7.2 Coagulant dipping

In coagulant dipping, the relationship between deposit thickness and dwell time has received much attention (e.g., 22,24). The main variables which affect deposit thickness are the dwell time, the TSC and the viscosity of the latex, and the nature and concentration of the coagulant. For a given coagulant system, the relationships between the deposit thickness and dwell time and viscosity are illustrated in Figures 1.1 and 1.2 respectively. The viscosity has a small effect upon the deposit thickness, but the dwell time has a

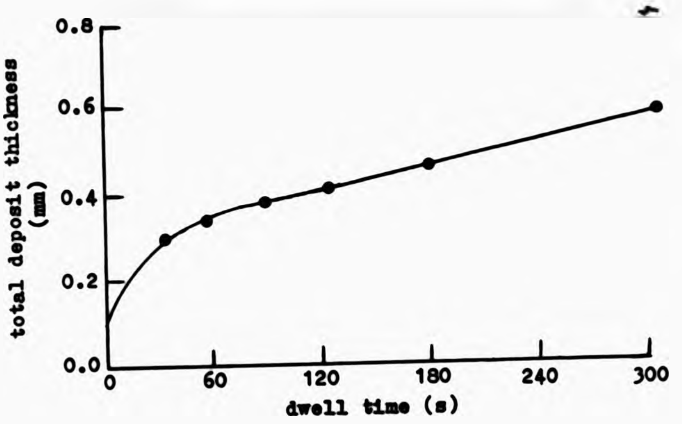


Figure 1.1 Effect of dwell time upon deposit thickness in coagulant dipping using 30% calcium nitrate (20)

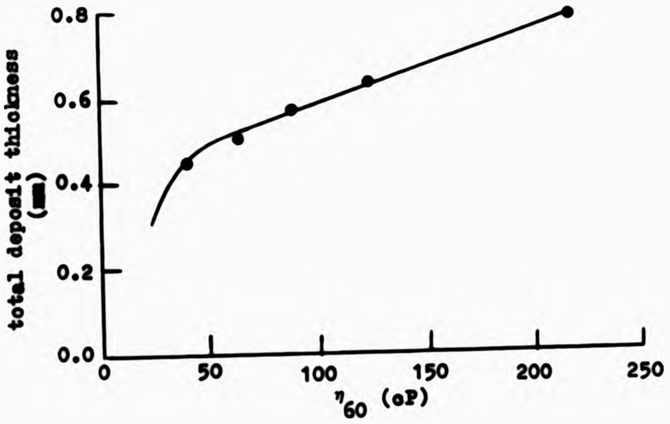


Figure 1.2 Effect of latex viscosity upon deposit thickness in coagulant dipping (20)

greater effect upon the deposit thickness, especially at short times.

A schematic diagram showing a cross-section of the different regions in the vicinity of the formation of a latex deposit by coagulant dipping is presented in Figure 1.3. There are various regions designated as follows:

Region I - the coagulant layer
Region II - the coagulant deposit
Region III - latex compound

As the former with the coagulant layer is immersed in the latex, Region II forms immediately. This results from migration of coagulant from Region I into the latex. As the former is allowed to dwell in the latex, the coagulant from Region I becomes dissolved and diffuses through Region II into Region III. As a consequence, Region II becomes progressively thicker with a subsequent decrease in thickness of Region III. The aqueous phase within the particle interstices in the coagulum dissolves the coagulant ions which then diffuse through the coagulum into the latex to form more coagulum. A

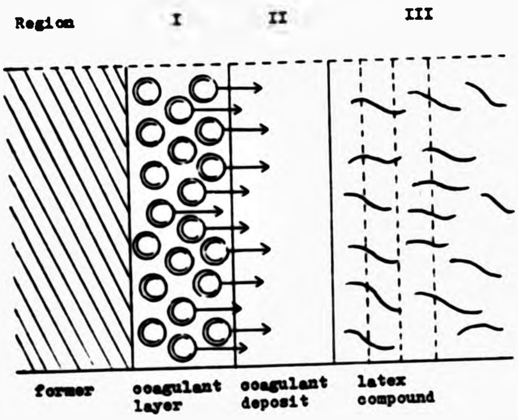


Figure 1.3 Schematic diagram of cross-section of different regions in vicinity of the formation of a latex deposit by coagulant dipping

concentration gradient is thus set up which depends upon the rate of diffusion of the coagulant ions. As the coagulum grows in thickness, the coagulant concentration gradient falls because of serum dilution, and the coagulant ions take longer to reach the uncoagulated latex. The TSC of the latex is a major factor in determining the initial pore size of the coagulum through which the coagulant cations have to pass (31). Finally, it has been shown (20) that, as expected, there is a direct relationship between the concentration of coagulant and the thickness of deposit, i.e., the greater the concentration of coagulant, the thicker is the rubber deposit obtained.

1.7.3 Mathematical relationship between deposit thickness and dwell time

Numerous mathematical equations to describe the relationship between the deposit thickness and dwell time have been proposed. For example, Gorton (21) proposed the equation:

$$l_d = A + K\, t_D^{\frac{1}{2}} \log_{10} \eta \qquad (1.2)$$

where l_d is the deposit thickness, t_D is the dwell time (up to 5 minutes), η is the viscosity of latex and A and K are constants.

In contrast, Sandomirskii and Korsunskii (22) proposed a different equation to describe the deposit thickness-time relationship. In its simplest form, it is:

$$q = K' + t_D^{Y} \qquad (1.3)$$

where q is the weight of deposit, t_D is the dwell time and K and Y are constants, and $0 \leqslant Y < 0.5$.

As can be seen, according to Gorton (21,23), the total deposit thickness is directly proportional to the square root of the dwell time. This implies a conventional diffusion process. Sandomirskii and Korsunskii (22), however, state that the total deposit thickness is directly proportional to a power of Y of the dwell time which is between zero and 0.5.

Numerous other and more complex relationships have been obtained (32,33), but there is no general agreement on a relationship. For example, Gouw (32) has investigated the deposit thickness-time relationship for uncompounded NR latex. The stability of the latex was varied by adding either ammonium acetate to reduce the stability or adding potassium oleate to increase the stability. The TSC of the latex was adjusted to about 59% by adding distilled water. The results showed that the more stable latex produced thinner deposits compared with the less stable latex. Gouw has stated that the equation 1.2 proposed by Gorton (21) is only valid for dwell time less than or equal to 9 minutes. Subsequently he has proposed that,

$$l_d = l_\infty (1-e^{-kt_D}) \qquad (1.4)$$

and

$$l_\infty = a - k \log C_m \qquad (1.5)$$

where l_D is the thickness of the dry deposit, k and a are the constants, t_D is the dwell time and C_m is the measured chemical stability of the latex.

Teoh (33) has postulated a series of equations:

$$l_d = l_\infty (1-e^{-kt_D}) \qquad (1.6)$$

$$l_d = l_\infty \tanh kt_D \qquad (1.7)$$

$$l_d = l_\infty (2/\pi) \tan^{-1} kt_D \qquad (1.8)$$

$$l_d = l_\infty \operatorname{erf} (kt_D) \qquad (1.9)$$

$$l_d = l_\infty (1-e^{-k\sqrt{t_D}}) \qquad (1.10)$$

where l_d is the dry deposit thickness, l_∞ is the limiting deposit thickness, and k is the constant and t_D is the dwell time.

All these equations predict a typical deposit thickness-time relationship. Using Gouw's experimental data, Teoh tested Equations 1.6 to 1.9 and found that they did not fit the data well, especially at longer dwell times (t_D > 10 minutes). However, Equation 1.10 fitted the experimental data well, even when stabilisers were added to the particular latex. Furthermore, it was found that the value of l_∞ depends upon the stabiliser content, while that of k is independent of the stabiliser content. It follows that the deposit thickness-time relationship at a given level of stabiliser will be characterised by the values of l_∞ and k.

1.8 Objectives of the present project

A considerable amount of literature is available on the subject of NR latex. Much attention has been paid to the properties of raw latex and the changes which occur when zinc compounds are added (e.g., 24, 25 and 26). Although the prevulcanisation of NR latex has been extensively studied, the published literature is mainly concerned with the investigation of the rate and extent of prevulcanisation, and with the effects of the extent of prevulcanisation upon the physical properties of products made from prevulcanised latex (e.g., 27 to 30). In the view of the author, although there is a general awareness amongst latex suppliers and users of the problems associated with the processing behaviour of NR latex with reference to dipped products, very little work has been carried out regarding the correlations between initial latex properties, processing behaviour and the properties of the product.

The objectives of the project described in this thesis were as follows:

1. To make a preliminary investigation of the characterisation of NR latex in both the unvulcanised and the prevulcanised state, to acquire a deeper understanding of the behaviour of latex in relation to the addition of compounding ingredients and the changes which occur on heating the latex.
2. (i) To assess the effect of selected latex variables upon the processing behaviour of NR latex, with particular reference to the straight- and coagulant-dipping processes.
   (ii) To investigate the relationship between processing behaviour and product properties in the wet and dry states.

It was expected that this study would increase knowledge of the fundamental science underlying latex dipping processes, as well as accumulating useful empirical data concerning the relationships between latex properties, processing behaviour and product properties.

CHAPTER 2 : LITERATURE SURVEY

2.1 Mechanical properties of latex deposits

2.1.1 Introduction

An understanding of the mechanical properties of the latex deposits in the wet and dry states is important industrially. When these properties are known, it enables the technologist to treat latex materials on a scientific rather than an empirical basis.

Numerous reports (11-24) are available on the subject of mechanical properties of the dry rubber deposits. These will be discussed in Section 2.1.5. In contrast, very little work has been published (1-10) on the properties and characterisation of wet latex gels. This may seem surprising at first sight, because a knowledge of the properties of latex gels is exceedingly important in the latex industry. This is primarily because the wet gel formed in industrial processes is often subjected to a certain amount of mechanical handling. It is therefore important to know whether the wet gel is able to sustain such handling without being damaged or distorted.

The problems arising in the removal of the deposit from a former or other substrate render measurements of the physical properties of wet gels difficult. It is obvious, therefore, that the inherent weakness of the gels limits not only the measuring of its tensile properties but also its usage in many latex processes. The tensile properties of the wet gels are far inferior to those of the corresponding dried deposits.

2.1.2 Methods of measuring wet-gel strength of latex deposits

The term 'wet-gel strength' is used to denote the tensile strength of the freshly-deposited latex films. There are several methods which have been reported for the measurement of wet-gel strength. Firstly, Medalia *et al*. (1) have developed a so-called 'paper dip' method. Essentially, the method is based upon a latex film which is deposited directly on a strip of paper of low wet-gel strength by coagulant dipping. The strip of paper which is of dumb-bell shape, is impregnated with calcium nitrate and then dipped into latex for 30 seconds. The strip, together with the adhering coagulant-dipped film is removed and rinsed in water. The tensile properties are then measured using a special tensile testing machine designed for films of high elongation at break and low tensile strength.

Although the 'paper dip' method seems to be the most widely reported, it is not the best of the methods described so far. Its principal disadvantage is that it does not resemble closely the conditions under which wet gels are produced in industrial processes for coagulant-dipped products. For example, the moist strip of paper is sandwiched between the layers of wet gel, and the effect of this composite structures upon the test-piece, and hence the wet-gel strength of the film, is not very clear.

The second method was developed by Savinkova et al. (2). In this method, the latex gels were prepared in the form of rings, as this was the most convenient form for the subsequent determination of mechanical properties. The latex compound was poured into special cylindrical metal moulds fitted with removable cores. After spontaneous gelling the latex, the core was extracted and ring removed from the mould. Mechanical tests were conducted by placing the rings of the gel on special grips in the shape of rollers on a dynamometer. The tensile properties were then determined. The tensile strength and elongation at break of the gel was calculated from the following breaking load and ultimate extension using the following standard relationships:

$$\sigma = \frac{L_B}{2A} \quad (\text{kg cm}^{-2}) \qquad (2.1)$$

and

$$\lambda = \frac{d - d_o}{d_o} \times 100 \quad (\%) \qquad (2.2)$$

where σ is the tensile strength of the gel, L_B is the breaking load, A is the initial cross-sectional area of the ring, λ is the breaking elongation (strain) of the gel, d_o is the distance between the grips of the dynamometer before stretching the ring of the gel, and d is the distance between the grips at the time the ring breaks. Since this method was designed to study the effect of the syneresis occurring within the wet gel, a few modifications are necessary in order for it to be applicable in the measurement of the wet-gel strength. For example, the removal of ring samples and then subjecting them to dynamometer must be a speedy process to minimise the effects of syneresis.

A third method, developed by Golberg et al. (3), is based upon the use of a special device which produces two-dimensional deformation of the wet gel on inflation. The pressure required for the inflation of the gel is measured by means of a U-tube manometer. The stress and strain are then calculated from the formulae:

$$\sigma = \frac{P\,\lambda^3 R_0}{10^4 . 2 l_0} \quad (\mathrm{kg\ cm^{-2}}) \qquad (2.3)$$

and

$$\lambda = \sqrt[3]{\frac{V_\tau}{V_0}} \qquad (2.4)$$

where σ is the stress in two-dimensional deformation (calculated on the actual cross-sectional area), P is the air pressure below the inflated gel, R_0 is the radius of the inflated sphere prior to deformation, l_0 is the thickness of the gel before deformation, λ is the elongation (strain) ratio in two-dimensional deformation, V_τ is the volume of air below the inflated gel and V_0 is the volume of air in the inflated gel prior to deformation. However, this method has appeared to be unpopular, probably because of the difficulties encountered in the preparation of the test-piece.

More recently, a method has been developed by Shukri (4). This appears to be the most satisfactory of the methods which have been published so far. In this method, the wet gel deposits are prepared by immersing the former with a very viscous layer of coagulant into the latex and withdrawing it. The gel is then carefully removed from the former, and placed on a plastic sheet in a closed container saturated with water. Thereafter, it is removed from the container after a predetermined time and dumb-bell test-pieces cut from it and immediately subjected to tension in a suitable tensile testing machine (such as an Instron) at room temperature.

2.1.3 Effect of syneresis on properties of latex gels

Much has been published on the subject of the syneresis of latex gels and its effect upon the mechanical properties of latex gels. However, very little effort, if any, has been made to discuss the structure of the gels and principal mechanisms underlying the observations. This is primarily due to the lack of knowledge concerning this subject. Latex gels do not have a constant composition or structure. Once a gel has formed, it may, depending upon the ambient conditions, begin to undergo the process known as syneresis. Syneresis is the spontaneous exudation of aqueous phase from the gel, and concomitant shrinkage of the gel. The occurrence of syneresis increases the strength of the gel because of the increased area of contact between latex particles and also because of the reduced water content. The increased area of inter-particle coalescence is induced by interfacial forces. In addition, syneresis promotes a more rapid drying of the latex film, because during syneresis the moisture content of the gel decreases and hygroscopic salts which prevent moisture from being removed from the gel in drying are expelled to the surface.

Many workers (5,8) have made attempts to study syneresis. Their principal finding has been that the syneresis conditions like medium, temperature and time, all have a considerable effect upon the syneresis process, and hence upon the strength of latex gels. Savinkova et al. (6) have shown that syneresis occurs most rapidly during the first 2 to 3 hours, and then slows up considerably. They also showed that syneresis occurs more rapidly in water than in air. This is in good agreement with the observations made by Voyutskii et al. (8) and by Sandomirskii et al. (9). Syneresis was also found to occur faster in hot water than in cold water. This was explained not only by the fact that heating increases the rate of syneresis itself, but also by the fact that increased temperature assists the mutual coalescence of the rubber particles. The strength at any given moisture content was also found to be greatest when syneresis was conducted in hot water. The use of hot water is said to assist the removal of the adsorbed stabilisers and thus to accelerate the coalescence of individual particles. In addition, it was observed that syneresis occurs rapidly in xylitan, triethanolamine and ethyl alcohol, apparently because of the dehydrating action of the hydroxyl groups of these compounds. Figure 2.1 shows the effect of syneresis upon the wet-gel strength. Prior to syneresis, the gel has little strength, but as syneresis progresses the wet-gel strength increases considerably, especially in xylitan or a hot water medium.

In the view of the author, there seems to be confusion between syneresis and leaching . For example, much of the reported work regards the syneresis process as comprising not only the exudation of aqueous phase from the wet gel, but also the extraction of soluble material from the wet gel. It is necessary, therefore, to make a clear distinction between these processes before drawing any definite conclusions.

2.1.4 Factors affecting mechanical properties of wet latex deposits

The strength of wet gels is governed by either

(a) the diffusion of long flexible chains of rubbers across the boundary between one latex particle and another and/or
(b) the strength of rubber itself.

There are several factors that affect the wet-gel strength of a latex deposit. Firstly, the strength of a latex gel is affected by the degree of ageing of the latex (5,7,10). Shepelev *et al*. (7) have found that the ageing of polychloroprene latex reduces the wet-gel strength and elongation at break of the gel. The reason given for this observation is that the rubber within each polymer molecule becomes more crosslinked, thus reducing the mobility of the molecules. The reduced mobility impedes coalescence of the particles into a strong gel.

The concentration and type of added soap (1,4,5,8) also appear to affect the wet-gel strength. Shukri (4) investigated the effect of added potassium stearate and an ethoxylate surfactant upon wet-gel strength. He found that increasing stabiliser content is accompanied by decreasing wet-gel strength. This is in good agreement with the observation made

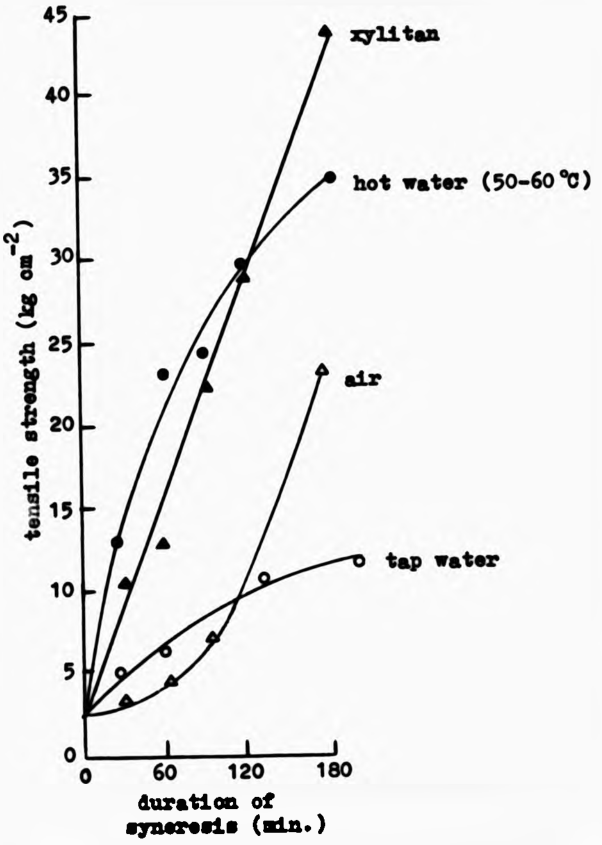


Figure 2.1 Tensile strength of wet gels prepared from Qualitex latex subjected to syneresis in various media in relation to the duration of the process (2)

by Voyutskii *et al.* (8). The most likely reason for the observed effect is thought to be that the absorbed soap molecules affect the ability of latex particles to coalesce.

Shepelev *et al.* (7) have shown that the wet gels obtained from latices containing ammonium fatty-acid salts as stabiliser have relatively high tensile strength and modulus but low elongation at break. On the other hand, the gels prepared from latices containing a sulphonate-type stabiliser (Nekal) are characterised by low tensile strength and modulus and a high elongation at break. Medalia *et al.* (1) have found that the addition of a non-ionic soap such as an alkyl phenoxypolyoxyethylene ethanol (Igepal CA-633) to a large-particle latex causes a reduction in the wet-gel strength. Medalia *et al.* (1) have also found that the wet-gel strength of latex gels prepared from a butadiene-based copolymer latex are far inferior to those prepared from NR latex. Neoprene Types 571 and 735 are intermediate between these two extremes, whilst Neoprene Type 572 gives slightly higher wet-gel strength than does the NR latex. The higher wet-gel strength of Neoprene Type 572 is thought to be a consequence of a greater crystallinity.

The degree of prevulcanisation of latex particles has a considerable effect upon the properties of wet gels derived from the latex. Medalia *et al.* (1) have shown that the tensile strength and elongation at break of latex gels from prevulcanised NR latex are considerably lower than are those from the NR latex from which the prevulcanised latex was prepared. Both the wet-gel strength and the elongation at break decrease with increasing degree of vulcanisation. This is thought to be a consequence of the rubber within each polymer particle becoming more crosslinked, thus discouraging interparticle coalescence.

The mechanical properties of wet gels are also affected by the degree of drying of the deposit (1). It was found that the wet-gel strength of NR latex gel is about 7% of that of dry film, and for gels from butadiene-based copolymer latices and nitriles latices the ratio is about 12%. Shukri (4) found that the tensile strength of the wet-gel is approximately 10% that of the dry film.

Shukri (4) has found a linear relationship between the TSC of the gel and the TSC of the latex from which it was obtained. He showed that the wet-gel strength increases with increasing gel TSC. This was explained by assuming the TSC of the gel to be an approximate measure of the area of particle contacts within the gel. The higher is the TSC of gel, the higher is the number and area of particles in contact with each other, and thus the greater is the tensile strength of the gel.

2.1.5 Factors affecting mechanical properties of dry latex deposits

Systematic studies have been carried out on the influence of salt coagulants on the properties of dry latex deposits obtained by the dipping process (11,14-19). In general, it has been concluded that the coagulating agents have a deleterious effect upon the properties of rubber films. Thorsrud (11) examined the effect of the cation and the anion of salts. The anions were added in the form of ammonium salts, and the cations were introduced in the form of salts of a strong acid or in the form of an acetate. He observed that the tensile strength decreases with the addition of salts. The decrease in tensile strength becomes more pronounced as the content of salt is increased. The effect is greater for the coagulant salts than for the ammonium salts. The results generally agreed with those of other workers (14-19).

The effect of ageing of polychloroprene latex upon the mechanical properties of the vulcanisates obtained by coagulant dipping has also been reported (10). It was found that the tensile strength and elongation at break decrease, whilst the modulus increases. The tensile strength and elongation at break of polychloroprene rubber films have been found to decrease with increase in the soap content (8). This is attributed to the increased degree of coverage of the particle surface by the stabiliser, thus discouraging interparticle coalescence.

In addition, the mechanical properties of dry latex deposits appear to be affected by the type of contained polymer (1,12), the degree of shrinkage upon drying or stretching (7,12), the degree of maturation of the latex (13), the degree of prevulcanisation of the latex (1, 20 to 24), and the thickness of the deposit (7).

Much of the above work is not strictly related to the present study, and therefore only the more relevant work has been discussed. In the view of the author, although one may be aware of the principal underlying differences between the mechanical properties of a latex deposit in its wet and dry states, and also of the effects of certain variables upon such properties, very little attention has been paid to gaining an insight into the resulting physical properties. It has therefore to be concluded that the subject is but poorly understood at present.

2.1.6 Structure of latex gels

By means of electron microscopy, it has been possible to study the structure of the surface of latex gels, which are partially or completely dry (25-28). However, no published reports have been found which describe the internal structure of latex gels. Guzman (27) has attempted to develop a simplified mathematical model which would give some representation of the structure of the gel in relation to its strength. In its simplest form, the model comprises a cubic lattice whose edges consisted of struts, each one of which is regarded as formed by a succession of spherical rubber particles. He found that the stronger the gel, the tighter was the network of the rubber particles. However, the model was not able to predict the experimental results satisfactorily.

Some workers (28) have examined the surface structure of coagulant-dipped wet gels by replication with gelatin. The transmission electron microscopy revealed a highly fissured structure in which all primary particles have aggregated into agglomerates 1 to 10 μm in diameter, and these in turn are partially separated by fissures. When these gels were leached for short periods, the small fissures disappeared and the large fissures increased in size. However, a prolonged period of leaching caused the disappearance of most of fissures, thus increasing coalescence in the gel.

2.1.7. Structure of dry latex films from prevulcanised NR latex

A film cast from NR latex is coherent and possesses a tensile strength which is appreciably lower than that obtained by drying down prevulcanised NR latex. However, since the former is not strictly related to this study, only the latter will be discussed further. There are three theories which have been proposed to explain the strength of films from prevulcanised NR latex. In the first theory, the strength is attributed to primary valence bonds between the particles. These bonds are presumed to be formed during the drying of a latex film because other evidence proves that intraparticle bonds are formed during the prevulcanisation reaction. However, it is found that the strong coherent films are still formed even when films are produced under conditions which are most unlikely to cause the formation of crosslinks between particles, thus proving the invalidity of the theory. The second theory regards the film as made up of discrete particles of vulcanised rubber cemented together by means of non-rubber constituents derived from the initial latex. Thus, removal of the non-rubber constituents should cause the film to disintegrate. Humphreys and Wake (29) have shown that the presence of the non-rubber constituents contributes very little to the strength of the film. Thus, this theory fails to explain the strength and the coherent nature of prevulcanised NR latex.

The third theory seeks to explain the strength of films in terms of secondary valence bonds formed between the molecules of adjacent rubber particles. Each particle contains a large number of individual rubber molecules which are arranged in a tangled, haphazard manner. During the vulcanisation reaction, all the molecules of any one particle become linked to one another, so that the particle itself becomes as one giant molecular network. Although the secondary valence bonds set up between any two molecules of adjacent particles are very weak, the totality of such forces between two given particles becomes appreciable as each particle contains a large number of individual primary rubber molecules. This third theory is regarded as the most convincing, since it explains some aspects of the behaviour of prevulcanised films. For example, the theory offers an explanation for the physical properties of a prevulcanised film. Blackley (30) explained the tensile stress-strain behaviour of films dried down from both unvulcanised and prevulcanised NR latex. His explanation is based on the proposal that when a latex film is dried down, the particles cohere together to give regions of overlap between the particles. In these regions of overlap, secondary valence bonds between the rubber molecules of different particles are formed. Thus when a film is subjected to a tensile stress, the initial extension leads to a rearrangement of the molecules in the region of overlap between the particles. At this stage, the stress-strain curve of prevulcanised latex films resemble the stress-strain curve of unvulcanised latex films. As a further stress is applied, the molecules in the regions of overlap are not able to move independently of one another because they are attached to large number of other molecules by means of crosslinks. Hence, in order to separate the particles, it is now necessary to overcome at the same time, the secondary valence bonds which have formed between a large number of molecules. Merrill (32) and Loh (31) have found the interpretation of the tensile stress-strain results for dried films obtained from prevulcanised NR latex to be consistent with the secondary valence theory.

2.2 Factors affecting drying of NR latex films

2.2.1 Introduction

Although considerable effort has been expended (33) in understanding the mechanism of latex film formation, very little work has been carried out on the rate of drying of dipped films. Most of the work on the subject of the rate of drying of latex films has been carried out within the last decade. Some of the more important work on drying is described below.

2.2.2 Development of techniques for investigating the rate of drying of latex films

Sheetz (34) determined the rate of water evaporation gravimetrically by saturating blotting paper with latex and weighing at regular intervals. Willhoit (35) followed rate of evaporation of water by using the general Electric Inframike Moisture Meter. De La Court (36) devised a method whereby he measured the light passing through the film and reflected from the underlying substrate to determine the point and extent of coalescence. Mahr (37) and Bertha and Ikeda (38) described the use of thermogravimetric analysis and differential scanning calorimetry to study the rate of drying of films. Vanderhoff (39) described a method which involves the direct drying of cast films. He used gravimetric analysis, but without the blotting paper technique used by Sheetz (34). More recently, Gazeley and Swinyard (40) studied the drying rates of NR latex films under controlled conditions of drying as regards variables such as temperature and humidity.

2.2.3 Mechanisms of film formation

Industrially, the phenomenon of the formation of continuous films by the evaporation of water from a dipped latex article is of considerable practical importance. However, the elucidation of the mechanisms in explaining all the observations for this phenomenon has not been very satisfactory. In the process of the formation of continuous films from latices, deformed spheres become held together by physical forces. Dillon et al. (41) proposed that after the evaporation of water, the particles fuse together by virtue of the forces arising from the polymer-air interfacial tension and are thus surface-tension forces. Sheetz (34) referred to this as the dry-sintering mechanism. He objected to it on the grounds that it showed inconsistency with the observation that film formation and water evaporation are inseparable events. Brown (42) stated that it is the capillary forces which arise from the water-air interfacial tension that are responsible for the coalescence of the film. He proposed the capillary theory, which is based upon the hypothesis that when the water loss is appreciable, the repulsive forces become small compared with the attractive forces, thus causing flocculation.

Based on Brown's assumption, Sheetz (34) pointed out that when the flocculation occurs, the surface spheres commence emerging from the liquid. As a consequence, they are subjected to capillarity compression forces due to the water-air interface. He suggested that these compression forces compress the matrix of particles under the surface, thus causing the deformation of the individual interior particles and/or the compaction of the matrix of spheres. By such mechanisms the water can be exuded to the surface, thus allowing the surface layer of particles to remain at least half immersed.

Vanderhoff et al. (39) examined the process of coalescence of the flocculated particles while immersed in water. Theoretically, he showed that the driving force is the free energy of the polymer-water interface.

Sheetz (34) analysed the contributions made, the mechanisms proposed by Dillon et al. (41) (exclusively all surface-tension forces), Brown (42) (exclusively capillary forces), and Vanderhoff et al. (39) (both types of forces), to the film-formation process. He proposed a new theory, the essential features of which are that:

(i) the energy required for film formation is the heat of the surroundings which is converted to useful work by evaporation of water.
(ii) an important contribution to the mechanism is that the evaporation of water does useful work by encouraging the diffusion of water through the polymer particles.

The contributions from capillary forces and the wet-sintering mechanism to the film-forming process are found to be of greatest importance during the first-half stage of the particle coalescence process.

Schuller (43) and Sukhareva et al. (44) showed that the resistivity of latex increases sharply at the point of coalescence of the particles. Voyutskii (45) claimed that the physical forces alone could not account for the physical properties displayed by latex films of polymers whose glass-transition temperatures are below the ambient drying temperature. Alternatively, he postulated a mechanism whereby the mutual interdiffusion of free polymer chain ends across the particle-particle interfaces makes the film more homogeneous and improves its physical properties. He referred to this as the autohesion mechanism. This concept of autohesion (46) is consistent with the further gradual coalescence (47) that occurs upon ageing in dry latex films of polymers whose glass-transition temperatures are below the ambient drying temperature.

Vanderhoff (39) proposed that the evaporation of water from a latex film occurs in three stages:

1. The first stage involves the evaporation of the water from the surface of the film. The particles move about with their characteristic Brownian motion. During this stage, the rate of water loss is linear with time, and is the same as that of pure water. This stage ends at the polymer volume fraction of about 0.60 to 0.75 when

the particles are forced into irreversible contact by water-air interfacial tension.

2. The intermediate stage begins after the particles come into irreversible contact. Then the combined interfacial tensions of the water-air and water-polymer surfaces cause coalescence of particles. The decreasing water-air interfacial area results in a rapid reduction in the rate of evaporation of water to 5 to 10% of the initial value.
3. The final stage is one in which water escapes from the film by diffusion through capillary channels or through the polymer itself. The water evaporation rate is low and decreases exponentially.

Gazeley and Swinyard (40) investigated the drying effects in unvulcanised and prevulcanised NR latex films. They concluded that films from prevulcanised latex dry more rapidly than do unvulcanised films in later stages of drying, under similar conditions (Figure 2.2). According to the mechanisms discussed by Vanderhoff (39), it would be anticipated that the first-stage drying rates for unvulcanised and prevulcanised films would be similar. However, under good drying conditions, e.g., high temperature, it is likely that water will evaporate from the surface faster than it can be transported through the bulk of the film. This causes coalescence of the rubber particles in the surface layer, thus resulting in a degree of diffusion control at the early stage. By the same argument, the slower coalescence of prevulcanised particles would result in faster drying rates than for unvulcanised films.

Gazeley and Swinyard (40) also studied the drying rates of cast films and coagulant-dipped gels, and found that there was no significant difference between the two. This led to the suggestion that, in the early stages of drying of films, the contribution of free Brownian motion of the rubber particles is not significant. This is because the Brownian motion is non-existent in gelled films.

Based on their observations, the first stage of drying is attributed to the passage of water through the gel, i.e., through the capillary network formed by partial coalescence of rubber particles, at the rate equivalent to its removal from the surface. Loss of water by evaporation allows further coalescence with a reduction in the size of the capillary

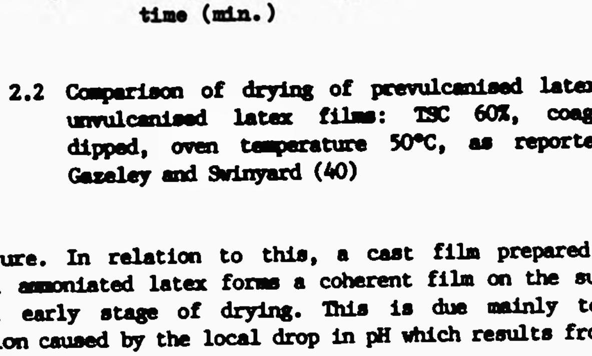


Figure 2.2 Comparison of drying of prevulcanised latex and unvulcanised latex films: TSC 60%, coagulant dipped, oven temperature 50°C, as reported by Gazeley and Swinyard (40)

structure. In relation to this, a cast film prepared from normal ammoniated latex forms a coherent film on the surface at an early stage of drying. This is due mainly to the gelation caused by the local drop in pH which results from the loss of ammonia at the surface.

Hansen (48) investigated the mechanism of the evaporation of water and solvent from latex paint films. He concluded that the rate of loss of solvent is controlled by surface factors rather than by diffusion, even at long evaporation times. Andrews (49) examined the influence of ethylene and propylene glycols on the drying characteristics of latex paints, under five different environmental conditions. He found that the paints containing ethylene glycol were more hygroscopic than those containing propylene glycol, and that paints containing ethylene glycol exhibited slower overall drying rates compared to the corresponding paints containing propylene glycol. Sullivan (50) investigated the evaporation of both water and solvent from latex and latex paint films. Evaporation of volatiles from latex coatings prior to film formation was found to be controlled by surface factors. The evaporation of volatiles after film formation in some cases was not diffusion controlled, depending upon the solvent involved and the interactions between different volatile materials.

2.3 Colloid stability of latex

2.3.1 Introduction

One of the most important properties of a latex is its colloid stability. The colloid stability of a latex is largely determined by the electrostatic charge on the latex particles (51.57), the degree of hydration (51,54), the steric effect of adsorbed macromolecules or polymers (52,53) and/or the free polymer in the dispersion medium (depletion stabilisation) (55,56). NR latex is known to vary in both the mechanical and chemical aspects of colloid stability.

2.3.2. Mechanical stability of NR latex

The mechanical stability of a latex is defined as its resistance to destabilisation by mechanical agitation or shear forces. This characteristic is of great practical importance whenever latex is handled. During concentration, in pumping and transportation, and in compounding and processing, mechanical forces are applied, and the possibility of destabilisation exists. The measurement and control of mechanical stability is therefore of considerable importance to both producers and consumers of latex.

It has been reported that the mechanical stability of NR latex is affected by the concentration (67) and types of added soaps (52,68-73), the concentration and types of added alkalis (72,74,75), the TSC of latex (68,74,75,81,82), and the addition of alcohols (67,68). It has also been found that the mechanical stability of NR latex is very dependent upon the test variables such as stirrer speed and temperature (74). Some of the investigations referred to above are not strictly related to this study, and therefore only the more relevant work will be discussed further.

2.3.2.1 Effect of added fatty-acid soaps

It is well known (68,76) that the mechanical stability of NR latex is greatly enhanced by the addition of small amounts of fatty-acid soaps. The efficacy of fatty-acid soaps in enhancing the mechanical stability of NR latex is believed to be due to their adsorption at the latex particle interface and the consequent increase in particle charge and repulsive potential. However, the change in the physical nature of the adsorbed soap may be more important in some cases. It is not certain whether the adsorption of soaps occurs at vacant sites on the particle surface or by displacement of naturally-occurring protein or soaps. It has been demonstrated, however, that displacement of proteins by soap can occur in NR latex (77), and that proteins (e.g., casein) are relatively poor mechanical stabilisers in comparison with fatty-acid soaps (78). For these reasons it is probable that displacement of proteins by added soaps is the most likely explanation.

Madge *et al.* (68) found that the addition of as little as 1.26x10^{-3} mole of potassium laurate per 100g latex solids caused an approximately 12-fold increase in mechanical stability. Cockbain and Philpott (52) also showed that the mechanical stability of latex was approximately doubled by the addition of as little as 1.0x10^{-4} mole of potassium decanoate per 100g latex solids. Blackley *et al.* (69) proposed that the large enhancement of mechanical stability of NR latex brought about by very small additions of fatty-acid soaps such as potassium laurate is primarily due to a more efficient utilisation of the indigenous anions at the rubber-aqueous interface. The indigenous soap anions, having long alkyl chains, become strongly adsorbed at the rubber-aqueous interface and may tend to cohere in clusters. The coherence in clusters of the adsorbed fatty-acid anions may reduce their efficiency as enhancers of mechanical stability. It was postulated that when two particles approached one another, the clusters were readily repelled away from the regions of impending contact. Since, the probability of such clusters returning to the regions of contact was low, the repulsive forces between these particles were less than those between particles stabilised by fatty-acid anions which were gaseous in nature at the rubber-aqueous interface. It was suggested that the alkyl chain of the added laurate anions was sufficiently long for the soap anions to be strongly adsorbed at the rubber-aqueous interface, but sufficiently short to disrupt the coherence of the clusters of indigenous adsorbed soap anions. Thus, the efficiency of these soaps in enhancing mechanical stability was seen as a consequencey of strong adsorption tendency combined with efficiency in reducing the coherence of clusters of indigenous fatty-acid anions.

Blackley *et al*. (69) also showed that the mechanical stability passes through a maximum as the alkyl chain length of the potassium saturated fatty-acid soap is increased. The relative effectivenesses for the higher fatty-acid soaps were observed to be in the following order:

laurate > myristate > palmitate >stearate

This is in good agreement with the observations made by Cockbain and Philpott (52). Again, the results were explained in terms of the adsorption behaviour of the added soap and its effect upon the physical nature of the adsorbed layer of soap anions (69). Addition of soap anions of sufficiently short alkyl chain length or long alkyl chain length, causes a decrease in the mechanical stability. The former are not strongly adsorbed and the latter are relatively ineffective in reducing the coherence of the clusters of indigenous adsorbed soap anions. However, addition of soap anions of an intermediate alkyl chain length are strongly adsorbed and also show a marked tendency to disrupt the coherence of the clusters of indigenous adsorbed soap anions, thereby causing a pronounced increase in mechanical stability.

Blackley and Azas (70) have investigated the effect of various added potassium C_{18} carboxylate soaps, namely, stearate, oleate, elaidate, linoleate, 1,2-hydroxystearate, 9,10-dihydroxystearate and ricinoleate upon the mechanical stability of NR latex. The effects observed when potassium C_{18} carboxylate soaps are added to NR latex are consistent with the hypothesis put forward previously (69) to explain the effects of added potassium n-alkanoates. All the C_{18} soaps investigated were found to increase the mechanical stability. The magnitude of the effect depends on the nature of the hydrophobe chain of the soap. The increase in mechanical stability can be satisfactorily accounted for by the hypothesis that the added soap is adsorbed at the rubber-aqueous interface and thereby modifies the mechanical properties of the adsorbed indigenous anions.

Gorton and Pendle (67) reported the effect of added fatty-acid soaps upon the mechanical stability of NR latex. They showed that there is little difference in the stabilising power of sodium and potassium salts of given fatty acids, but the ammonium salts are generally less effective. Blackley and Haynes (71) showed that the ability of a laurate soap to enhance the mechanical stability of NR latex depends upon the counter-ion of the soap. The order of increasing effectiveness appears to be:

ammonium < lithium < sodium < potassium

More recently, Tan (73) confirmed the two findings which have been reported by previous workers (52,68,69). They are:

(i) A large enhancement of the mechanical stability of NR latex can be brought about by small additions of potassium fatty-acid soaps (up to $4x10^{-4}$ mole per 100g latex solids).
(ii) The effectiveness of potassium fatty-acid soaps in enhancing the mechanical stability of the latex depends upon the chain length of its alkyl group.

2.3.2.2 Effect of added alkalis

In compounding NR latex, particularly for the production of dipped goods, a fixed proportion of alkali, e.g., potassium hydroxide, is normally added. Addition of these alkalis have the effect of maintaining latex pH at adequate levels despite losses of ammonia by evaporation and of reducing the rate of skin formation at the surface of the compounding latex. These alkalis also have the effect of increasing the mechanical stability (67,72-75).

Dawson (74) studied the effect of ammonia content upon the mechanical stability of concentrated NR latex. He used various concentrations of ammonia ranging from 0.1 to 1.2% on the aqueous medium. It was reported that at concentrations of ammonia less than 0.4%, the mechanical stability decreased rapidly with decreasing ammonia concentrations. At concentrations of ammonia greater than 0.4%, the mechanical stability increased slightly with increasing ammonia concentrations. Loha (72) determined the mechanical stability of a series of NR latex samples having various ammonia contents. He varied the ammonia content both by deammoniation by aeration and by the addition of aqueous ammonia (1%) to the original latex. He showed that progressive deammoniation was accompanied by a decrease in the mechanical stability of the latex. The mechanical stability was found to increase with increasing ammonia content. Above a certain ammonia content (ca. 0.5% on the whole latex), the mechanical stability was relatively constant when further ammonia was added. It was suggested that at low ammonia content, and therefore at low pH, the fatty-acid soaps in the latex were partially converted to free fatty acids, thus lowering the mechanical stability. Tan (73) confirmed these findings. However, he speculated that the increase in mechanical stability which accompanies increasing ammonia content (i.e., at high pH) may be a consequence not only of the ionisation of higher fatty-acid soap, but also of an effect upon the hydration layer surrounding the rubber particles.

Minoura (75) investigated the effect of ammonium, sodium, potassium and calcium hydroxides upon the mechanical stability of ammoniated NR latex. He showed that progressive additions of ammonium hydroxide are accompanied by an increase in mechanical stability until a certain concentration is attained, above which the mechanical stability is not significantly affected by further increase in concentration of ammonia. Progressive additions of potassium hydroxide and sodium hydroxide cause a sharp initial increase in mechanical stability, followed by a rapid decrease to very low values with further additions. The point at which the mechanical stability begins to decrease corresponds approximately to the potassium hydroxide number of the latex, but is lower for sodium hydroxide than for potassium hydroxide. Additions of calcium hydroxide are found to be accompanied by a very sharp fall in the mechanical stability. The initial increase in mechanical stability was explained as a consequence of the reaction of alkalis with the indigenous fatty acids in the latex to form soaps, which acted as stabilisers. The decrease in mechanical stability with further additions of potassium and sodium hydroxides was attributed to the common-ion effect. By this was meant that the ionic dissociation of potassium and sodium salts of fatty acids decreased due to the potassium hydroxide and sodium hydroxide being the strong bases. In comparison, however, since ammonium hydroxide is a weak base and is not completely ionised at high concentrations and therefore does not function as a strong electrolyte, there is no decrease in the mechanical stability. In the case of calcium hydroxide, the calcium ions are believed to have reacted with the adsorbed fatty-acid anions to form a soap which then precipitated out. Consequently, the charge on the latex particles was reduced, thus causing a decrease in the mechanical stability. Minoura (75) also found that there is a linear relationship between the logarithm of the mechanical stability time and the molar concentration of added alkalis.

Gorton and Pendle (67) also studied the effect of alkalis upon the mechanical stability of ammoniated NR latex. Their observations are in accordance with those of Minoura. However, they explained that the initial increase in the mechanical stability at low levels of added strong alkali was a consequence of suppression of the ionisation of ammonium salts, that is to say, the concentration of ammonium ions is reduced and the ammonium soaps are replaced by the corresponding potassium or sodium soaps. The sharp loss of stability that occurs at the higher levels of addition of sodium hydroxide and potassium hydroxide may be due to the high ionic strength of the aqueous phase at those levels. Loha (72) failed to prove that the reduction in mechanical stability brought about by excess potassium hydroxide can be explained on the basis of ionic strength alone. He found that the mechanical stability can be drastically reduced without, apparently, greatly affecting the charge on the particles. He suggested that the additional factor responsible for the reduction in mechanical stability in the presence of excess potassium hydroxide is that it probably interferes with the ability of the electric charges to promote hydration of the particles. Tan (73) also investigated the effect of sodium hydroxide and potassium hydroxide upon the mechanical stability of ammoniated NR latex. His findings are in accordance with these observations.

2.3.2.3 Effect of added electrolytes

It is well-known that the stability of latex can be profoundly reduced by the addition of electrolytes. This may be a consequence of:

(i) increased ionic strength of the aqueous medium, resulting in the compression of the diffuse double layer surrounding the particles;

(ii) reduction in the Stern potential due to the increased adsorption of cations into the Stern layer;

(iii) chemical reaction between the cation of the electrolyte and the fatty-acid anions adsorbed at the surface of the rubber particles.

According to the Deryagin and Landau (79) and Verwey and Overbeek (80) theory of the stability of lyophobic colloids, any of these mechanisms will reduce the potential energy barrier to flocculation. Thus, the colloid destabilisation of the latex occurs more easily.

The effect of added electrolyte upon the mechanical stability of NR latex has been reported by several workers (52,67,72,73). Cockbain and Philpott (52) studied the effect of addition of potassium chloride upon the mechanical stability of NR latex. On adding potassium chloride, the mechanical stability was found to be decreased. This phenomenon was explained as arising from a reduction both in the Stern potential and in the thickness of electric double layer surrounding the rubber particles.

Loha (72) investigated the effect of monovalent, divalent and trivalent metal chlorides upon the mechanical stability of ammonia-preserved NR latex. In all cases, the mechanical stability was found to decrease progressively with an increase in concentration of metal chloride. In the case of the monovalent metal chlorides, on a molal basis of addition, lithium chloride caused a much greater reduction of mechanical stability than did either sodium chloride or potassium chloride. This was explained as being possibly due to the low solubility of the lithium salts of long-chain fatty acids. Loha (72) also showed that the addition of divalent metal chlorides caused a more severe effect in reducing mechanical stability than did any of the monovalent metal chlorides. The order of increasing effectiveness of the ions appeared to be:

beryllium < magnesium ≈ zinc < cadmium < barium ≈ calcium

The reaction of divalent metal ions with adsorbed fatty-acid anions to form insoluble salts may be partly responsible for the rapid reduction in mechanical stability. In comparison, however, the effect of aluminium chloride upon mechanical stability was found to be less drastic than that of the divalent metal chlorides. This is rather surprising at first, and may be explained by extensive hydration of aluminium ions in aqueous solution.

A recent review of the mechanical stability of NR latex by Gorton and Pendle (67) reports that there is a rapid reduction in the mechanical stability of NR latex with an increase in ammonium acetate concentration. This may be attributed to the corresponding increase in the ionic strength of the aqueous phase, and the resultant compression of the electrical double layers surrounding the rubber particles.

More recently, Tan (73) examined the effect of potassium chloride, potassium sulphate and magnesium chloride upon the mechanical stability of ammonia-preserved NR latex. His findings are in good agreement with previous observations by other workers (52,72). He showed that magnesium chloride has a more severe effect in reducing mechanical stability than does either potassium chloride or potassium sulphate. It was suggested that the reduction in mechanical stability brought about by magnesium chloride is undoubtedly greater than can be explained on the basis of ionic strength alone. He postulated that the interaction between the added magnesium ions and the higher fatty acids, thereby forming insoluble magnesium salts, may be responsible for the sharp fall in mechanical stability.

2.3.3 Chemical stability of NR latex

The chemical stability of a latex is defined as the ability of a latex to withstand the coagulating or flocculating effects of added substances. For most anionic latices, such substances include acids, metallic ions, polymer miscible organic solvents and cationic surface active-agents. According to Blackley (58), the concept of chemical stability is loose and ill-defined, but is nevertheless very important in connection with the practical application of latices. Generally speaking, a latex must be sufficiently stable towards chemicals for it be able to tolerate the addition of various substances during the compounding stage, but not so stable as to withstand the coacervative influences which may be brought to bear upon it, for example, during a dipping process. Preserving the balance between too high and too low stability constitutes a major challenge in latex technology.

The variability in chemical stability, which has important implication for processibility, is much greater than the variability in mechanical stability. This is believed to be due, in part at least, to the unpredictability of interactions between NR latex and zinc oxide or between NR latex and zinc ions (59-61). It is known that dissolved zinc is capable of precipitating some of the naturally-occurring stabilisers, principally fatty-acid soaps, and that this reduces colloid stability (62-66). If the fatty-acid soap content, as regards composition as well as amount, of latices was markedly variable, then this could account for variations in processibility.

The possibility of predicting the processibility of NR latex by a single chemical stability test, namely, one involving destabilisation of latex by the zinc ammine system, has been studied by many workers (78,83-85). Amongst the early proposals, the methods preferred fall into three classes:

(1) measurement of mechanical stability of NR latex compounded with either zinc oxide or zinc acetate with or without addition of surfactant (64,86);
(2) determination of viscosity change with time, in the presence of zinc oxide (64,86,87); and
(3) determination of gelation time at elevated temperature in the presence of zinc acetate (88,89).

The destabilisation of latex by the zinc ammine system is normally thought to require the presence of a source of zinc ions, ammonium ions, free ammonia and a latex which is stabilised by adsorbed anions which are capable of forming insoluble zinc salts. The cause of destabilisation of latex has been studied in detail by Nithi-Uthai (90). The following equilibria are probably established in a model system which comprises zinc oxide/aqueous ammonia/ ammonium salt:

$$ZnO + H_2O \longrightarrow Zn(OH)_2$$

$$Zn(OH)_2 \rightleftharpoons Zn^{++} + 2OH^-$$

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

$$Zn^{++} + nNH_3 \rightleftharpoons Zn(NH_3)_n{}^{++}$$

$$Zn(NH_3)_n^{++} + 2RCOO^- \longrightarrow [Zn(NH_3)_n^{++}]\ [RCOO^-]_2 \downarrow$$

insoluble zinc salt
precipitated in the
surface of particles causes
destabilisation of latex

Thus, the processibility of compounded NR latex, i.e., NR latex which contains vulcanisation ingredients, protective agents, stabilisers and fillers, is determined by the reactions of solubilised zinc in the compound (91). Its control may be affected in several ways as follows:

1. Removal of zinc oxide: This eliminates the source of destabilising influences, but, this is not feasible since zinc oxide is required for vulcanisation of latex. However, alternatives to zinc oxide have been proposed which, although containing zinc, appear to be less active in promoting colloid destabilisation. A recent compound of this type is a zinc ammine isocyanurate.

2(a) Reduction in free ammonia: The free ammonia has two opposing effects. On the one hand, it encourages the formation of zinc ammine complexes, thereby causing the coagulation of latex. On the other hand, it increases the formation of tetrammine complexes if present in excess. The zinc tri- and tetra-ammine complexes are less effective in destabilising the latex than are the lower ammine complexes (92). Thus, the stability of the latex is increased. It appears, therefore, that reduction in ammonia content causes a reduction in the destabilisation of latex by reducing the formation of zinc ammine complexes.

(b) Reduction in ammonia ions: The increase in destabilisation by ammonium ions is a consequence of two effects. Firstly, the ammonium salts have a direct effect by increasing the ionic strength of the latex. The increase in ionic strength tends to compress the electrical double layer which is associated with the rubber-serum interface. As a consequence, the colloid stability of the latex is reduced. Secondly, according to the model zinc oxide/ammonia/ammonium salt system shown above, the introduction of ammonium salts suppresses the concentration of hydroxyl ions and hence increases the initial concentration of zinc ions with a subsequent increase in the concentration of zinc ammine complexes. Thus, a reduction in ammonium salts hinders not only the formation of zinc ammine complexes but also reduces the ionic strength of the aqueous serum.

3. Addition of fixed alkalis: Additions of fixed alkalis (i.e., hydroxyl ions) increase the ratio of $[NH_3]$ to $[NH_4^+]$. Thus the formation of zinc ammine complexes is reduced. The alkalis may also interfere with the zinc soap formation and solubility, as well as suppressing the initial zinc ion concentration by common-ion effect.
4. Addition of surfactants: The addition of appropriate surfactants increases the colloidal stability in the presence of zinc ammine ions.

Additional factors which influence the solubility of zinc oxide in NR latex are probably the non-rubber serum constituents. Wechsberg (93) showed that the concentrations of mono- and di-carboxylic acids (glycine and aspartic acid) may be the other variables which control the solubility of zinc oxide in NR latex.

The volatile fatty acids present in ammonia-preserved latex as their ammonium salts reduce the chemical stability. This may be attributed to the increase in ionic strength of the aqueous phase, and hence a reduction in the thickness of the electrical double layer surrounding the particles. Also, the ammonium ion concentration increases with the VFA No. and presumably this has an effect. It is also possible that there may be a specific effect of the acetate anions, since Nithi-Uthai (90) has shown that acetate anions have a greater destabilising effect in latices containing zinc oxide than do many other anions.

Nithi-Uthai (90) examined the effect of added soaps upon the stability of NR latex which contained zinc oxide. He found that, for a given homologous series, the addition of potassium laurate to NR latex containing zinc oxide gave the most unstable latex. An explanation of the minimum stability of latex stabilised with laurate soap, has been given by considering the overall effect of the following factors:

1. Extent of soap adsorption on latex particles: The longer is the chain length of the fatty-acid soap, the greater

is the tendency for it to become adsorbed onto the surface of rubber particles, and hence the higher is the increase of surface potential. Thus, for a given homologous series, latex stabilised with potassium stearate is expected to be the most stable, and latex stabilised with potassium hexanoate to be the least stable.

2. Modification of Hamaker constant of latex particles: It can be shown that the Hamaker constant of fatty-acids increases with increasing chain length. Thus, latex stabilised by stearate soap has a greater attractive interparticle potential energy than does latex stabilised by laurate soap or by fatty-acid soaps of shorter chain length. Consequently, the stearate-stabilised latex is expected to be the most stable and the hexanoate-stabilised latex to be the least stable.
3. Reactivity of soap towards zinc ammine ions: In the presence of zinc ammine complexes, adsorbed soap has the possibility of reacting with the zinc ammine ions. It has been shown (65) that soaps with longer chain lengths are more reactive towards zinc ammine ions than are soaps with shorter chain lengths. Thus the stearate-stabilised latex has higher reactivity towards zinc ammine ions. This reduces the concentration of adsorbed soap molecules on the surface of the latex particles and hence lowers the Stern potential. For this reason, the stearate soaps are more effective in enhancing the zinc-ammine destabilisation of latex than are the hexanoate soaps.

It thus appears that the effect of added soap upon the colloid stability of NR latex containing zinc oxide is due to the operation of all three factors.

Nithi-Uthai (90) also investigated the effect of concentration of added soap upon the colloid stability of latex which contained zinc oxide. He reported that, at low soap concentration, the addition of soap increases the stability of latex towards zinc ammine ions. At high soap concentration, the added soap reduces the stability of NR latex containing zinc oxide. This phenomenon was explained by the extent of adsorption of soap on to the latex particles, as described above.

Gorton and Pendle (60) have reported a study of the physical and chemical properties of samples of mature commercial high-ammonia NR latex concentrate. They measured 40 properties of each of 20 latices. In many respects, the latices were found to be relatively consistent, but significant variability was found in their response to the addition of zinc ammine ions. The variability was considered to relate to the variable processing behaviour sometimes observed in user factories. However, no information was given concerning the processing characteristics of these latices.

Gorton and Pendle (60) failed to discover any strong relationship between zinc ion sensitivity and any other measured property. However, it was tentatively suggested that there was a direct relationship between adsorbed soap levels and the sensitivity to zinc salts. It appears, therefore, that the sensitivity of high-ammonia latex to zinc ions is determined by a combination of several factors the nature of which remains to be established.

CHAPTER 3 : MATERIALS, EQUIPMENT AND EXPERIMENTAL PROCEDURES

3.1 Materials

3.1.1 NR latex

The NR latex used for the bulk of the investigation was a high-ammonia latex supplied by London International Group plc, which contained 0.7% ammonia by weight. A single batch was used for each set of experiments in the programme in order to avoid batch-to-batch variations.

3.1.2 Vulcanisation ingredients

In the preliminary studies, the vulcanising ingredients used include sulphur, S, zinc diethyldithiocarbamate, ZDEC, and zinc oxide, ZnO. Velvet sulphur was supplied by Anchor Chemical Company Ltd. It was added to the latex as 33% aqueous dispersion prepared by ball-milling. The formulation for this dispersion is shown in Table 3.1.

Table 3.1 Formulation for preparation of 33% aqueous dispersion of sulphur

	parts by weight
sulphur	33
Belloid TD	1
casein solution (10%)	7
distilled water	5

Zinc oxide, ZnO, and industrial-grade ZDEC, also supplied by Anchor Chemical Company Ltd., were added to the latex as 33% aqueous dispersions prepared by ball-milling. The formulation for these dispersions is shown in Table 3.2.

Table 3.2 Formulation for preparation of 33% aqueous dispersions of ZDEC and ZnO

	parts by weight
solid ingredient*	33
Belloid TD	1
casein solution (10%)	6
distilled water	60

* solid ingredient was either ZDEC or ZnO

3.1.3 Dispersing agent

The dispersing agent used was the disodium salt of a methylene di-naphthalene sulphonic acid. It was supplied by Anchor Chemical Company Ltd. as Belloid TD, and was used as received.

3.1.4 Colloid stabiliser

To improve the colloid stability, a 10% solution of lactic casein was used. This was prepared using the formulation given in Table 3.3. The powdered lactic casein, supplied by Anchor Chemical Company Ltd., was added gradually under rapid stirring to hot water containing the borax and preservative.

Table 3.3 Formulation for preparation of 10% aqueous casein solution

	parts by weight
powdered casein	10.0
borax	1.5
p-chlor-m-cresol	0.1
distilled water	88.4

3.1.5 Inorganic electrolyte

The inorganic electrolyte used was magnesium chloride. It was supplied by BDH Chemicals Ltd. and was of analytical grade. It was used as received.

3.1.6 Ammonia solution

Analar-grade ammonia solution (35%) was supplied by Koch-Light Laboratories Ltd. The ammonia solution was diluted with distilled water to appropriate concentrations, in particular 1.6%, as required in the experimental work.

3.1.7 Fatty-acid soap

A specially-pure grade of lauric acid was supplied by Fisons Ltd. It was said to have a minimum assay of 99%, and was used without further purification.

Potassium laurate was prepared by neutralising the lauric acid with potassium hydroxide. The calculated amount of lauric acid and water required to produce 10% (w/w) potassium fatty-acid soap solution were accurately weighed into a pre-weighed bottle (250-ml). The contents of the bottle were warmed to about 60°C in a thermostatically-heated water bath. Potassium hydroxide solution (56ml of 10% solution) was slowly added to the warmed fatty acid and maintained at 60°C for a further 30 minutes. The contents of the bottle were cooled to room temperature. The pH of the soap solution was ca. 10.4.

3.1.8 Nonionic stabiliser

The nonionic stabiliser used in this work was ethylene oxide-fatty alcohol condensate, which was of the form $RO(CH_2CH_2O)_iH$, where R was $C_{17}H_{35}$, and the average value of i was 10. This condensate was supplied by ABH Chemicals Ltd., and was prepared as a 10% aqueous solution. It was used without further purification.

3.1.9 Formaldehyde

Analytical-reagent grade formaldehyde, obtained from Koch-Light Laboratories Ltd., as an aqueous solution of concentration 37-40% w/v, was diluted to the required concentrations with distilled water.

3.1.10 Calcium sulphate

In the development of the calcium stability test, laboratory-grade calcium sulphate (anhydrous) supplied by Aldrich Chemicals Company Ltd. was used as various dispersions. The dispersions were prepared as follows: A known weight of calcium sulphate was weighed accurately into a 100-ml volumetric flask, and then made up to volume with distilled water.

3.1.11 Distilled water

All the distilled water used in the present investigation was obtained from an electrical still supplied by Manesty Machines Ltd.

3.1.12 Other chemicals

All other chemicals, such as acetic acid, sulphuric acid, potassium hydroxide, ammonium acetate etc., used for the investigation were general-purpose laboratory grades, and were used as received.

3.2 Equipment

3.2.1 Dipping machine

To investigate the dipping behaviour of NR latex, a Cotswald Patent Dipping Machine was used. The hydraulic fluid used in this machine was Shell Tellus Oil 27.

3.2.2 Drying cabinet

To study the processing behaviour of dipped films, it was necessary to maintain controlled drying conditions as regards temperature, humidity and rate of air flow. A drying cabinet was designed which satisfied these requirements. An illustration of the drying cabinet is shown in Figure 3.1. Principally, the drying cabinet was a rectangular-shaped cabinet, having dimensions 50x65x70cm. Five sides were made of plywood, and the front side was made of Perspex sheet.

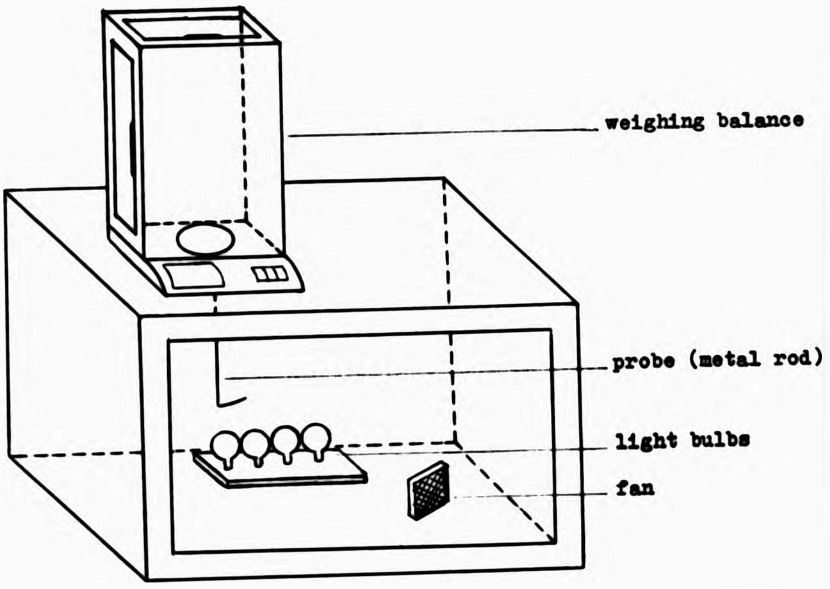


Figure 3.1 Illustration of the drying cabinet

Heat losses and gains were kept to a minimum by insulating the plywood with polystyrene foam. In doing so, the rate of heat loss from the cabinet was calculated to have reduced from 17 $Js^{-1}{\bullet}C^{-1}$ to 0.8 $Js^{-1}{\bullet}C^{-1}$. The heat input requirement was provided by means of electric light bulbs. Four light bulbs of powers 40, 60, 100 and 100 watts were located inside the cabinet. Three light bulbs were used for the purpose of raising the temperature to just below the required temperature. The different combinations of light bulbs required to produce various temperatures are given in Table 3.4. One light bulb of power 100 watts was connected to the temperature control relay, to control the temperature to exactly that required. The reason for using one of the two most powerful of the four heat sources to control the temperature to the required value is that, by so doing, the heat source remained switched off for a longer time than it remained switched on. The control circuit used to maintain the temperature at the required value is shown in Figure 3.2. Basically, the temperature transducer, in this case a thermocouple, comprises a variable temperature node and a fixed temperature node. The variable temperature node of voltage V_T is connected to the negative terminal of the comparator and the fixed reference temperature node of voltage $V_{ref.}$ is connected to the positive terminal of the comparator. The output voltage, V_O, of the comparator is driven either positive or negative depending upon which of the comparator terminals is at the greater voltage. However, since the current at the output of the comparator is insufficient to

Table 3.4 Permanent power of light bulbs required to raise the temperature of drying cabinet, such that the controlled light bulb flashes on and off at regular time intervals of approximately 30s

temperature (°C)	permanent power of light bulbs required (watts)
< 45	0
45 > 55	40
55 > 65	60
>65	100

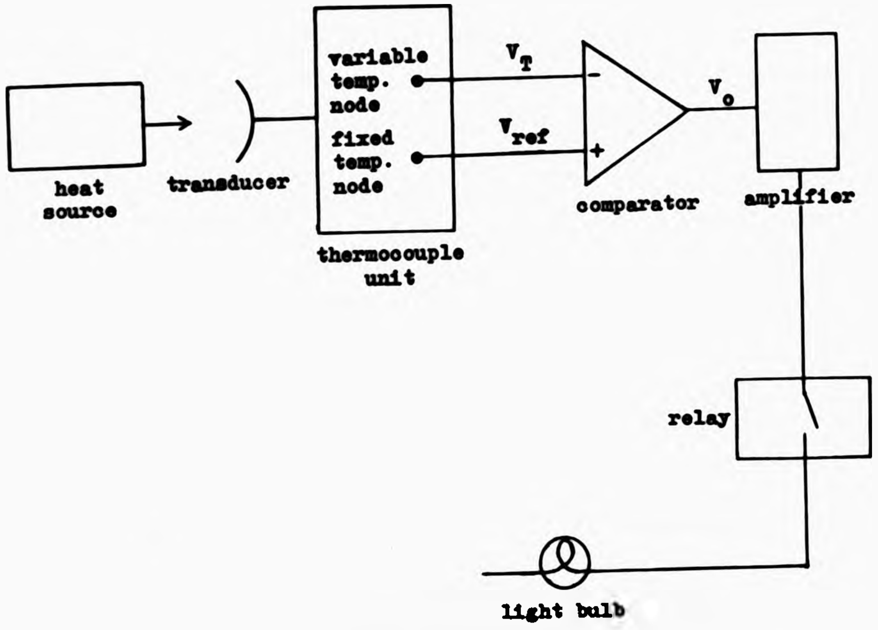


Figure 3.2 Circuit used to maintain temperature at the required value

drive the magnetic relay in series with the light bulb, i.e., to make or break the circuit, an amplifier is necessary. Thus, a negative output at the comparator will demagnetise the relay, thereby breaking the circuit and switching off the light bulb. By contrast, a positive output at the comparator will magnetise the relay, thus causing the light bulb to switch on.

Also, a fan was placed in the drying cabinet. It was positioned in such a manner that the temperature distribution in the entire cabinet was kept as uniform as possible. The difference in temperature in different regions of the cabinet was a maximum of ± 1°C. The range of temperature at any one point was ± 0.1°C. In addition, a Sartorius Model 1702 electronic weighing balance was placed above the cabinet. A metal rod, attached to the weighing arm, protruded into the cabinet, to enable samples to be weighed during the drying process (Figure 3.1).

The relative humidity of the drying cabinet was varied by introducing plates of either silica gel, to reduce the relative humidity, or water, to increase the relative humidity. In this manner, it was possible to maintain a constant value of relative humidity during the entire experimental period of 15-30 minutes. The relative humidity was measured using a horse-hair hygrometer.

3.3 Test methods for determination of latex properties

3.3.1 Basic properties of NR latex

Basic properties such as TSC, DRC, alkalinity, KOH No., VFA No. and MST were determined by the procedures specified in BS 1672:1972.

3.3.2 Determination of viscosity

The concentric-cylindrical Haake-Rotovisko viscometer was used to measure the viscosity of the latex. The instrument measures the torque which is applied to the bob (inner cylinder) as it rotates with a constant angular velocity in a fixed cylindrical cup containing the latex under investigation. The bob was inserted into the latex, which was maintained at a temperature of 25±1°C. The bob was then rotated at a constant shear rate, usually $190s^{-1}$ (speed factor, ν , is 6). The dial reading, S, was noted after 30 seconds. The latex viscosity, η , was calculated using the equation:

$$\eta = 0.271 \times \nu \times S \text{ (centipoise, cP)} \qquad (3.1)$$

The measurements were carried out in duplicate. The reproducibility was of the order of ± 0.5 units.

3.3.3 Determination of particle size

The Coulter Nano-sizer model TM was used for the determination of latex particle size. The instrument measures the average size of particles in suspension. A small quantity of latex was diluted with distilled water such that the suspension appeared slightly turbid and generally translucent. The particle size and the polydispersity were then measured using the procedure described in the instrument manual.

3.3.4 Determination of pH

The pH of the sample was measured at 25±1°C using a digital pH meter, Philips model PW 9409. The meter was equipped with a glass electrode and a calomel electrode. It was calibrated with buffer solutions having pH values of 7 and 9. The sample was conditioned at 25±1°C before measuring its pH.

3.3.5 Determination of zinc ammonium acetate viscosity (ZAAV)

NR latex was compounded according to the formulation given in Table 3.5. The latex samples, contained in 250-ml bottles, were immersed in a thermostated water bath at 25±1°C for 30 minutes to allow the thickening to occur under controlled conditions. The viscosity was then measured at a constant shear rate of $190s^{-1}$, as described in Section 3.3.2.

3.4 Development of a test for microgel content

3.4.1 Introduction

In commercial dipping plants, small amounts of microgel are observed to be formed during the dipping process. Microgel may be defined as agglomerates of two or more rubber particles to

Table 3.5 Formulation used for ZAAV test

ingredient	parts by dry weight
latex sample	100.00
potassium stearate (10%)	0.25
zinc oxide (50%)	3.50
ammonium acetate (20%)	0.60

form larger particles. At this stage, the original interface between the particles may or may not still exist.

It is not clear whether this microgel is formed during the prevulcanisation or during the actual dipping process. Although commonly observed, there are no reports in the literature as to the size of the microgel particles, their quantity or their effect on the properties of the dipped products. In fact, there have not been any published reports concerning the visualisation and determination of microgel content in NR latex. Consequently, an attempt was made to isolate and characterise these microgel particles. Since NR has a density of 920kg m^{-3}, the particles tend to rise to the surface. It is observed that the larger the particle size, the faster is the rate of rise (Figure 3.3). In order to separate the microgel particles from the remainder of the latex particles, the latex was repeatedly diluted and creamed. Repeated dilution/creaming of the microgel layer eventually lead to the reduction of the proportion of normal-size particles in the top layer. The maximum number of dilutions was three.

3.4.2 Concentration of microgel layer

About 8g of the sample was diluted with 100ml of distilled water and stabilised with small amounts (ca. 0.5g) of potassium stearate. The sample was allowed to settle for 24 hours. The top layer was then removed (ca. 10ml) and further diluted with 100ml water plus potassium stearate stabiliser. Again, the sample was allowed to settle for 24 hours, and the top layer was then removed for the study of microgel.

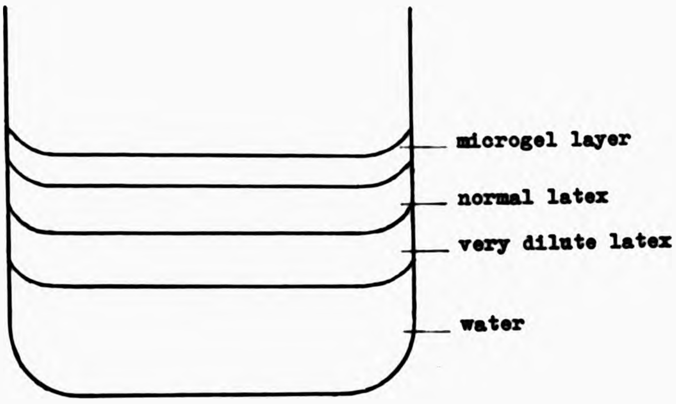


Figure 3.3 Creaming of latex for separation of microgel showing the different layers that form

3.4.3 Microscopic studies

The microgel layer was diluted by a factor of 250 with distilled water. A drop of diluted latex was placed on a microscope slide and covered with a cover slip. The slides were then examined under an optical microscope (Zeiss model 211) at a magnification of x1000 using an oil-immersion objective lens. Microphotographs were taken by the author for selected latex samples. These microphotographs were magnified 10 times using a "Projectina-optik", which allowed the particle diameter to be measured directly. A minimum of 20 particles were measured per microphotograph, and the average was taken. This gave a direct measurement of the size of the microgel particles.

3.4.4 Nano-sizer measurements

The size of the microgel particles was also measured as described in Section 3.3.3.

3.5 Calcium stability test

3.5.1 Introduction

This test was investigated primarily as a possible aid to the prediction of processing behaviour in coagulant dipping,in which, the latex particles are deposited on a former following destabilisation with calcium salts. Consequently, it was thought desirable to device a test which measured the colloid stability of latex towards calcium ions.

3.5.2 Precursor of the calcium stability test

This test is analogous to the ZAAV test. Initially, an attempt was made to device a calcium stability test in which the viscosity of NR latex was determined after the addition of various amounts of calcium sulphate dispersions of various concentrations. Various dispersions of calcium sulphate were prepared (Section 3.1.10), and added to the latex as shown in Table 3.6. For each latex sample, the viscosity was measured at various storage times, using the Haake-Rotovisko viscometer. However, there was no consistent pattern of results and therefore the process below was developed.

Table 3.6 Weights of various calcium sulphate dispersions added to latex, to investigate the effect of these dispersions upon the viscosity of ammonia-preserved NR latex

weight of calcium sulphate (g/167g latex)	calcium sulphate dispersion					
	3%	5%	6%	7%	8%	10%
0.05	1.67	1.00	0.83	0.71	0.63	0.50
0.08	2.67	1.60	1.33	1.14	1.00	0.80
0.11	3.67	2.20	1.83	1.57	1.38	1.10
0.14	4.67	2.80	2.33	2.00	1.75	1.40
0.17	5.67	3.40	2.83	2.43	2.13	1.70
0.20	6.67	4.00	3.33	2.86	2.50	2.00
0.23	7.67	4.60	3.83	3.29	2.88	2.30

3.5.3 The calcium stability test

The calcium stability test was devised, which appeared to be more satisfactory than the test in which the latex viscosity was determined after the addition of calcium sulphate. Basically, the calcium stability test involves the measurement of the coagulation time after the addition of a definite amount of calcium sulphate. The coagulation time (or calcium stability time, CST) is defined as the time taken for the latex containing 100g total solids to coagulate completely after addition of a known weight of calcium sulphate in the form of a suitable dispersion.

In developing a standard calcium stability test, certain preliminary investigations were undertaken. They included:

1. Investigation of the required weight of 7% dispersion of calcium sulphate to give a convenient coagulation time: It was found that the addition of 10g of 7% calcium sulphate dispersion to 50g latex (i.e., 2.34g calcium sulphate/100g rubber) gave a convenient coagulation time of 200s.
2. Investigation of the effect of temperature upon coagulation time: It was observed that at higher

temperatures (40-60°C) greater difficulty in obtaining reproducible coagulation times were encountered. The discrepancy between duplicates is > ± 25%. Consequently, the temperature selected for the calcium stability test was 25±1°C.

3.5.4 Procedure for calcium stability test

The apparatus was set up as shown in Figure 3.4. Essentially, it consisted of a 120-ml bottle placed in a beaker which contained water maintained at 25±1°C, thus acting as a water bath. The fluctuations in temperature were minimised by using polystyrene balls for insulation purposes. About 50g of latex was weighed into a 120-ml bottle and stirred vigorously with the aid of a magnetic stirrer. About 10g of freshly-prepared 7% dispersion of calcium sulphate was added to the latex in an amount equivalent to 2.34g calcium sulphate/100g rubber. A stop-clock was started, and the coagulation time (or calcium stability time, CST) recorded. The detection of coagulation was aided by using a glass rod to stir the latex gently. This was necessary as the magnetic follower became almost immobilised due to the highly viscous nature of the latex nearer the end-point. The measurements were carried out in duplicate. The reproducibility was in the order of ± 2.5%.

3.6 Investigation of effects of heating upon properties of NR latex

A study was conducted to investigate the effect of heating upon some of the basic properties of NR latex, both as regards the latex as received and the compounded latex. The composition and heating conditions applied to each of the six latices are shown in Table 3.7. The apparatus used to heat samples B, D and E is shown in Figure 3.5. About 1500g of high-ammonia NR latex was weighed into a 2-litre reaction vessel. With the aid of a mechanical stirrer, the latex was agitated for the entire heating period to minimise creaming effects. Heating of the latex was brought about by means of a thermostated water bath, set at 60±1°C. The basic latex properties were determined as described in Section 3.3.

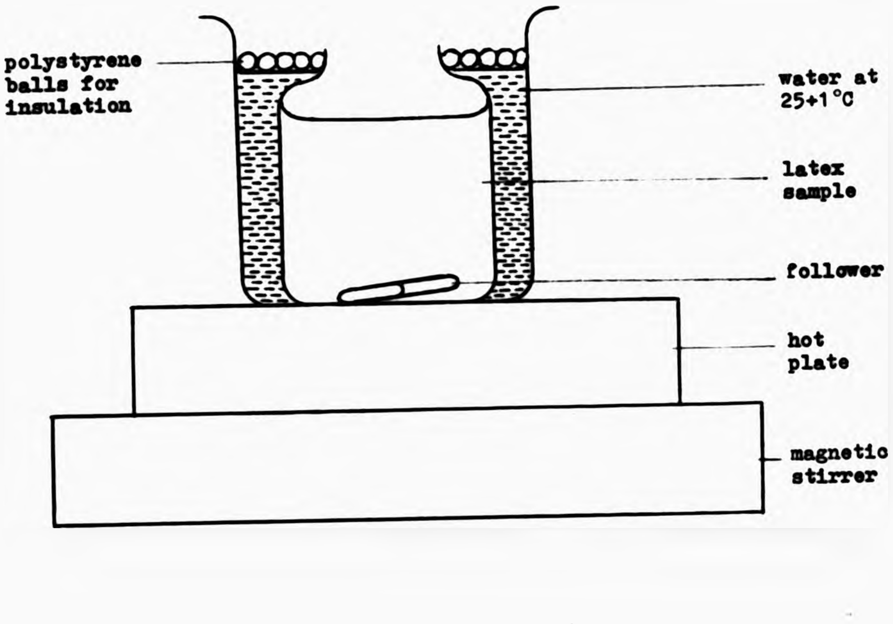


Figure 3.4 Apparatus for calcium stability test

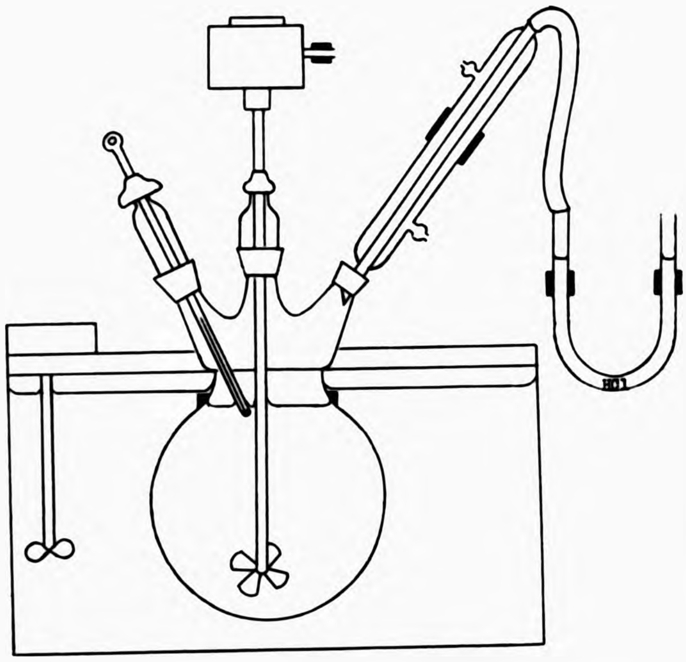


Figure 3.5 Apparatus for heating latex samples in 2-litre reaction vessel. The U-tube was incorporated in later experiment to determine the loss of ammonia.

Table 3.7 Composition and heating conditions applied to latex samples (A to E) prior to carrying out basic latex tests

	parts by dry weight					
	A	B	C	D	E	F
NR latex	100	100	100	100	100	100
sulphur	-	-	1.0	1.0	1.0	1.0
zinc oxide	-	-	0.5	0.5	-	-
ZDEC	-	-	0.8	0.8	0.8	0.8
KOH	-	-	0.5	0.5	0.5	0.5
stored at room temperature	✓	-	✓	-	✓	-
heated at 60°C for 5 hours	-	✓	-	✓	-	✓

3.7 Methods for assessing latex processing behaviour

To investigate the processing behaviour of NR latex with special reference to latex dipping, various test methods were developed. These are described in the following sections.

3.7.1 Determination of rate of drying of dipped films

The total volatile content, TVC, (mostly water) of a latex is defined as the total grams of volatiles per 100g original latex. This decreases on drying, and is therefore a measure of the extent of drying. The following procedure was used to determine TVC: A glass slide was dipped into a beaker of prevulcanised latex at fixed immersion and withdrawal rates. Both the immersion and withdrawal rates were 7.8cm min^{-1}. Immediately after withdrawal of the slide, a stopwatch was started. The slide was then transferred from the dipping machine into the drying cabinet, set at a given constant temperature. The duration of the transfer process was approximately 30s. With the aid of an electronic balance, the weight loss of the dipped films was recorded at various intervals, to constant weight. The determination was made in duplicate. The reproducibility was found to be satisfactory, i.e., the differences between duplicate determinations were no more than 1%. The total volatile content, TVC, was calculated as:

$$\% \text{ TVC} = [(W_t / W_o) \times 100] - (\text{TSC})_o \qquad (3.2)$$

where W_t is the weight of latex sample at time t, W_o is the initial weight of the latex sample and $(\text{TSC})_o$ is the initial percentage total solids content in the latex. Because W_o could not be directly determined with precision, it was calculated from the weight of the latex sample after complete drying, W, using the formula

$$W_o = [100 / (\text{TSC})_o] \times W \qquad (3.3)$$

3.7.2 Determination of rate of evaporation of ammonia during drying of dipped films

The total ammonia content, TAC, of a latex is defined as the total grams of ammonia per 100g original latex. This is used as a measure of the extent of evaporation of ammonia from the latex.

3.7.2.1 Preparation of sample

A glass slide was dipped into a beaker of prevulcanised latex at constant immersion and withdrawal rates of 7.8cm min^{-1}. Immediately after withdrawing the slide, a stopwatch was started. The slide was then transferred into the drying cabinet, and the weight recorded. The transfer process required approximately 30s. The slide was then left to dry for a given drying time. After drying, the sample on the slide was washed off with 50ml distilled water into an open-necked bottle and stoppered. The process was repeated at various drying times, and the ammonia content and pH of the latex washings determined.

3.7.2.2 Determination of ammonia content

The quantity of ammonia in the sample was determined by titration with standard sulphuric acid according to the procedure described in BS 1672:1972. About 100ml water and 5ml of 5% nonionic stabiliser at pH 6 were added to a 250-ml beaker. The total ammonia content, TAC, was calculated as:

$$\% \text{ TAC} = \frac{17V}{10^5} \times \frac{50 + W_1}{W_2} \times \frac{100}{W_1} \qquad (3.4)$$

where V is the titre volume of 0.01N sulphuric acid (ml), W_1 is the weight of latex on slide (g), and W_2 is the weight of diluted latex (g). The derivation of this equation is shown in Appendix A.

3.7.2.3 Determination of pH

A more rapid alternative way of determining ammonia content was to measure pH and then use a calibration curve of pH versus ammonia content. The calibration curve was obtained by determining ammonia content as described in Section 3.7.2.2. The pH was measured according to the procedure given in Section 3.3.4.

3.7.3 Determination of set time of dipped films

For the purposes of this project, the set time, t_S, of a dipped latex film was defined as the time taken for a given thickness of latex to set completely under controlled conditions of temperature and relative humidity. To determine the set time, a slide was immersed into, and withdrawn from, prevulcanised latex at constant immersion and withdrawal rates of 7.8cm min^{-1}. The slide was then transferred into the drying cabinet. The set time of the film was determined by having a known weight (and hence thickness since area of the film was constant) of sample of latex on the slide and measuring the time taken for the film to set completely. The sample thicknesses were varied by varying the withdrawal rates. The setting of the film was detected by allowing the tip of the finger to touch gently the surface of the film. In doing so, some of the latex was transferred from the slide onto the fingertip. However, when the film was completely set, no more latex was transferred, but instead the fingerprint was left on the surface of the film. A sharp end-point was obtained; the setting process occurred over a 10-20 second period (Figure 3.6).

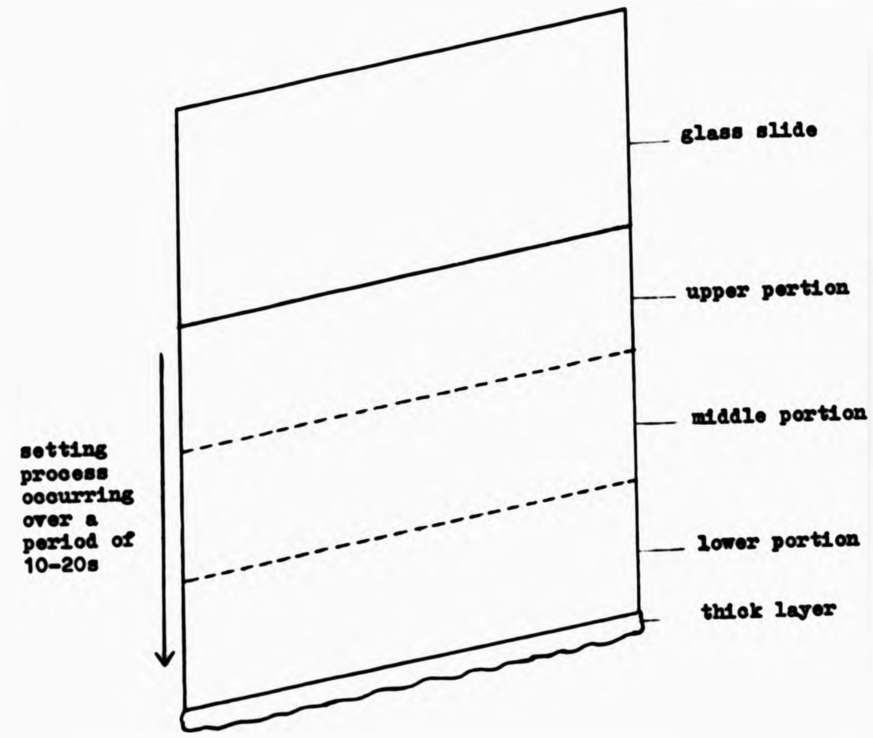


Figure 3.6 Illustration of a dipped film showing the occurrence of the setting process

3.7.4 Determination of 'curtaining effect'

The 'curtaining effect' for a film obtained by latex dipping is defined as the irregularities arising as a consequence of the non-uniform flow of the latex down the former prior to its setting. To investigate this effect, a film was cast by immersing a glass slide into a beaker containing prevulcanised NR latex and then withdrawing it. Both the immersion and the withdrawal rates were 7.8cm min^{-1}. The dipped latex film was then allowed to dry at room temperature. Once the film was dry, it was dusted with talc and removed from the former. The film was then sandwiched between two PVC sheets, and circular samples were punched from it at regular intervals using a hole punch. The labelling of the samples is shown in Figure 3.7. A diagram of weight against sample position was prepared, as shown in Figure 3.8. The variation in film thickness was taken as a measure of the 'curtaining effect'.

This procedure was used to investigate:

(a) the effect of withdrawal speed upon the 'curtaining effect';
(b) the induced 'curtaining effect', i.e., a deliberate 'curtaining effect' caused by immersing a slide into, and withdrawing from, a beaker containing 'lumpy' latex, at constant immersion and withdrawal rates of 7.8cm min^{-1}. By 'lumpy' latex is meant, a semi-liquid latex which was obtained by leaving latex exposed to the atmosphere for about 6 hours, followed by its thorough stirring;
(c) possible factors which may cause the 'curtaining effect'; and
(d) the effect of unwashed and washed formers upon the 'curtaining effect'.

3.8 Test methods for determining mechanical properties of latex films

The mechanical properties of the latex films that were determined in the present investigation were tensile strength, elongation at break and wet-gel strength.

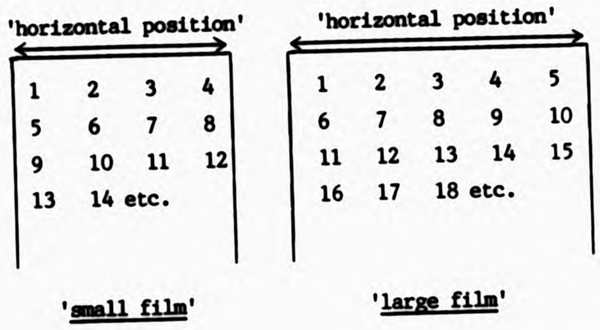


Figure 3.7 Labelling of dipped latex films for investigation of 'curtaining effect'

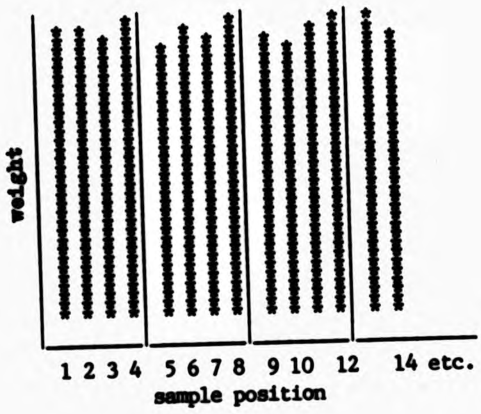


Figure 3.8 A typical diagram of a 'small film'

3.8.1 Tensile strength and elongation at break

Tensile strength is defined as the stress required to break a strip of rubber, based upon the initial cross-sectional area of the test-piece. The term 'elongation at break' is defined as the increase in length, expressed as a percentage of the original length, of a strip of rubber at the moment of rupture.

To measure the tensile properties, the test-pieces used were of the dumb-bell type. The dumb-bells were stamped from the film using a sharp die free from any imperfections. The thickness of the test-piece along the central parallel portion was measured in three places to 0.001mm using a dial gauge. The average of the three thicknesses was taken as an estimate of the thickness of the test-piece.

The tensile strength and elongation at break of the test-piece were measured using a tensile testing machine, Universal Instron 1026. The grips used to hold the dumb-bell were of the pneumatic type. The rate of grip separation was 500±50 mm min^{-1}. A plot of stress versus strain during extension was recorded directly by a chart recorder. For each sample, four dumb-bells were used and the results averaged. The cross-sectional area used to calculate the tensile strength was the initial cross-sectional area before stretching.

3.8.2 Wet-gel strength

The term 'wet-gel strength' of a latex film is used to denote the tensile strength of the freshly deposited latex films.

To determine the wet-gel strength, a glass slide of dimensions approximately 10x3x0.4cm was cleaned thoroughly with soap solution, then washed with distilled water and dried in oven at 70°C. It was first immersed (immersion rate, 7.8cm min^{-1}) into the coagulant solution to a depth of approximately 9.0cm and then withdrawn (withdrawal rate, 7.8cm min^{-1}). Excess coagulant solution was allowed to drip off and the volatile solvent was allowed to evaporate (assisted by the heat of the former), leaving a very viscous layer of coagulant on the former. The temperature of the former was allowed to drop to near room temperature; this occurred about 2-3 minutes after withdrawal from the coagulant solution. The former was then immersed into the latex at a constant immersion rate of 7.8cm min^{-1}, and allowed to dwell for 60s. The former was withdrawn at a constant withdrawal rate of 7.8cm min^{-1}. The gel was carefully removed and placed on a metal gauze coated with rubber, in a closed container saturated with water, for approximately three minutes before determining its wet-gel strength. The metal gauze was coated with rubber to prevent rusting when in contact with water. The coating of the metal gauze with rubber was carried out as follows: Essentially, a metal gauze was immersed into, and withdrawn from NR latex followed by its drying at room temperature. This procedure was repeated several times until a sufficient thickness of the rubber was deposited onto the gauze.

To measure the wet-gel strength, dumb-bell test-pieces were cut from the gel using a standard cutter. The remainder of the gel was placed back into the container and its thickness determined at a later time. The dumb-bell test-piece was immediately stretched on the Instron machine, model Universal Instron 1026, at room temperature. The tensile strength was measured at a standard rate of jaw separation of 20cm min^{-1}. For each sample, four dumb-bells were used and the results averaged. The cross-sectional area used to calculate the wet-gel strength was the initial cross-sectional area before stretching.

3.9 Determination of concentration of crosslinks in vulcanised rubber films by swelling measurements

On the molecular scale, the swelling of vulcanised rubber is similar to the process by which non-crosslinked polymers dissolve in solvents. Thus the theory of the thermodynamics of polymer solutions can be applied to the swelling of vulcanised rubber films. However, one important difference is that because of the presence of the crosslinks, the rubber cannot disperse as individual chain molecules throughout the solvent. Instead, as solvation of the rubber occurs and the chains assume elongated conformations, the crosslinks constrain the swelling because elastic retractive forces develop which oppose the swelling process. These forces are identical to the force which develops when a rubber test-piece is stretched. In consequence, use can be made of the theory of rubber elasticity in calculating the equilibrium extent of swelling. At equilibrium, the elastic and swelling forces balance. By combining the theory of thermodynamics of polymer solutions with the theory of rubber elasticity, it is possible to derive an expression relating the equilibrium degree of swelling to the molecular weight of polymer chains between the crosslinks. The result is known as the Flory-Rehner equation (1,2):

$$M_c = \frac{V_1 \, V_r^{1/3} \, \rho}{\ln(1-V_r)+V_r+\chi V_r^2} \qquad (3.5)$$

where M_c is the molecular weight between crosslinks, V_1 is the molar volume of the solvent, ρ is the density of unswollen rubber, χ is the rubber/solvent interaction parameter, which is taken as 0.36 (3), and V_r is the volume fraction of rubber in the swollen gel at swelling equilibrium. In the derivation of this equation, the correction for loose end imperfections in the network is ignored. The concentration of crosslinks in the rubber network, [X], is related to M_c by the equation,

$$[X] = \tfrac{1}{2} M_c \qquad (3.6)$$

The procedure used to determine the concentration of crosslinks in the prevulcanised rubber films was as follows: A strip of the film weighing about 0.1 to 0.2g was cut and weighed accurately. It was then immersed in a conical flask containing toluene (about 50ml), and phenyl-β-naphthylamine (0.5g). The purpose of this latter substance was to ensure that no oxidative chain scission reactions occurred. The flask was stoppered and left in a dark cupboard for one week for equilibrium swelling to occur. After this time, the excess toluene was poured off, and the swollen rubber gel was dropped into a previously weighed bottle, which was immediately closed and reweighed.

The density of the unswollen rubber was determined as follows: A strip of rubber, about 5cm long, was placed in water (about 25ml) in a beaker, where it floated. Methanol was run in from burette, with agitation, until the pieces neither floated nor sank. The densities of the rubber and the methanol/water mixture were now equal, and the density of the liquid was determined by using a specific gravity bottle.

CHAPTER 4 : CALCIUM STABILITY TEST

4.1 Development of calcium stability test

The reason for the development of the calcium stability test was to investigate in more detail, than hitherto, the effect of calcium ions upon the stability of NR latex, and thereby to be able to predict the processing behaviour of NR latex during coagulant dipping. Normally, the coagulant solution used in coagulant dipping is calcium chloride in methylated spirit. However, if a solution of calcium chloride is added to the latex, an immediate flocculation or coagulation occurs, and so this would not provide the basis for a very sensitive test. Therefore, in this test calcium sulphate was used as the source of calcium ions. The reason for this is that calcium sulphate is only sparingly soluble in water. It can thus be added to the latex, as a dispersion in water, without immediate coagulation occurring. However, over a period of time, calcium ions react with fatty-acid soap anions in the latex, and further calcium sulphate, from the calcium sulphate particles, dissolves to maintain the equilibrium. This results in progressive colloidal destabilisation of the latex, which is accompanied by a progressive increase in viscosity of the latex with time. Additionally, it simulates the coagulant dipping process, in which calcium ions diffuse from the former into the latex to bring about destabilisation of the latex.

4.2 "Calcium viscosity test" (CVT)

4.2.1 Introduction

It had been observed that additions of calcium sulphate to the latex caused the viscosity to rise with time. Thus, it was decided to investigate whether this increase in viscosity was reproducible and, if so, whether it could be used as a measure of the susceptibility of the latex to colloidal destabilisation by calcium ions.

4.2.2 Procedure

The experimental method is described in detail in Section 3.5.2. Basically, known weights of calcium sulphate dispersions (containing various concentrations of calcium sulphate ranging from 3 to 10% by weight) were added to the latex, and the viscosity was measured after various periods of time. Some of the results are shown in Figure 4.1.

4.2.3 Discussion

When the same weight of calcium sulphate was added to a fixed weight of latex using different dispersion concentrations, the increase in viscosity was not regularly related to the concentration of calcium sulphate in the dispersion (Figure 4.1). This is rather surprising that the viscosity increase should depend upon the concentration of calcium sulphate dispersion, if the amount of added calcium sulphate to the latex was fixed. A possibility for this observation may be that the increase in the concentration of the dispersion increases the number of particles and hence increases the rate of dissolution of calcium sulphate. This is thought to be a likely explanation, since, in each case, the addition of calcium sulphate to latex was made by preparing a fresh dispersion and not by a mere dilution of a concentrated dispersion. In any case, the results suggest that the viscosity does increase with time, on adding calcium sulphate to the latex. When different weights of calcium sulphate were added in the form of a dispersion of given concentration (7%), it is clearly seen that the viscosity is related to the weight of calcium sulphate added (Figure 4.2). In general, the initial slope of curves in Figure 4.2 increases with increasing level of calcium sulphate. Again, it is speculated that the effect of increasing the number of particles increases the rate of dissolution of calcium sulphate. The predicted maximum amount of calcium sulphate would dissolve in the aqueous phase of the latex assuming that the aqueous phase was pure water is 0.084g/100g latex. This compares with the various additions of calcium sulphate ranging from 0.05 to 0.23g/100g latex. Finally, when viscosity, after maturing the latex for a fixed period (24 hours), is plotted against weight of calcium sulphate added to the latex (Figure 4.3), there is again no relationship between viscosity and dispersion concentration. However, the peaks shown in Figure 4.3 are very interesting. In this respect, since no consistent pattern of results was observed, it was concluded that this type of calcium viscosity test did not show much promise as a method of assessing the susceptibility of NR latex to colloidal

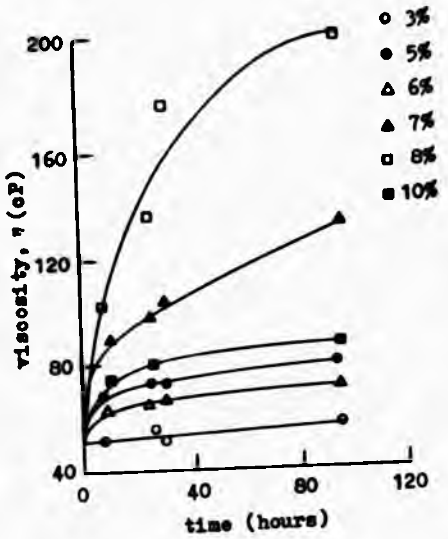


Figure 4.1 Viscosity versus time for latices containing 0.05g calcium sulphate added as various dispersions to the fixed weight of latex sample of 100g.

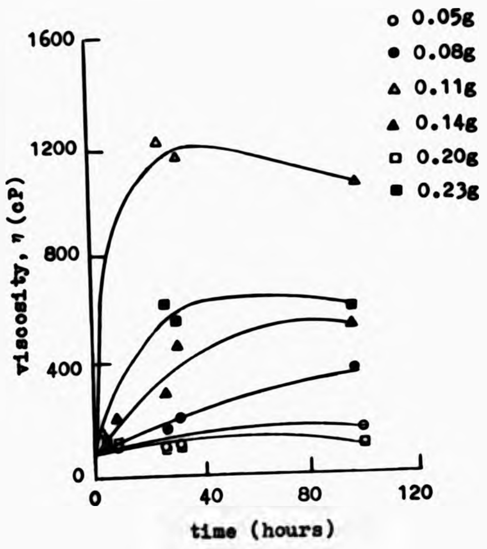


Figure 4.2 Viscosity versus time for latices containing various weights of calcium sulphate added as a 7% dispersion to the fixed weight of latex sample of 100g.

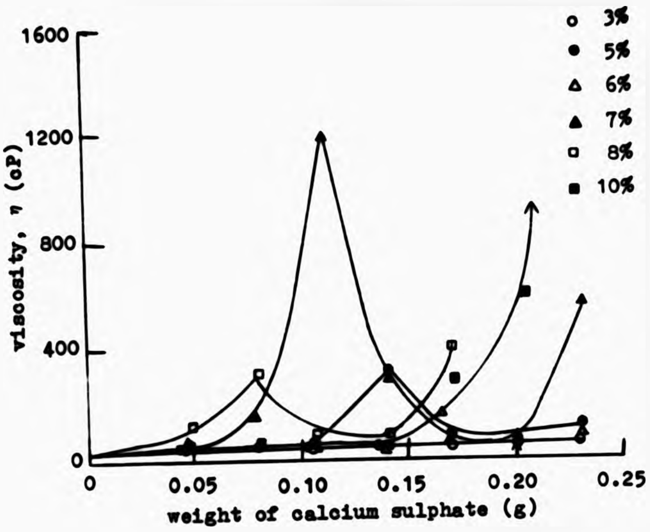


Figure 4.3 Viscosity versus weight of calcium sulphate after maturation for 24 hours. The additions of calcium sulphate were made as various dispersions to the fixed weight of latex sample of 100g.

destabilisation by calcium ions.

4.3 Calcium stability test

4.3.1 Introduction

It was decided to investigate a method of assessing the stability of NR latex to calcium ions by causing complete coagulation of latex by addition of calcium sulphate. The time required for complete coagulation was determined as a measure of stability to calcium sulphate. The factors which affected the coagulation time (or calcium stability time, CST) were determined as described in Section 3.5.3. However, basic standard conditions were selected for the calcium stability test from the results described in the subsequent sections.

4.3.2 Selection of weight of calcium sulphate to be added: discussion of coagulation time versus weight of 7% calcium sulphate dispersion

The results for the determination of the effect of the weight of 7% dispersion of calcium sulphate upon the coagulation time are given in Figure 4.4. As can be seen, there is a very sharp rise in coagulation time as the amount of calcium sulphate dispersion is reduced below about 6g/50g latex. However, lack of sensitivity is observed at high levels of addition of calcium sulphate. It is thought that the initial sharp increase in the coagulation time at low levels of addition of calcium sulphate, i.e., below about 6g/50g latex, is a consequence of the reduction in the number of particles of calcium sulphate and hence a reduction in the rate of dissolution of calcium sulphate. This results in reduced colloidal destabilisation of the latex which is accompanied by an increase in the coagulation time. However, the lack of sensitivity at high levels of addition of calcium sulphate may be attributed to the effect of the saturation of the aqueous phase. When the additions of calcium sulphate are compared with the amount of calcium sulphate required to saturate the aqueous phase of the latex (as predicted from the equilibrium solubility of calcium sulphate in water at 25°C), it is found that 0.6g of 7% dispersion of calcium sulphate per 50g latex is required to saturate the aqueous phase of the latex, assuming that the aqueous phase was pure water. Clearly, the value is approximately 10 times smaller than the observed

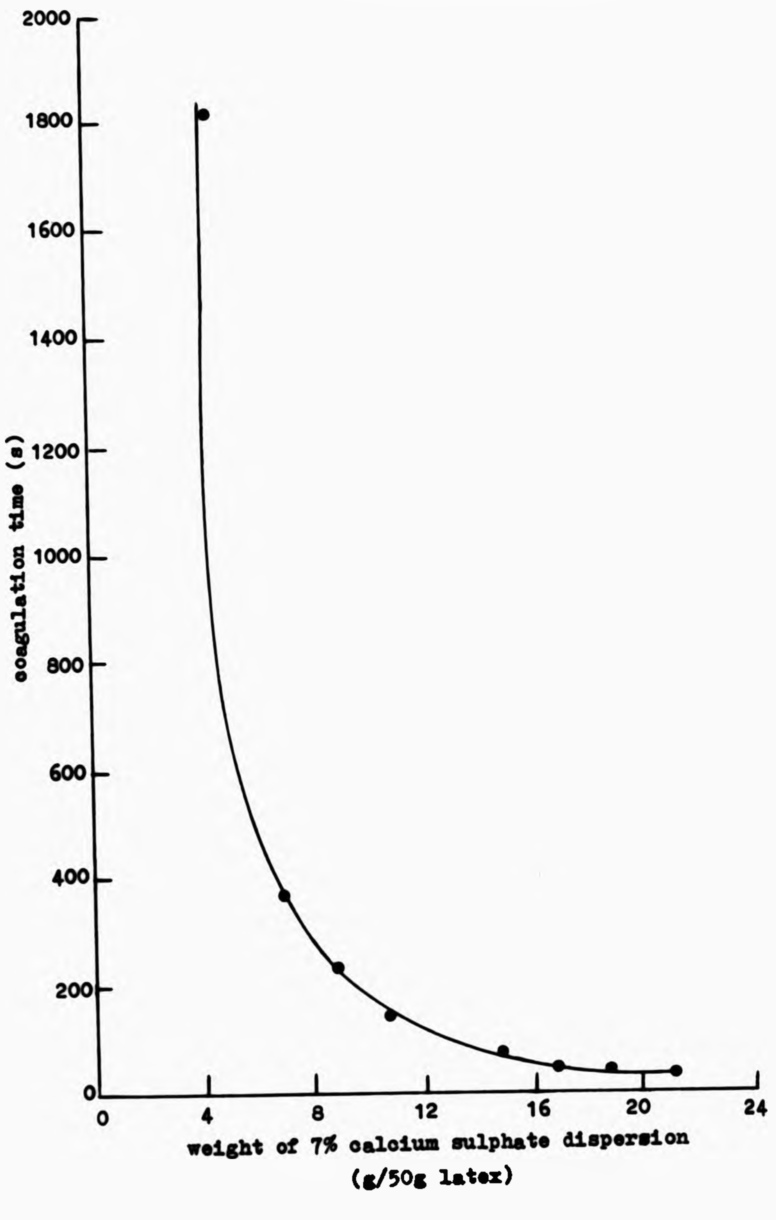


Figure 4.4 Coagulation time at 25°C versus weight of 7% dispersion of calcium sulphate added

critical value of 6g/50g latex, above or below which the coagulation time changes drastically. Since the sharp fall in coagulation time with increasing calcium sulphate addition does not seem to be related to the equilibrium solubility in the aqueous phase, the next possibility to consider is that it is a consequence of the amount of calcium sulphate which is required to react with higher fatty-acid soaps in the latex. Thus, the "critical" value of 6g of 7% calcium sulphate per 50g latex is compared with ca. 1/3(KOH No.-VFA No.) (1). The latter gives some indication to the content of higher fatty-acid soaps in the latex. It is found that the content of higher fatty-acid soaps in the latex is about 0.054g per 50g latex. Clearly, there is no approximate equivalence between the "critical" value of 6g of 7% calcium sulphate per 50g latex and the content of higher fatty-acid soaps. It is thus difficult to understand the observed shape of the curve in Figure 4.4.

4.3.3 Selection of temperature of test

The results for the determination of the effect of temperature upon coagulation time are shown in Figure 4.5. As can be seen, the coagulation time decreased initially with an increase in temperature. However, as the temperature was further increased, i.e., above 40°C, the coagulation time became more or less constant. The initial decrease in coagulation time may be attributed to the calcium sulphate dissolving more rapidly as the temperature is increased. However, it is not thought to be a likely explanation, because the solubility of calcium sulphate is 0.209g/100g water at 30°C and 0.162g/100g water at 100°C (2). The constancy of coagulation time above 40°C, however, may be a consequence of the following:

1. At higher temperatures, the viscosity of the latex is increased, leading to difficulties in maintaining satisfactory continuous stirring.
2. Preliminary coagulation of some of the latex.

Thus, a temperature of 25±1°C was selected for this test.

4.3.4 Conditions chosen for standard calcium stability test

The conditions selected for the calcium stability test were as follows: 20g of 7% calcium sulphate dispersion was added to

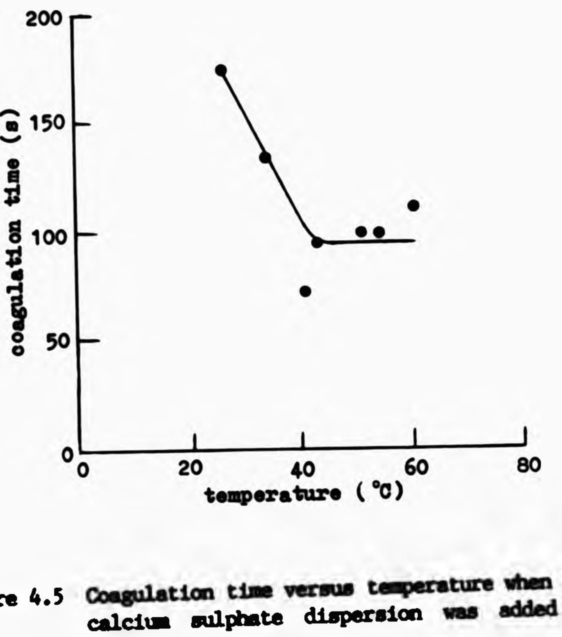


Figure 4.5 Coagulation time versus temperature when 20g of 7% calcium sulphate dispersion was added to 100g latex

100g latex at 25±1°C. The time taken to coagulate the latex completely was measured. This time was taken as the coagulation time (i.e., the calcium stability time, CST). The reproducibility of this test was in the order of ± 2.5%.

4.4 Effect of repeated coagulant dipping upon calcium stability time, CST, of NR latex

The effect of repeated coagulant dipping upon the calcium stability of NR latex is shown in Figure 4.6. As can be seen, repeated coagulant dipping of NR latex reduces the calcium stability time gradually. This was expected, because repeated coagulant dipping increases the calcium content of the latex through diffusion of calcium ions from the former into the bulk of the latex. The increased concentration of calcium ions lowers the stability of the latex. There are two possible mechanisms which may account for this:

1. compression of the electrical double layer surrounding the latex particles due to the increased ionic strength of the aqueous medium - this mechanism will be discussed in detail in Chapter 8.
2. direct chemical interaction between the calcium ions and the stabilising higher fatty-acid anions, forming an insoluble, unionised and unhydrated metal soap, viz.

$$Ca^{++} + 2RCOO^{-} \longrightarrow (RCOO)_2Ca \downarrow$$

The rate of destabilisation of latex by acquired calcium ions and hence the CST value was expected to depend upon the following factors:

(a) weight of latex in the beaker;
(b) surface area of the coagulant layer;
(c) TSC of the latex;
(d) coagulant solution concentration; and
(e) dwell time.

All these factors affect the concentration of calcium ions and hence the stability of the bulk latex.

It is not surprising that there is only a small reduction in the CST with an increase in the number of dips. This is because the dwell time selected was 45s. Hence, only a short

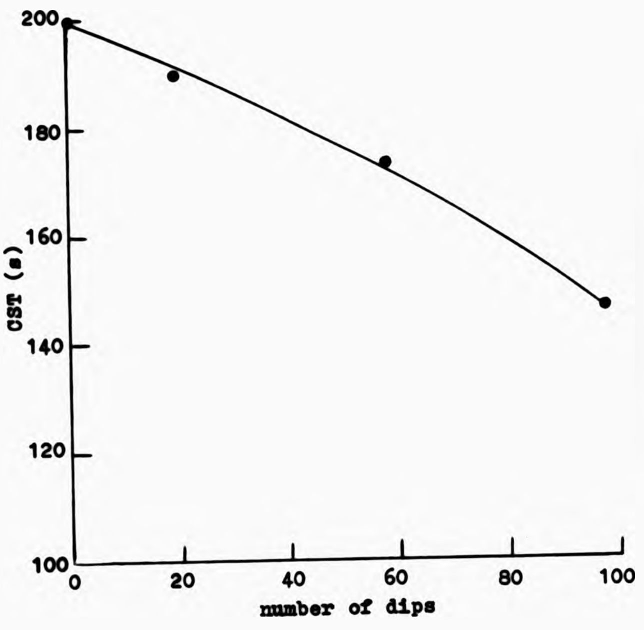


Figure 4.6 Effect of repeated coagulant dipping upon calcium stability time of NR latex

time was available for diffusion of calcium ions from the former into the bulk of the latex. Thus, only low concentrations of calcium ions were introduced into the bulk of the latex, and these produced only small changes in the CST value.

CHAPTER 5 : EFFECT OF HEATING UPON PROPERTIES OF NR LATEX AS RECEIVED AND WHEN COMPOUNDED

5.1 Introduction

Essentially, to investigate the effect of heating upon some of the basic properties of NR latex both as regards the latex as received, (Formulation A⟶B), and the compounded latex containing the principal vulcanising ingredients (Formulation C⟶D), four latex samples were prepared. They were as shown in Table 5.1. However, to study the factors affecting the stability of NR latex other than the effects associated with the presence of zinc oxide, two additional latex samples, namely, E and F were prepared in the absence of zinc oxide (Table 5.1). The procedure used to heat latex samples A, C and E to give B, D and F respectively is described in Section 3.6. The properties of these latex samples were investigated using the procedures described in Chapter 3. The results are summarised in Tables 5.2 to 5.7.

5.2 Effect of heating latex samples upon TSC and DRC

The results for the effects of heating upon the TSC and DRC are shown in Table 5.2. It can be seen that, as expected, there were no significant changes in TSC and DRC brought about by heating the latices. The TSC and DRC of latex samples C and D are lower than for samples A and B respectively. This effect is a consequence of dilution of latex samples during the compounding process.

5.3 Effect of heating latex samples upon VFA No.

The results for the effect of heating latex samples upon VFA No. are given in Table 5.3. It is seen that the VFA No. remained approximately constant, thereby indicating that the latex was well-preserved in that no further micro-organic activity occurred during the heating. This is hardly surprising, since the high pH (pH 10) and the high final temperature (60°C), are not conducive to bacterial action. But some micro-organisms are resistant to temperature of *ca*. 60°C, and in any case there was the rise to 60°C.

Table 5.1 Preparation of latex samples to investigate effects of heating upon properties of high ammonia-preserved NR latex

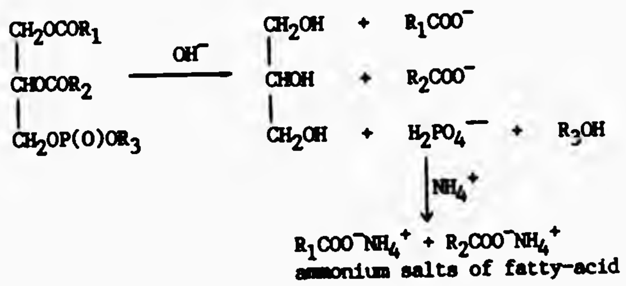
	parts by dry weight					
	A	B	C	D	E	F
NR latex (%)	100	100	100	100	100	100
sulphur (%)	-	-	1.0	1.0	1.0	1.0
zinc oxide (%)	-	-	0.5	0.5	-	-
ZDEC (%)	-	-	0.8	0.8	0.8	0.8
KOH (%)	-	-	0.5	0.5	0.5	0.5
stored at room temperature	✓	-	✓	-	✓	-
heated at 60°C for 5 hours	-	✓	-	✓	-	✓

Table 5.2 Effect of heating upon TSC and DRC of NR latex as received and when compounded

latex sample	property	
	TSC (%)	DRC (%)
A	62.6	60.3
B	62.7	60.5
C	60.4	59.1
D	60.5	59.1

5.4 Effect of heating latex samples upon KOH No.

The results for the effect of heating latex samples upon KOH No. are given in Table 5.3. It is seen that the KOH No. increased significantly on heating the latex samples. This is in agreement with the results found by Martosugito (1). Possible reasons for the increase in KOH No. are hydrolysis of the phospholipids and hydrolysis of the proteins in the latex. Phospholipids are hydrolysed to glycerol, fatty-acid anions, phosphate anions and organic bases as follows:



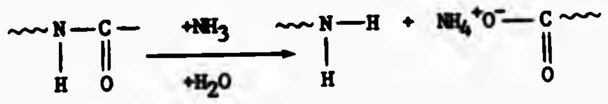
$$\begin{array}{l} CH_2OCOR_1 \\ | \\ CHOCOR_2 \\ | \\ CH_2OP(O)OR_3 \end{array} \xrightarrow{OH^-} \begin{array}{l} CH_2OH \; + \; R_1COO^- \\ | \\ CHOH \; + \; R_2COO^- \\ | \\ CH_2OH \; + \; H_2PO_4^- \; + \; R_3OH \end{array}$$

$$\downarrow NH_4^+$$

$$R_1COO^-NH_4^+ + R_2COO^-NH_4^+$$

where R_1 and R_2 are fatty-acid radicals and R_3 is $-CH_2CH_2N^+(CH_3)_3OH^-$.

Polypeptides are hydrolysed as follows:



$$\sim\!\sim\!\sim \underset{\substack{| \\ H}}{N} - \underset{\substack{\| \\ O}}{C} - \xrightarrow[+H_2O]{+NH_3} \sim\!\sim\!\sim \underset{\substack{| \\ H}}{N} - H + NH_4^+O^- - \underset{\substack{\| \\ O}}{C} \sim\!\sim\!\sim$$

The hydrolysis of phospholipids and polypeptides may have been accelerated by heating, thus yielding an increase in acid anions and a consequent increase in KOH No.

5.5 Effect of heating latex samples upon pH

The results for the effect of heating latex samples upon the pH values are shown in Table 5.3. A significant reduction in pH was observed. This is qualitatively consistent with the production of acids by hydrolysis of proteins and lipids (Section 5.4). The hydroxyl ions (OH^-) are removed as a consequence of the reduction of acid anions, thus reducing the pH value (Appendix B). However, the reduction in pH

Table 5.3 Effect of heating upon VFA No., KOH No., pH, MST and alkalinity of NR latex as received and when compounded

latex sample	property				
	VFA No.	KOH No.	pH	MST (s)	alkalinity*
A	0.08	0.62	11.42	1455	1.87
B	0.07	0.79	10.32	3397	1.67
C	0.06	0.65	10.70	40	1.76
D	0.08	0.71	10.50	820	1.54
E	—	—	—	1138	—
F	—	—	—	823	—

* in g NH_3/100g aqueous phase

quantitatively is not consistent with the increase in KOH No., for a given latex sample. For example, the reduction of ammonia from pH results (Appendix B, 3) indicates the further hydrolysis of 0.02g lipid/100g latex. By contrast, the increase in KOH No. results (Section 5.15.2) indicates the reduction of ammonia by further hydrolysis of 0.38g lipid/100g latex.

Also, the pH of latex sample C was found to be lower than that of A (Table 5.3), when the former contained 0.5 pphr potassium hydroxide and the latter did not. However, this may be a consequence of the effect of zinc oxide.

5.6 Effect of heating latex samples upon alkalinity

The results for the effect of heating latex samples upon the alkalinity are given in Table 5.3. The observed reduction in alkalinity is a consequence of reduced ammonia content in the latex. Possible reasons for this reduction of ammonia are as follows:

(a) Some evaporation of ammonia occurred during heating of the latex samples. It was found by a separate experiment (see Figure 3.5) that on heating the latex samples A and C, the loss of ammonia to the atmosphere is about 0.11g NH_3/100g aqueous phase and 0.17g NH_3/100g aqueous phase respectively.

(b) The reaction of ammonia with fatty acids and amino acids formed by the hydrolysis of phospholipids and proteins (see Section 5.4).

Estimates of reductions in ammonia content by both these processes are summarised in Table 5.4. From Table 5.4, it can be seen that on heating latex sample A, there was a loss of ammonia of 0.2g NH_3/100g aqueous phase (or 10.7%) as measured by alkalinity determination experiment. The estimated loss of ammonia by evaporation (5.9%) and by reaction with acids (4.3%, calculated from the KOH No.) totals 10.2%. This value is in excellent agreement with the experimental value of 10.7%, and suggests that the ammonia loss was indeed a consequence of both evaporation and reaction with acids formed on heating. For the effect of heating upon latex sample C, the experimental value of loss of ammonia (12.5%) is also in close agreement with the estimated value (11.4%). This further confirms that the loss of ammonia was both by evaporation and by reaction with acids formed on heating.

Table 5.4 Comparison of total loss of ammonia as indicated by alkalinity determination with possible losses by evaporation and reaction with acids

latex sample	concentration of ammonia ($g\ NH_3$/100g aqueous phase)					
	alkalinity results				KOH No.* results	
	original latex	after heating	loss on heating	estimated loss by evaporation (a)	reaction with acids (b)	total loss (a+b)
A⟶B	1.87 **100**	1.67 **89.3**	0.20 **10.7**	0.11 **5.9**	0.08 **4.3**	0.19 **10.2**
C⟶D	1.76 **100**	1.54 **87.5**	0.22 **12.5**	0.17 **9.7**	0.03 **1.7**	0.20 **11.4**

Note: values typed in bold are percentages

* see Appendix B for calculation

5.7 Effect of heating latex samples upon mechanical stability

The results for the effect of heating latex samples upon mechanical stability are shown in Table 5.3. It is observed that on heating the latex there is a very large increase in the mechanical stability. The percentage increase is 57%. This observation is consistent with that of Martosugito (1). However, the percentage increase is somewhat higher than that observed by him under similar conditions of heating. He found that the mechanical stability increases by 35% on heating the latex for 6 hours at 60°C. He showed that the increase in the mechanical stability depends on:

(i) the duration of heating at 50°C, the maximum increase being attained over a heating period of 16 to 24 hours; and

(ii) the temperature of heating: when the latex was heated for 5 hours, the optimum enhancement of mechanical stability was observed at 50°C.

As before, a possible explanation for the enhancement of the mechanical stability of ammonia-preserved latex by heating is the hydrolysis of phospholipids and proteins. Although it is generally assumed that the hydrolysis of the phospholipids is complete when the latex is received, the results suggest that the hydrolysis of phospholipids may in fact be incomplete on receipt, and that the hydrolysis of residual phospholipids can be accelerated by heating.

Phospholipids are hydrolysed to glycerol, fatty-acid anions, phosphate anions and organic bases (see Section 5.4). The adsorption of the ammonium salts of these fatty acids at the particle interface would produce a higher surface charge and therefore a higher repulsive force between approaching latex particles. Hence the mechanical stability increases.

An additional contributor to the enhanced mechanical stability may arise from the hydrolysis of proteins, whereby the formation of polypeptides to amino acids occurs (see Section 5.4). Such hydrolysis would also result in increased charge, which, if it remained on the surface of particles, would increase the mechanical stability of latex. However, if the charged species were water soluble, it would lower the stability. Additionally, hydrolysis of the proteins would reduce their effectiveness as steric stabilisers even if they remain adsorbed, and might also lead to desorption. Both these effects would reduce the mechanical stability. Also, the ionic strength will increase, thereby reducing the mechanical stability.

There is also the possibility that heating "plasticises", i.e., makes the individual anions more mobile, the aggregates of fatty-acid anions already adsorbed at the particle surface, thereby making the fatty-acid anions more effective as colloid stabilisers. This may well be the principal cause of the mechanical stability increase.

In the case of compounded latex (samples C and D), another factor, namely, effects associated with the presence of zinc oxide, should also be taken into consideration. As can be seen from the mechanical stability results (samples A⟶C and B⟶D) (Table 5.3), the addition of zinc oxide reduces the mechanical stability considerably. This observation agrees well with the reported literature (2,4) for the effect of added zinc oxide upon the colloid stability of ammonia-preserved NR latex. The presence of other vulcanising ingredients, however, appears to have only a small effect upon mechanical stability (compare samples A and E).

5.8 Correlation of KOH No., alkalinity, MST and pH

In summary, the hydrolysis of lipids and proteins accounts for the increased KOH No. and mechanical stability and the reduced pH and alkalinity . Thus, it is expected that there should be a correlation between:

(a) reduced alkalinity and increased KOH No.

Unfortunately, the results obtained in the present investigation are insufficient to confirm or refute the existence of a correlation. However, when an attempt was made to compare these results with those of Martosugito (1), there was no obvious correlation between the reduced alkalinity and the increased KOH No. (Figure 5.1).

(b) increased mechanical stability and increased KOH No.

Martosugito (1) found an approximate linear relationship between the mechanical stability and the KOH No. in the absence of zinc oxide. However, the results obtained in the present investigation failed to fit with his correlation (Figure 5.2).

(c) reduced pH and reduced alkalinity

Since there were insufficient results to obtain the correlation between the reduced pH and the reduced alkalinity, an attempt was made to correlate and compare with the results of Martosugito (1). The results are given in Figure 5.3 and show the lack of correlation between the reduced pH and the reduced alkalinity.

(d) reduced pH and increased KOH No.

Again, there were not sufficient results to obtain the relationship between the reduced pH and the increased KOH No. Thus, it was decided to correlate and compare the results with those of Martosugito, as shown in Figure 5.4. However, no obvious relationship between the reduced pH and the increased KOH No. was achieved.

5.9 Effect of heating latex samples upon viscosity

The viscosity was determined as described in Section 3.3.2. The results are shown in Table 5.5, from which it is evident that there is a significant increase in viscosity on heating ammonia-preserved NR latex. The factors which affect the viscosity of latices are mainly the TSC of latex, the particle size and size distribution, the temperature and the particle aggregation. The degree of hydration, affecting the effective hydrodynamic particle size and the effective volume fraction of disperse phase is also important. However, since the TSC of latex samples was approximately constant, and the temperature was maintained at 25±1°C, it was possible that the reason for the increase in viscosity are changes in particle size and size distribution. From the results given in Table 5.5, however, it is concluded that, since the particle size remained approximately constant, the possibility of increase in viscosity due to changes in particle size is ruled out. The most probable cause of small increases in viscosity is, therefore, an increased degree of loose, reversible agglomeration of the particles. This would probably not be detectable by the Nanosizer because the latex was diluted so

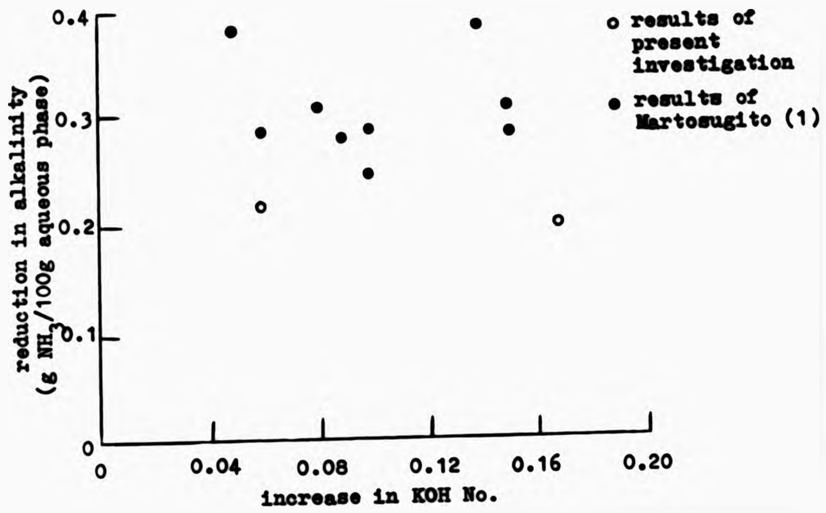


Figure 5.1 Correlation of reduction in alkalinity with increase in KOH No.

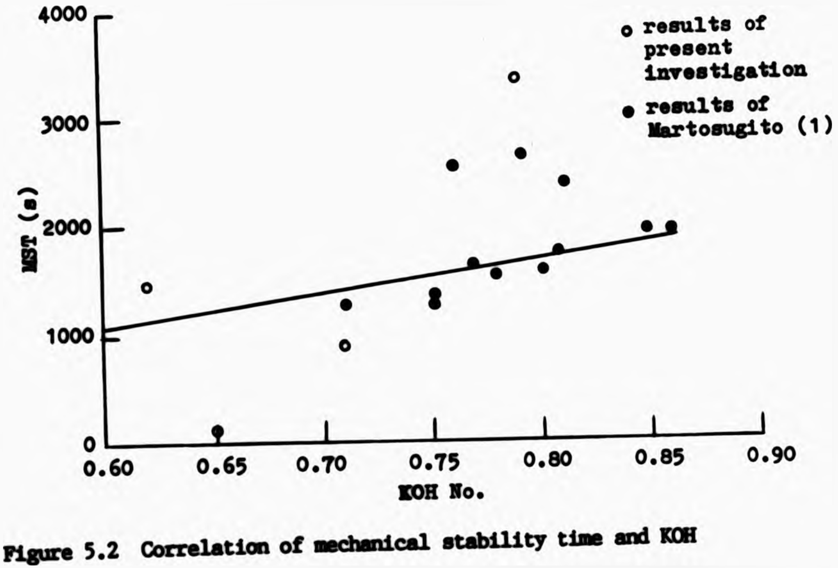


Figure 5.2 Correlation of mechanical stability time and KOH No.

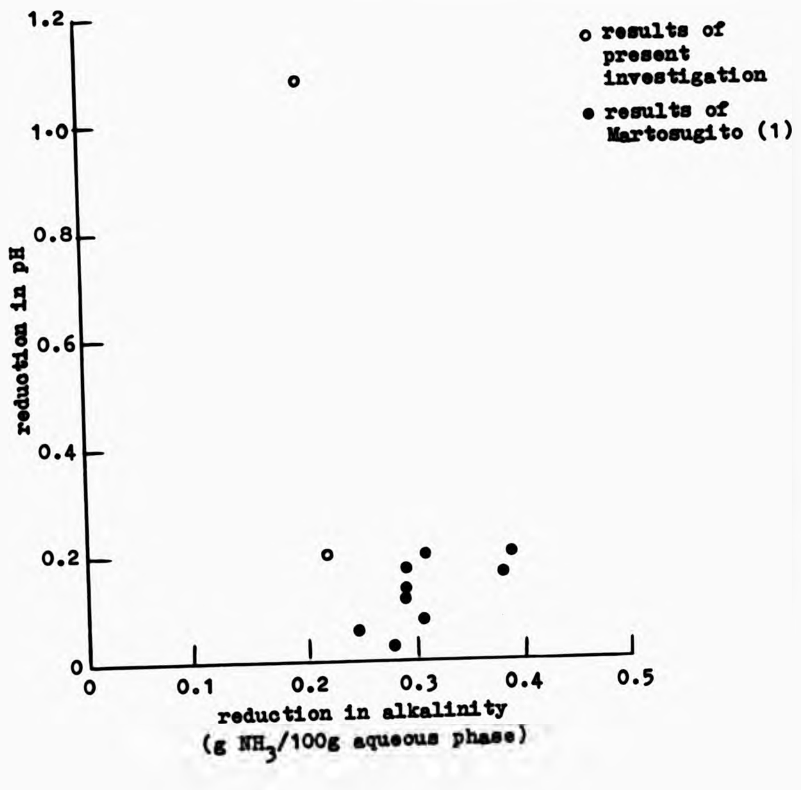


Figure 5.3 Correlation of reduction in pH with reduction in alkalinity

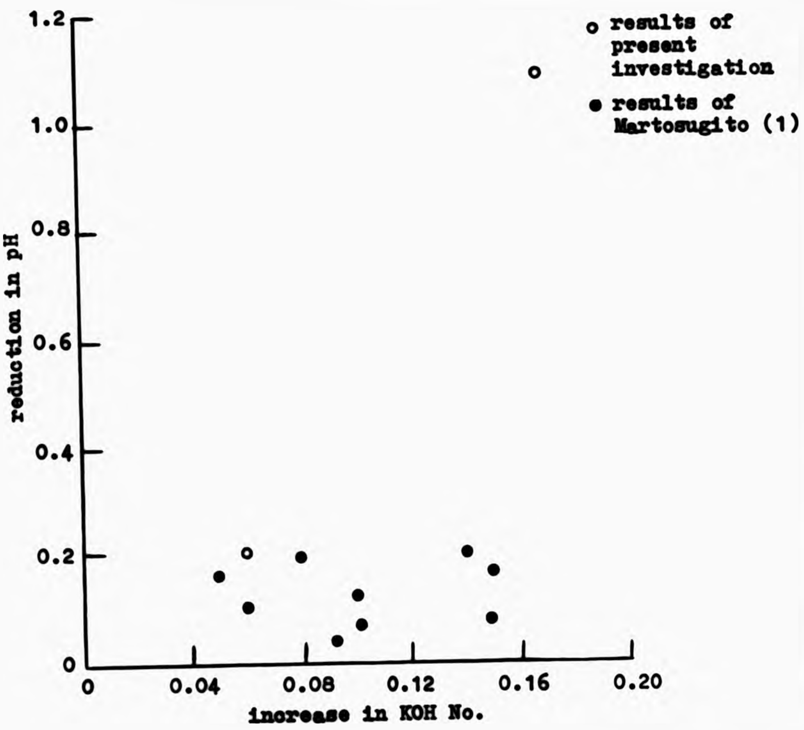


Figure 5.4 Correlation of reduction in pH with increase in KOH No.

extensively before the measurement. The dilution of latex would cause the aggregates to dissociate. The cause of the increased particle aggregation might be the denaturation of the proteins on heating. Increase in the degree of particle hydration, with an increase in effective hydrodynamic particle size, seems less likely as a cause of the viscosity increases, because the Nanosizer would probably detect such increases in effective particle size.

The percentage increase in viscosity from sample A⟶B and from sample C⟶D are very similar. This is rather surprising at first, since sample C contains zinc oxide. However, the increase would probably have been greater if the potassium hydroxide had not been present.

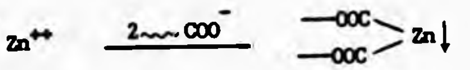
5.10 Effect of heating latex samples upon ZAAV

The zinc ammonium acetate viscosity, ZAAV, test was carried out as described in Section 3.3.5. The results are given in Table 5.5. In general, an increase in viscosity is found to accompany the addition of zinc ammonium acetate to the latex sample. The reactions which occur when zinc ammonium acetate is added may be as follows:

(a) $ZnO + 2NH_4^+OH^- + 2NH_4^+Ac^- \longrightarrow [Zn(NH_3)_4]^{++} + 2Ac^- + 3H_2O$

(b) $[Zn(NH_3)_4]^{++} \rightleftharpoons Zn^{++} + 4NH_3$

(c)



$$Zn^{++} \xrightarrow{2\sim\sim COO^-} (\text{—OOC})_2Zn\downarrow$$

Thus, the removal of the adsorbed fatty-acid anions on the particle surface lead to an increase in the particle aggregation and hence an increase in the viscosity.

It is observed that heating latex samples in the presence of zinc ammonium acetate, results in an increased viscosity. This is in accordance with previous observations (2,7-9). Possible explanations for such observations are that at increased temperatures the concentrations of zinc diammine and lower ammines is increased, and hence the reaction of the adsorbed stabiliser with an enhanced concentration of lower zinc ammine complexes increases. Thus, the destabilisation of latex,

Table 5.5 Effect of heating upon viscosity, ZAAV and particle size of NR latex as received and when compounded

latex sample	property		
	viscosity (cP)	ZAAV (cP)	particle size (nm)*
A	48.8	49.0	418
B	53.7	66.9	400
C	43.1	46.6	445
D	47.2	55.9	431
E	-	41.5	-
F	-	49.9	-

* average particle size as determined by Nanosizer

containing zinc ammine ions, increases with an increase in temperature. The reactions which may occur on heating can be summarised as follows:

$$[Zn(NH_3)_4]^{++} + 4H_2O \rightleftharpoons [Zn(H_2O)(NH_3)_3]^{++} + 3H_2O + NH_3$$

$$\upharpoonleft\downharpoonright$$

$$[Zn(H_2O)_2(NH_3)_2]^{++} + 2H_2O + 2NH_3$$

$$\upharpoonleft\downharpoonright$$

$$[Zn(H_2O)_3(NH_3)]^{++} + H_2O + 3NH_3$$

$$\upharpoonleft\downharpoonright$$

$$[Zn(H_2O)_4]^{++} + 4NH_3$$

concentrations
of these species
increases at high
temperatures (2)

and $$NH_3 + H_2O \rightleftharpoons NH_4^{+}OH^{-}$$

However, Nithi-Uthai (2) postulated that additional factors responsible for the destabilisation of latex by zinc ammine ions are:

(a) the reduction in the potential energy barrier with a consequent reduction in the colloid stability of the latex;

(b) the increase in ammonium ion concentration, which compresses the electrical double layer associated with rubber-serum interface, thereby causing destabilisation of the latex; and

(c) the formation of a precipitate of zinc hydroxide, in the presence of solid zinc oxide, which causes desorption of the adsorbed stabiliser on the surface of latex particles.

All these factors contribute to the colloid destabilisation of the latex. The reduced colloidal stability will lead to increased viscosity, probably due to the increased reversible particle aggregation. Thus, an increase in viscosity with an increase in temperature may be due to the operation of all these effects.

When zinc ammonium acetate viscosity results are compared with the viscosity results, it is found that:

(i) as expected, the latex sample treated with zinc ammonium acetate has a higher viscosity than the latex sample without zinc ammonium acetate;

(ii) an approximate linear relationship is obtained, when zinc ammonium acetate is plotted against viscosity for the same latex sample (Figure 5.5). This looks interesting. As far as the author is aware, there is no published literature reporting a similar relationship. When linear regression analysis was performed on these results, a regression coefficient, r, of value 0.87 was obtained. This suggests that there is a good correlation between zinc ammonium acetate viscosity and viscosity. However, more observations are certainly desirable in order to confirm (or refute) this correlation.

5.11 Effect of heating latex samples upon microgel content

In latex, microgel may be defined as the larger particles formed by the association of two or more rubber particles. At this stage, an interface between the original particles may or may not exist. The procedure for measuring the microgel

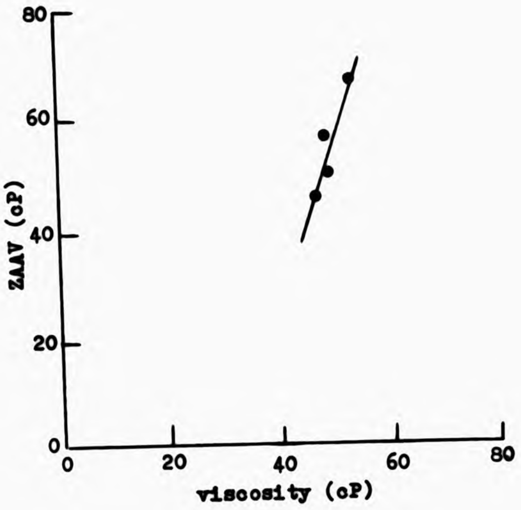


Figure 5.5 Zinc ammonium acetate viscosity, ZAAV, versus viscosity of the latex prior to ZAAV test

content is described in Section 3.4. Basically, the microgel studies were carried out using both the Nanosizer and the optical microscope. The former allowed a quantitative measurement of the microgel size, whereas the latter not only measured the size of the microgel but also gave indications of the structure of the microgel. The results are shown in Table 5.6.

The results obtained by microscopic studies show similar trends to the results obtained using the Nanosizer. For example, microscopic studies indicate that all the samples possess microgel mostly in the form of doublets and triplets (Figure 5.6), thus confirming the small microgel size detected by the Nanosizer. In addition, sample C consists of macroparticles (Figure 5.7). This is confirmed by the large microgel size measured by the Nanosizer.

The heating of uncompounded latex does not affect microgel size to any extent (compare samples A and B). However, addition of zinc oxide caused a marked increase in microgel size (compare samples A and C). The other compounding

Table 5.6 Effect of heating upon microgel present in NR latex as received and when compounded

latex sample	property		
	average* microgel size (nm)	microgel size** (no. of particles in aggregates)	microgel** structure
A	580	2-3	d and t
B	518	2-3	d and t
C	1300	2-18	m
D	613	2-3	d and t
E	1074	3-4	t and q
F	700	3-4	t and q

abbreviations used in table: d = doublets, t = triplets, q = quadruplets and m = macroparticles

* by Nanosizer
** by microscopic studies

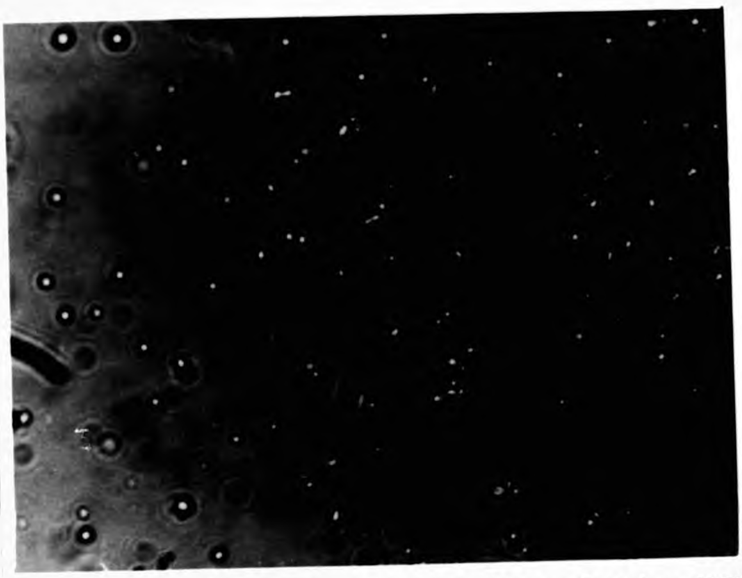


Figure 5.6 Micrograph of latex sample A (magnification x1000)

Figure 5.7 Micrograph of latex sample C (magnification x1000)

ingredients, such as sulphur and ZDEC also caused an increase in the microgel size (compare samples A and E).

The heating of samples C and E to give samples D and F respectively, caused an apparent reduction in the microgel size, as well as in the microgel number. This may be a result of:

(a) coalescence of large aggregates, which are removed from the latex as skin. However, this is unlikely since no skin was observed.
(b) dispersal of loose aggregates (microgel structure) formed by zinc oxide and other vulcanising ingredients. At room temperature, the formation of loose aggregates may interfere in both the microgel and the Nanosizer measurements. However, by raising the temperature the loose aggregates may disperse to participate in the processes indicated schematically in Figure 5.8. The dispersal process is probably initiated to some extent by the extra carboxylate anions arising from the hydrolysis of proteins and lipids when latex is heated. It is probable that the dispersal of loose aggregates is the most likely explanation for the reduction in microgel size.

5.12 Correlation of particle size with MST

The large particle size may account for the reduction in mechanical stability. For example, the presence of large particles in sample C, as shown by microscopic studies and by Nanosizer measurements, may contribute to the very low mechanical stability for this latex sample. However, in contrast, sample E has a relatively high microgel size together with a high mechanical stability. This leads to the suggestion that in the presence of zinc oxide (sample C), the desorption of soap from latex particles occurs. Thus, a net reduction in the repulsive charge causes the mechanical stability to decrease. However, by heating the latex to give sample D, carboxylate anions, formed from the hydrolysis of lipids, become adsorbed on to the particle surface, thereby restoring the repulsive charge. Consequently, the mechanical stability increases. This is also consistent with the hypothesis that carboxylate anions play a part in the initiation of the process of dispersal of loose aggregates

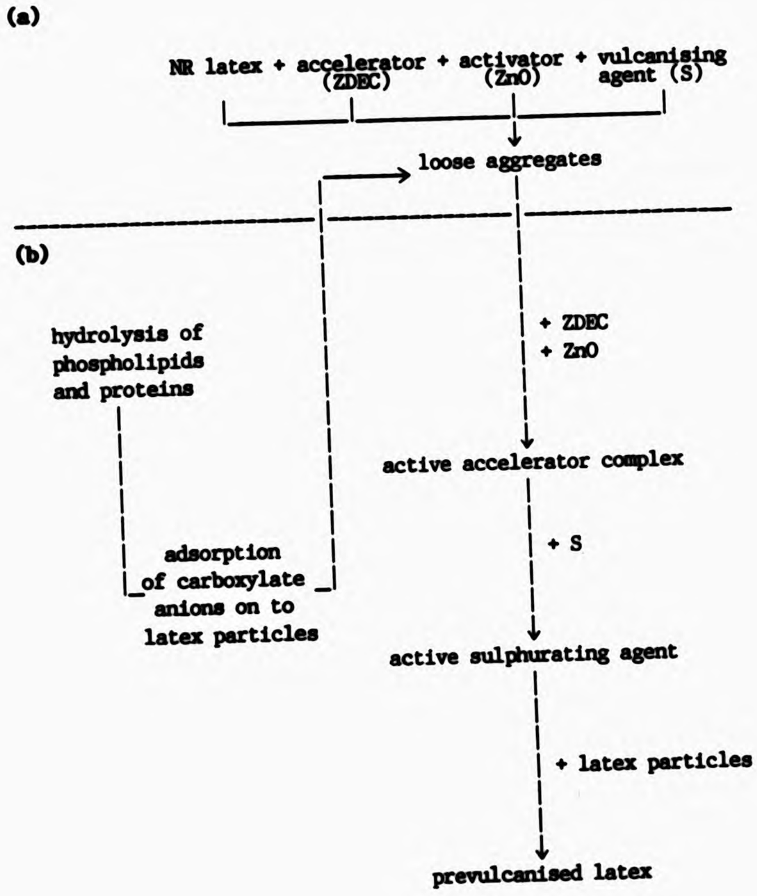


Figure 5.8 Schematic representation of main processes occurring during heating of (a) compounded and (b) prevulcanised NR latex containing ZDEC, ZnO and S

(see Section 5.11).

5.13 Effect of heating latex samples upon calcium stability

The calcium stability test was carried out as described in Section 3.5. The results for the effect of heating latex samples upon the calcium stability time, CST, are given in Table 5.7. As can be seen, there is a marked enhancement in the stability of NR latex to the calcium ions. This is really rather surprising since it was expected that the introduction of calcium ions would cause a catastrophic effect in the destabilisation of the latex, irrespective of heating latex. Also, it is observed that compounding the latex with vulcanising ingredients massively reduces the stability of the latex to the calcium ions. Possible explanations for these observations are believed to be similar to those given for the mechanical stability. In summary, they include:

(i) hydrolysis of phospholipids and proteins; and
(ii) effects associated with the presence of zinc oxide.

Table 5.7 Effect of heating upon CST of NR latex as received and when compounded

latex sample	CST (s)
A	200
B	500
C	5
D	100

5.14 Correlation of mechanical stability and calcium stability

The mechanical stability, MST, results are correlated with the calcium stability, CST, results in Figure 5.9. As can be seen, a straight line passing almost through the origin is obtained, indicating a linear relationship between the mechanical stability and the calcium stability. When linear regression analysis was carried out on these results, a

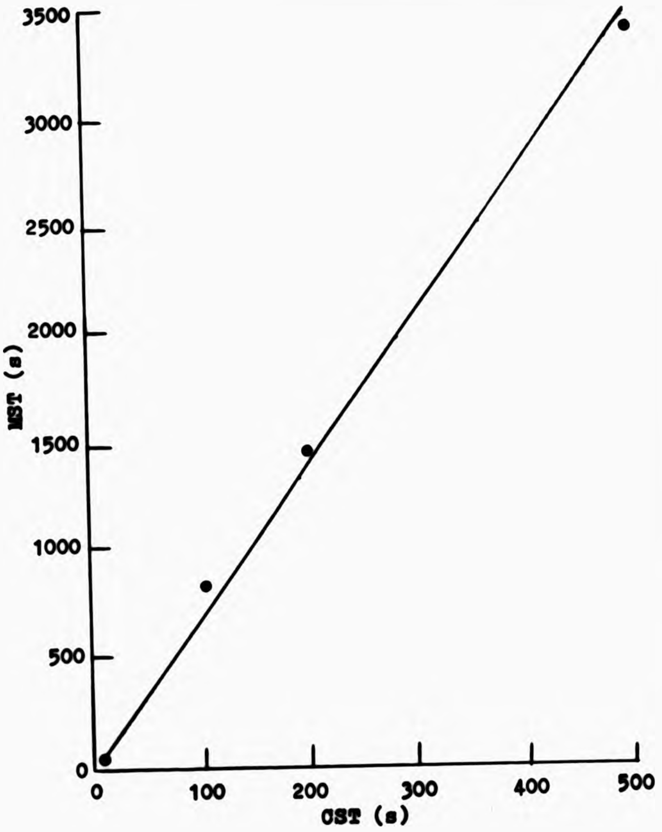


Figure 5.9 Correlation between mechanical stability time, MST, and calcium stability time, CST

regression coefficient of 1.00 was obtained. This suggests that there is an excellent correlation between mechanical stability and calcium stability. This is rather an unusual speculation and will be discussed further in Chapter 8. However, this confirms that, in general, the factors which affect the mechanical stability also affect the calcium stability of latex similarly.

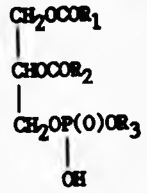
5.15 Further consideration of the hypothesis that increased hydrolysis of lipids occur on heating

5.15.1 Introduction

In summary, it is observed that, on heating the latex:

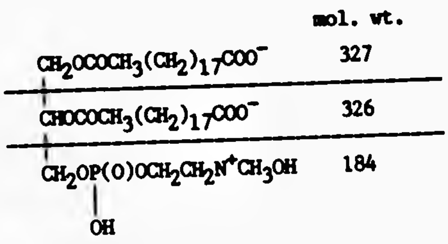
(a) the KOH No. increases, thus indicating an increase in the content of ammonium salts which titrate in the KOH No. determination;
(b) the alkalinity decreases, which indicates that the ammonia has either evaporated and/or reacted with acids; and
(c) the mechanical stability increases, thus indicating that the colloid stability of the latex has increased, possibly partly because more charge is now present on the rubber particles.

These observations are all consistent with further hydrolysis of the phospholipids in NR latex having occurred during the heating. In NR latex, the phospholipids are predominantly of the lecithin type, but a proportion of kephalins is also present. The structure of these phospholipids is,



$$\begin{array}{l} CH_2OCOR_1 \\ | \\ CHOCOR_2 \\ | \\ CH_2OP(O)OR_3 \\ \quad\quad\ \ | \\ \quad\quad\ OH \end{array}$$

where R_1 and R_2 are fatty-acid radicals and R_3 is, $-CH_2CH_2N^+CH_3OH$ in lecithin or $-CH_2CH_2NH_2$ in kephalins. Assuming, fatty-acid radicals are of stearic type, it follows that the molecular weight of a lecithin of this type is 837.



$$\begin{array}{ll} & \text{mol. wt.} \\ CH_2OCOCH_3(CH_2)_{17}COO^- & 327 \\ \hline CHOCOCH_3(CH_2)_{17}COO^- & 326 \\ \hline CH_2OP(O)(OH)OCH_2CH_2N^+CH_3OH & 184 \end{array}$$

5.15.2 Further consideration of KOH No. results

On heating the NR latex the KOH No. increased from 0.62 to 0.79. Thus, the difference is equivalent to

$$\frac{0.17}{56} \times \frac{1}{4} \times 837 \qquad \text{g lipid/100g latex solids}$$

i.e., to 0.64g lipids/100g latex solids
i.e., to 0.38g lipids/100g latex,
the factor 4 in the denominator being a consequence of the lipid molecule giving two stearate anions and one phosphate anion when it fully reacts. Thus the KOH No. results are consistent with the hydrolysis of lipids.

5.15.3 Further consideration of alkalinity results

The alkalinity results indicate that the alkalinity reduced from 1.87 to 1.67g NH_3/100g aqueous phase (i.e., 0.2g NH_3/100g aqueous phase). The ammonia evaporation experiment (Section 3.6, Figure 3.5), indicates that the total loss of ammonia by evaporation was 0.11g NH_3/100g aqueous phase. Thus, the loss of 0.09g NH_3/100g aqueous phase may have occurred due to the reaction with acids generated during the heating of the latex.

Assuming that the acid which reacts with ammonia is PO_4^{---} from hydrolysis of lipid, then four moles of ammonia will react with one mole of phosphate and two moles stearic acid. The reduction of ammonia content of 0.09g NH_3/100g aqueous phase is therefore consistent with the further hydrolysis of,

$$0.25 \times \frac{100}{250} \times \frac{837}{95} \times \frac{1}{2} \quad \text{g lipid/100g latex}$$

i.e., with the further hydrolysis of 0.44g lipid/100g latex. The alkalinity results are therefore consistent with the further hydrolysis of lipids. Also, it is interesting to note that the values 0.44g lipid/100g latex from alkalinity results and 0.38g lipid/100g latex from KOH No. results are surprisingly close.

5.15.4 Further consideration of MST results

From the mechanical stability results, it is observed that on heating the latex the mechanical stability increased from 1455s to 3397s. Again, the results are consistent with the further hydrolysis of lipids. It appears, therefore, that the addition of about 0.4g stearate type soap/100g latex increases the mechanical stability from 1455s to 3397s. However, this does not agree satisfactorily with the observations made by previous workers (7,11,12). For example, Tan (12) reported that the mechanical stability increases from 1100s to 1700s by adding about 0.1g potassium stearate/100g latex. The increase observed in the present investigation is far greater than that observed by Tan (x2.33 as compared to x1.55), and greater than that observed by other workers (7,12). It seems likely that the other factors are involved besides the mere generation of additional soap anions. This is further confirmed by the inconsistency of the reduction in pH with the increase in KOH No., quantitatively (Section 5.5).

5.15.5 Summary

The further considerations of the results reported in this chapter show that they are consistent with heating NR latex, causing further hydrolysis of lipids to occur to the extent of about 0.40g lipid/100g latex. Although, it is generally assumed that the hydrolysis of lipids is complete when the latex is received, the results indicate that the hydrolysis is incomplete on receipt, and that further hydrolysis can occur on heating. Jurado and Mayhan (13) have reported that 1% of the latex solids from NR latex are lipids (i.e., 0.6g lipid/100g latex). Thus, the values obtained in the present investigation are consistent with their work.

CHAPTER 6 : EFFECT OF SELECTED LATEX VARIABLES UPON THE PROCESSING BEHAVIOUR OF NR LATEX WITH REFERENCE TO STRAIGHT DIPPING

6.1 Introduction

Straight dipped films were prepared as described in Chapter 3. The former and film were transferred to the drying cabinet, as described in Section 3.7.1, and the weight of film as a function of time was determined. This allowed both the weight of water evaporated and the rate of evaporation to be calculated. Before commencing any experiments, it was decided to check the reliability of the horse-hair hygrometer as described in the next section.

6.2 Reliability of horse-hair hygrometer to measure relative humidity of drying cabinet

The reliability of the horse-hair hygrometer to measure the relative humidity of the drying cabinet was determined by comparing the experimental values at any given temperature with those calculated from the measured value for the same atmosphere at one particular temperature. The calculation is shown in Appendix C. In this calculation it is assumed that the hygrometer gives the correct value at one temperature and then it is checked whether or not it gives the correct values at other temperatures, i.e., the reliability is checked as regards the temperature-variation of the measured relative humidity. The results are shown in Table 6.1. Experimental and theoretical relative humidity values as a function of temperature are shown in Figure 6.1. It is observed that the difference in the curves is small at low temperatures. However, at high temperatures (>60°C), the difference is noticeable, thereby suggesting that the sensitivity to temperature variations of the horse-hair hygrometer becomes significant at temperatures above 60°C.

6.3 Investigation of reproducibility of drying of dipped latex films

The reproducibility of the drying of dipped latex films was investigated at a temperature of 45°C and a relative humidity

Table 6.1 Results for theoretical and experimental values of relative humidity in drying cabinet

temperature (°C)	RH_E (%)	P_2 ($N\ m^{-2}$)	$P_S(1)$ ($N\ m^{-2}$)	RH_T P_2/P_S (%)
30	-	138684	4246	32.7
35	25.0	140973	5627	25.0
40	20.0	143261	7381	19.4
45	18.5	145550	9590	15.2
50	13.0	147838	12342	12.0
55	10.5	150126	15748	9.5
60	8.0	152415	19930	7.7
65	7.4	154704	25021	6.2
70	7.0	156993	31179	5.0

RH_E is the experimental relative humidity
RH_T is the theoretical relative humidity
P_2 is the water vapour pressure for 0.079 moles of water vapour in the drying cabinet
P_S is the saturated water vapour pressure

of 25%. The procedure is described in Section 3.7. It can be seen from Figure 6.2 that the reproducibility of the results is good. This indicates that the accuracy of the technique used for following the drying of dipped latex films at constant temperature and relative humidity conditions was adequate.

6.4 Effect of cabinet conditions upon drying of dipped latex films

6.4.1 Effect of temperature at constant relative humidity

The total volatile content, TVC, (mostly water) of a latex is defined as the total grams of volatiles per 100g original latex. This decreases on drying, and is therefore a measure of the extent of drying. The method for determining the TVC at various temperatures and at a constant relative humidity of 25% is given in Section 3.7.1. The results are shown in Table 6.2 and Figure 6.3. As expected, it is found that, at higher

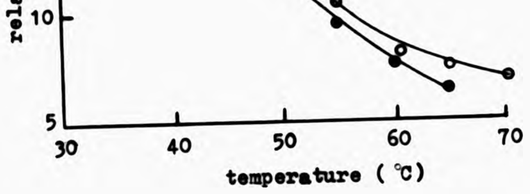


Figure 6.1 Variation of experimental relative humidity, (o), determined by horse-hair hygrometer, and theoretical relative humidity, (●), (see Appendix B), with temperature within the drying cabinet

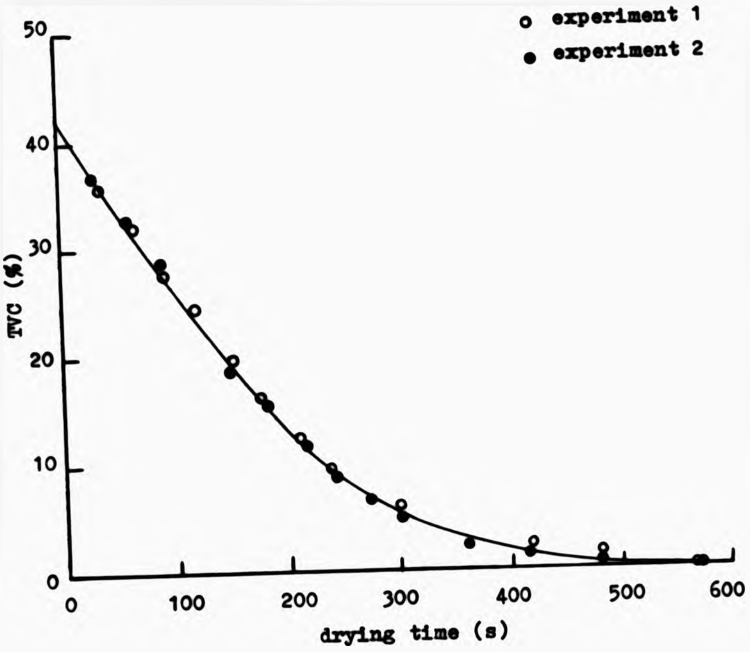


Figure 6.2 Reproducibility of results of duplicate experiments for TVC versus drying time at constant temperature 45°C and relative humidity 25%. The weight of film when completely dry was about 0.3g.

Table 6.2 Effect of temperature on TVC at various drying times and constant relative humidity (25%). These data are for the drying of straight dipped films from prevulcanised NR latex. The weight of the film when completely dry was 0.3g.

drying	temperature (°C)						
time	30	35	40	45	50	55	60
(s)	TVC of drying films expressed as a % of the original weight						
0	41.4	41.4	41.4	41.4	41.4	41.4	41.4
30	35.3	35.5	35.4	36.3	35.9	34.5	—
40	—	—	—	—	—	—	32.4
45	33.7	33.8	34.3	35.0	34.2	32.7	—
60	32.3	32.4	32.9	33.4	32.3	30.8	26.5
75	30.8	31.2	30.8	32.1	30.6	28.5	21.9
90	29.4	29.7	29.6	30.2	28.6	25.6	17.2
105	28.1	28.5	28.3	28.5	26.6	23.8	13.2
180	—	—	20.9	20.7	17.7	13.2	2.3
210	19.4	19.6	18.2	17.2	14.4	9.8	0.9
240	16.9	17.1	15.3	14.8	11.6	6.5	0.5
270	14.2	14.9	13.1	12.2	8.8	4.2	—
300	12.8	12.6	10.6	9.5	6.5	2.4	0.1
360	8.8	8.8	6.7	5.6	3.1	1.0	0.0
420	—	—	3.9	3.2	—	—	0.0
480	3.5	3.4	—	—	0.8	0.3	0.0
600	0.8	1.1	0.6	0.9	0.4	0.1	0.0
780	—	0.1	—	0.1	0.0	0.0	0.0
900	0.0	0.0	0.0	0.0	0.0	0.0	0.0

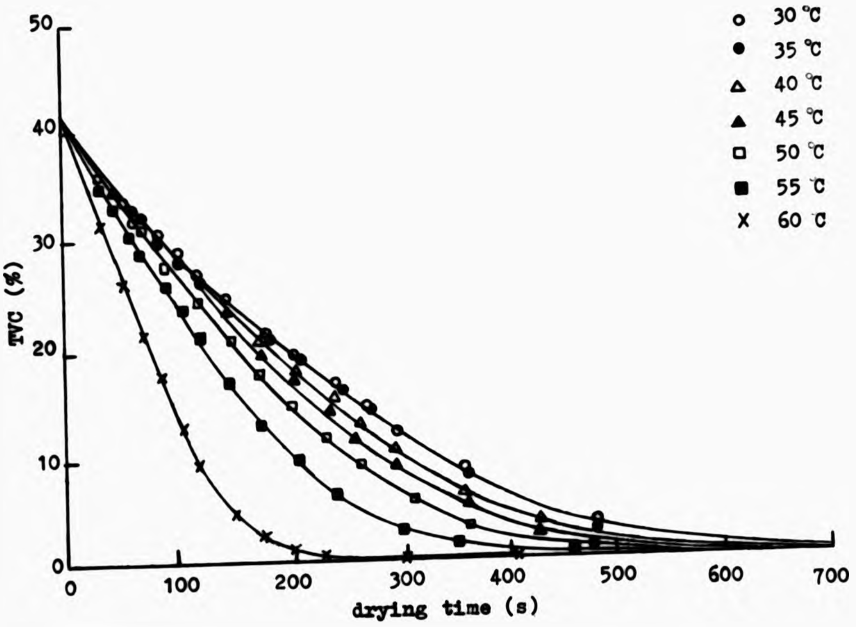


Figure 6.3 TVC versus drying time at various temperatures and constant relative humidity (25%). The weight of the film when completely dry was about 0.3g.

temperatures, water is lost more rapidly from dipped latex films than at lower temperatures.

6.4.2 Effect of relative humidity at constant temperature

The procedure for determining the effect of relative humidity upon the drying of dipped latex films at a constant temperature is given in Section 3.7.1. The results are shown in Table 6.3 and Figure 6.4. Figure 6.4 shows TVC plotted as a function of drying time at various relative humidities and a constant temperature of 30°C. It is observed that the effect of relative humidity upon the variation of TVC with drying time at a given temperature (30°C) is negligible at values of relative humidity less than 35%, but becomes appreciable above this value.

6.5 Initial analysis of drying behaviour of dipped films from prevulcanised NR latex

Attempts have been made to analyse the results for the variation of TVC with drying time in various ways. At first sight, it appeared that an exponential type of relationship might exist between TVC and drying time. Thus a relationship of the following type might exist:

$$\mathrm{TVC} = \exp.^{-nt}$$

or

$$\ln \mathrm{TVC} = -nt \qquad (6.1)$$

where t is the drying time and n is a constant. Typical graphs of ln TVC versus t are shown in Figure 6.5. As can be seen, a straight line is not obtained, thus demonstrating that the relationship between TVC and drying time is not of the simple exponential form indicated above.

6.6 Analysis in terms of diffusion

6.6.1 Introduction

It is possible that the rate-controlling step in the drying of latex films is the diffusion of water through the film. Hence, an attempt was made to analyse the results on this basis. Diffusion may be defined as a molecular process in which molecules are transported from a region of higher concentration to one of lower concentration as a result of

Table 6.3 Effect of relative humidity on TVC at various drying times and constant temperature (30°C). These data are for the drying of straight dipped films from prevulcanised NR latex. The weight of the film when completely dry was 0.3g.

drying	relative humidity (%)							
time	17	20	23	29	33	46	55	60
(s)	TVC of drying films expressed as a % of the original weight							
0	42.2	42.2	42.2	42.2	42.2	42.2	42.2	42.2
30	34.9	33.2	—	34.9	34.0	34.5	—	35.9
45	32.6	31.2	32.2	33.4	32.9	33.5	33.2	34.9
60	30.5	29.5	30.1	30.9	30.5	32.1	32.6	33.9
75	28.5	27.8	27.8	29.2	28.8	31.0	31.7	33.0
90	26.3	25.7	25.7	27.0	27.4	29.6	30.5	31.9
120	22.5	22.2	22.0	23.2	23.2	27.3	28.3	29.8
150	19.2	18.7	18.8	19.6	19.6	24.5	25.8	27.7
180	16.0	15.4	15.3	16.1	16.3	22.0	23.3	25.4
210	12.6	12.7	12.0	12.8	13.2	19.9	20.9	23.5
240	9.9	9.7	9.2	9.5	9.9	17.3	19.0	21.4
300	5.2	5.2	5.1	4.3	5.2	12.9	14.8	17.5
360	2.3	2.0	2.7	1.5	2.4	8.4	11.0	13.8
480	0.7	0.4	0.9	0.2	0.5	1.8	4.7	7.2
600	0.4	0.2	0.3	0.0	0.0	0.1	1.6	2.7
900	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1

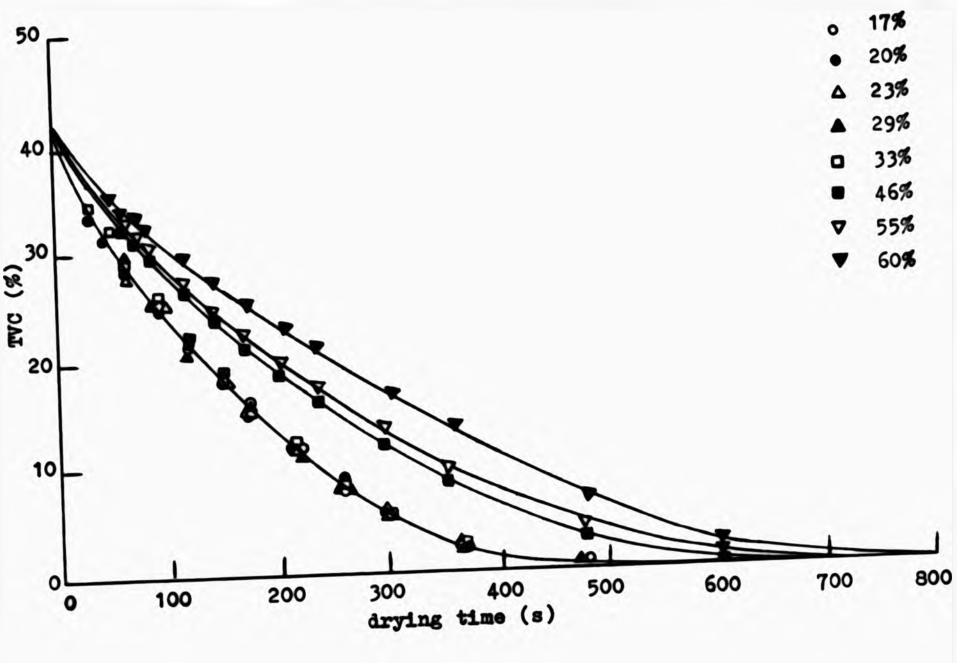


Figure 6.4 TVC versus drying time at various relative humidities and at constant temperature (30°C). The weight of the film when completely dry was about 0.3g.

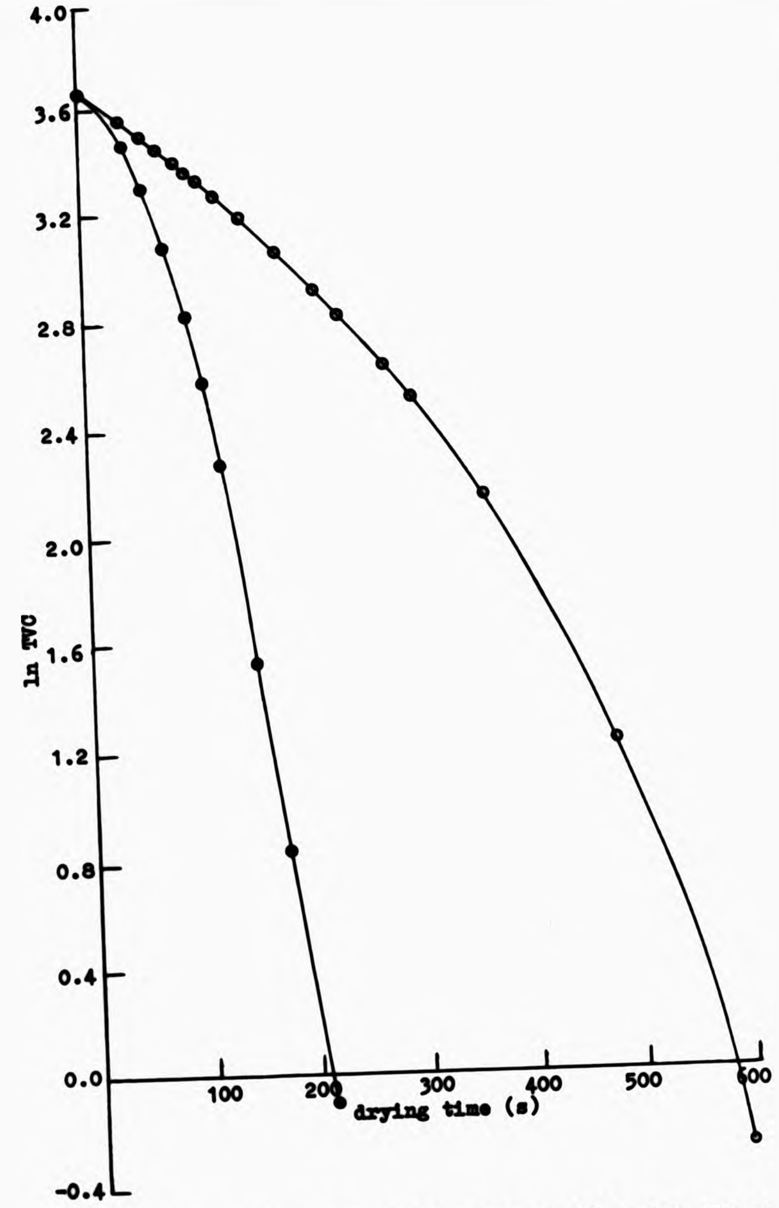


Figure 6.5 ln TVC versus drying time at 30°C, (o) and at 60°C, (●), at constant relative humidity (25%). The weight of the film when completely dry was about 0.3g.

thermal motion. The transport of liquid into and from rubber is a process which conforms to this definition.

The fundamental diffusion equations are due to Fick (2), who formulated them in 1855. The first law of diffusion states that the rate of transfer of diffusant, R_D, across a section of unit area is proportional to the concentration gradient, dc/dx, normal to the section. This can be expressed as,

$$R_D = -D \frac{dc}{dx} \qquad (6.2)$$

where D is the proportionality constant, known as diffusion coefficient. Fick's second law of diffusion in one dimension relates the time-variation of concentration to the distance-variation as follows:

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \qquad (6.3)$$

where t denotes time and x distance.

It can be shown that for Fickian diffusion the rate of transfer of diffusant, R_D, is directly proportional to the square root of the diffusion time, i.e.,

$$R_D \propto t^{\frac{1}{2}} \qquad (6.4)$$

However, since R_D is difficult to measure accurately, the method described below was employed.

Consider a typical mass-uptake curve for a liquid being absorbed into a solid such as a rubber film. The curve is typically as shown in Figure 6.6, in which M_∞ is the maximum mass of liquid absorbed and M_t is the mass of liquid absorbed at time, t. It has been shown (2) that the variation of M_t/M_∞ with t is dependent upon D. The argument is as follows:

Consider, a plane sheet that occupies the region $-l < x < l$, l being half the total thickness of the sheet and x being 0 at the centre of the sheet, as shown in Figure 6.7. It is assumed that the initial concentration of liquid in the solid, c_0, is zero, and that the concentration in the solid at equilibrium,

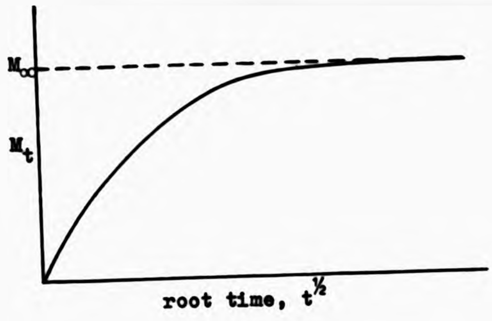


Figure 6.6 Typical mass-uptake curve for liquid being absorbed into a solid

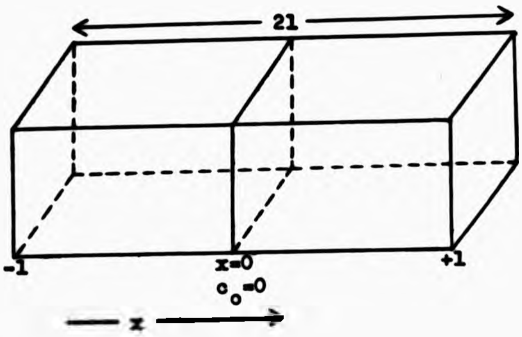


Figure 6.7 Section of plane sheet occupying region $-1 < x < 1$

c_∞, is constant. The concentration of liquid, c_t, at a time, t, is related to the distance x below the surface (2) by

$$\frac{c_t - c_0}{c_\infty - c_0} = \sum_{n=0}^{n=\infty} (-1)^n \operatorname{erf} \frac{(2n+1)l - x}{2(Dt)^{\frac{1}{2}}} + \sum_{n=0}^{n=\infty} (-1)^n \operatorname{erf} \frac{(2n+1)l + x}{2(Dt)^{\frac{1}{2}}} \qquad (6.5)$$

The error function of x, erf x, is given in mathematical tables. If M_t is the total amount of liquid absorbed at time t, and M_∞ the corresponding quantity after infinite time, then (2)

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{l^2}\right)^{\frac{1}{2}} \left\{ \pi^{-\frac{1}{2}} + 2\sum_{n=1}^{n=\infty} (-1)^n \operatorname{ierf} \frac{nl}{(Dt)^{\frac{1}{2}}} \right\} \qquad (6.6)$$

In the early stages of diffusion, the infinite series in the right-hand side of equation 6.6, is comparatively smaller than $\pi^{-\frac{1}{2}}$, hence is ignored. The expression is then simplified to,

$$\frac{M_t}{M_\infty} = 2\,\frac{(Dt)^{\frac{1}{2}}}{l\pi^{\frac{1}{2}}} \qquad (6.7)$$

It can be seen from equation 6.7 that a plot of M_t/M_∞ versus the square root of the diffusion time, $t^{\frac{1}{2}}$, should produce a straight line of slope $2D^{\frac{1}{2}}/l\pi^{\frac{1}{2}}$, thereby enabling D to be calculated. In the present investigation, the desorption of water from a dipped film from prevulcanised NR latex was measured. Thus assuming the desorption process to be of a similar nature to the absorption process, all other things being equal, the results have been treated in the manner indicated by the above analysis.

6.6.2 TVC as a function of square root of diffusion time, $t^{\frac{1}{2}}$

In the experiment for the determination of water loss from a dipped film, M_t was equivalent to TVC (expressed as a percentage) and M_∞ was 41.4 (again expressed as a percentage). Initially, the thickness, L, of the dipped film was assumed to be constant. The plots of TVC versus $t^{\frac{1}{2}}$ shown in Figure 6.8 were obtained. The curves are obviously non-linear. It was then realised that it might be necessary to make allowance for the change in L during the desorption process.

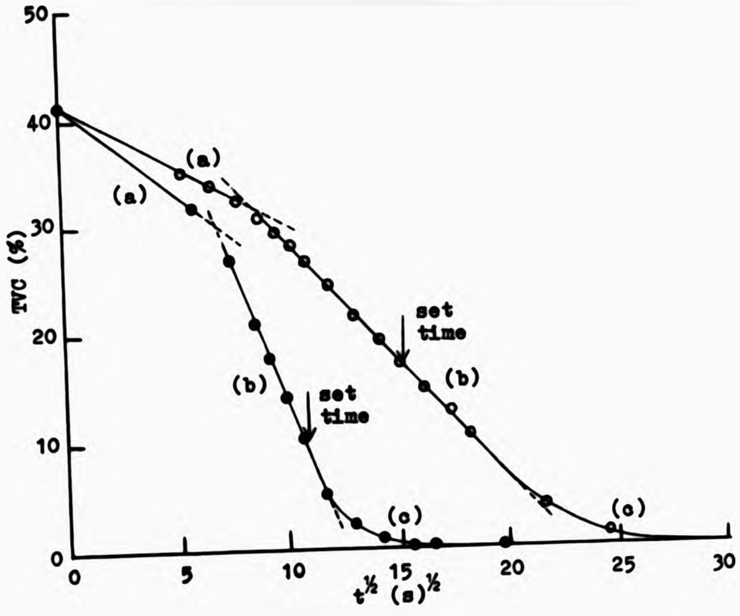


Figure 6.8 TVC against square root of diffusion time, $t^{1/2}$, at 30°C, (o), and at 60°C, (●). Note: Plots for only two extreme temperatures are shown. The plots for other temperatures between 30-60°C follow the same trend and lie within these extremes.

6.6.3 TVC as a function of square root of diffusion time per unit thickness, $t^{\frac{1}{2}}/L$

Again, M_t was regarded as equivalent to TVC (%) and M_∞ was taken as 41.4 (%). The value of L at any particular diffusion time was calculated from the known area of the latex films and the TVC at that time. A typical calculation is given below. The example chosen is for the initial thickness of the latex film before drying commences.

Knowing (a) the area of film, a_f, $25cm^2$
(b) the weight of film, w_f, 0.5g
(c) the density of (i) water, ρ_W, $1gcm^{-3}$,
(ii) rubber, ρ_R, $0.92gcm^{-3}$
and (d) TVC_∞, 41.4%,

the thickness of a film at any time, t, can be calculated. Thus, at $TVC_\infty = 41.4\%$, the thickness due to

(i) rubber, L_R, is given by

$$L_R = \frac{w_f\,[(100-TVC_\infty)/100]}{\rho_R\, a_f} = 0.13mm$$

(ii) water, L_W, is given by

$$L_W = \frac{w_f\,(TVC_\infty/100)}{\rho_W\, a_f} = 0.08mm$$

Hence, the thickness of the dipped film, L, at zero time is

$$L = L_R + L_W = 0.13 + 0.08 = 0.21mm$$

Values of L_R, L_W and L at other times of drying were calculated similarly using the appropriate value of TVC. The values of square root of diffusion time per unit thickness at time t, i.e., $t^{\frac{1}{2}}/L$, were then calculated and are shown in Table 6.4. Graphs of TVC as a function of square root of diffusion time per unit thickness of film at time t for given temperatures of 30°C and 60°C are shown in Figure 6.9. It can be seen from Figure 6.9 that TVC varies linearly with the square root of diffusion time per unit thickness during the

Table 6.4 Values of TVC and square root of diffusion time per unit thickness, $t^{\frac{1}{2}}/L$, at 30, 40, 50 and 60°C

drying time	temperature (°C)							
	30		40		50		60	
(s)	TVC (%)	$t^{\frac{1}{2}}/L$ $(s)^{\frac{1}{2}}$/mm	TVC (%)	$t^{\frac{1}{2}}/L$ $(s)^{\frac{1}{2}}$/mm	TVC (%)	$t^{\frac{1}{2}}/L$ $(s)^{\frac{1}{2}}$/mm	TVC (%)	$t^{\frac{1}{2}}/L$ $(s)^{\frac{1}{2}}$/mm
0	41.4	0	41.4	0	41.4	0	41.4	0
30	35.3	28	35.4	28	35.9	27	—	—
40	—	—	—	—	—	—	32.4	33
45	33.7	34	34.3	34	34.2	34	—	—
60	32.3	40	32.9	40	32.3	40	26.5	43
75	30.8	46	30.8	46	30.6	46	21.9	50
90	29.4	51	29.6	51	28.6	51	17.2	59
105	28.1	56	28.3	55	26.6	57	13.2	67
180	21.7	79	20.9	79	17.7	82	2.3	101
210	19.4	87	18.2	88	14.4	92	0.9	112
240	16.9	96	15.3	97	11.6	103	0.5	120
270	14.2	105	13.1	107	8.8	113	—	—
300	12.8	113	10.6	116	6.5	123	0.1	135
360	8.8	130	6.7	135	3.1	137	0.0	146
420	—	—	3.9	152	—	—	—	—
480	3.5	162	—	—	0.8	152	—	—
600	0.8	189	0.6	189	0.4	189	—	—
900	0.0	234	—	—	0.0	218	—	—

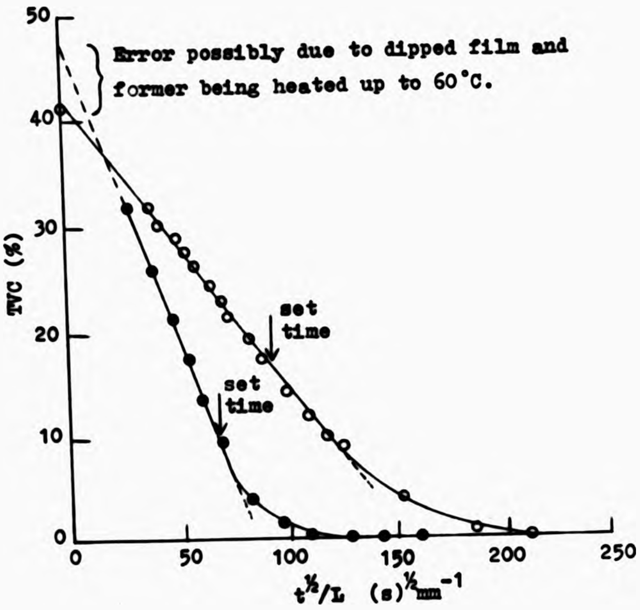


Figure 6.9 TVC against square root of diffusion time per unit thickness, $t^{\frac{1}{2}}/L$, at 30°C, (o), and at 60°C, (●). Note: Plots for only the two extreme temperatures are shown. The plots for other temperatures between 30-60°C follow the same trend and lie within these two extremes.

early stages of drying. This suggests that there is single diffusion process which governs the rate of drying of dipped latex films.

6.6.4 Calculation of diffusion coefficient, D, of water

The diffusion coefficient, D, of water through the latex films was calculated as described in Section 6.6.1. The slope, which was determined by the method of least squares (linear regression), in Figure 6.9 is equal to $2D^{\frac{1}{2}}TVC_{\infty}/\pi^{\frac{1}{2}}$, thus enabling the value of D to be calculated. The results are shown in Table 6.5. As can be seen from the results, the diffusion coefficient increases with an increase in temperature. This is hardly surprising, since at high temperatures the thermal energy and hence the kinetic energy of the molecules is higher than at low temperatures. Thus the rate of movement of water molecules through the latex film (characterised by D) is expected to increase with increasing temperature.

It may be argued that the soluble materials present in the latex film may affect the diffusion coefficient because such substances are removed by leaching. For example, Gazeley (3)

Table 6.5 Values of diffusion coefficient for water molecules through latex films obtained from slopes of TVC versus $t^{\frac{1}{2}}/L$ plots at various temperatures, T

T (°C)	$(T)^{-1}$ $(K)^{-1}$	slope* $(s\ mm^{-2})^{\frac{1}{2}}$	D (cm^2s^{-1})	ln D
30	$3.30x10^{-3}$	0.25	$0.3x10^{-6}$	-15.1
35	$3.25x10^{-3}$	0.26	$0.3x10^{-6}$	-15.0
40	$3.20x10^{-3}$	0.28	$0.4x10^{-6}$	-14.8
45	$3.15x10^{-3}$	0.30	$0.4x10^{-6}$	-14.7
50	$3.10x10^{-3}$	0.32	$0.5x10^{-6}$	-14.6
55	$3.05x10^{-3}$	0.35	$0.6x10^{-6}$	-14.4
60	$3.00x10^{-3}$	0.50	$1.2x10^{-6}$	-13.7

* determined using the least square method

showed that the rate of extraction of soluble materials was reduced significantly by increasing the temperature from 25°C to 70°C. The reason given for this was that the solubility of some of the non-rubber materials is reduced by a denaturing process as the temperature is increased, thus reducing the rate of extraction. However, Gick (4) has shown that the leaching process has a negligible effect upon the calculation of the diffusion coefficient for water molecules in rubber films.

6.6.5 Calculation of activation energy, E_A, for diffusion of water through latex film

The variation of diffusion coefficient with temperature can be expressed by the Arrhenius equation as follows:

$$D = A\,e^{-E_A/RT}$$

or

$$\ln D = \ln A - E_A/RT \qquad (6.9)$$

where A is the Arrhenius pre-factor, R is the gas constant, 8.314J mol^{-1} K^{-1}, T is the absolute temperature and E_A is the activation energy for the diffusion process. It can be seen from equation 6.9 that a plot of ln D versus T^{-1} enables the activation energy, E_A, to be determined. When ln D is plotted as a function of T^{-1} (see Figure 6.10), a linear relationship is obtained up to temperatures in the region of 50-55°C (Section (a)). This indicates that the Arrhenius equation holds up to *ca.* 50°C. The activation energy calculated from the slope of the line, using the method of least squares (linear regression), was found to be 1.4kJ mol^{-1}. At temperatures greater than 55°C, however, an abrupt change in slope occurs (Section (b)). It is not certain whether this change is a consequence of experimental errors or a genuine change. However, the latter seems to be the more likely, because if the former was true then the values obtained at temperatures 50-55°C would also be expected to be affected by experimental error to a certain degree. Obviously, more work needs to be carried out on this aspect, before drawing any definite conclusions.

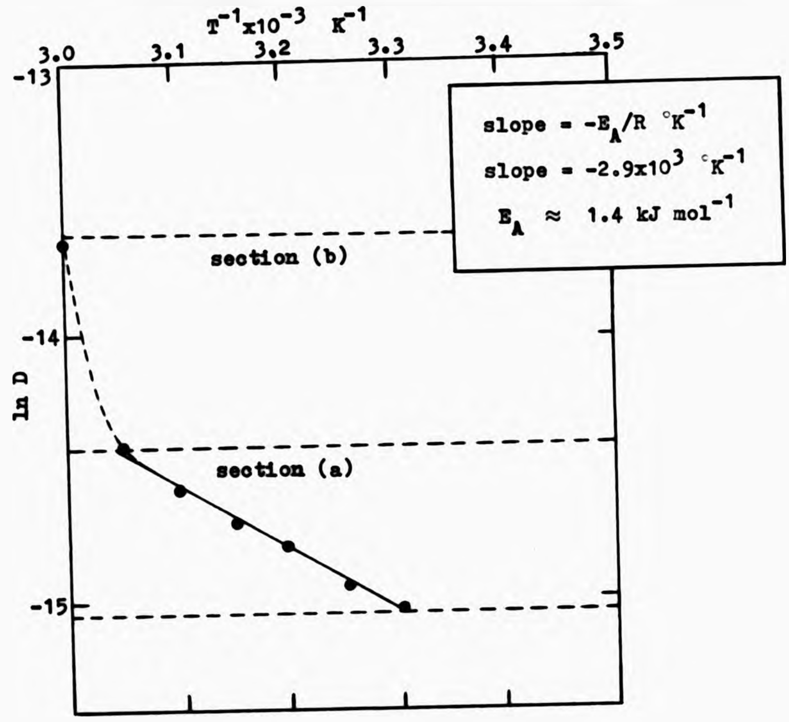


Figure 6.10 Arrhenius plot of ln D versus reciprocal absolute temperature, T^{-1}, for diffusion of water through dipped films from prevulcanised NR latex during drying

6.7 Discussion of analysis of results for drying of latex films on assumption that the rate-controlling process is diffusion of water molecules through film

6.7.1 Introduction

A number of studies have been made on the drying and formation of latex films, as discussed in Chapter 2. A common mechanism seems to apply, which has been discussed by Vanderhoff (5). It involves three stages for the process of drying. These three stages can be summarised as follows:

1. In the first stage, the particles move about with their characteristic Brownian motion and the water evaporates from the latex at the same rate as for pure water. This stage ends when particles are forced into irreversible contact by water-air interfacial tension. This occurs at a polymer volume fraction of about 0.6-0.75 (6).
2. The intermediate stage begins when the particles come into irreversible contact with one another and ends with their coalescence to form a continuous film. During this stage, the rate of evaporation decreases rapidly to a value 10-20 times smaller than that observed during the first stage. This is a consequence of reduction in the water-air interfacial area.
3. In the final stage, any residual water trapped in the bulk of the film escapes by diffusion either through capillary channels between the deformed spherical particles or through the polymer itself. The rate of evaporation is very much smaller than the first two stages, and decreases very slowly with time.

6.7.2 Discussion of TVC versus $t^{\frac{1}{2}}/L$ plots

From the mechanisms discussed by Vanderhoff (5,6), it would be anticipated that the loss of water would be linear with time during the first stage of drying. However, Figure 6.9 shows that the TVC is linearly related to the square root of diffusion time per unit thickness during the early stages of drying. This suggests that there is single diffusion mechanism which governs the drying of dipped films. The single diffusion process is probably a consequence of the formation of a coherent film on the surface of the film during the early stages of drying. This may be due mainly to the gelation caused by the local drop in pH resulting from loss of ammonia at the surface. The gelation due to loss of ammonia will be discussed further in Section 6.8.7.

6.7.3 Confirmation of coalescence of surface layer particles

6.7.3.1 Procedure

An experiment was carried out in which approximately 10g of latex was weighed accurately and placed in a weighing bottle. The area of the base of the bottle was $\sim 26cm^2$, which is equivalent to area of films on the slide. The bottle was then allowed to stand exposed to atmosphere at room temperature and relative humidity of 52%. After a predetermined time, it was filtered through a microporous gauze, (25 μ), previously weighed. The gauze was re-weighed after filteration. Thus the weight of residue on the gauze after filteration was known. The procedure was repeated after various drying times. The results are given in Table 6.6.

6.7.3.2 Results and discussion

As can be seen from Table 6.6, the weight of residue on the gauze increased with increase in the drying time, suggesting that there is an increase in the amount of inter-particle structure within the latex. This increase of structure produces aggregates of particles which are undoubtedly larger than the size of micropores, and hence do not pass through the filter. At this stage, however, it was uncertain whether the phenomenon of increase of inter-particle structure within the latex occurred in the bulk of the latex or in the surface, or in both. Hence, a further experiment was carried out in which various weights (and hence thicknesses) of latex were placed in the bottle and exposed to the atmosphere for a fixed drying time of 10 minutes. The weights of residue on the gauze after filteration were determined. The results are shown in Table 6.7.

It was expected that, on the one hand, if the increase of inter-particle structure, and hence in the coalescence of rubber particles, occurred at the surface of the latex, then the amount of residue would be independent of the thickness (or area) of latex samples. On the other hand, if the increase

Table 6.6 Results of experiment to investigate coalescence of surface layer of latex film: effect of drying time upon weight of residue upon gauze after filteration

drying time (s)	weight of residue on gauze (g)
0	0.1626
30	0.3028
60	0.3366
120	0.3563
180	0.3664
300	0.3671
600	0.3707
900	0.3865

Table 6.7 Results of experiment to investigate coalescence of surface layer of latex film: effect of variation of initial sample weight upon weight of residue upon gauze after filteration, at the fixed drying time of 10 minutes

weight of latex sample (g)	weight of residue on gauze (g)
5.0425	0.3900
10.0067	0.3879
15.6574	0.3868
19.9025	0.3866
25.0117	0.3926
30.1640	0.3972

of inter-particle structure occurred in the bulk of the latex, then the amount of residue would be expected to increase with reduction in the thickness of latex samples. In fact, Table 6.7 shows that the weight of residue on the gauze was approximately constant, irrespective of the thickness of the latex sample. This also indicates that the increase of inter-particle structure and coalescence of rubber particles in the surface occurs during the very early stages of drying, i.e., < 30s.

6.7.4 Effect of coalescence of surface particles upon drying

The coalescence of the particles at the surface of a dipped latex film causes a capillary structure to form. The water can then pass through the surface layer by diffusion at a rate equal to that at which it is removed from the surface by evaporation. The capillary structure is maintained by interstitial water. The evaporation of water causes further coalescence of particles with consequent gradual disappearance of the capillary structure.

The further development of this hypothesis of coalescence of surface layer particles leads to the conclusion that, if the rate of loss of water from the surface is by evaporation which is at a rate equal to the rate at which water is transported through the surface by diffusion, then the latter should be independent of the thickness of the film at that time. However, Figure 6.9 shows that the loss of water from the film has a strong dependency upon the changing thickness of the film with time (c.f. Figure 6.8). It is thought that this phenomenon arises from the operation of two opposing effects.

(i) The time-dependent thickening of the surface film together with increasing coalescence of its constituent particles reduces the water content near the surface of the film.

(ii) A gradual build-up of water from the bulk of the film to near the surface increases the water content near the surface of the film. This build-up of water near the surface is a consequence of a concentration gradient being set-up as more water evaporates from the film. As a consequence more water moves outwards from bulk to near surface by osmosis.

Thus, the balance of these two opposing effects ensures an adequate supply of water near the surface of the film to replenish the water which is lost by evaporation by the passage of water through the surface of the film by diffusion.

6.7.5 Relationship between rate of diffusion, R_D, rate of evaporation, R_E, and surface area, A_S

In the above discussion, it has been proposed that the rate of loss of water from the surface by evaporation is at a rate equal to the passage of water through the surface by diffusion, for a given size of capillaries. In order to probe the credibility of this proposition, an attempt has been made to derive an expression which relates these processes. Also, the factors affecting such a relationship are discussed.

It is assumed that, to a first approximation, the percentage of water present in the film is equivalent to the area of water, and hence to the size of the capillaries, at the surface. The rate of loss of water by evaporation is thus expected to be directly proportional to the surface area. This effect was investigated by determining the slopes for a given drying time from Figure 6.3, which yielded the corresponding rate of evaporation of water. The surface area was calculated from the percentage of water present in the film. The results are shown in Table 6.8 and Figure 6.11. Clearly, the results indicate that there is a linear relationship between the rate of evaporation of water from the film and the surface area of water at the surface, and hence the aggregate size of the capillaries at the surface. Thus:

$$R_E = KA_S \qquad (6.10)$$

where R_E is the rate of evaporation of water, A_S is the surface area of water (which is proportional to the aggregate size of the capillaries at the surface), and K is the proportionality constant, known as evaporation coefficient. The evaporation coefficient, K, is expected to depend upon

(a) drying conditions, e.g., the temperature and relative humidity: It is seen from Table 6.9 that the value of K increases with increase in temperature. It is well known that the rate of evaporation of water is temperature-dependent. Thus from equation 6.10, if the

Table 6.8 Relationship between rate of evaporation of water, R_E, and surface area of water, A_S, at various temperatures

drying time (s)	R_E $((\%)s^{-1})$	TVC (%)	TSC (%)	$A_S = \frac{TVC}{TVC+TSC} \times 100$
		temperature 30°C		
0	16.8	42.0	58.0	42.0
100	11.4	28.2	58.0	32.7
200	8.5	18.3	58.0	24.0
300	6.4	12.1	58.0	17.3
400	5.0	5.1	58.0	8.1
		temperature 40°C		
0	16.8	42.0	58.0	42.0
100	11.4	28.1	58.0	32.6
200	8.6	18.5	58.0	24.2
300	7.1	10.5	58.0	15.3
400	5.0	4.5	58.0	7.2
		temperature 55°C		
0	24.0	42.0	58.0	42.0
100	15.3	23.5	58.0	28.8
200	11.2	10.0	58.0	14.7
300	3.7	2.5	58.0	4.1
400	1.6	0.5	58.0	0.9
		temperature 60°C		
0	35.0	42.0	58.0	42.0
100	25.2	14.5	58.0	20.0
150	11.6	6.0	58.0	9.4
200	3.4	1.5	58.0	2.5

Figure 6.11 Rate of evaporation, R_E, versus surface area of water, A_S, for dipped latex films drying at various temperatures

surface area of water for evaporation remains constant, the value of K increases with an increase in temperature.

(b) rate of diffusion of water, R_D, through the surface layer: The rate of diffusion of water, R_D, through the surface layer of a latex film is expected to depend upon the natures and amounts of the non-rubber substances which are present in the aqueous phase of latex.

6.7.6 Effect of non-rubber constituents of latex upon rate of drying of dipped latex films

When water evaporates from a latex film, the concentration of salts in the aqueous phase increases, thereby reducing the rate of passage of water through the surface by diffusion. To investigate whether such an effect causes any significant changes in the overall drying process of a latex film, an experiment was carried out in which ammonium acetate solution was diluted with distilled water to appropriate concentrations. The rate of loss of water was determined by means of weight loss-time curve, for a given concentration of ammonium acetate. The results are shown in Figure 6.12. It is observed that, on increasing the concentration of ammonium acetate solution, the rate of loss of water from it was reduced. However, the increased concentration of salt during the early stages of drying of a dipped latex film seems to have only a small effect upon the rate of loss of water from the film. This is because, in a latex film, the concentration of salts increases from about 2.5 to 10% in the early stages of drying; and from Figure 6.12, it is estimated that the rate of loss of water is thereby reduces from 1.30g hr^{-1} to 1.12g hr^{-1} (or $3.6 x 10^{-4}$g s^{-1} to $3.1 x 10^{-4}$g s^{-1}) when the salt concentration increases from 2.5 to 10%.

6.7.7 Diffusion coefficient, D, of water through dipped latex films

The values of D (Table 6.5) have been found to be of the order of $10^{-6} cm^2 s^{-1}$. These values agree satisfactorily with the values for the diffusion coefficient of, for example, weak electrolytes in water. The D-value for citric acid in water at 25°C is $0.07 x 10^{-6} cm^2 s^{-1}$ (6). The D-value for citric acid is selected, since it is a weak acid and hence is expected to behave in a similar way to acetic and formic acids, which are

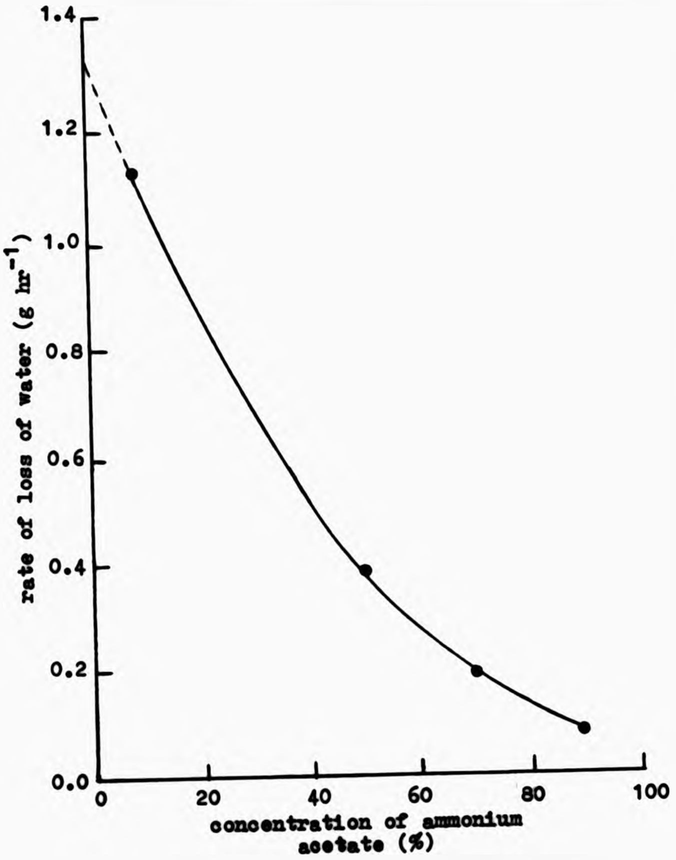


Figure 6.12 Effect of concentration of ammonium acetate solution upon rate of loss of water from this solution. The concentration of undiluted ammonium acetate solution was assumed to be 100%.

known to be present in NR latex. The literature values of D for the diffusion of water through various polymers are typically $10^{-10} cm^2 s^{-1}$ (4). Clearly, this suggests that, in the early stages of the drying of dipped latex films, the loss of water is by diffusion through capillaries formed by coalescence of latex particles and not through the rubber itself. This conclusion agrees with that reached by Gazeley and Swinyard (7).

6.7.8 Activation energy, E_A, of water

The activation energy for the diffusion of water from a dipped film from prevulcanised NR latex has been found to be 1.4kJ mol^{-1} (Figure 6.10). This value is much lower than the reported values for the diffusion of various substances through a wide range of rubbers. For example, Frensdorff (8) found 2.5-4.7kJ mol^{-1} for the activation energy for the diffusion of benzene in ethylene-propylene copolymers; Gick (4) reported 3.5kJ mol^{-1} for the diffusion of aviation fuel in polysulphide sealants. The result for the activation energy, therefore confirms that the diffusion of water is not through the polymer in the early stages of the drying of dipped latex films.

6.7.9 Relationship between D and K

It has been assumed that the rate of evaporation of water from the surface of a latex film occurs at a rate equal to the rate of diffusion of water through the surface. It is thus expected the rate of evaporation (characterised by the evaporation coefficient, K) will be linearly related to the rate of diffusion (characterised by the diffusion coefficient, D), all other things being equal. Values of K for various temperatures were calculated from the slopes, the latter being determined by the method of least squares (linear regression), of plots shown in Figure 6.11. These values have been plotted versus the diffusion coefficient, D, at the same temperature. The results are shown in Table 6.9 and Figure 6.13. From Figure 6.13, it is seen that there is an excellent straight line, bearing in mind all the experimental uncertainties, thus indicating that there is indeed a linear relationship between K and D. However, it should be noted that the line does not go through the origin. Thus, the main feature of the first stage of drying appears to be that the rate of passage of water through the surface by diffusion occurs at a rate equal to that at which it is removed from the surface by evaporation.

Table 6.9 Values of D and K at various temperatures

temperature (°C)	D (cm^2s^{-1})	K (s^{-1})
30	$0.29x10^{-6}$	$0.36x10^{-6}$
40	$0.37x10^{-6}$	$0.39x10^{-2}$
55	$0.55x10^{-6}$	$0.60x10^{-2}$
60	$1.16x10^{-6}$	$1.04x10^{-2}$

6.7.10 Comparisons with published work

Vanderhoff (5) stated that the initial stage of the loss of water from a latex film involves the evaporation of water at a rate equal to that for pure water, irrespective of the polymer particles which are present. The latex particles are in Brownian motion, and are deemed not to penetrate the surface (9). However, the results of the present investigation are not consistent with this mechanism, since the rate of loss of water is non-linear with time, even during the early stages of drying. This is further supported by confirming the linearity with time of the loss of water from pure water as follows: an experiment was carried out in which the rate of evaporation of pure water was determined under the same conditions as those used for latex films (i.e., temperature of 30°C and relative humidity of 25%). The relationship for weight loss versus time (Figure 6.14) was linear throughout the drying process, except at the point where the water disjoined from the wall or bottom of the dish (the latter not shown). The rate of evaporation of water was calculated to be $2.5x10^{-4}g\ min^{-1}cm^{-2}$. This value is in good agreement with the value reported by Vanderhoff *et al.* (6) for pure water at 22°C and relative humidity 50%, which is in the range $2.1\text{-}2.2x10^{-4}g\ min^{-1}cm^{-2}$. The small difference arises from the different conditions used.

That the contribution of the Brownian motion of the rubber particles during the early stages of the drying of latex films is insignificant accords with the conclusion reached by

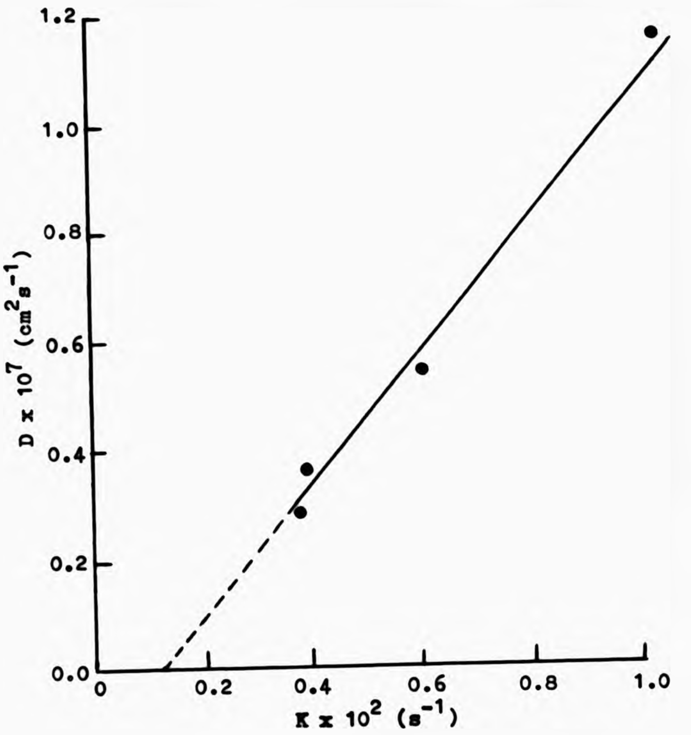


Figure 6.13 Relationship between D and K at various temperatures

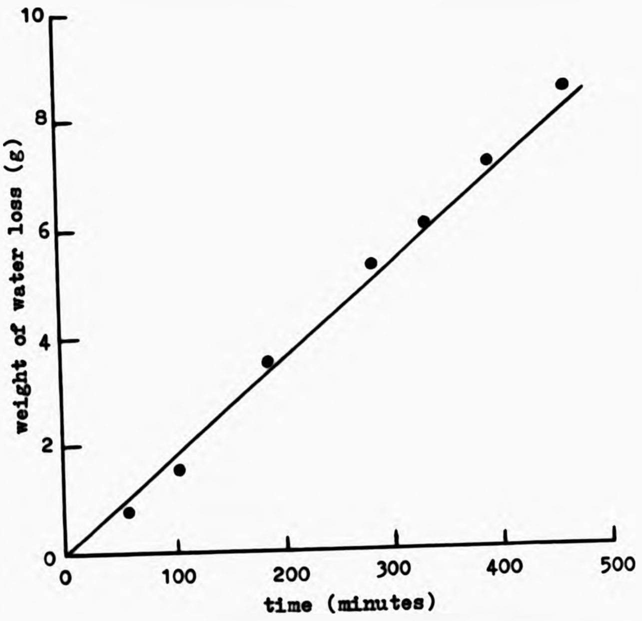


Figure 6.14 Weight of water loss from pure water versus time at constant temperature 30°C and relative humidity 25%

Gazeley and Swinyard (7). They found that there was no significant difference between the results from cast films and those from coagulant dipped gels (in which Brownian motion was completely suppressed), other conditions being equal.

6.7.11 Summary

In a film prepared from normal ammoniated latex, a coherent film forms on the surface at an early stage of drying. This is thought to be mainly a consequence of gelation caused by the local drop in pH resulting from loss of ammonia at the surface (7). The principal feature of this stage of drying is that the water passes through the surface by diffusion at a rate equal to that at which it is removed from the surface by evaporation. The rate of evaporation of water, R_E, from the surface depends upon the surface area, A_S, of water, and hence upon the aggregate size of the capillaries present in the surface. It has been found that,

$$R_E = KA_S$$

The evaporation coefficient, K, depends upon:

(a) the drying conditions, e.g., temperature and relative humidity; and
(b) the rate of diffusion of water through the surface of the latex film.

The rate of diffusion of water may be affected by the concentration of salts present in the aqueous phase of the latex. However, it has been found that the increased concentration of salts in the latex aqueous phase as drying proceeds has little effect upon the rate of drying of latex films.

The diffusion coefficient for the diffusion of water through latex films has been found to be of the order of $10^{-6}cm^2s^{-1}$. The activation energy has been found to be $1.4kJ\ mol^{-1}$. These values indicate that the diffusion of water is not through the rubber itself but through the capillaries which form on the surface during the early stages of drying of dipped latex films.

A linear relationship has been observed between the diffusion coefficient, D, and the evaporation coefficient, K, for a given type of dipped latex film drying at various temperatures.

6.8 Effect of temperature upon ammonia content, TAC, during drying of dipped films from prevulcanised NR latex

6.8.1 Introduction

The total ammonia content, TAC, of a latex is defined as the total grams of ammonia content per 100g original latex. This is used as a measure of the extent of evaporation of ammonia from the latex. The procedure for determining TAC is given in Section 3.7.2. The results are arrived at by using a calibration curve for total ammonia content versus pH. The calibration curve was obtained for a batch of latex samples for which both the TAC and the pH were determined. The resultant calibration curve for TAC versus pH is shown in Figure 6.15. A logarithmic relationship was expected but surprisingly a linear relationship was obtained. However, since the pH variation was in such a small range, the overall relationship probably remained unaffected. Thus, this curve was regarded as acceptable. The main advantage of using a calibration curve as compared to the direct determination of ammonia content by the alkalinity experiment is that the pH measurements are rapid compared with the direct determination of TAC. It must be stressed that the calibration curve obtained is linear only in the specified range.

6.8.2 Results for effect of temperature on TAC

The results for the effect of temperature on TAC after various times of drying at a constant relative humidity of 25% are shown in Table 6.10 and Figure 6.16. As expected, it is observed that the loss of ammonia is more rapid at higher temperatures than at lower temperatures.

A striking feature of the plots of TAC versus drying time (Figure 6.16 (a)) is that initially there is a very sharp decrease in TAC with an increase in drying time. A possible reason for this may be that, as soon as the thin latex films are exposed to the atmosphere, the ammonia which is present in

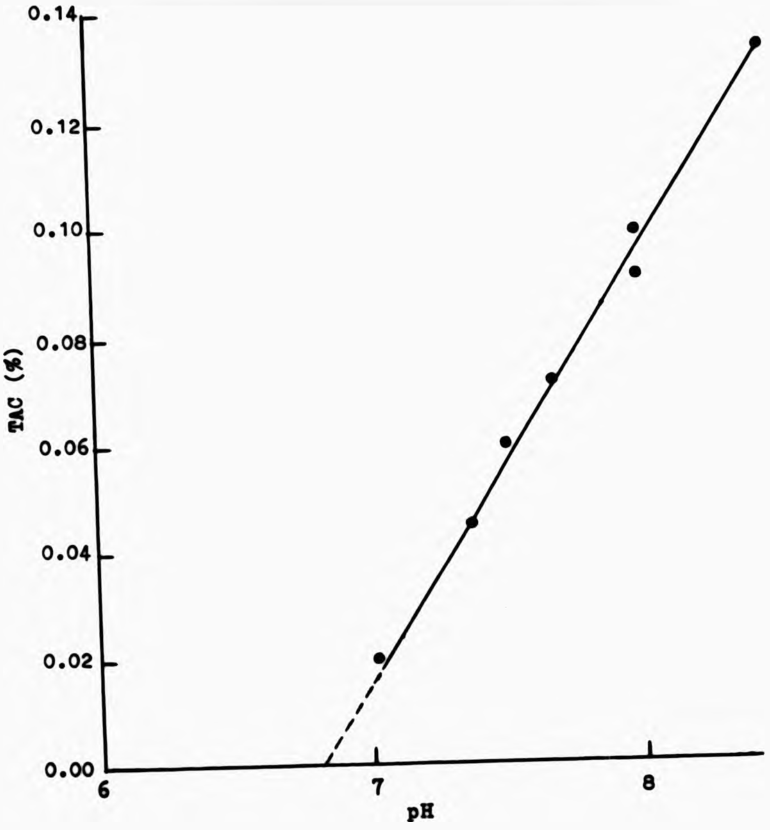


Figure 6.15 Calibration curve for total ammonia content, TAC, versus pH

the aqueous phase in equilibrium with ammonium ions volatilises almost instantly. This initial rapid loss of ammonia in a very short time is probably very important technologically. As far as is known, no previous work has been carried out on this aspect of the investigation. However, the further subsequent loss of ammonia may be a result of the gradual dissociation of ammonium ions. In order to test these hypotheses, the results are analysed further in Section 6.8.4.

Table 6.10 Effect of temperature on TAC at various drying times and a constant relative humidity of 25%

drying time (s)	temperature (°C) 30	35	40	45	50	55	60
	TAC (g ammonia/100g original latex)						
30	0.12	0.11	0.11	0.10	0.09	0.06	0.02
60	0.10	0.09	0.08	0.08	0.07	0.03	0.00
90	0.09	0.08	0.08	0.06	0.05	0.02	—
120	0.08	0.07	0.06	0.05	0.03	0.01	—
180	0.08	0.05	0.04	0.02	0.02	0.00	—
240	0.05	0.03	0.03	0.01	0.01	—	—

6.8.3 Analysis of results for loss of ammonia from dipped latex films on assumption that rate of loss is diffusion-controlled

As for the results for loss of water (see Section 6.6), the results for the loss of ammonia from dipped latex films were analysed by plotting TAC against the square root of time per unit thickness of film at time t, for loss of ammonia at various temperatures and constant relative humidity of 25%. The results are shown in Figure 6.17. In all cases, a linear relationship between TAC and square root of time per unit film thickness at time t, $t^{\frac{1}{2}}/L$, is observed. This suggests that, after the initial rapid loss of ammonia within 30s, (Figure 6.17 (a)), the further loss of ammonia (i.e., possibly ammonia combined with acids) is by a diffusion process.

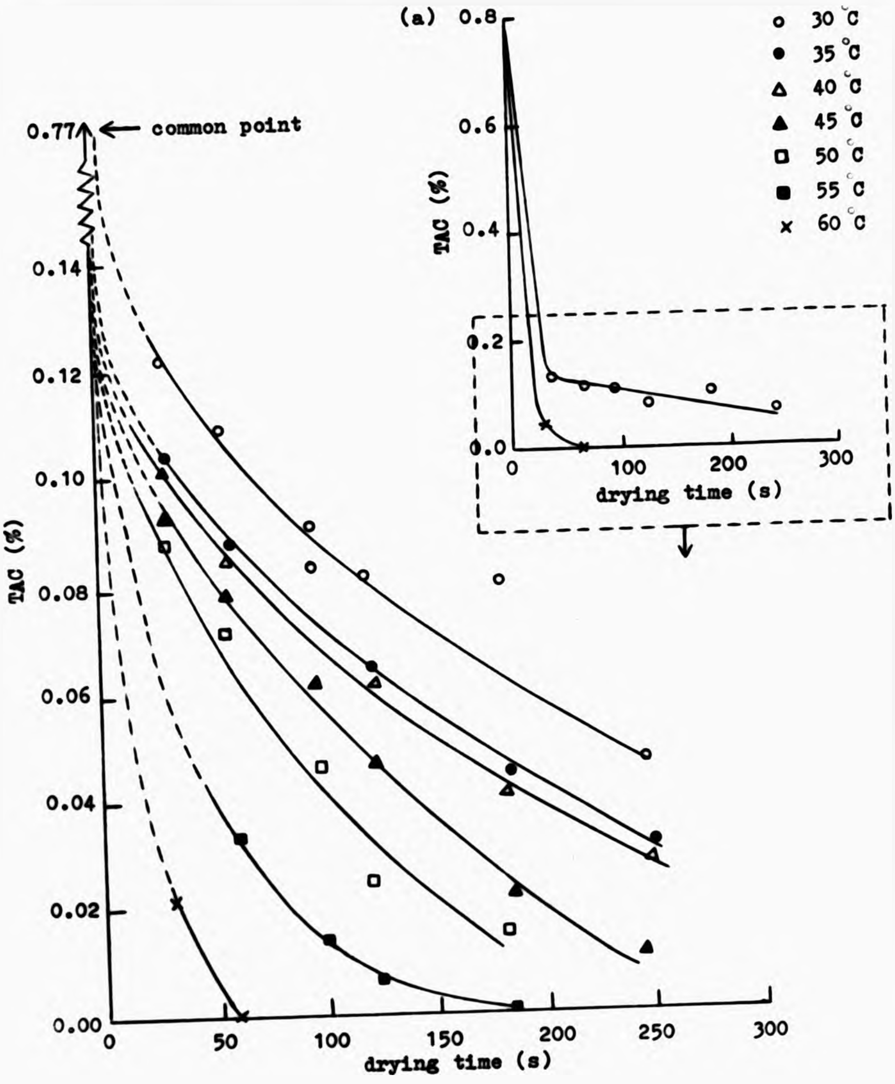


Figure 6.16 TAC versus drying time at various temperatures and constant relative humidity (25%)

6.8.4 Analysis of results for TAC versus $t^{\frac{1}{2}}/L$

The results of TAC as a function of $t^{\frac{1}{2}}/L$ at various temperatures (Figure 6.17 (a)) confirm that the initial loss of ammonia is a rapid process. This has been interpreted as rapid initial volatilisation of ammonia in equilibrium with ammonium ions in the aqueous phase, followed by a further loss of ammonia resulting from probably a gradual dissociation of ammonium ions. In order to test this interpretation, the results for TAC versus $t^{\frac{1}{2}}/L$ have been analysed further. Because a linear relationship is observed between TAC and $t^{\frac{1}{2}}/L$ after the initial rapid loss of ammonia (Figure 6.17), the total amount of ammonia present for loss by diffusion is then readily obtained by interpolation of the plots to zero time. This yielded the total amount of ammonia, TAC_{∞}, available for loss of ammonia by diffusion, presumably present not only as ammonia combined as ammonium ions but also as ammonia in equilibrium with ammonium ions in the aqueous phase. The point at which the dissociation of ammonium ions begins was found from KOH No. titration. It should be noted that the essential reaction which occurs in the KOH No. titration is:

$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$$

The results are shown in Table 6.11 and Figure 6.18.

It can be seen from Table 6.11 and Figure 6.18 that, as the temperature increased, the amount of total ammonia, TAC_{∞}, available for loss by diffusion decreased. This implies that the total loss by diffusion of ammonia in equilibrium with ammonium ions in the aqueous phase decreases. However, at temperatures above 50°C, the further loss of ammonia by diffusion is wholly due to the dissociation of ammonium ions, as is indicated by the negative values for A-B in Table 6.11, A-B being interpreted as the amount of total ammonia in equilibrium with ammonium ions in the aqueous phase. This effect can be easily demonstrated by drawing tangents to the two parts of the curve for TAC_{∞} versus temperature, as shown in Figure 6.18. The point where the two tangents intersect corresponds almost exactly to the KOH No. This implies that the loss by diffusion of ammonia as ammonium ions alone occurs at temperatures above about 50°C. It appears that the further analysis of the results for the loss of ammonia during the drying of films from prevulcanised NR latex is consistent with

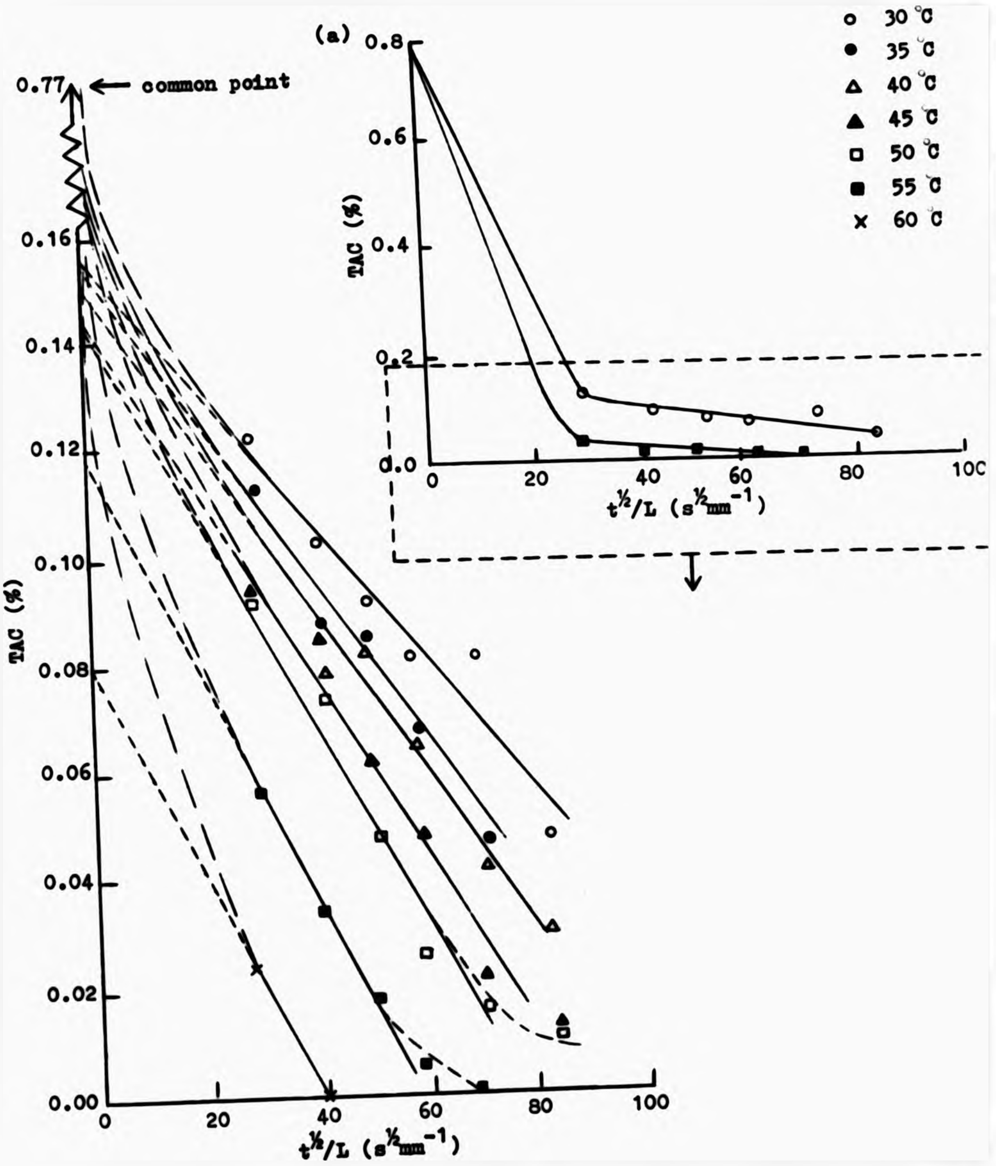


Figure 6.17 TAC versus square root of diffusion time per unit film thickness, $t^{1/2}/L$, at various temperatures

Table 6.11 Total ammonia, TAC_{∞}, present for loss by diffusion at various temperatures, and its relationship to the amount of ammonia equivalent to the KOH No.

temperature (°C)	TAC_{∞} * ($g\ NH_3/100g$ original latex), A	amount of ammonia equivalent to KOH No. ($g\ NH_3/100g$ original latex), B	A-B ($g\ NH_3/100g$ original latex)
30	0.16	0.14	0.02
35	0.15	0.14	0.01
40	0.15	0.14	0.01
45	0.14	0.14	0.00
50	0.14	0.14	0.00
55	0.11	0.14	-0.03
60	0.08	0.14	-0.06

* calculated using the method of least squares (linear regression), since all the points lie near or on the straight line.

the interpretation which has been proposed above. It is also very interesting to note that there is such an abrupt change of slope. This change though very significant never appears to have been observed previously.

The effect can be summarised by separating the curve of TAC versus $t^{\frac{1}{2}}/L$ at a given temperature, into three regions which correlate well with the proposed origins of the ammonia as the latex film dries. This is illustrated in Figure 6.19. The first region involves the loss by evaporation of ammonia which is entirely in equilibrium with ammonium ions in the aqueous phase. In the intermediate region, the ammonia which is lost by diffusion is derived both from the ammonia in equilibrium with ammonium ions in the aqueous phase and the ammonium ions themselves. In the final region, the ammonia which is lost by diffusion is solely from the ammonium ions. However, as the temperature is increased, the transition from evaporation (Region I) to diffusion (Region III) is accelerated. Above about 50°C, no intermediate stage is observed.

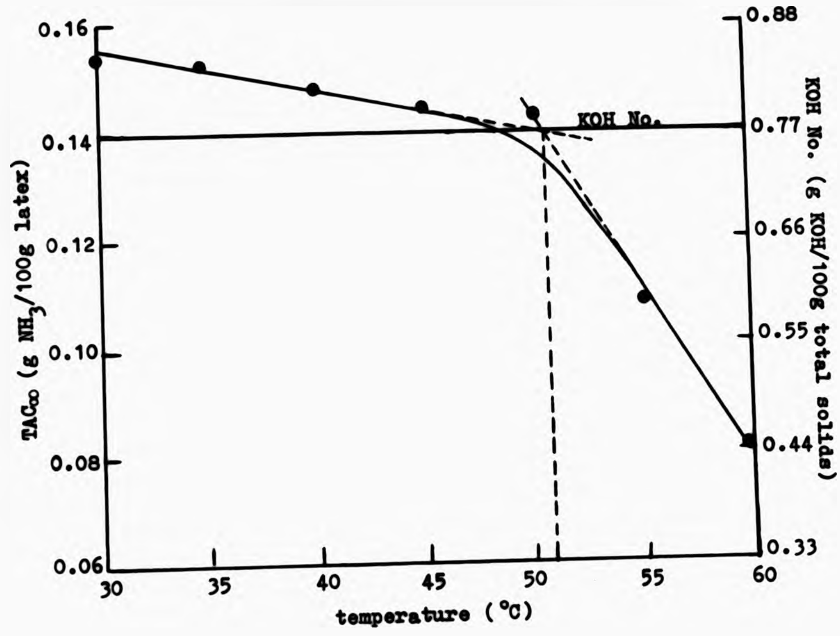


Figure 6.18 TAC∞ versus temperature and its relationship to the KOH No.

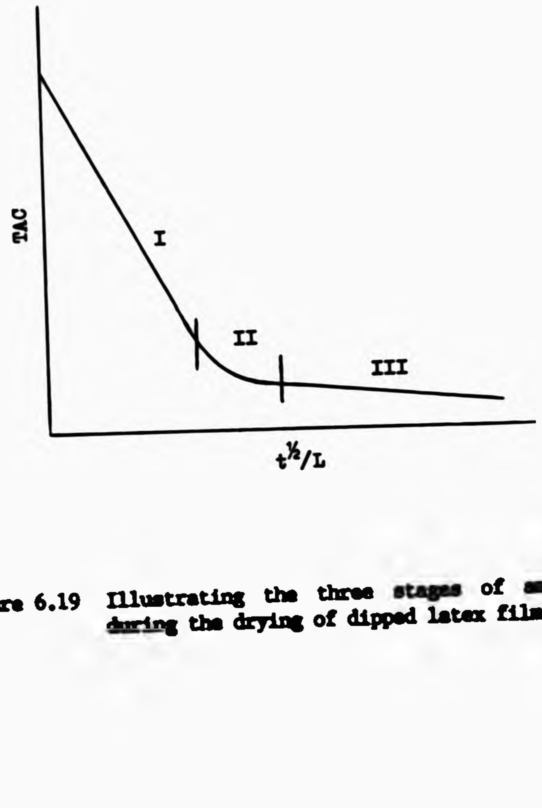


Figure 6.19 Illustrating the three stages of ammonia loss during the drying of dipped latex films

6.8.5 Calculation of diffusion coefficient, D, for ammonia in a latex film

The diffusion coefficient, D, of ammonia during the drying of a dipped latex film was calculated as described in Section 6.6.1. Values of D have been estimated from the plots of TAC versus $t^{\frac{1}{2}}/L$ shown in Figure 6.17. Assuming that the diffusion of ammonia through the latex film obeys the Fickian diffusion equation, it follows that,

$$\frac{TAC_t}{TAC_\infty} = \frac{2(Dt)^{\frac{1}{2}}}{\pi^{\frac{1}{2}}L} \qquad (6.11)$$

where TAC_t is the weight of ammonia at time t and TAC_∞ is the maximum weight of ammonia for loss by diffusion. The diffusion coefficient, D, can therefore be calculated for the diffusion of ammonia through the latex film. The results are shown in Table 6.12. As the temperature is increased, the diffusion coefficient increases. This was expected, because at higher temperatures the thermal motion of the molecules is increased relative to the motion at lower temperatures, thereby increasing the diffusion coefficient.

Table 6.12 Values of diffusion coefficient for ammonia molecules through latex films obtained from slopes of TAC versus $t^{\frac{1}{2}}/L$ plots at various temperatures, T

T (°C)	$(T)^{-1}$ $(K)^{-1}$	TAC (%)	slope* $(s\ mm^{-2})^{\frac{1}{2}}$	D (cm^2s^{-1})	ln D
30	$3.30x10^{-3}$	0.16	$1.2x10^{-3}$	$0.5x10^{-6}$	-14.5
35	$3.25x10^{-3}$	0.15	$1.5x10^{-3}$	$0.7x10^{-6}$	-14.1
40	$3.20x10^{-3}$	0.15	$1.4x10^{-3}$	$0.7x10^{-6}$	-14.1
45	$3.15x10^{-3}$	0.14	$1.6x10^{-3}$	$1.0x10^{-6}$	-13.8
50	$3.10x10^{-3}$	0.14	$1.9x10^{-3}$	$1.3x10^{-6}$	-13.5
55	$3.05x10^{-3}$	0.11	$1.8x10^{-3}$	$2.1x10^{-6}$	-13.1
60	$3.00x10^{-3}$	0.08	$1.9x10^{-3}$	$4.5x10^{-6}$	-12.3

* determined using the least squares method.

The diffusion coefficient for ammonia through latex films has been compared with the diffusion coefficient for water through latex films. In general, the D values for the diffusion of ammonia are higher than those for the diffusion of water. A plausible reason for this is that the ammonia loss process is more rapid than the water loss process in the drying of an ammoniated NR latex film. This is because ammonia molecules are more mobile and volatile than water molecules as they are not associated to the same extent (note that the molecular weights are virtually identical). Thus, the concentration gradient set up for the former is comparatively high, and hence higher values of D for loss of ammonia are obtained.

When the values of D for water are plotted against the values of D for ammonia at the same temperature, the graph shown in Figure 6.20 is obtained. A linear relationship between the two diffusion coefficients is obtained. This suggests that the factors which influence the rate of loss of water during the drying of a latex film also influence the rate of loss ammonia from the film, all other things being equal. Furthermore, it is noted that the line does not go through the origin, i.e., there is a positive intercept on the diffusion for water axis. This is interesting, and it implies that at a sufficiently low temperature the latex film is impermeable to ammonia but permeable to water. Again, it seems unlikely that these interesting observations have ever been made previously.

6.8.6 Calculation of activation energy, E_A, for diffusion of ammonia through latex films

When ln D for ammonia diffusing through a latex film is plotted versus 1/T (Figure 6.21), the Arrhenius relationship is seen to be obeyed up to a temperature of about 55°C, above which a deviation occurs. A similar observation was made when ln D for the diffusion of water was plotted versus 1/T (see Section 6.6.5, Figure 6.10). The activation energy calculated from the slope, which was determined using least squares method, of the linear portion was found to be about 2.6kJ mol^{-1}. This value is almost double the value for the diffusion of water through latex film (1.4kJ mol^{-1}). It is possible that this difference is due in part to the bulky size of the hydrated ammonium ion.

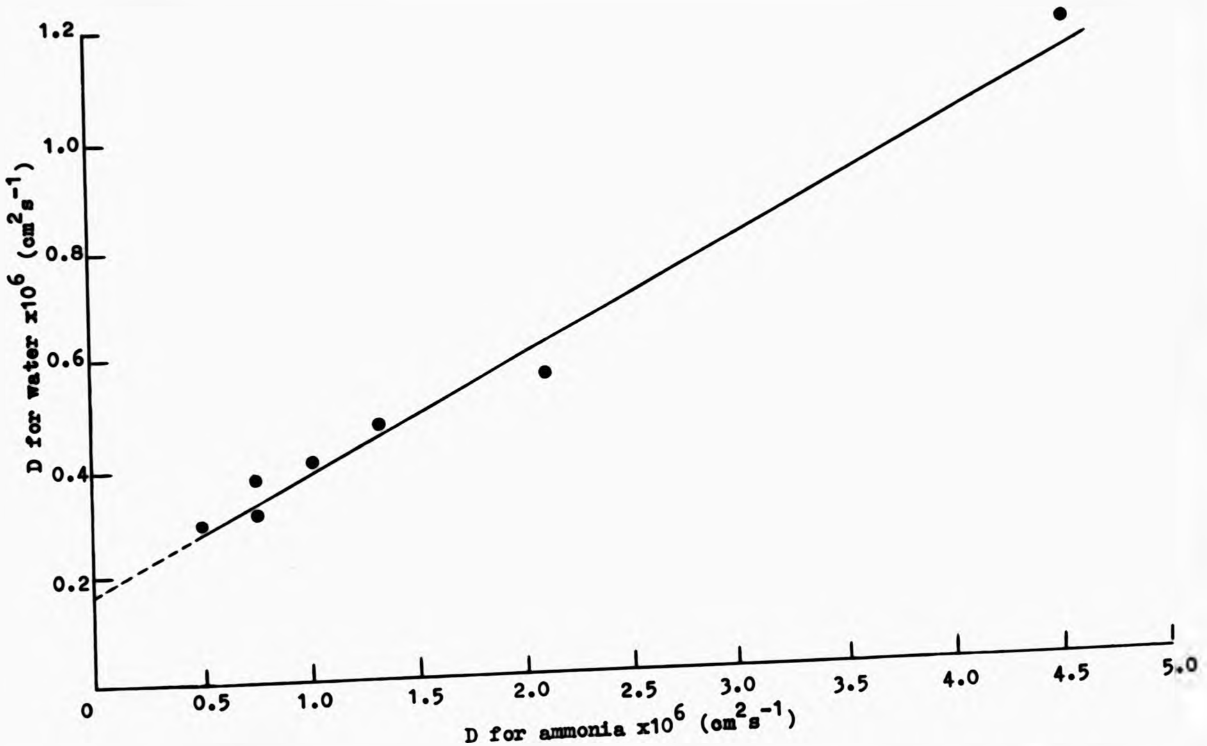


Figure 6.20 Relationship between D for water and D for ammonia through latex films at various temperatures

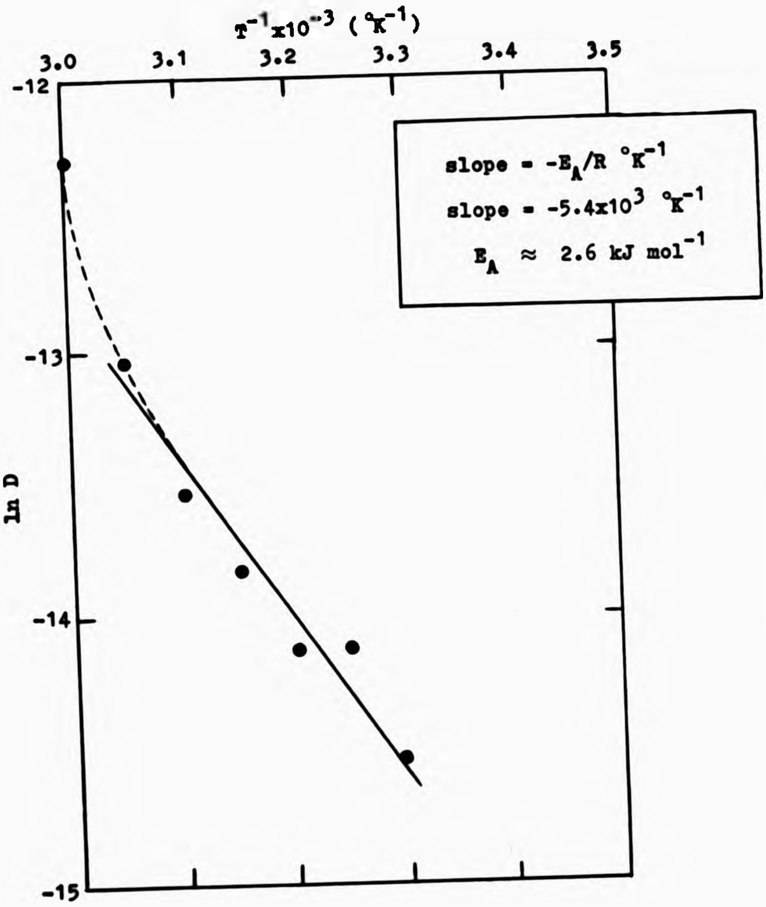


Figure 6.21 Arrhenius plot of ln D versus reciprocal absolute temperature, T^{-1}, for diffusion of ammonia through dipped films from prevulacnised NR latex during drying

Unfortunately, no previous investigations of this aspect of latex science and technology have been reported, hence no direct comparisons can be made. However, some interesting results have been obtained in this work, which merit further study. For example, deviations from the Arrhenius relationship have been observed at higher temperatures, but no further investigation of this matter has been possible because of the limited time available.

6.8.7 Correlation of TAC and TVC

It was not considered worthwhile to consider in great detail the relationship between the results for TVC and those for TAC. This is because a very large percentage of the total ammonia is lost from the film in a very short time compared with a percentage of the total water lost from the film. Nevertheless, the TVC results suggest that a coherent surface layer forms on the surface of the film at an early stage of drying (Section 6.7). A possible reason for this is that a local drop in pH occurs which results from loss of ammonia at the surface. As a consequence, coalescence of the particles occurs at the surface. The TAC results (Figure 6.16) confirm this hypothesis, since there is an initial sharp drop in TAC in less than 30s. This initial sharp drop is followed by a gradual loss in TAC on drying of the dipped latex film. To consider further the implications of this latter observation, the percentage concentrations of ammonia present at various times of drying of a dipped latex film at various temperatures and a constant relative humidity of 25%, have been calculated as follows:

$$\text{Percentage ammonia concentration} = \frac{\text{TAC at a specified drying time}}{\text{TVC at that specified drying time}} \times 100$$

The results are summarised in Table 6.13 and Figure 6.22. It is observed that over the first 30s or so there is a rapid decrease in ammonia concentration.

6.9 Effect of temperature upon set time, t_S, of dipped films from prevulcanised NR latex

For the purposes of this project, the set time, t_S, of a dipped latex film was defined as the time taken for a given

Table 6.13 Percentage ammonia concentration at various temperatures and drying times for drying of dipped latex films at 25% relative humidity

drying time (s)	temperature (°C)					
	30	35	40	45	50	55
	ammonia content (g NH_3/100g aqueous phase)					
0	1.86	1.86	1.86	1.86	1.86	1.86
30	0.35	0.31	0.31	0.25	0.25	0.16
60	0.31	0.27	0.24	0.25	0.22	0.16
90	0.31	0.28	0.28	0.21	0.17	0.07
120	0.31	0.24	0.24	0.18	0.10	0.02
180	0.37	0.21	0.20	0.11	0.09	—
240	0.28	0.18	0.20	0.08	0.01	—

Note: The ammonia content values at zero drying times are derived from the initial alkalinity of the latex.

weight (and hence thickness since the area was constant) of latex to set completely under controlled conditions of temperature and relative humidity. The procedure for investigating the effect of temperature upon the set time of a dipped film from prevulcanised NR latex is given in Section 3.7.3. The results for the effect of weight, and hence the thickness of the film since it was at a constant surface area of 45cm^2, are given in Table 6.14 and Figure 6.23. It is seen that a straight line is obtained, thus indicating a linear relationship between the set time and weight of a dipped latex film. Furthermore, all the lines pass through the origin. As expected, it was found that, as the weight of the dipped latex film was increased, the set time, t_S, under the same conditions of temperature and relative humidity also increased. The most likely explanation for this is that the thicker is the film, the smaller is the proportion of latex aqueous phase which is lost by evaporation in a given time at any particular temperature, i.e., the smaller is the increase in solids content in a given time. Thus the thicker the film, the larger is the time required to attain the minimum solids

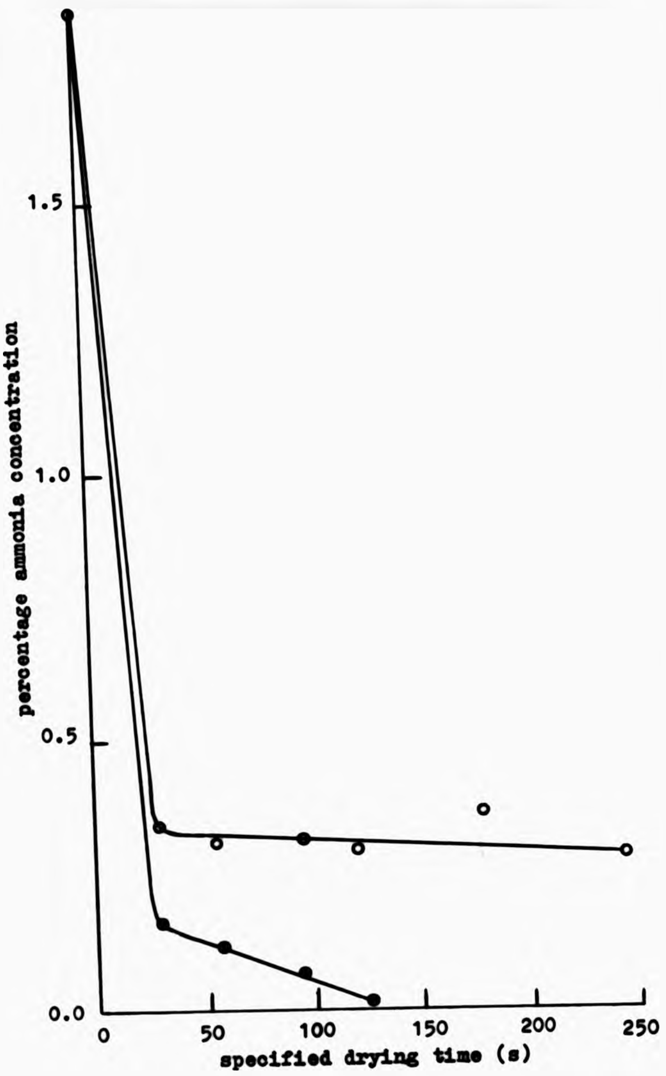


Figure 6.22 Percentage ammonia concentration versus drying time at 30°C, (o), and 55°C, (●), for drying of dipped latex films at 25% relative humidity

Table 6.14 Effect of film weight, W, upon set time, t_S, for dipped latex films drying at various temperatures and constant relative humidity of 25%. The constant surface area of the films was 45cm^2.

temperature (°C)													
30		35		40		45		50		55		60	
W (g)	t_S (s)	W (g)	t_S (s)	W (g)	t_S (s)	W (g)	t_S (s)	W (g)	t_S (s)	W (g)	t_S (s)	W (g)	t_S (s)
0.2657	184	0.2492	148	0.2613	142	0.2895	140	0.2713	120	0.2634	96	0.2420	81
0.2736	194	0.2573	153	0.2758	147	0.3113	151	0.2768	123	0.2659	99	0.2931	97
0.2755	196	0.2823	160	0.3285	173	0.3450	170	0.2844	126	0.2753	101	0.2978	92
0.2867	202	0.2891	171	0.3547	183	0.3587	167	0.3131	132	0.3347	115	0.3138	101
0.3237	213	0.3342	179	0.4017	201	0.3602	178	0.3413	149	0.3364	118	0.3405	115
0.3415	223	0.3671	190	0.4101	205	0.3714	181	0.3622	156	0.3483	124	0.3489	118
0.3648	239	0.3911	211	0.4728	236	—	-	0.4204	164	—	-	0.3781	132
—	-	0.4001	219	—	-	—	-	—	-	—	-	0.4273	135
—	-	—	-	—	-	—	-	—	-	—	-	0.4538	150
—	-	—	-	—	-	—	-	—	-	—	-	0.4758	150
—	-	—	-	—	-	—	-	—	-	—	-	0.5065	155

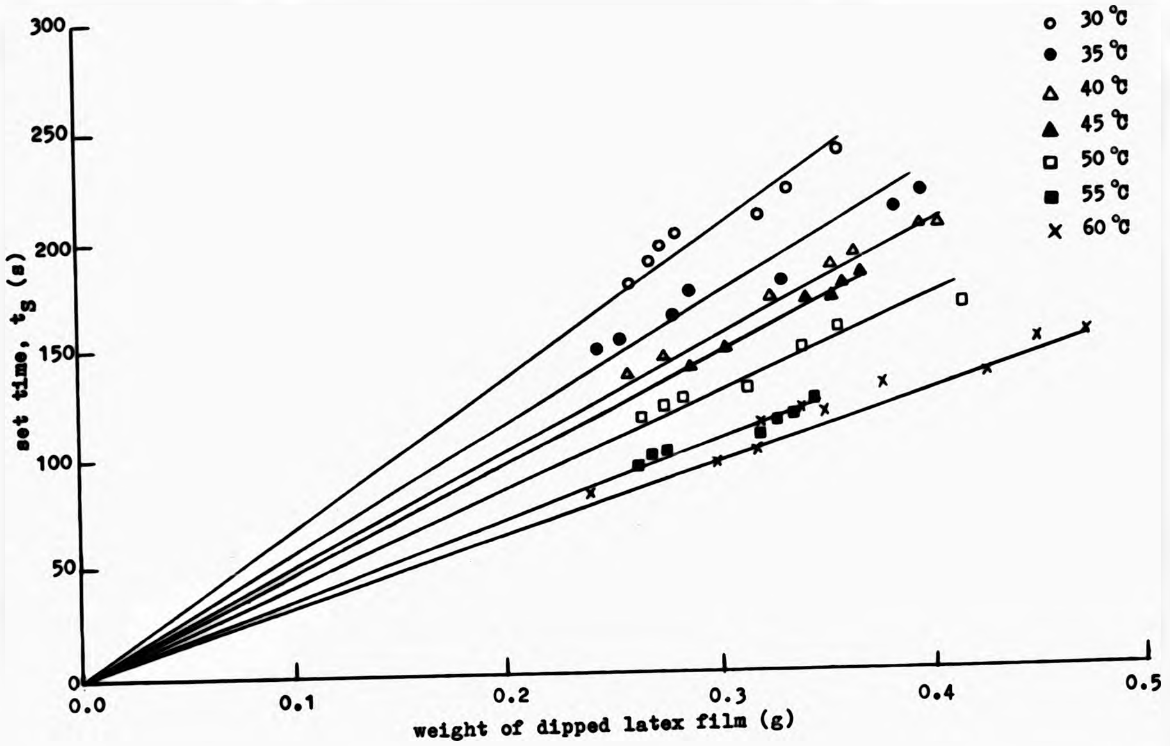


Figure 6.23 Effect of film weight upon set time for dipped latex films drying at various temperatures and at 25% relative humidity. The surface area of the films was 45cm^2.

content necessary for the film to set, i.e., the greater is t_S.

This explanation can be illustrated by considering the two NR latex films shown in Figure 6.24. Both films A and B initially had 60% TSC, and are drying under identical conditions of temperature and relative humidity. However, film B was initially twice the weight, and therefore twice the thickness of film A. The rates of evaporation of water from both A and B are the same because the surface areas of the films are the same (see Section 6.7.5). Thus, when water evaporates, the increase in TSC is higher for film A than for film B. It is well known that an increased concentration of latex particles increases the tendency for coalescence of the particles. The set time is the time at which the particles in film as a whole coalesce. It is thus postulated that when the initial thickness (or weight) of a drying dipped latex film is increased, there is a reduction in the tendency of the rubber particles to coalesce after a given time, because the average distance of separation between the particles after any given time of drying is greater than it is in thinner films. As a consequence, the set time increases provided that the other factors remain constant. As expected, as the temperature of drying of a dipped latex film is increased, the set time decreases (Figure 6.25). This phenomenon is directly attributable to the increased rate of evaporation of water. This enables the critical TSC for setting to be attained more rapidly. Thus the set time is reduced.

An attempt has been made to obtain a parameter which represents a "standardised" set time for any particular film drying under given conditions. For this purpose, the set time per unit weight per unit thickness has been calculated from the slope of the graph of set time versus the initial weight of the dipped latex films (Figure 6.23). This gives a measure of the set time per unit weight of a dipped latex film. Experimentally, because t_S is directly proportional to W, the slope of t_S versus W is independent of W at any given temperature. The surface area of a dipped latex film is approximately 45cm^2. Hence, the set time per unit weight per unit area could be calculated. The results are shown in Table 6.15.

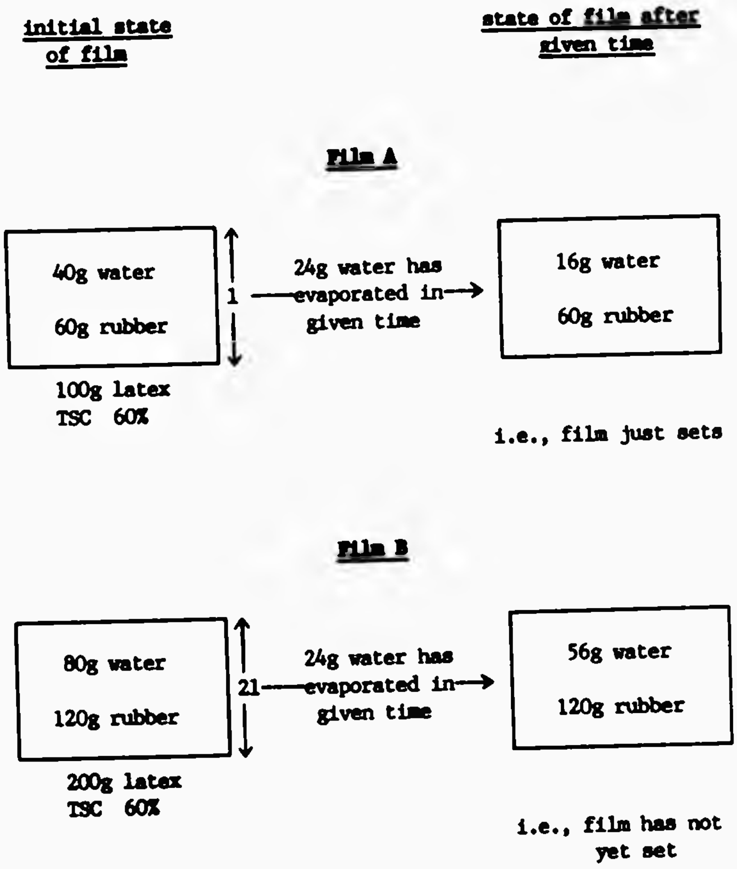


Figure 6.24 Pictorial representation of effect of film thickness (and hence film weight) upon set time at constant temperature and relative humidity. It is assumed that the film sets when the water content has been reduced to about 16%.

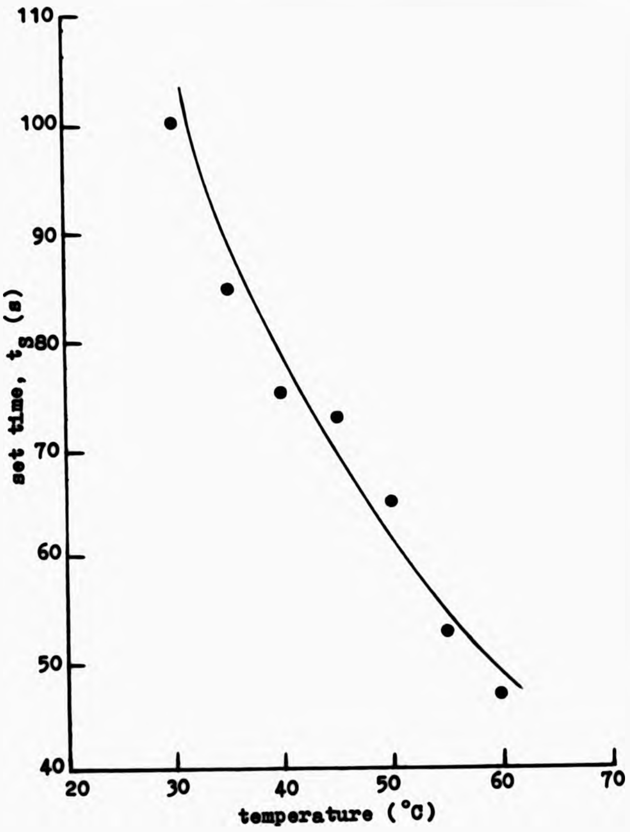


Figure 6.25 Effect of temperature upon set time, t_s, of constant weight (0.15g) of a dipped latex film drying under constant relative humidity (25%)

Table 6.15 Results for "standardised" set time parameter for dipped latex films at various temperatures and at 25% relative humidity. The initial TSC was 59% and the surface area of the film was 45cm^2.

temperature (°C)	standard set time parameter (s $g^{-1}cm^{-2}$)
30	15.2
35	12.7
40	11.8
45	11.1
50	9.5
55	7.5
60	7.1

6.10 Effect of TVC upon set time, t_s, of dipped latex films

The effect of TVC upon set time of dipped latex films was investigated by diluting the latex with distilled water. The results are shown in Figure 6.26. An approximately linear relationship is observed for the data from this experiment. It would certainly be expected that, for a dipped latex film of given weight as the TVC is increased, the set time would also increase. This is expected, because, as the TVC is increased, so also does the time required for sufficient water to evaporate from latex to reduce the TVC to the critical value for setting.

An additional point has been added to Figure 6.26, namely, a point for a film which is just about to set, and therefore has zero set time. The TVC for such a film was inferred by correlating the set time with the volume fraction of rubber particles in the film at the time of setting, as indicated by the curves shown in Figure 6.3. The results are given in Table 6.16. They show that the coalescence of rubber particles takes place at about 83% TSC. It has been reported that the volume fraction of rubber in NR latex can exceed 0.8 before the particles are forced into irreversible contact (7). This agrees closely with the experimental values obtained in the present work. The average volume fraction is found to be 0.83.

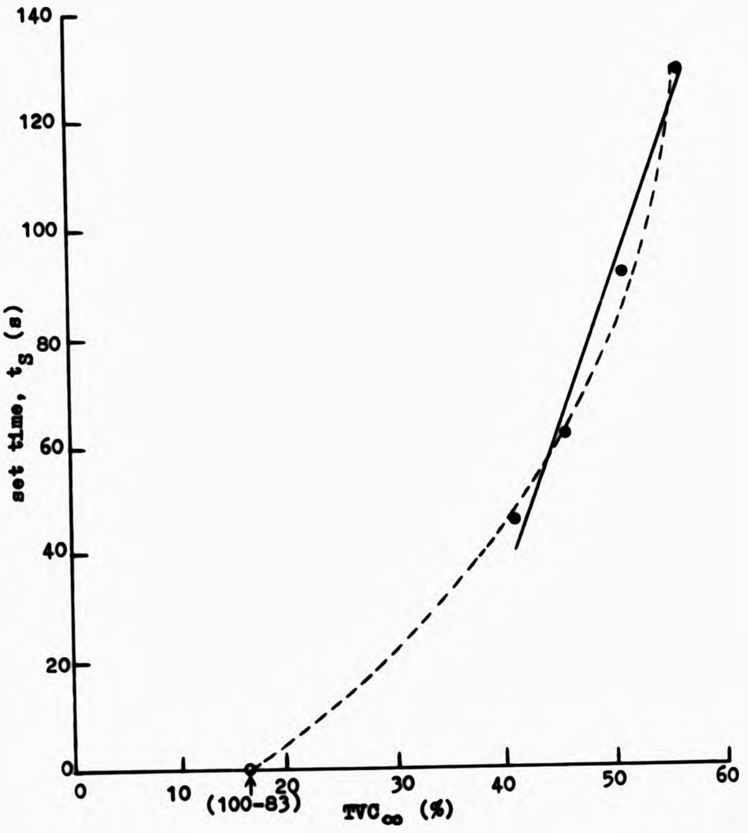


Figure 6.26 Set time, t_S, versus TVC_{∞} at 60°C and relative humidity 25% for 0.15g weight of dipped latex films (see text for significance of lines --- (o) and —— (●))

Table 6.16 Correlation of set time, t_S, with volume fraction of particles at time of setting for films drying at various temperatures, T. The TVC at the set time was determined from Figure 6.3.

T (°C)	t_S (s)	TVC (%)	TSC (%)	V_r*
30	245	16.5	83.5	0.85
35	215	18.9	81.1	0.82
40	205	18.5	81.5	0.83
45	196	18.5	81.5	0.83
50	165	18.6	81.4	0.83
55	135	19.0	81.0	0.82
60	130	8.2	91.8	0.92
average volume fraction of rubber				0.83

* V_r is the volume fraction of rubber at time of setting and was calculated as

$$V_r = \frac{m_r/\rho_r}{m_r/\rho_r + m_a/\rho_a}$$

where m_r and m_a are the masses of rubber and aqueous phase respectively, and ρ_r and ρ_a are the densities of rubber and aqueous phase respectively.

The volume fraction of uniform spheres in close hexagonal packing is known to be $\pi/3(2)^{\frac{1}{2}}$, i.e., 0.74. This would be expected to be the set time if the latex particles were all spherical and of the same size. A higher value found is thus consistent with the latex being non-uniform in particle size, and with the particles perhaps deforming slightly from their spherical shape as they come into irreversible contact. Both factors would increase packing efficiency at the point of setting. When this additional point is included on the graph of set time versus TVC, it is concluded that the relationship between set time and TVC, which appeared to be approximately linear, shown as —— in Figure 6.26, is in fact a reasonably smooth curve, shown as --- in Figure 6.26.

6.11 Correlation of TAC with set time

The TAC results, taken from Figure 6.16, and set time results, taken from Figure 6.23, are correlated in Table 6.17. It can be seen that, in general, the set time, t_S, is lower than the t_d. By t_d is meant, the time taken for the concentration of ammonia, TAC, to approach zero for a dipped latex film of given weight of 0.45g. Also, the concentration of ammonia, TAC, in the completely set dipped latex film ranges from 0.00 to 0.03% of the original weight of latex. At first sight, it seems rather surprising that the latex does not coagulate completely when virtually all ammonia has evaporated. However, since prevulcanised latex was used, it contained sufficient potassium hydroxide to ensure the stability of latex even in the complete absence of ammonia.

6.12 Effect of latex dipping conditions upon 'curtaining effect'

6.12.1 Introduction

The 'curtaining effect' for a film obtained by latex dipping is defined as the irregularities arising as a consequence of the non-uniform flow of the latex down the former prior to setting. The procedure for investigating the 'curtaining effect' is described in Section 3.7.4. Basically, circular samples were cut from the dried latex film using a hole punch. The positions of the samples are shown in Figure 6.27. Each circular sample was weighed. The results are shown in Table 6.18. A diagram of weight of sample against sample position

Table 6.17 Correlation of set time, t_S, with TAC at the time of setting for films drying at various temperatures.

temperature (°C)	TAC at t_S (%)	t_S (s)	t_d^* (s)
30	0.03	315	470
35	0.03	260	425
40	0.03	245	385
45	0.02	225	275
50	0.02	180	225
55	0.01	165	180
60	0.00	135	60

* t_d is the drying time of a dipped latex film of weight 0.45g when TAC approaches zero.

was constructed, for each latex dipping experiment. A typical diagram is shown in Figure 6.28. This shows that there was some variation in the thickness of the film in adjacent positions.

The 'curtaining effect' was quantified by considering the weight differences between adjacent circular samples as shown in Figure 6.29. A quantitative measure of the 'curtaining effect', CE, was then calculated as

$$CE = (\sum(\Delta W_i)^2/N)^{\frac{1}{2}} \quad (g) \qquad (6.11)$$

where ΔW_i is typical entry either for the 'across' differences shown in Figure 6.29 (a) or for the 'down' differences shown in Figure 6.29 (b), and N is the total number of entries in either Figure 6.29 (a) or Figure 6.29 (b), i.e., 20. This is a statistical measure of the variation of the differences in the weights of adjacent samples. To eliminate the negative values of the weight differences, the CE values were calculated using ΔW_i^2 rather than ΔW_i.

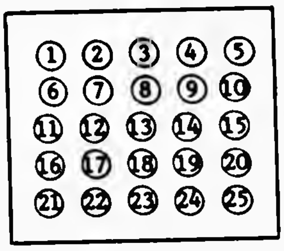


Figure 6.27 Positions of circular samples punched from latex film for investigation of 'curtaining effect'

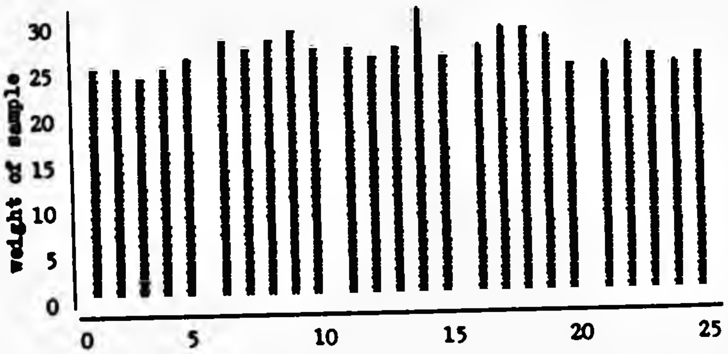


Figure 6.28 Typical diagram showing weight of sample at various sample positions. The dipped films were withdrawn at a constant rate of $1.0mm\ s^{-1}$.

Table 6.18 Results of weight measurements (grams) to investigate effect upon curtaining effect of (A) withdrawal rate, (B) induced curtaining, (C) factors which might affect curtaining and (D) use of unwashed and washed formers

sample	(A) (mm s^{-1})				(B)			(C)			(D)	
position	10.7	1.0	1.3	3.6	immersion of former in creamed latex	withdrawal of former by free hand	disturbance when former withdrawn	talc-dusted former	lightly greased former	heavily greased former	unwashed former	washed former
1	0.0013	0.0024	0.0020	0.0024	0.0040	0.0020	0.0019	0.0022	0.0020	0.0022	0.0023	0.0015
2	0.0012	0.0021	0.0018	0.0020	0.0068	0.0021	0.0016	0.0024	0.0022	0.0024	0.0031	0.0016
3	0.0012	0.0022	0.0021	0.0021	0.0093	0.0018	0.0016	0.0020	0.0024	0.0019	0.0029	0.0014
4	0.0013	0.0023	0.0020	0.0023	0.0080	0.0021	0.0016	0.0022	0.0020	0.0024	0.0027	0.0015
5	0.0014	0.0022	0.0020	0.0024	0.0070	0.0024	0.0017	—	0.0018	0.0021	0.0027	0.0014
6	0.0013	0.0023	0.0024	0.0025	0.0085	0.0021	0.0021	0.0024	0.0019	0.0024	0.0029	0.0020
7	0.0012	0.0021	0.0020	0.0029	0.0068	0.0021	0.0019	0.0027	0.0020	0.0025	0.0036	0.0020
8	0.0012	0.0018	0.0029	0.0029	0.0084	0.0027	0.0018	0.0028	0.0023	0.0023	0.0029	0.0017
9	0.0012	0.0019	0.0022	0.0031	0.0115	0.0024	0.0023	0.0028	0.0023	0.0024	0.0036	0.0019
10	0.0014	0.0017	0.0028	0.0030	0.0120	0.0026	0.0023	0.0024	0.0019	0.0023	0.0032	0.0018
11	0.0013	0.0022	0.0035	0.0026	0.0115	0.0024	0.0023	0.0024	0.0023	0.0028	0.0036	0.0019
12	0.0014	0.0022	0.0031	0.0026	0.0069	0.0035	0.0022	0.0026	0.0024	0.0028	0.0034	0.0019
13	0.0013	0.0022	0.0028	0.0030	0.0220	0.0029	0.0023	0.0029	0.0026	0.0028	0.0035	0.0018
14	0.0014	0.0021	0.0028	0.0031	0.0203	0.0030	0.0024	0.0029	0.0024	0.0022	0.0039	0.0018
15	0.0013	0.0022	0.0027	0.0032	0.0170	0.0025	0.0024	0.0028	0.0018	0.0024	0.0034	0.0018
16	0.0014	0.0024	0.0025	0.0029	0.0128	0.0034	0.0025	0.0028	0.0021	0.0024	0.0029	0.0020
17	0.0012	0.0019	0.0028	0.0031	0.0165	0.0035	0.0024	0.0027	0.0021	0.0022	0.0032	0.0018
18	0.0013	0.0020	0.0029	0.0029	0.0208	0.0029	0.0029	0.0029	0.0024	0.0028	0.0036	0.0016
19	0.0015	0.0021	0.0030	0.0029	0.0125	0.0024	0.0026	0.0031	0.0023	0.0025	0.0037	0.0019
20	0.0014	0.0020	0.0028	0.0030	0.0081	0.0034	0.0024	0.0022	0.0025	0.0022	0.0034	0.0019
21	—	0.0022	—	—	0.0164	0.0029	0.0023	0.0029	—	0.0026	0.0033	0.0017
22	—	0.0025	—	—	0.0154	0.0032	0.0025	0.0026	0.0027	0.0025	0.0033	0.0019
23	—	0.0024	—	—	0.0140	0.0031	0.0025	0.0026	0.0025	0.0022	0.0031	0.0019
24	—	0.0023	—	—	0.0121	0.0040	0.0027	0.0027	0.0024	0.0025	0.0035	0.0019
25	—	0.0025	—	—	—	—	0.0025	0.0026	0.0025	0.0024	0.0039	0.0018

(a)

A	(1-2)	(2-3)	(3-4)	(4-5)
B	(6-7)	(7-8)	(8-9)	(9-10)
C	(11-12)	(12-13)	(13-14)	(14-15)
D	(16-17)	(17-18)	(18-19)	(19-20)
E	(21-22)	(22-23)	(23-24)	(24-25)

(b)

a	b	c	d	e
(1-6)	(2-7)	(3-8)	(4-9)	(5-10)
(6-11)	(7-12)	(8-13)	(9-14)	(10-15)
(11-16)	(12-17)	(13-18)	(14-19)	(15-20)
(16-21)	(17-22)	(18-23)	(19-24)	(20-25)

Figure 6.29 Quantification of 'curtaining effect' by use of weight differences between adjacent circular samples, (a) 'across' and (b) 'down', a dipped latex film

6.12.2 Reproducibility of results for 'curtaining effect'

The reproducibility of the results for the 'curtaining effect' was difficult to assess, because the probability of the same error recurring at the same point in the film was negligible, unless the former upon which the film was produced was defective at that point.

6.12.3 Investigation of induced curtaining

Attempts were made to induce enhanced curtaining in order to ascertain the sensitivity of the test for the 'curtaining effect'. To this end, curtaining was enhanced by preparing a series of dipped latex films from prevulcanised NR latex as follows:

(i) a former was immersed into the creamed latex, i.e., into latex which had been left exposed to the atmosphere to form a dense film on the surface and had then been stirred, and withdrawing at a constant rate of 1.3mm s^{-1};
(ii) a former was withdrawn from the latex by free hand, after it had been immersed into a beaker of prevulcanised NR latex; and
(iii) a former was vibrated as it was being withdrawn from latex at a constant rate of 1.3mm s^{-1}.

The 'curtaining effect' was then investigated as described in Section 3.7.4. The results are given in Table 6.18. They were analysed by the procedure described in Section 6.12.1. The CE values are shown in Table 6.19. As expected, the 'curtaining effect' was observed both 'across' and 'down' the dipped latex films. CE values across the sheet are generally less than those down the sheet. This is discussed further subsequently. As can be seen in Table 6.19 the CE values ranged from 2.2 to 5.4. Values of CE equal to or less than 2.5 are taken as indicating the absence of any curtaining effect. It is thought that values of CE equal to or less than 2.5 are not significant, because of experimental uncertainties. These include,

(a) uncertainties in the weighings (± 0.0002g); and
(b) experimental uncertainties arising from, for example, moisture absorption.

Table 6.19 CE values obtained from experiments in which effect of enhancing curtaining in dipped film from prevulcanised NR latex was investigated

method used to produce latex film	CE values (g)	
	across dipped film	down dipped film
former immersed in creamed latex	2.6×10^{-4}	4.2×10^{-4}
former withdrawn from latex by hand	5.4×10^{-4}	4.5×10^{-4}
former vibrated when withdrawn from latex	2.2×10^{-4}	3.5×10^{-4}

6.12.4 Effect of withdrawal rate upon curtaining effect

The procedure for determining the curtaining effect is described in Section 3.7.4. The effect of withdrawal rate upon the curtaining effect was investigated by producing latex film at various withdrawal rates. The results were analysed by the method described in Section 6.12.1. The results of this analysis are shown in Table 6.20. In general, the results indicate that at all withdrawal rates, there is no significant curtaining effect across the dipped films. However, as the withdrawal rate is increased from 1.3 to 3.6mm s^{-1}, the CE value increases down the dipped latex film. This may be a consequence of rapid flow down the former associated with high withdrawal rates when the film is partially set, referred to in Table 6.20 as the 'flowing effect'. It is thus concluded that, within experimental error, the curtaining is negligible provided that the former is withdrawn at a constant rate using reasonable withdrawal rates, e.g., 0.7 or 1.0mm s^{-1}.

It is also concluded that the 'flowing effect', which can be described as a uniform variation of film thickness, is more important than the 'curtaining effect', which can be described as a non-uniform variation in film thickness. For this reason, the 'flowing effect' has been further investigated.

Table 6.20 Effect of withdrawal rate upon CE values for dipped films from prevulcanised NR latex. An estimate of the 'flowing effect' is also given.

withdrawal rate (mm s^{-1})	CE values (g)		'flowing effect', (D-A), (g)*
	across dipped film, A	down dipped film, D	
0.7	1.1×10^{-4}	1.2×10^{-4}	0.1×10^{-4}
1.0	1.9×10^{-4}	2.3×10^{-4}	0.4×10^{-4}
1.3	2.4×10^{-4}	3.8×10^{-4}	1.4×10^{-4}
3.6	2.2×10^{-4}	4.2×10^{-4}	2.0×10^{-4}

* see text

6.12.5 Further consideration of 'flowing effect'

The 'flowing effect' was quantified as the variation of film thickness with distance from the top of the dipped latex film. The weights of samples punched at various distances from the top of the film were determined for films produced at various withdrawal rates. The results are shown in Table 6.21 and graphically in Figure 6.30. As expected, a gradual increase in average sample weight (hence film thickness) was observed with increase in distance from the top of the film. This effect may be attributed to the flow of the latex down the former, prior to its setting. The effect is more pronounced at a higher withdrawal rate, e.g., 3.6mm s^{-1}, than at a lower withdrawal rate, e.g., 0.7mm s^{-1}.

6.12.6 Investigation of possible factors causing curtaining of dipped latex films

The procedure for determining the curtaining effect is described in Section 3.7.4. Possible factors which may cause curtaining in latex films were investigated by producing films

Table 6.21 **Average weights* of punched circular samples punched at various distances from top of films punched at various withdrawal rates**

distance of sample from top of film (mm)	withdrawal rate (mm s^{-1})			
	0.7	1.0	1.3	3.6
2	0.0012 **0.6x10^{-4}**	0.0021 **1.1x10^{-4}**	0.0021 **1.3x10^{-4}**	0.0022 **1.8x10^{-4}**
12	0.0013 **1.0x10^{-4}**	0.0020 **2.4x10^{-4}**	0.0023 **4.2x10^{-4}**	0.0027 **2.6x10^{-4}**
22	0.0013 **1.0x10^{-4}**	0.0022 **0.4x10^{-4}**	0.0026 **5.5x10^{-4}**	0.0028 **2.6x10^{-4}**
32	0.0014 **0.6x10^{-4}**	0.0021 **1.9x10^{-4}**	0.0027 **1.4x10^{-4}**	0.0031 **1.3x10^{-4}**
42	0.0014 **1.3x10^{-4}**	0.0022 **1.3x10^{-4}**	0.0029 **1.0x10^{-4}**	0.0030 **1.0x10^{-4}**

Note: values typed in bold are standard deviations, calculated from weight measurements given in Table 6.18

* 4-5 separate determinations went into each average

Table 6.22 **CE values across and down the dipped film from prevulcanised NR latex to measure the possible factors causing 'curtaining effect'**

treatment of former	CE values (g)	
	across	down
dusted with talc	3.0x10^{-4}	3.5x10^{-4}
lightly-greased	2.5x10^{-4}	2.9x10^{-4}
heavily-greased	3.2x10^{-4}	3.9x10^{-4}

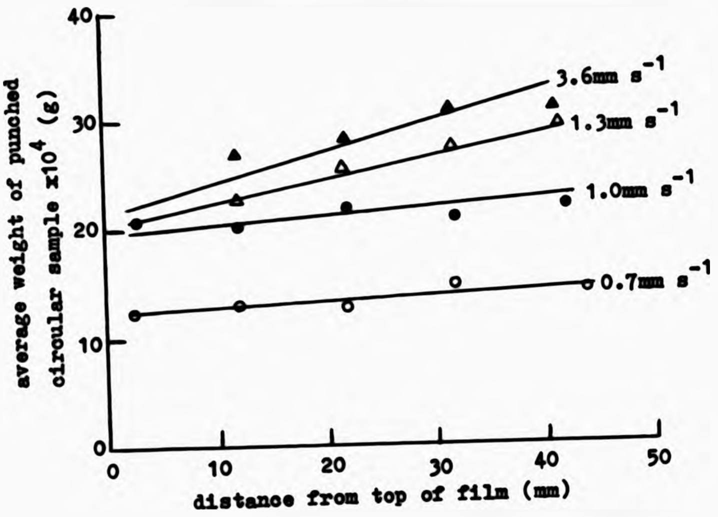


Figure 6.30 Average weight versus distance from top of film for films produced at various withdrawal rates (shown alongside the curves)

by immersing formers treated as follows, into latex and withdrawing at a constant withdrawal rate of 1.3mm s^{-1}:

(a) former dusted with talc
(b) lightly-greased former
(c) heavily-greased former

The results are given in Table 6.22. As can be seen, all the CE values are greater than the reference value of 2.5. This indicated that factors such as talc-dusting and/or greasy formers can contribute to the curtaining effect.

6.12.7 Effect of unwashed and washed formers upon curtaining effect

To confirm the importance of a thorough cleaning of the formers, dipped latex films were produced by immersing,

(a) an unwashed former (i.e., a former which was used directly after the previous dipped film had been produced), and
(b) a washed former (i.e., a former which had been thoroughly cleaned) into latex and withdrawing at a constant withdrawal rate of 1.3mm s^{-1}.

The results are shown in Table 6.23. It is observed that the curtaining effect is absent in dipped latex film which was produced by using a washed former. In comparison, however, the results for the dipped latex film which was produced by using an unwashed former indicates the presence of a substantial curtaining effect. It is therefore essential to clean formers thoroughly to eliminate the curtaining effect.

Table 6.23 Effect of using unwashed and washed former upon the curtaining effect in dipped latex films

conditions of former	CE values (g)	
	across	down
unwashed	5.3×10^{-4}	7.4×10^{-4}
washed	1.5×10^{-4}	2.2×10^{-4}

CHAPTER 7 : EFFECT OF SELECTED PROCESS VARIABLES UPON THE DRYING BEHAVIOUR OF COAGULANT-DIPPED LATEX FILMS

7.1 Introduction

One of the most important conclusions reached so far in this investigation is that the rate of drying of straight-dipped films from prevulcanised NR latex is a diffusion-controlled process, even in the early stages of drying. The main feature of this stage of drying is that the water can pass through the surface by diffusion at a rate equal to that at which it is removed from the surface by evaporation. The rate of evaporation of water is found to be directly proportional to the surface area of water, and hence depends upon the aggregate size of the capillaries present in the surface. It was intended to extend this work to coagulant dipped films where variations in thickness and in the aggregate size of the capillaries, can easily be achieved in principle, thus allowing the importance of such variables to be further investigated. The selected process variables, namely, concentration of coagulant solution, TSC of latex and dwell time, all are expected to affect the thickness of the deposit, and hence the drying behaviour of dipped films.

The formation of coagulant-dipped films occurs principally by diffusion of coagulant ions from the former into the latex. This causes destabilisation of the latex particles adjacent to the former by removing charges which surround the particles. The other processes like syneresis and dehydration are also thought to play some role in bringing about destabilisation, the nature of which is still not clear.

In light of the above, the purpose of this chapter is to draw together the many results which have been obtained for the various aspects of this part of the investigation. On the basis of these results, an attempt will be made to postulate a mechanism for the early stages of drying of coagulant-dipped latex films.

The study of the drying behaviour in the later stages for coagulant-dipped films has not been carried out. Drying during the later stages is believed to be a very slow process, and may well therefore be diffusion-controlled.

7.2 Preparation of gelled films

In coagulant dipping, the deposit thickness appears to be affected one way or another by certain variables. It is thus important to employ a procedure in which these variables are controlled. The procedure which used the dipping machine seemed to be unsatisfactory, because it produces films of progressively increasing thickness down the former. It was necessary, therefore, to use an alternative procedure. This was as follows: To a clean petri-dish which was at 70°C, the coagulant solution prepared according to the formulation given in Table 7.1, was added. A sufficient amount (ca. 5-10ml) was added such that the bottom of the dish was covered completely. The excess was then discarded. The solvent (IMS) was allowed to evaporate (assisted by the heat from the dish), thus leaving a concentrated layer of coagulant (ca. 0.2-0.4g) in the dish. The temperature of the dish was allowed to fall to room temperature; the time taken was about one to two minutes. After this time, sufficient latex was added to the dish and left for a predetermined dwell time of 60s. The excess latex was poured out. A rectangular piece was cut from the freshly-prepared gel and its area measured. The piece was then rinsed in distilled water to remove any residual calcium salts and other impurities (see Section 7.3.1), and the excess water was removed by blotting with paper. The gel was then transferred

Table 7.1 Formulation for 30% coagulant solution

ingredient	weight
$CaCl_2.6H_2O$	15
$Ca(NO_3)_2.4H_2O$	15
cetyltrimethyl-ammonium bromide	0.1
IMS	60
deionised water	10

to the drying cabinet set at constant temperature (30°C) and relative humidity (25%) for the weight measurements. From the water-loss measurements were calculated the percentages by weight of total volatile content, TVC, for given drying times, t.

The following were investigated:

(a) Effect of dwell time at constant TSC of 59% and coagulant solution concentration of 30%;
(b) Effect of TSC at constant dwell time of 60s and coagulant solution concentration of 30%; and
(c) Effect of concentration of coagulant solution at constant TSC of 59% and dwell time of 60s.

Essentially, the objective of experiment (a) was to investigate the effect of film thickness, and the objective of experiments (b) and (c) was to investigate the effect of the aggregate size of the capillaries in the surface, upon the rate of drying of the dipped films.

7.3 Preliminary studies

7.3.1 Effect of washing of wet gels with water upon rate of drying

This effect was investigated because it was realised that residual calcium salts might be present on the surface of the wet gel, and that these salts might cause some unnecessary complexities in the interpretation of the final results. Figure 7.1 shows the effect of washing the wet gel with water upon the rate of loss of water from the gel. As can be seen, the residual calcium salts have a significant retarding effect upon the rate of drying of gelled films. The initial rate of evaporation of water is reduced from 6.45×10^{-4} to 5.58×10^{-4}g min^{-1}cm^{-2}. The reason for this is probably that the hygroscopic nature of the calcium salts retards evaporation of water from the surface of the gel. On the other hand, however, the calcium salts may also encourage removal of water from the gel to the surface by dehydration process, thereby interfering with the diffusion process. Thus, it was decided to wash the gel as described in Section 7.2 before determining the drying behaviour of coagulant dipped films.

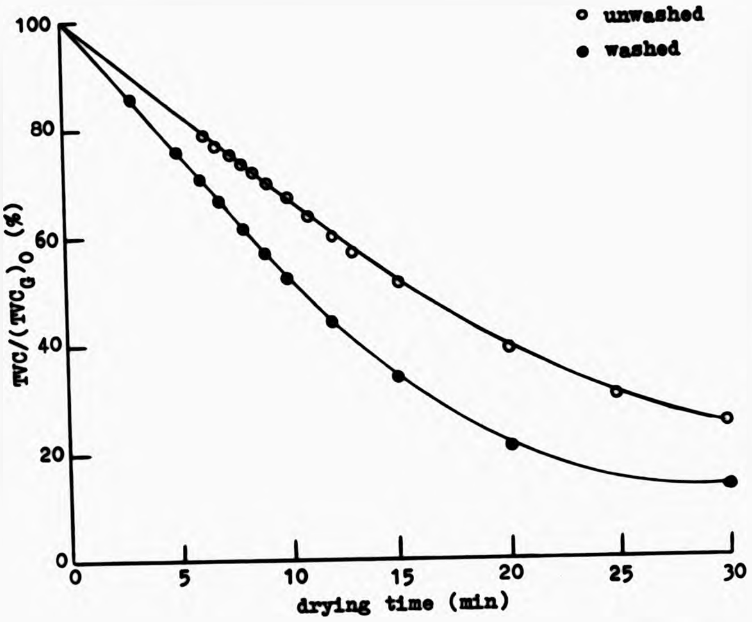


Figure 7.1 Effect of washing of wet gel with water upon rate of evaporation of water: TSC 59%, coagulant solution concentration 30%, dwell time 60s

7.3.2 Treatment of data

Initially, the TVC of a coagulant-dipped film at zero drying time, $(TVC_G)_0$, was calculated in a similar way to that for a straight-dipped film (see Chapter 6), that is to say, it was assumed that the TSC of the gel is equal to that of the latex from which it was formed. However, subsequent work showed that the TSC of the gel is somewhat higher than that of the latex from which it was formed. This may possibly be due to the dehydration and/or the syneresis of the gel. Thus, the TVC results were recalculated based on the TSC of the gel at zero drying time. The true TVC at zero drying time denoted by $(TVC_G)_0$, was obtained by extrapolating the weight loss-time curve to zero time, as shown in Figure 7.2. It is seen that, for a given dipped film, the TSC of the gel (66.1%) is higher than the TSC of the latex (59%) from which it is formed. In subsequent work, the TVC results are those based upon the TSC of the gel. A typical treatment of the data obtained for the weight measurements is shown in Table 7.2.

7.4 Results and discussion

7.4.1 Introduction

In general, the early stages of the drying process for coagulant-dipped films can be divided into two regions. In the first region, an initial constant rate of water loss is observed which persists to 70-90% volume rubber. The second region begins when the rate drops off rapidly to a value 15-25 times smaller than that for the first region. This effect is illustrated schematically in Figure 7.3. These results are in general agreement with published work (1-3).

7.4.2 Effect of dwell time upon rate of drying

The effect of dwell time upon the drying behaviour of the gelled films at a TSC of 59% and coagulant solution concentration of 30%, is shown in Figure 7.4. As can be seen, there was an initial linear decrease in $TVC/(TVC_G)_0$ with drying time (Region I), followed by a non-linear decrease in $TVC/(TVC_G)_0$ as the drying continued (Region II). This effect was more pronounced for films obtained at short dwell times than for films obtained at long dwell times. The shapes of these curves are of similar form to those obtained by other workers (2,3).

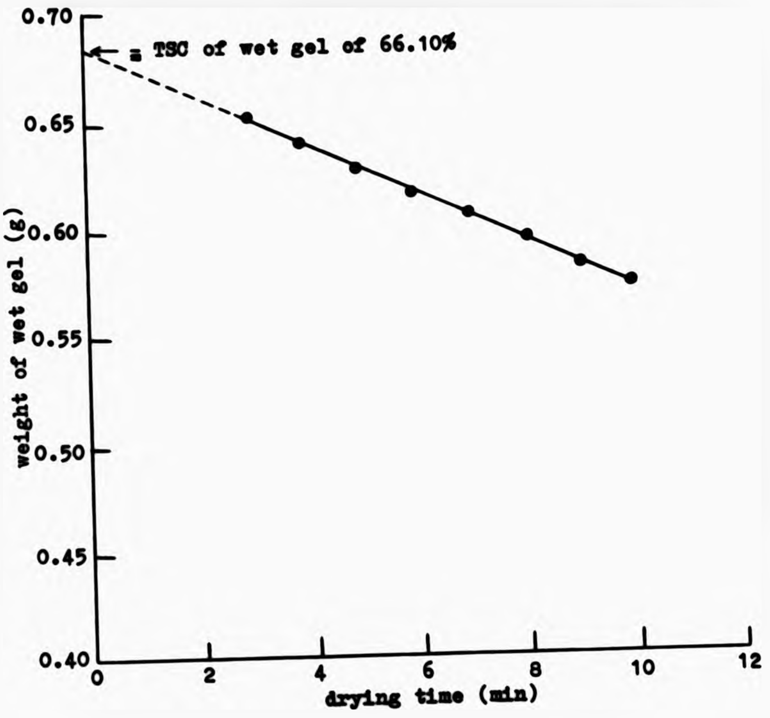


Figure 7.2 Extrapolation of weight loss-time curve to obtain TSC of wet gel at zero drying time

Table 7.2 Treatment of typical data for weight-loss measurements of a wet gel: dwell time 60s, TSC 59% and coagulant solution concentration 30%; drying conditions: temperature 30°C, relative humidity 25%. The area of wet gel was 8cm^2, and the weight of the wet gel when completely dry was 0.45g.

drying time, t (min)	weight of wet gel (g)	TSC+TVC (%)	TVC (%)	$TVC/(TVC_G)_0$ (%)	$^*L_W$ (mm)	$^*L$ (mm)	$t^{1/2}/L$ ($s^{1/2}$/mm)
0	$^+$0.6809	100.0	33.9	100.0	0.27	0.88	0
3	0.6484	95.2	29.1	85.9	0.23	0.84	15.9
4	0.6373	93.6	27.5	81.1	0.22	0.83	18.7
5	0.6252	91.8	25.7	75.9	0.20	0.82	21.3
6	0.6133	90.1	24.0	70.7	0.19	0.80	23.7
7	0.6030	88.6	22.5	66.3	0.18	0.79	26.0
8	0.5918	86.9	20.8	61.4	0.17	0.78	28.2
9	0.5806	85.3	19.2	56.6	0.15	0.76	30.5
10	0.5717	84.0	17.9	52.7	0.14	0.75	32.5
12	0.5532	81.3	15.2	44.7	0.12	0.73	36.7
15	0.5280	77.5	11.4	33.8	0.09	0.70	42.7
20	0.4981	73.2	7.1	20.8	0.06	0.67	51.9
30	0.4797	70.5	4.4	12.8	0.03	0.65	65.7

$^+$ weight of a wet gel at zero drying time was obtained from extrapolation of weight versus drying time, as shown in Figure 7.2. Since all the points lie on or near the straight line, the least square method was employed to obtain the parameters of the straight line.

* calculation of L_W and L is described in Section 6.6.3.

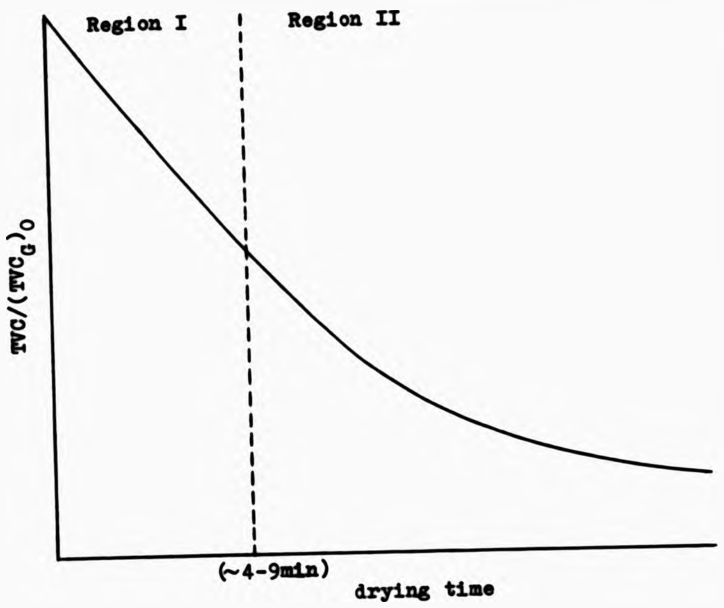


Figure 7.3 Illustrating drying behaviour of a gelled latex film at 30°C and relative humidity of 25% (see text for significance of Regions I and II)

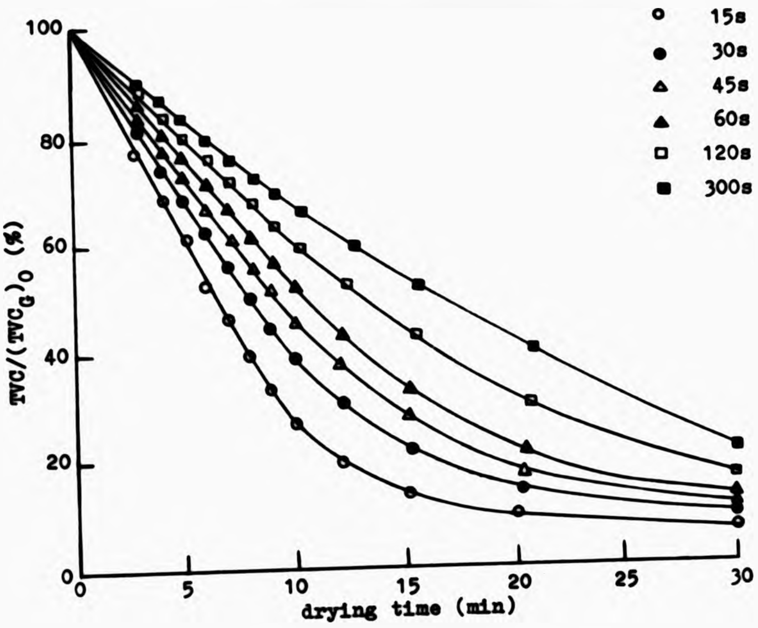


Figure 7.4 Effect of dwell time upon rate of drying of a gelled film: TSC 59%, coagulant solution concentration 30%; drying conditions: temperature 30°C, relative humidity 25%

Before attempting to explain the nature of these results, it was necessary to consider an important factor, namely, the rate of deposition of latex on the former. This rate is believed to control the composition and structure of the gel, and hence the rate of evaporation of water. The rate of deposition was measured by plotting the thickness of the wet gel at zero drying time, $(L_G)_0$, against dwell time for a given TSC of 59% and coagulant solution concentration of 30%. The results are shown in Figure 7.5. The thickness of the wet gel at zero drying time was measured as described in the previous chapter, Section 6.6.3. It is observed from Figure 7.5 that the initial rate of deposition is high, and that deposition slows down as the time of dwell increases. This observation is in agreement with that made by Shukri (4). Several workers (4-6) have suggested that the deposition of rubber particles on the former is a diffusion-controlled process. Hence, the data in Figure 7.5 have been re-plotted in Figure 7.6 as wet-gel deposit thickness at zero drying time, $(L_G)_0$, versus square root of dwell time. The results plotted in this way support the view that the deposition of the rubber particles on the former is indeed a diffusion-controlled process at short dwell times. However, deviations from linearity occur at high dwell times. Shukri (4) attributed this effect to the excess latex dripping off the former at high dwell times. The procedure employed in this investigation, however, did not entail any dripping (see Section 7.2). Thus, it is thought that the deviation at high dwell times may be a consequence of high gelation of latex in the early stages of deposition, which renders difficult further diffusion of calcium ions through the gel. This is consistent with the observations reported in Section 7.4.4, from which changes in the concentration of the coagulant solution have been found to have an insignificant effect upon the rate of deposition of latex particles. Thus, it is postulated that at short dwell times, the rate of deposition of latex particles is high, thereby forming gels of close-packed structures. Hence, the water per unit volume of the gel is reduced with a consequent reduction in the rate of evaporation of water. This hypothesis that strong coherent latex gels form at short dwell times is supported by the plots of the total solids content of the gel at zero drying time, $(TSC_G)_0$, versus dwell time shown in Figure 7.7. Clearly, the results show that increase in $(TSC_G)_0$, and hence in the rate of deposition of latex particles, is greater at short dwell times than at long dwell times.

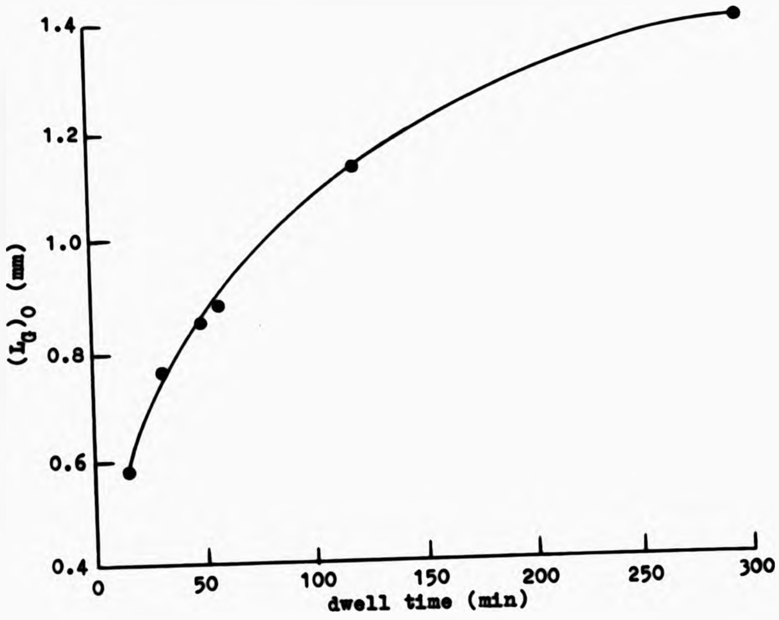


Figure 7.5 Relationship between thickness of wet gel at drying time 0, $(L_G)_0$, and dwell time: TSC 59%, coagulant solution concentration 30%

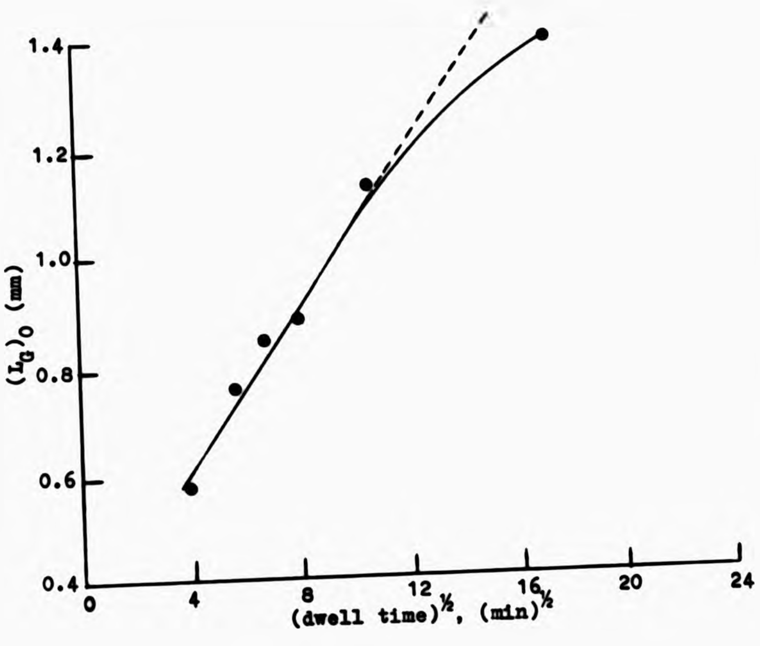


Figure 7.6 Relationship between thickness of wet gel at drying time 0, $(L_G)_0$, and square root of dwell time: TSC 59%, coagulant solution concentration 30%

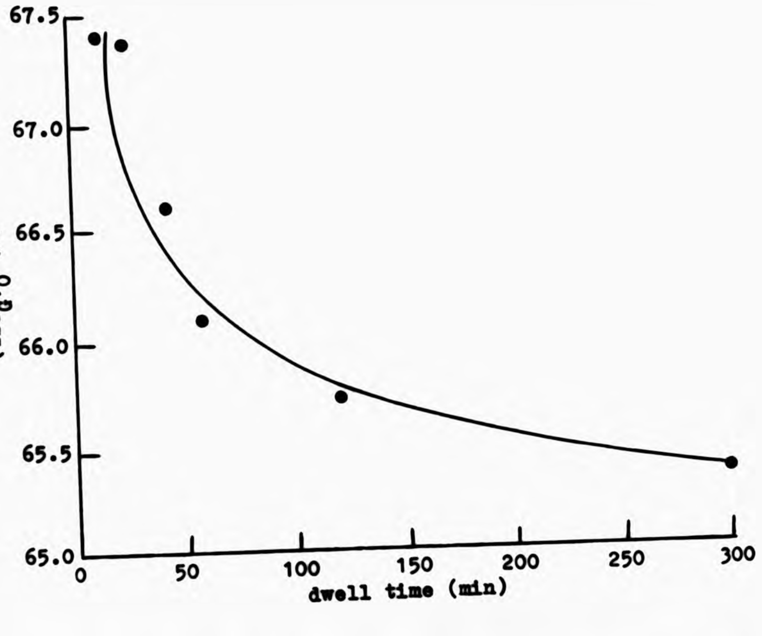


Figure 7.7 Plot of TSC of gel at zero drying time, $(TSC_G)_0$, versus dwell time: TSC 59%; coagulant solution concentration 30%

7.4.3 Effect of TSC of latex upon rate of drying of wet gels

The purpose of this investigation was to alter the composition and structure of the wet gel, thus perhaps producing changes in the rate of evaporation of water. Figure 7.8 shows the effect of the TSC upon rate of drying of gels at a given dwell time of 60s and a coagulant solution concentration of 30%. When $TVC/(TVC_G)_0$ was plotted against drying time, as shown in Figure 7.8, a series of curves were obtained. Again, a linear rate of evaporation is observed initially. This is followed by a gradual decrease in rate of evaporation. It is also observed that the TSC of the latex appears to have an insignificant effect upon the rate of evaporation from the subsequent gel. At first glance, this may seem surprising, because it is expected that the water content per unit volume of gel would be higher at low TSC than at high TSC, and hence that the rate of evaporation would be higher in the former than in the latter.

This conflicting observation, however, may be explained by considering the results shown in Figure 7.9. Figure 7.9 shows the relationship between the wet-gel deposit thickness at zero drying time, $(L_G)_0$, and the TSC of the latex. It is seen that the thickness of the wet-gel deposit at zero drying time, and hence the rate of deposition of the rubber particles, is virtually independent of the TSC of the latex over the range 30-60%. The approximately constant thickness of the wet deposit when the TSC of the latex is varied over the range 59-30% agrees satisfactorily with the results of Shukri (4). It should be noted that, when the TSC is zero, the thickness is due entirely to the coagulant layer (0.1mm), plus due to the water (0.08mm).

It is possible that the constancy of thickness of the wet gel at various TSCs can be attributed to the balance between the following two factors:

(i) At low TSC, the rate of diffusion of calcium ions from the former to the latex is high. This is mainly due to the low resistance offered by the reduced concentration of latex particles.

(ii) At high TSC, the rate of diffusion of calcium ions is retarded by the increased concentration of latex

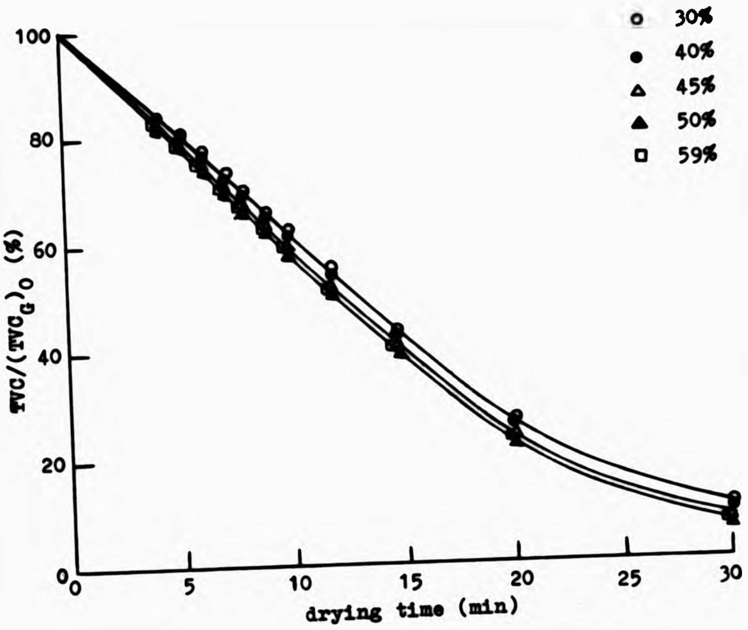


Figure 7.8 Effect of TSC of latex upon rate of drying of a gelled film: dwell time 60s, coagulant solution concentration 30%; drying conditions: temperature 30°C, relative humidity 25%

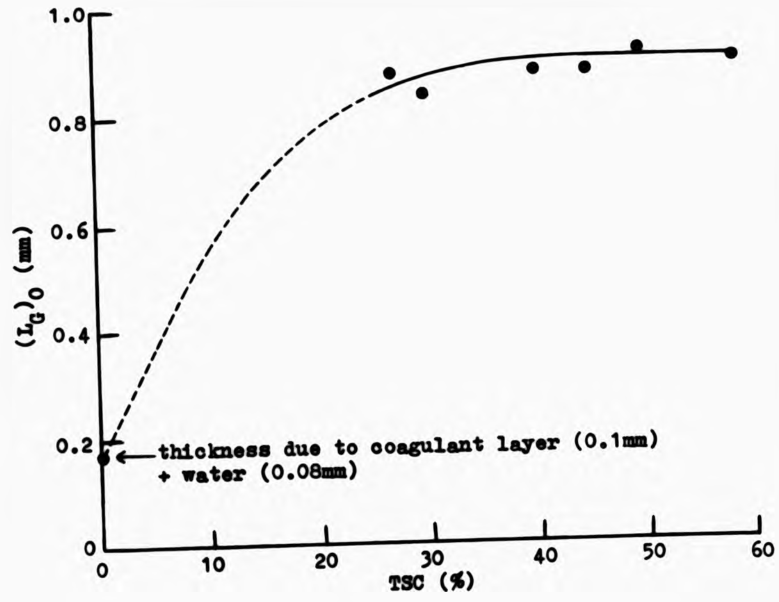


Figure 7.9 Relationship between thickness of wet gel at zero drying time, $(L_G)_0$, and TSC of latex: dwell time 60s; coagulant solution concentration 30%

particles, but the probability of the diffused calcium ions interacting with the latex particles is increased.

Thus, the operation of these two effects maintains approximately constant composition and structure of the wet gel. Hence, the water content per unit volume of the wet gel is virtually constant. Hence, the TSC of the latex has insignificant effect upon the rate of evaporation of water from the gelled deposit.

This hypothesis that gels have constant composition or structure at various latex TSCs is further investigated by considering the initial volume fraction of rubber in the wet gel, $(V_G)_0$. The results are presented in Table 7.3. When $(V_G)_0$ was plotted against TSC of latex, as shown in Figure 7.10, a curve was obtained. As can be seen, the initial volume fraction of rubber in the wet gel increases marginally with increasing latex TSC. This suggests that the composition of the gel varies slightly with the TSC of the latex from which the gel was derived.

7.4.4 Effect of concentration of coagulant solution upon rate of drying of gelled latex films

Again, the purpose of this investigation was to attempt to vary the aggregate size of the capillaries in the gel. It was thought that the amount of calcium salts on the former would determine the concentration gradient for calcium ions in the latex gel, and hence the rate of diffusion of calcium ions through the latex and the rate of deposition of latex particles on the former. Results have been obtained for $TVC/(TVC_G)_0$ as a function of drying time for gels formed using coagulant solutions of various concentrations. The dwell time was 60s and the latex TSC 59%. The results are shown graphically in Figure 7.11. As can be seen, no noticeable changes occur on varying the concentration of coagulant solution. This suggests that the coagulant solution has two opposing effects upon the rate of deposition of latex on the former: On the one hand, an increased thickening effect by causing greater coalescence of the latex particles due to the high concentration of coagulant solution; and on the other hand, a reduced thickening effect by preventing further

Table 7.3 Effect of TSC of latex upon the initial volume fraction of rubber in the wet gel, $(V_G)_0$: dwell time 60s and coagulant solution concentration 30%.

TSC (%)	$(L_G)_0$ (mm)	$(TSC_G)_0$ (%)	$(V_G)_0$*
30.2	0.84	60.1	0.62
40.1	0.87	62.5	0.64
45.3	0.87	63.4	0.65
50.1	0.91	62.4	0.64
59.0	0.88	66.1	0.68

* $(V_G)_0$ is the volume fraction of the wet gel at zero drying time. It is given by:

$$\frac{(TSC_G)_0/\rho_r}{(TSC_G)_0/\rho_r + (100 - (TSC_G)_0)/\rho_w}$$

where ρ_r is the density of rubber ($0.92gcm^{-3}$) and ρ_w is the density of water ($1.00gcm^{-3}$).

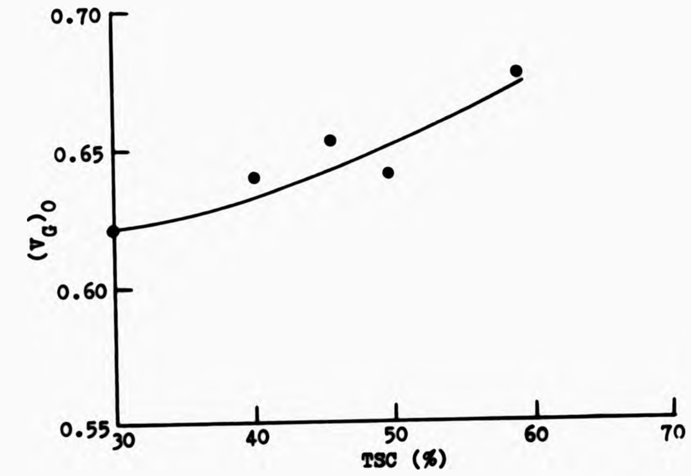


Figure 7.10 Effect of TSC of latex upon the initial volume fraction of rubber in the wet gel, $(V_G)_0$,: dwell time 60s; coagulant solution concentration 30%

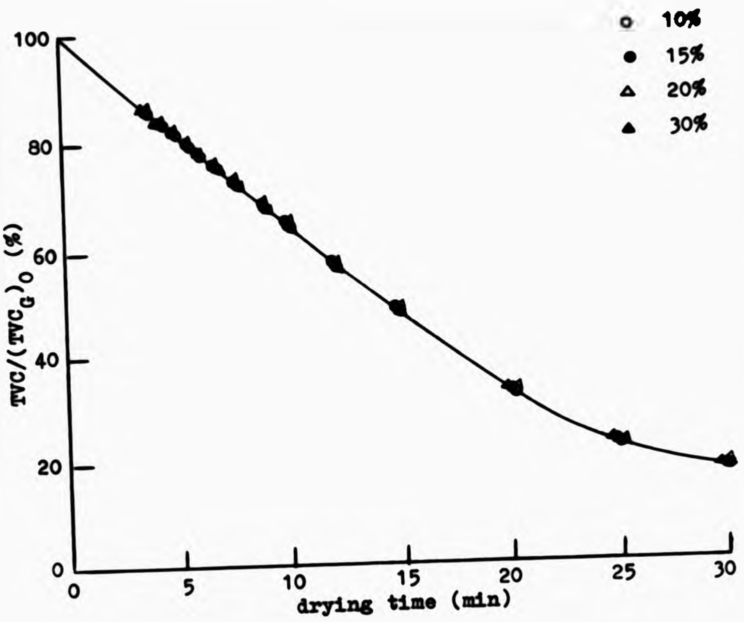


Figure 7.11 Effect of concentration of coagulant solution upon rate of drying of a gelled latex film: TSC 59%, dwell time 60s; drying conditions: temperature 30°C, relative humidity 25%

diffusion of calcium ions due to the high gelation of the latex particles.

The opposition of these two effects produces gels of constant thickness, as can be seen by plotting the thickness of wet-gel deposit at zero drying time, $(L_G)_0$, against the concentration of the coagulant solution (Figure 7.12). The results show that the thickness increases slightly with increasing coagulant solution concentration. The thickness at zero coagulant solution concentration corresponds to the thickness of wet deposit obtained by straight dipping.

7.5 Analysis of results for rate of evaporation of water from wet gels

7.5.1 Introduction

Before attempting to analyse the results of rate of evaporation of coagulant dipped films under constant conditions of temperature (30°C) and relative humidity (25%), it must be pointed out that there is an additional process known as syneresis which occurs concomitantly with the drying process. Much of the reported work (7-11) on the subject of syneresis has been confused with the evaporation process. In this work, an effort is made to separate the process of syneresis from the process of evaporation.

Syneresis is defined as the spontaneous exudation of aqueous phase from the gel, with consequent shrinkage of the gel. Thus, the occurrence of syneresis promotes the removal of water from the gel and may therefore promote the drying of gelled films. The effect of syneresis can easily be observed by comparing the results of the TSC of the latex with the TSC of the gel at zero drying time, $(TSC_G)_0$, as shown in Table 7.4. The results suggest that serum is exuded during the formation of the gel, in that the TSC of the gel is significantly greater than that of the latex from which it was formed. These results have been discussed in Section 7.4.3.

7.5.2 The $TVC/(TVC_G)_0$ versus drying time plot

The results presented in Figures 7.4, 7.8 and 7.11 show that the $TVC/(TVC_G)_0$ versus drying time plots in the early stages of drying of coagulant dipped films indicate two distinct

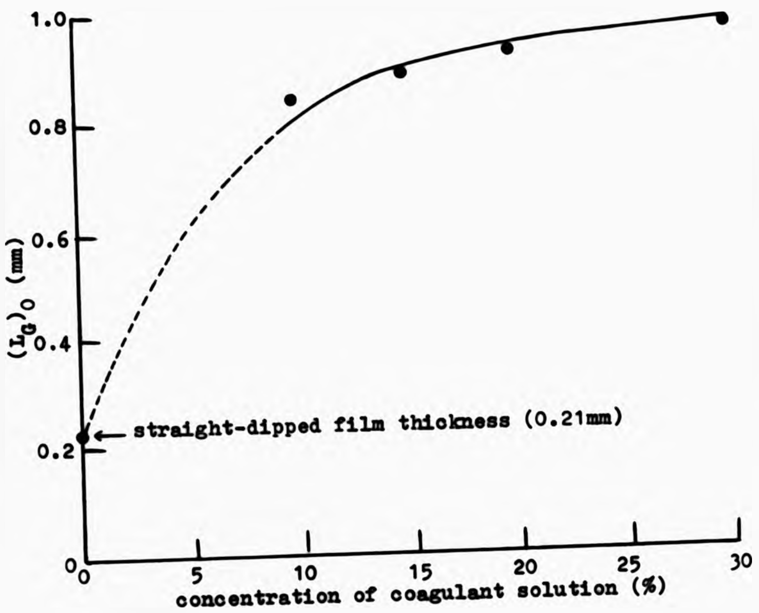


Figure 7.12 Relationship between thickness of wet gel at zero drying time, $(L_G)_0$, and concentration of coagulant solution: TSC 59%; dwell time 60s

Table 7.4 Comparison of TSC of latex with TSC of gel at zero drying time, $(TSC_G)_0$

TSC of latex (%)	$(TSC_G)_0$ (%)
30.2	60.1
40.1	62.5
45.3	63.4
50.1	62.4
59.0	66.1

regions of drying. In the first region, the rate of evaporation is constant and in the second region it is not. This type of behaviour is in accordance with that obtained by other workers (2,3). However, the mechanism proposed by Vanderhoff (2) to explain the linearity of the constant-rate region for cast films is inappropriate here. This is because he postulated that the initial loss of water is the same as that for pure water and that the latex particles move about with their characteristic Brownian motion. This is obviously not the case in gelled films, because there is no Brownian motion of the rubber particles. It is thus necessary to consider these results further in order to gain a deeper understanding of the process before any attempts can be made to postulate a theory to account for the experimental observations.

7.5.3 Possible mechanisms for evaporation of water from wet gels

The evaporation of water from wet gels in the early stages may involve one or both of the following mechanisms:

(i) evaporation of that water which is exuded by syneresis; and

(ii) evaporation of that water which passes through the capillary network formed by partial coalescence of the latex particles. The capillary structure is maintained by interstitial water.

Both of these mechanisms will now be considered in some detail.

7.5.3.1 Evaporation of that water exuded by syneresis

After the formation of a gel, the gel sometimes continues to contract spontaneously such that the serum contained within the capillary network is squeezed out onto the surface. As a consequence, the total solids content of the gel increases above that of the latex from which it was formed (Table 7.4). Thus, it is possible that the rate of evaporation of water is directly proportional to the rate of syneresis. The rate of syneresis was measured as the volume percentage of serum exuded by using the equation 7.1. viz,

$$V_s = \frac{(TVC_G)_0 - (TVC_G)_t}{(TVC_G)_t} / \rho_w \times 100 \qquad (7.1)$$

where V_s is the volume percentage of serum exuded, $(TVC_G)_0$ is the total volatile content of gel at zero drying time, $(TVC_G)_t$ is the total volatile content of gel at drying time t, and ρ_w is the density of water (taken as 1g cm^{-3})

In order to minimise the loss of water by any other mechanisms as far as possible, the syneresis was measured after a drying time of two minutes. When the rate of evaporation, R_E, was plotted as a function of the volume percentage of serum exuded, V_s, (V_s being varied by varying the dwell time), a linear relationship was observed. The results are shown in Table 7.5 and Figure 7.13. The results suggest that the greater is the rate of syneresis, i.e., the greater is the volume percentage of serum exuded, the higher is the rate of evaporation of water. This is consistent with the observations made by Shukri (4). He showed that syneresis occurs rapidly within about five minutes of the formation of the gel, and that this rapidity of syneresis increases as the dwell decreases. The results further suggest that the value 2.6x10^{-4}g $min^{-1}cm^{-2}$ obtained by extrapolation of the rate of evaporation to zero volume of serum exuded, i.e., when syneresis is absent, is in surprisingly good agreement with the value of 2.5x10^{-4}g $min^{-1}cm^{-2}$ obtained for pure water under the same conditions of temperature (30°C) and relative humidity (25%) (Section 6.7.11). This is a very interesting

Table 7.5 Effect of volume percentage of serum exuded at drying time of two minutes, $(V_s)_2$, upon rate of evaporation of water, R_E, for gels produced at various dwell times

dwell time (s)	R_E ($gmin^{-1}cm^{-2}$)	$(V_s)_2$ (%)
15	6.8×10^{-4}	19.0
30	5.9×10^{-4}	15.0
45	5.5×10^{-4}	13.0
60	5.1×10^{-4}	12.3
120	4.6×10^{-4}	10.0
300	4.4×10^{-4}	8.0

observation. It seems unlikely that this observation has ever been made previously. However, with the limited data available, it is not clear whether this agreement is fortuitous or not. In any case, the results indicate that the gels dry faster than pure water and in some cases, twice as fast. It is thought that this may be a consequence of:

(a) possibly an increase in the surface area of water due to the formation of water droplets on the surface of gelled films. These water droplets are thought to arise from the process of spontaneous exudation of serum from the gel and concomitant contraction of the gel; and
(b) partly an increase in the kinetic energy of water molecules due to the extra energy supplied by the process of contraction of the gel.

The mechanism (b) may offer some explanations for the gels drying faster than pure water. However, it is thought that the mechanism (a) offers the most likely explanation for the marked increase in the rate of evaporation of water from gels than from pure water. This is because, visual examination of the gelled films appeared to show the presence of water droplets on the surface of the gel in the early stages of drying.

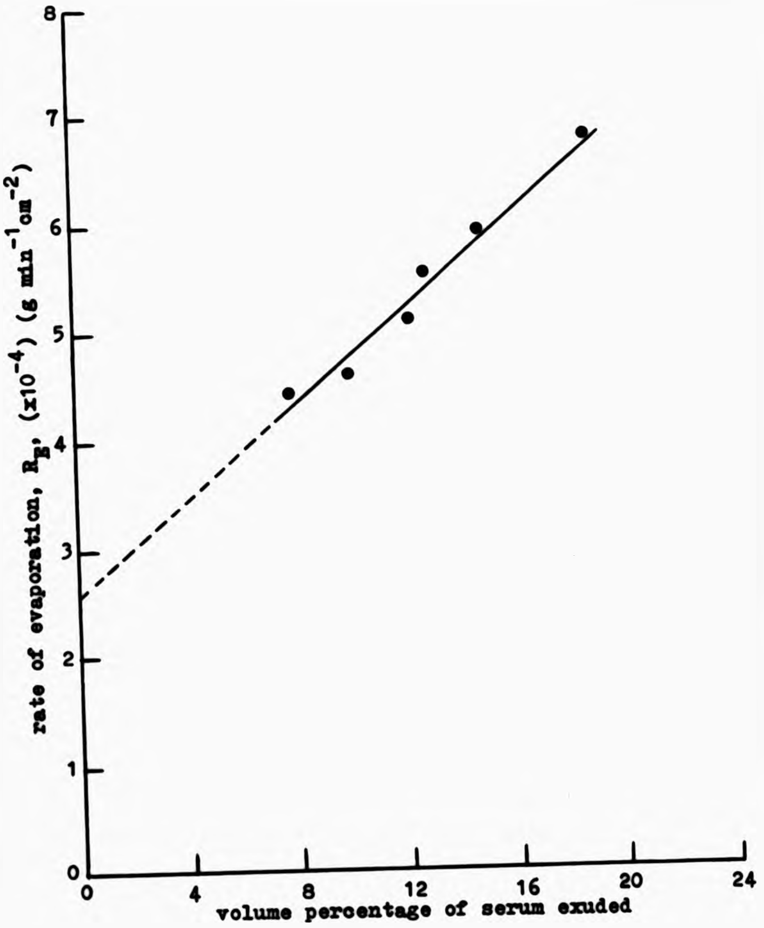


Figure 7.13 Relationship between rate of evaporation of water, R_E, and volume percentage of serum exuded for a given dwell time: TSC 59%; coagulant solution concentration 30%

7.5.3.2 Interstitial water evaporation

If the evaporation of water is due to the passage of water through the capillary network formed by the gel, it is expected to be dependent upon the surface area of capillaries. This effect was investigated by measuring the surface area of capillaries and then plotting the rate of evaporation, R_E, against the surface area, A_S, for a given dwell time. The surface area was measured as described in Section 6.7.5. In summary, it was assumed to a first approximation that the percentage of water present in the gel is equivalent to the surface area of water and hence to the aggregate size of the capillaries in the surface. The rate of evaporation of water is thus expected to be directly proportional to the surface area. The rate of evaporation of water was investigated by determining the slopes for a given drying time in Figure 7.4. The surface area was calculated from the percentage of water present in the film at that given drying time. The results for the effect of surface area, and hence the aggregate size of the capillaries, upon rate of evaporation of water, for gels produced at dwell times of 15s and 300s are shown in Table 7.6. A graph of rate of evaporation, R_E, versus surface area, A_S, was plotted for gels produced at various dwell times and at constant TSC of 59% and coagulant solution concentration of 30%. The results are shown in Figure 7.14. It is seen from Figure 7.14 that the rate of evaporation corresponding to short drying times (~ 4-9min) is independent of surface area of water (Region I). However, above the drying time of 4 to 9 minutes, it is linearly related to the surface area (Region II). Furthermore, the lines do not pass through the origin in Region II, thus suggesting that the water loss is by some mechanism other than passage through the capillary channels by diffusion. This other mechanism could well be syneresis. This is most likely to be true since Savinkova *et al*. (8) have shown that syneresis generally occurred very rapidly during the first 2 to 3 hours, and then slowed down considerably. Region II of Figure 7.14 also shows that the lines approach the origin more nearly on increasing the dwell time. This suggests that the dependency of rate of evaporation of water upon the surface area of capillaries alone becomes more apparent for gels produced at high dwell times. This is hardly surprising, because the composition or structure of the gel changes with changes in dwell time. The further significance of these results, however, will be discussed in Section 7.6.3.

Table 7.6 Relationship between rate of evaporation of water, R_E, and surface area, A_S, for gels produced at dwell times of 15s and 300s: TSC 59% and coagulant solution concentration 30%

drying time (min)	R_E ((%)/min)	TVC_G (%)	TSC_G (%)	A_S*
gel produced at dwell time of 15s				
2.5	8.0	26.4	32.6	44.8
5.0	8.0	19.9	32.6	37.9
7.5	8.0	13.4	32.6	29.1
10.0	4.1	9.1	32.6	21.9
12.5	2.1	6.5	32.6	16.0
15.0	1.6	4.6	32.6	12.3
17.5	1.0	3.6	32.6	10.9
gel produced at dwell time of 300s				
2.5	3.2	31.9	34.7	47.9
5.0	3.2	29.1	34.7	45.6
7.5	3.2	26.3	34.7	43.1
10.0	3.2	23.6	34.7	40.5
12.5	3.1	20.8	34.7	37.5
15.0	3.0	18.4	34.7	34.7
17.5	2.8	15.9	34.7	31.4

* $A_S = (TVC_G / (TVC_G + TSC_G)) \times 100$

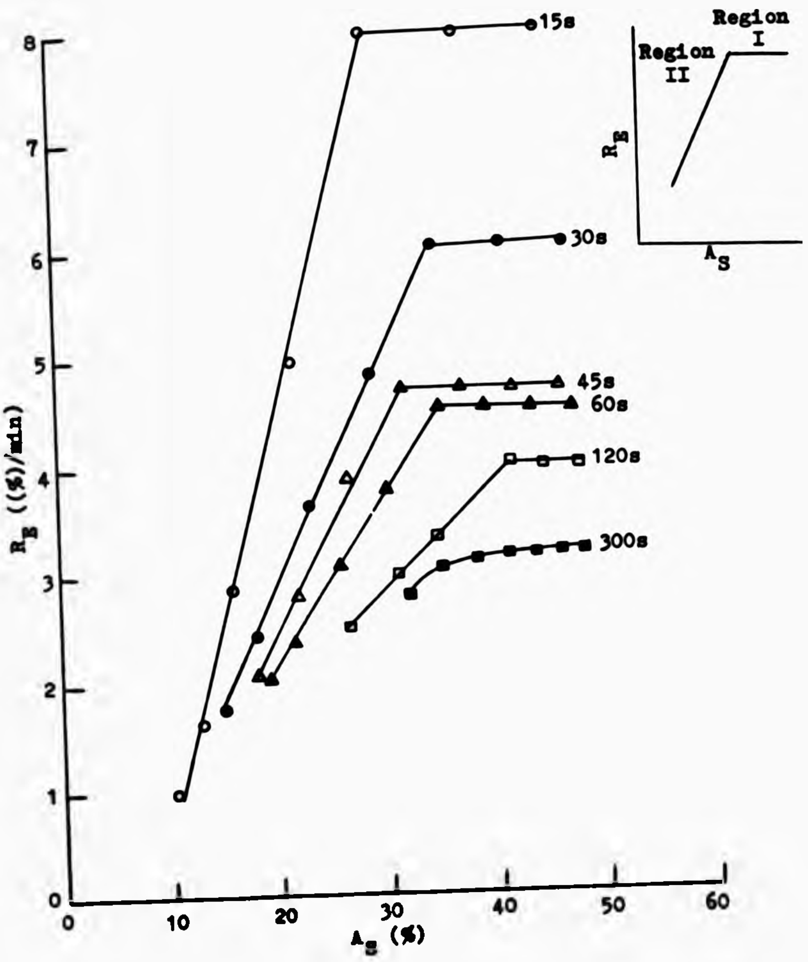


Figure 7.14 Relationship between rate of evaporation of water, R_E, and surface area of capillaries, A_S, for gels produced at various dwell times: TSC 59%; coagulant solution concentration 30% (see text for significance of Regions I and II)

The independency of rate of evaporation of water with the surface area in Region I is consistent with the effect of syneresis. However, as the drying of the gels continues, the further loss of water in Region II is predominantly by its passage through the capillary network by diffusion, at a rate equal to that at which it is removed from the surface by evaporation, although syneresis continues to persist.

7.5.4 Summary of conclusions concerning mechanism of evaporation of water from wet latex gels

In the early stages of the drying of the wet gels, the mechanisms in operation at all times are primarily the syneresis and the diffusion. However, the principal mechanism governing the loss of water in Region I is the evaporation of that water which is exuded via syneresis and in Region II is the evaporation of that water which passes through the capillary channels to the surface by diffusion. The effectiveness of such processes depends on the composition or structure of the gel (see Section 7.6.3).

It is not surprising that the Russian workers (7-11) have confused the syneresis process with the evaporation process. This is because the very early stages of the drying process of the wet gels (Region I) involves the evaporation of that water which is exuded via syneresis, thus generating the inseparable nature of the two. However, the separation of these two processes becomes more apparent at the later stages of the drying (Region II) when another process, namely, diffusion participates in the mechanism of the drying process.

7.6 Consideration of loss of water through wet gels by diffusion mechanism

7.6.1 Introduction

It is proposed that the loss of water in Region II of the drying process for the wet gels is by passage of water through the capillary network by diffusion, at a rate equal to that at which it is removed from the surface of the gel by evaporation. Hence, the data obtained for the rate of evaporation of water from the wet gels (Figures 7.4, 7.8 and 7.11) are presented as $TVC/(TVC_G)_0$ versus square root drying time per unit thickness at that drying time, $t^{\frac{1}{2}}/L$, in subsequent sections. The thickness of the wet gel at a given drying time was calculated using the method described in Section 6.6.3.

In general, the results plotted this way support the view that the loss of water from the wet gel in Region II is indeed a consequence of its passage through the capillary network by diffusion at a rate equal to at which it is removed from the surface by evaporation. This behaviour is illustrated schematically in Figure 7.15. As can be seen in Figure 7.15, two distinct mechanisms seem to be operative, one being dominant at short drying times and the other at long drying times. At short drying times, the rate of diffusion is low, and at long drying times the rate of diffusion is high. In addition, it is noted that the Region II of the rate of diffusion curve (Figure 7.15) begins more or less at the same drying time as the Region II of the rate of evaporation curve (Figure 7.3). Thus, the analysis of the rate of evaporation of the wet gels in Section 7.5 suggest that the discontinuity revealed by Figure 7.15 may be an artefact of syneresis in Region I and diffusion in Region II.

7.6.2 Explanation of discontinuity in $TVC/(TVC_G)_0$ versus $t^{\frac{1}{2}}/L$ plots

Since the process of syneresis occurs only in gelled films, it was decided to compare the results for the drying of coagulant-dipped films with the results for the drying of straight-dipped films, under constant conditions of temperature and relative humidity. The comparison is shown in Figure 7.16. This is a most interesting diagram. As far as the author is aware, no previous workers have published similar plots. The first and most obvious difference is that the coagulant-dipped films dry much faster than the straight-dipped films, at least when $t^{\frac{1}{2}}/L$ exceeds about $20 s^{\frac{1}{2}}$ mm^{-1}. At first glance this seems rather surprising. However, these results do support the mechanisms put forward for the early stages of drying of films produced by both straight and coagulant dipping. The further significance of these results will be discussed more fully in Section 7.8. Figure 7.16 also shows that the discontinuity occurs only in the drying of coagulant-dipped films. Thus, the discontinuity in plots of $TVC/(TVC_G)_0$ versus $t^{\frac{1}{2}}/L$ at short drying times (Region I), as shown in Figure 7.15, gives an indication of the occurrence of

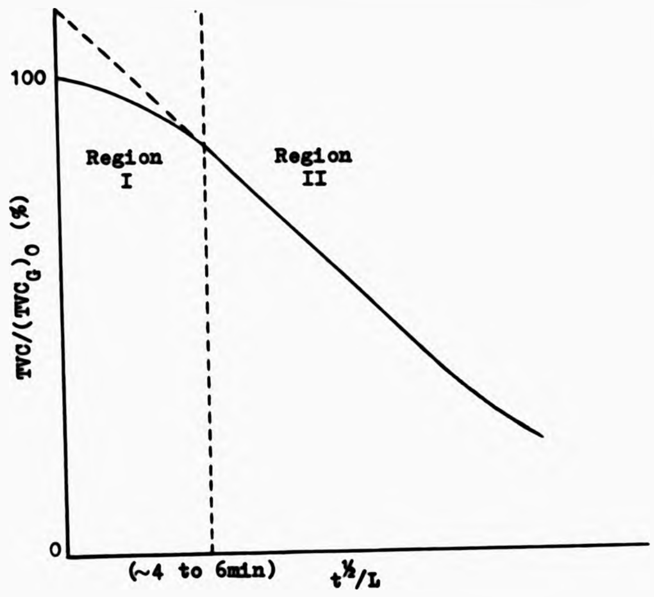


Figure 7.15 Schematic illustration of loss of water by diffusion from the wet gel (see text for significance of Regions I and II)

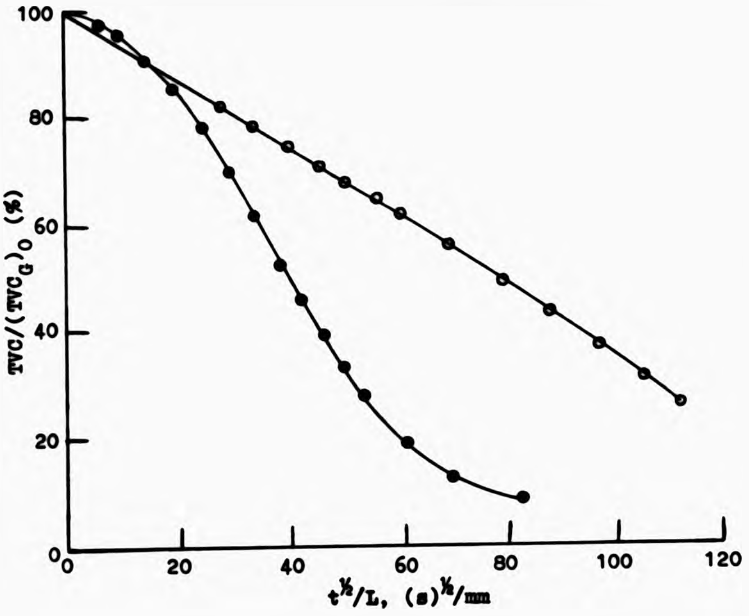


Figure 7.16 Comparison between drying behaviours of a straight-dipped film, (o), and of a coagulant-dipped film, (•), results plotted to test diffusion mechanism: TSC 59%; coagulant-dipped film conditions: dwell time 60s, coagulant solution concentration 30%; drying conditions: temperature 30°C, relative humidity 25%

syneresis. This supports the earlier suggestions put forward regarding the linearity of the plots of $TVC/(TVC_G)_0$ versus drying time (Figure 7.3, Region I).

7.6.3 Effect of dwell time upon rate of diffusion of water through wet gels

In contrast to the results for the rate of evaporation of water from gels formed at various dwell times, when a graph of $TVC/(TVC_G)_0$ versus $t^{\frac{1}{2}}/L$ is plotted for gels formed at various dwell times (Figure 7.17), it is observed that a reduction in the dwell time leads to a reduction in the rate of diffusion, provided that other factors such as TSC and coagulant solution concentration remain constant. Initially, it was speculated that it may be the thickness factor in the diffusion equation which led to this conclusion. For example, the thickness, L, of the wet gel increases with increasing dwell time, thereby reducing the factor $t^{\frac{1}{2}}/L$ in the diffusion equation 6.8. Thus, the rate of evaporation results were examined further by attempting to take into account the changing thickness at various dwell times. Hence, a graph of $TVC/(TVC_G)_0$ versus drying time per unit thickness, t/L, was plotted for gels formed at various dwell times, under constant conditions of temperature and relative humidity (Figure 7.18). It was found that all the data points could now be represented by a single curve. It is thus postulated that the diffusion of water through the wet gel is affected by some mechanism other than the rate of evaporation of water from the gel.

In practice, it is noticed that at long dwell times when the former is withdrawn from the latex, excess latex merely flows down to the bottom of the former where it remains as a drop, in extreme cases, the drop falls off the former. Shukri (4) attempted to evaluate the significance of such behaviour upon the overall structure of the wet gel by determining the viscosity of the latex which ran off the former. He showed the viscosity to be higher than that of the bulk of the latex. According to Shukri, the outer layer of the deposit which forms after long dwell times is in a critical condition of incipient gelation. Thus, it was proposed that the deposit which forms after long dwell times consists of two distinct regions. There is an inner region which resembles the deposit obtained at short dwell times in that it comprises a strong coherent latex gel. There is also an outer region which

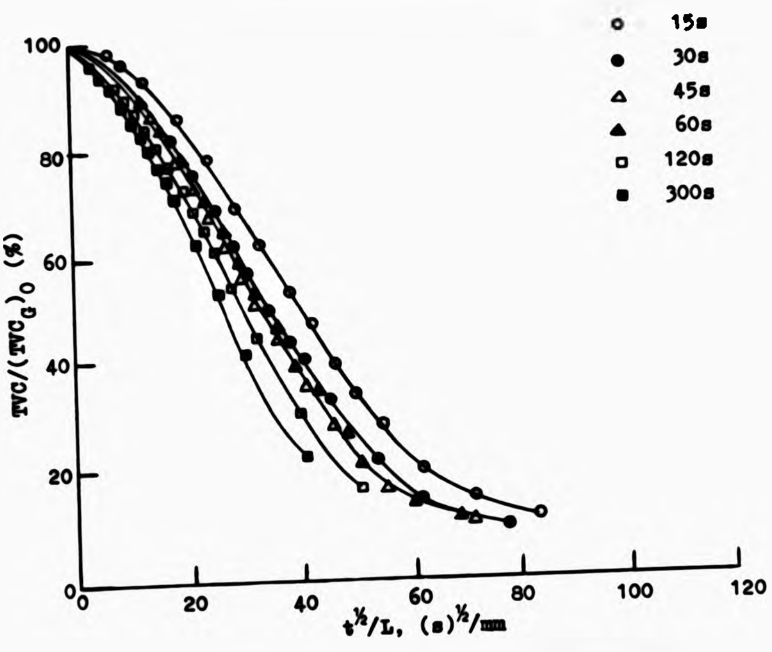


Figure 7.17 Effect of dwell time upon rate of diffusion of water through the wet gel: TSC 59%, coagulant solution concentration 30%; drying conditions: temperature 30°C, relative humidity 25%

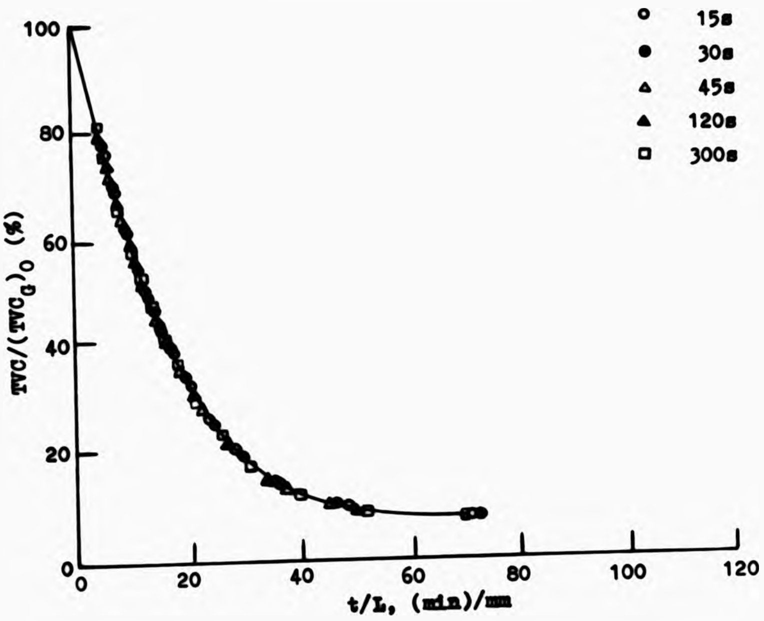


Figure 7.18 Effect of dwell time upon variation of TVC/(TVC$_G$)$_0$ with t/L: TSC 59%, coagulant solution concentration 30%; drying conditions: temperature 30°C, relative humidity 25%

comprises a highly viscous layer, i.e., the viscosity is sufficiently high for the layer to be withdrawn with the former but significantly low to cause the latex subsequently to flow off the former.

The results obtained in this investigation appear to support Shukri's finding, in that they suggest that the rate of diffusion of water per unit volume of the gel is lower for gels formed at short dwell times than for those formed at long dwell times. In other words, in the early stages of drying of the wet gels, the diffusion of water through a unit volume of the gel is reduced in the case of gels formed at short dwell times, because the gel comprises a more tightly-packed structure. However, as the dwell time is increased, the gel structure becomes more open, thereby increasing the rate of diffusion of water per unit volume of the gel. This also explains the enhancement of the rate of evaporation of water exuded by syneresis with reduction in the dwell time (Figure 7.14). That is to say, at short dwell times, the gel comprises a more compact structure and therefore the interfacial forces are considerably higher. As a consequence, water trapped in the gel is more readily forced out.

7.6.4 Effect of TSC of latex and concentration of coagulant solution upon rate of diffusion of water through wet gels

It is seen in Figure 7.8 and 7.11 that no noticeable changes occurred in the rate of evaporation of water from wet gels formed from latices having various TSCs (using coagulant solution having a constant concentration of 30%), or from wet gels obtained using coagulant solution of various concentrations and a latex of constant TSC of 59%, the gels being formed at a dwell time of 60s in each case. Thus, it was expected the rate of diffusion of water through a wet gel would also be independent of the TSC of the latex or of the concentration of the coagulant solution. This is because the results obtained so far have indicated that the rate of diffusion of water through the capillaries is equal to the rate of evaporation of water from the capillaries, for a given gel. Additionally, since the dwell time for the formation of the gel was constant throughout this entire investigation, the effects of variations in gel structure should be negligible. The effects of variations in gel structure due to the changes in either the TSC of the latex or the concentration of the coagulant solution should also be negligible (see Sections 7.4.3 and 7.4.4 respectively).

When a graph of $TVC/(TVC_G)_0$ versus $t^{\frac{1}{2}}/L$ was plotted for gels formed from latices of various TSCs using a coagulant solution of constant concentration of 30% and a dwell time of 60s (Figure 7.19), or for gels formed using coagulant solution having various concentrations and at a latex of constant TSC of 59% and a dwell time of 60s (Figure 7.20), no significant effects were observed. This was expected. The mechanisms postulated for such observations are given in Section 7.4.3 and 7.4.4 respectively. Also, the shapes of the plots in Figures 7.19 and 7.20 are consistent with the loss of water from the gel being a diffusion-controlled process. Again, the deviation in the early stages is attributed primarily due to the occurrence of syneresis.

7.7 Comparison of conclusions reached from analyses of drying behaviour of gelled films according to diffusion and evaporation models

7.7.1 Drying behaviour in Region I

The rate of movement of water through the wet gel (characterised by a diffusion coefficient, D) can be compared with the rate of removal of water from the gel (characterised by an evaporation coefficient, K). In summary, the former was obtained by determining the slopes of plots of $TVC/(TVC_G)_0$ versus $t^{\frac{1}{2}}/L$ (Figure 7.17) and calculating D by the method described in Section 6.6. The latter was determined directly from the slopes, using the least squares method, of plots of $TVC/(TVC_G)_0$ versus t (Figure 7.4) in the linear region, i.e., over the range of drying times from about 4 to 9 minutes. As shown in Section 6.7.5,

$$R_E = KA_S \qquad (7.2)$$

where R_E is the rate of evaporation of water, K is the evaporation coefficient, and A_S is the surface area of water which is equivalent to the aggregate cross-sectional area of the capillaries. In Region I, however, R_E is independent of A_S, as shown in Figure 7.14. Hence,

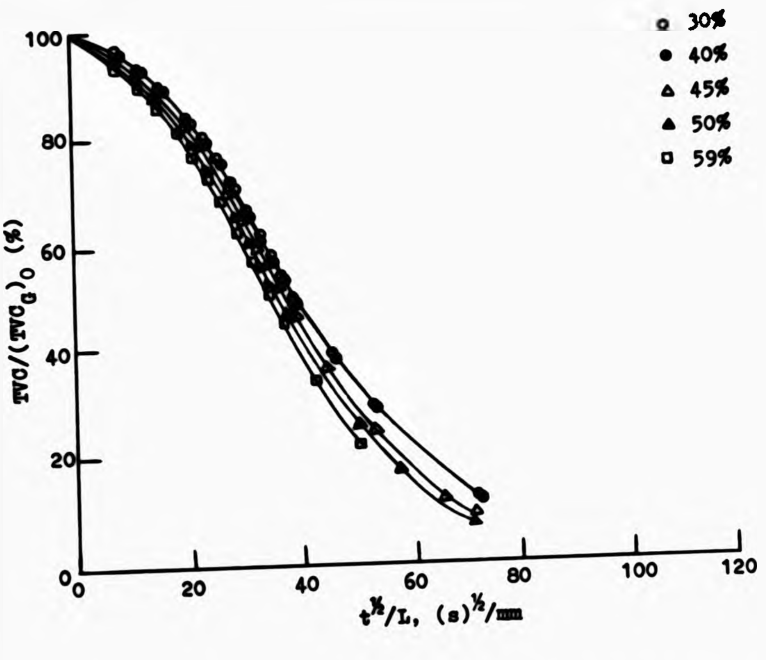


Figure 7.19 Effect of TSC of latex upon rate of diffusion of water through a gelled latex film: dwell time 60s, coagulant solution concentration 30%; drying conditions: temperature 30°C, relative humidity 25%

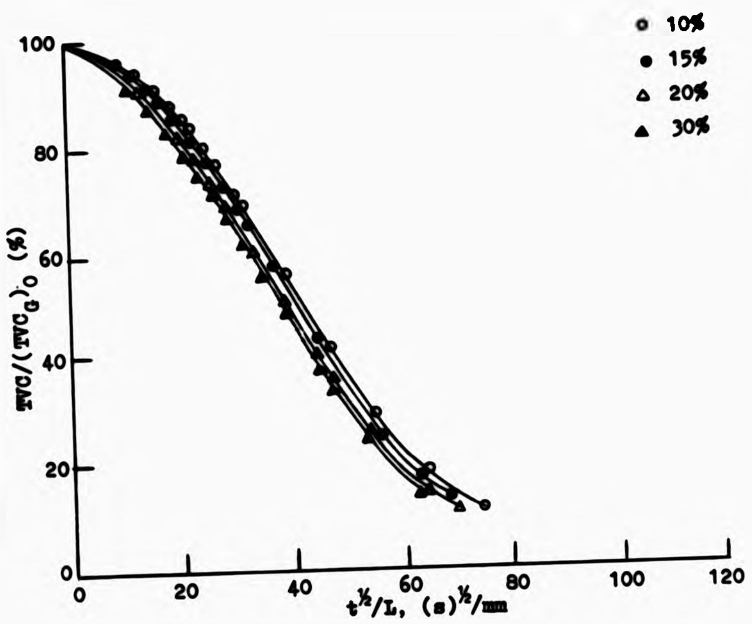


Figure 7.20 Effect of concentration of coagulant solution upon rate of diffusion of water through a gelled latex film: TSC 59%, dwell time 60s; drying conditions: temperature 30°C, relative humidity 25%

$$R_E = K \qquad (7.3)$$

A graph of D versus R_E (=K) has been plotted, as shown in Figure 7.21. As can be seen, a rather unusual plot was obtained. It can be divided into three sections, labelled A, B and C.

7.7.2 Drying behaviour in Region II

Again, the diffusion coefficient was obtained as summarised in above Section 7.7.1. However, the rate of evaporation is not constant in this region, but instead is found to be directly proportional to the surface area of the capillaries, A_S, at a given drying time (Figure 7.14). Thus, it obeys the equation 7.2. The evaporation coefficient, K, values were obtained by determining the slopes in Figure 7.14, using the least squares method. When a graph of D was plotted versus K (Figure 7.22), a curve of similar form to that for Region I (Figure 7.21) was obtained, showing three distinct sections, namely, A, B and C.

7.7.3 Discussion

The results shown in Figures 7.21 and 7.22 are very interesting indeed and almost certainly very significant. It seems unlikely that these very interesting observations have ever been made previously. Despite lack of knowledge available relating to the processes which occur during the drying of coagulant-dipped gels, an attempt has been made to elucidate mechanisms by separating processes such as diffusion, syneresis etc., all of which appear to be interrelated in a complex manner. The principal finding so far is that the main process governing drying in Region I is syneresis and in Region II is diffusion. The significance of such processes in relation to the effect of changes in the gel structure upon the nature of the curves shown in Figures 7.21 and 7.22, and hence upon the overall drying rate, is discussed in the subsequent sections.

7.7.3.1 Behaviour in Section A of Figures 7.21 and 7.22

At long dwell times (>60s), the wet gel has a more open structure compared with the wet gel formed at short dwell times. This allows the passage of water through the gel to be rapid, thereby increasing the rate of diffusion. However, the

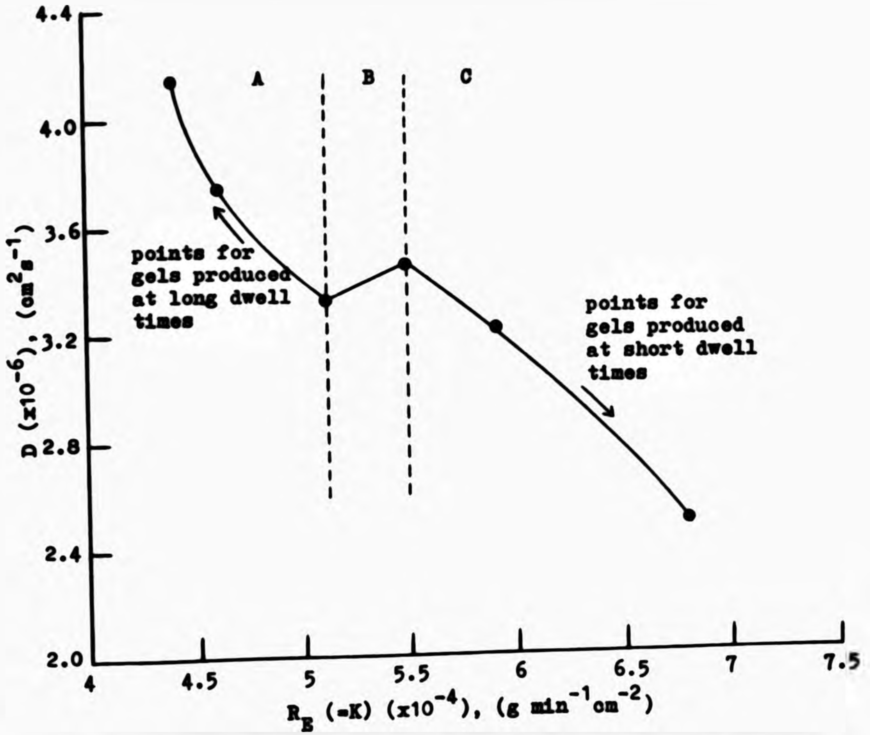


Figure 7.21 Relationship between D and R_E*, for gels produced at a given dwell time, which characterise drying behaviour in Region I: TSC 59%, coagulant solution concentration 30%; drying conditions: temperature 30°C, relative humidity 25% (see text for significance of Sections A, B and C)

* R_E = K from equation 7.3

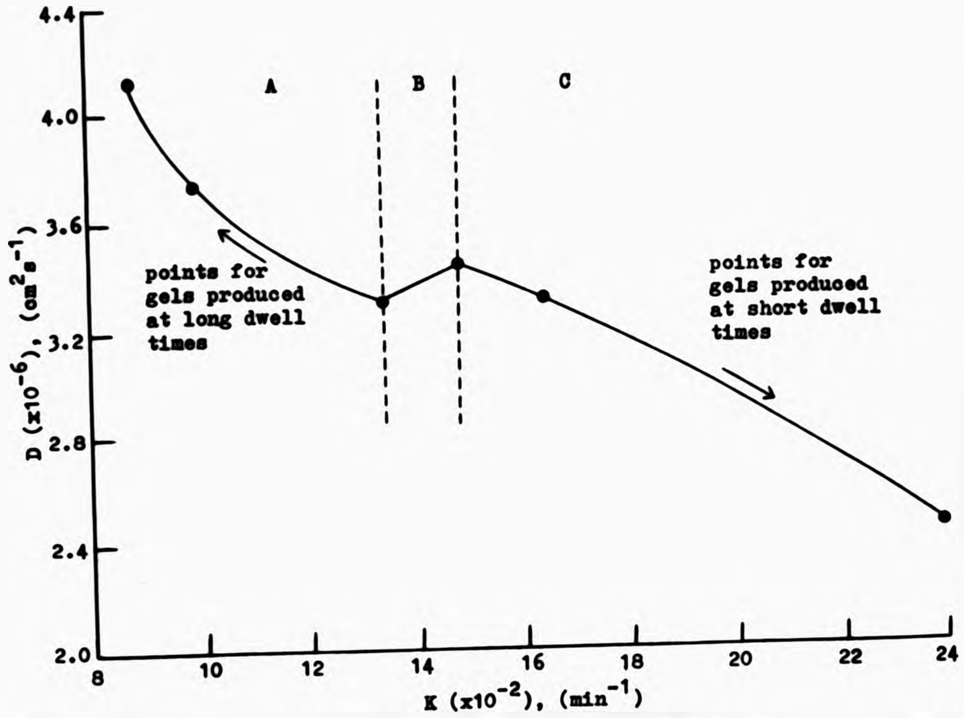


Figure 7.22 Relationship between D and K for gels produced at a given dwell time, which characterise drying behaviour in Region II: TSC 59%, coagulant solution concentration 30%; drying conditions: temperature 30°C, relative humidity 25% (see text for significance of Sections A, B and C)

rate of syneresis is reduced due to the reduction in the interfacial forces. Thus, the overall rate of evaporation of water is dependent upon the rate of diffusion alone, without the process of syneresis participating much in the mechanism. This effect may be stated as follows:

$$\begin{array}{c}\text{rate of}\\\text{evaporation}\end{array} = \begin{array}{c}\text{rate of}\\\text{diffusion}\end{array} > \begin{array}{c}\text{rate of}\\\text{syneresis}\end{array}$$

7.7.3.2 Behaviour in Section B of Figures 7.21 and 7.22

At mid-dwell times (45-60s), a transition state occurs in which the capillary structure changes from the more open structure to the more tightly packed structure. In this state, the rate of evaporation is governed equally by the rate of diffusion and the rate of syneresis. Thus, the overall rate of evaporation of water is a result of both, the water which is exuded by syneresis and which passes through the capillary network formed by partial coalescence of the latex particles. viz,

$$\begin{array}{c}\text{rate of}\\\text{evaporation}\end{array} = \begin{array}{c}\text{rate of}\\\text{diffusion}\end{array} \gtrless \begin{array}{c}\text{rate of}\\\text{syneresis}\end{array}$$

7.7.3.3 Behaviour in Section C of Figures 7.21 and 7.22

At short dwell times (<45s), the evaporation of water from the gel is mainly by exudation of water via syneresis, although diffusion process still occurs. This is because the wet gel formed comprises a tightly packed structure of latex particles, thereby increasing the interfacial forces and hence causing an increase in the rate of syneresis. Thus,

$$\begin{array}{c}\text{rate of}\\\text{evaporation}\end{array} = \begin{array}{c}\text{rate of}\\\text{diffusion}\end{array} < \begin{array}{c}\text{rate of}\\\text{syneresis}\end{array}$$

After the initial rapid occurrence of syneresis, syneresis continues to persist. However, the relative importance of syneresis is dictated by the overall nature of the gel structure. The persistence of syneresis for long periods of drying is in accordance with the work of Savinkova _et_ _al_. (8).

7.8 Comparison of drying processes for coagulant- and straight-dipped latex films

One of the fundamental differences between straight dipping and coagulant dipping is that the latter permits the production of much thicker films. The drying process is highly dependent upon the thickness of these films. An attempt has been made to compare the drying process for a coagulant-dipped film with that for a straight-dipped film, taking into account their different thicknesses where necessary. The $TVC/(TVC_G)_0$ versus t plots in Figure 7.23 compare the rate of evaporation of water from straight-dipped film with that of a coagulant-dipped film under constant conditions of temperature (30°C) and relative humidity (25%). Both films were produced from latex of 59% TSC. At first glance, it appears that the rate of evaporation from a straight-dipped film is higher than that from a coagulant-dipped film. However, this difference is thought to arise from the different film thicknesses. Hence, the data in Figure 7.23 are presented as $TVC/(TVC_G)_0$ versus drying time per unit thickness, t/L, in Figure 7.24. The results plotted in this way suggest that the rate of evaporation, in actual fact, is more rapid for films formed by coagulant dipping than by straight dipping. Thus, the results support the view that the syneresis promotes drying.

Similar observations have been made when a comparison of the drying of coagulant- and straight-dipped films is made on the assumption that the process is diffusion-controlled. It is seen in Figure 7.16 that the rate of diffusion of water through a coagulant-dipped film is comparatively higher than the rate of diffusion of water through a straight-dipped film. The value of diffusion coefficient, D, for a coagulant-dipped film is found to increase by a factor of 10 compared with the value for a straight-dipped film.

7.9 Summary

The early stages of the drying of wet latex gels formed by coagulant dipping can be divided into two regions:

(i) Region I - This is an initial region of constant rate which persists until the volume fraction of rubber has increased to 70-90%. In this region, the loss of water is principally by syneresis. Hence,

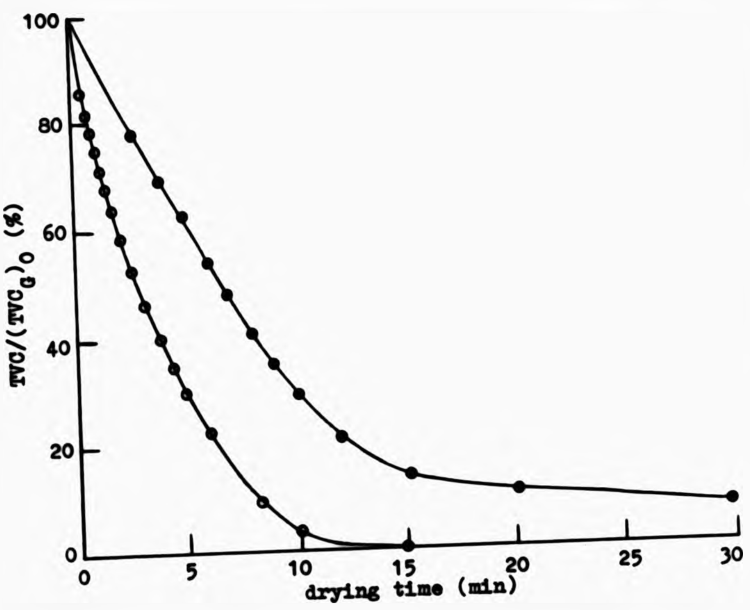


Figure 7.23 Comparison of drying behaviour of a straight-dipped film, (o), with that of a coagulant-dipped film, (●): TSC 59%; coagulant-dipped film conditions: dwell time 60s, coagulant solution concentration 30%; drying conditions: temperature 30°C, relative humidity 25%

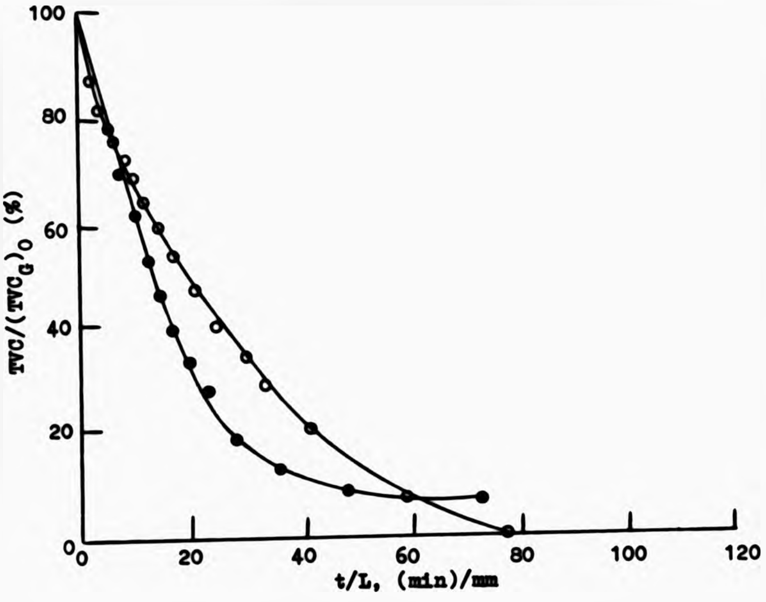


Figure 7.24 Comparison of curves for TVC/(TVC$_G$)$_0$ versus drying time per unit thickness for films formed by straight dipping, (o), and by coagulant dipping, (●): TSC 59%; coagulant-dipped film conditions: dwell time 60s, coagulant solution concentration 30%; drying conditions: temperature 30°C, relative humidity 25%

$$R_E = K$$

(ii) Region II - This is a region in which the rate of drying drops off readily to a value 15-25 times smaller than that for the Region I. The main feature of this stage of drying is that water can pass through a capillary network formed by partial coalescence of the rubber particles, at a rate equal to that at which it is removed from the surface. Thus,

$$R_E = KA_S$$

The rate of loss of water is strongly dependent upon the gel structure, as is evidenced by the results for gels produced at various dwell times under the conditions which favour the formation of a strong gel, e.g., short dwell times, some water is forced out by syneresis. The other process variables, such as latex TSC and coagulant solution concentration seem to have a negligible effect upon the gel structure as evidenced by effect upon the rate of evaporation of water.

A peculiar relationship between the diffusion coefficient, D, and the evaporation coefficient, K, (Figures 7.21 and 7.22) is achieved, which can be divided into three distinct sections, labelled A, B, and C. It is proposed that:

(a) in Section A, i.e., for gels produced at high dwell times (>60s),

$$\begin{array}{c}\text{rate of}\\\text{evaporation}\end{array} = \begin{array}{c}\text{rate of}\\\text{diffusion}\end{array} > \begin{array}{c}\text{rate of}\\\text{syneresis}\end{array} \; ;$$

(b) in Section B, i.e., for gels produced at mid-dwell times (45-60s),

$$\begin{array}{c}\text{rate of}\\\text{evaporation}\end{array} = \begin{array}{c}\text{rate of}\\\text{diffusion}\end{array} \gtrless \begin{array}{c}\text{rate of}\\\text{syneresis}\end{array} \; ; \text{ and}$$

(c) in Section C, i.e., for gels produced at low dwell times (<45s),

$$\begin{array}{c}\text{rate of}\\\text{evaporation}\end{array} = \begin{array}{c}\text{rate of}\\\text{diffusion}\end{array} < \begin{array}{c}\text{rate of}\\\text{syneresis}\end{array} \; .$$

Finally, a comparison of the drying behaviour of straight- and coagulant-dipped films suggests the occurrence of syneresis in the early stages of the drying process. For instance, the discontinuity in the relationship of $TVC/(TVC_G)_0$ versus $t^{\frac{1}{2}}/L$ (Figure 7.16), which is attributed to syneresis, is observed only in coagulant-dipped films. Also, the rate of loss of water in terms of drying time per unit thickness for a coagulant-dipped film is considerably higher than that for a straight-dipped film (Figure 7.24). The reason for this phenomenon is that syneresis promotes drying in the former.

CHAPTER 8 : EFFECT OF ADDED INGREDIENTS UPON PROCESSING PROPERTIES OF PREVULCANISED NR LATEX

8.1 Introduction

There is little understanding of the relationship between composition and properties of ammonia-preserved NR latex, especially in respect of the natures and amounts of non-rubber substances and the causes of variability in processing behaviour. The objective of the work described in this chapter was to attempt to throw some light on these areas, and hence, it was hoped, to gain deeper insight into the changes in NR latex properties which are brought about by the addition of various ingredients.

The effects of added ingredients upon the properties of prevulcanised NR latex were investigated by the procedures described in Chapter 3. The added ingredients were:

1. fatty-acid soap, e.g., potassium laurate
2. alkalis, e.g., ammonia and potassium hydroxide
3. salts of volatile fatty acids, e.g., ammonium acetate
4. metal salt, e.g., magnesium chloride

These particular additives were selected because all are known to affect the stability of the latex and hence the observed processibility variations. Various concentrations of each of these ingredients, together with the vulcanising ingredients, were added to the latex before prevulcanisation. Small amounts of each of these ingredients were added to the NR latex which were thought to bring about profound changes in the stability of the NR latex, as reported by previous workers (10-13,17,23). The properties examined were divided into three classes:

(i) latex properties: these were TSC, DRC, KOH No., VFA No., alkalinity, pH, viscosity, ZAAV, MST, CST and microgel content;
(ii) processing properties: these included a measure of water and ammonia loss from a dipped film, set time and curtaining effect (CE);
(iii) physical properties of latex deposits: these were the

tensile properties of a rubber deposit in both its wet and dry state.

8.2 Colloid stability of latex

The colloid stability of latex may be affected by the nature and the amount of the added ingredient. By 'colloid stability' in this context is meant the ability of the latex to withstand those influences which tend to bring about coalescence of the polymer particles, and the eventual separation of the latex into either an immobile gel or two bulk phases.

There are several important factors which are believed to be responsible for promoting the colloid stability. These include:

(a) reduction of the free energy associated with the interface which separates the polymer and the aqueous phase;
(b) the presence around the particles of a layer of tightly bound water molecules which act as a mechanical barrier against the coalescence of two latex particles;
(c) the presence upon the particle surfaces of electric charges of similar polarity which give rise to counter-ion clouds surrounding the particles which discourage the particles from approaching each other;
(d) the adsorption upon the particle surfaces of polymer molecules which give rise to steric stabilisation; and
(e) the presence of dissolved macromolecules in the dispersion medium which give rise to exclusion stabilisation.

Adsorption processes are almost invariably associated with a reduction in free energy. When two particles move towards each other from infinite separation, the change in Gibbs free energy, ΔG, at constant temperature and pressure is given by the expression

$$\Delta G = \Delta H - T\Delta S \qquad (8.1)$$

where ΔH is the change in enthalpy, ΔS is the change in entropy, and T is the absolute temperature. For a stable lyophobic colloid, this ΔG should be positive. It has been pointed out that there are the following three different ways in which a positive value of ΔG can be attained (1-3):

1. $\Delta G > 0$ when $\Delta H > 0$ and $\Delta S > 0$
2. $\Delta G > 0$ when $\Delta H < 0$ and $\Delta S < 0$ but $-T\Delta S >> -\Delta H$
3. $\Delta G > 0$ when $\Delta H > 0$ and $\Delta S < 0$

These give, respectively, colloids which are stabilised by enthalpic, entropic and enthalpic-entropic factors. The interfacial free energy, γ, on the other hand, is the change of ΔG per unit area when the particles have completely flocculated and coalesced to form bulk polymer. This ΔG is always negative, and γ is always positive (because γ is the ΔG per unit area for the reverse process, i.e., for the creation of unit area of interface from the bulk phases). Reducing γ to γ' will obviously reduce the ΔG for the complete flocculation and coalescence, and hence make the colloid more stable. It will also increase the ΔG for the close approach of particles, if other factors remain unchanged. The actual value of ΔG will depend upon the position of the particles relative to each other. But nevertheless γ is always positive and this ΔG is always negative. A schematic diagram showing the relationship between ΔG and γ when two particles move towards each other from infinite separation, is given in Figure 8.1.

The second factor which promotes colloid stability is the presence around the particle of a sheath of tightly bound water molecules. The extent to which hydration occurs is believed to depend upon the nature of the substances which are adsorbed at the particle interface.

The third factor which imparts stability to the latex is the presence of bound electric charges at the particle surfaces. The primary mechanism of electrostatic stabilisation is not mutual repulsions between the charges carried by the particles, but mutual repulsions between the ions in the counter-ion clouds which surround the particles. As a consequence, work has to be done to cause these counter-ion clouds to interpenetrate. Thus as regards colloid stability, it is not the charges on the particles themselves which are of primary importance, but the counter-ion clouds which those bound charges support. It is thus expected that the latex would remain indefinitely stable if the only forces operating between the particles were those arising from the mutual

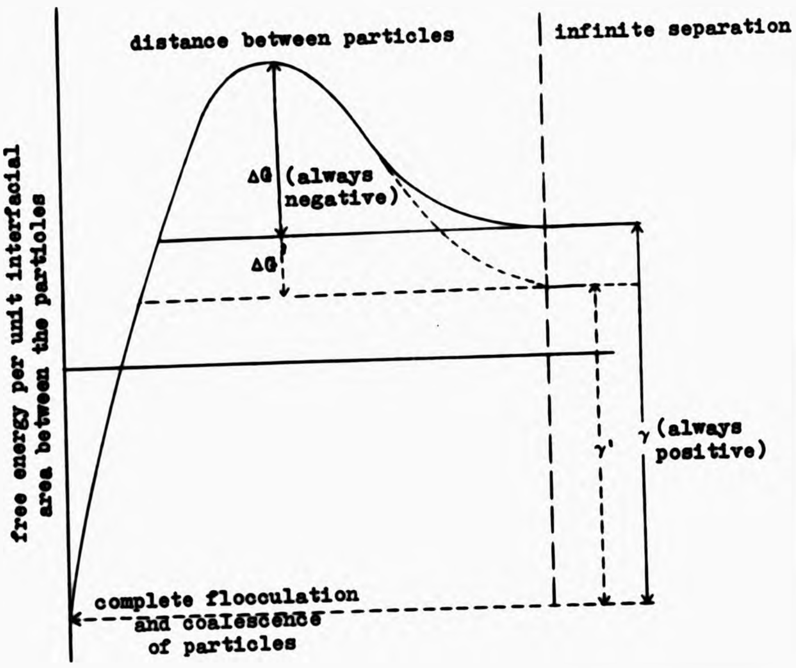


Figure 8.1 Schematic illustration of change in free energy per unit interfacial area as the particles approach one another from infinite separation

repulsion between the ions in the counter-ion clouds which surround the particles. However, it is well-known fact that flocculation occurs very slowly on storage of a latex. It is generally agreed, therefore, that there must also exist short-range forces of attraction between the particles. The overall behaviour of the colloid particles of latex is then considered to be determined by the balance between these two types of force.

The fourth factor, steric stabilisation is particularly important in general, and probably for NR latex in particular. Heller and Pugh (32) were the first to use the term 'steric stabilisation' to denote stabilisation by adsorbed macromolecules in the absence of any electrostatic component. When nonionic polymer chains adsorbed upon adjacent particles interact, the steric repulsive forces and interaction energy that occur originate from two possible mechanisms:

(i) If the distance of separation of two particles is less than twice the thickness of the adsorption layer, then mixing of the two adsorption layers occur. If this process is accompanied by a net increase in the free energy, repulsion occurs between the particles. Such a mechanism is very probable when the concentration of the polymer in the adsorption layer is low (33).

(ii) When the polymer concentration in the adsorption layer is high, the particles undergo pseudo-elastic collision on approach rather than mixing. The polymer molecule adsorbed on the particle loses configurational entropy. This mechanism is referred to as the 'denting mechanism' (34).

Steric stabilisation is obtained by balancing the attractive and steric repulsive energy of two particles on close approach. The total potential energy for sterically-stabilised particles, V_S, is given by

$$V_S = V_{SR} + V_A \qquad (8.2)$$

where V_{SR} is the steric repulsive potential energy and V_A is the attractive potential energy.

Finally, the colloid stability can be enhanced by the presence of dissolved nonionic polymer in the dispersion medium. The free polymer in the dispersion medium is responsible for the repulsion between the particles. Repulsion arises from an increase in the free energy due to almost complete exclusion of free polymer between the surfaces of the particles when they are in close proximity.

8.3 Theory of colloid stability

Fundamental studies have indicated that the colloid stability of NR latex can be profoundly affected by the natures and amounts of added ingredients (10-13,17,23). It was thus considered important to discuss the theory of colloid stability in some detail, and attempt to interpret the results of the effect of added ingredients upon the processing properties of NR latex on the basis of this theory.

A complete analysis of the theory of the stability of colloid particles in terms of long-range forces of repulsion and short-range forces of attraction has been given by Deryagin and Landau (5) and by Verwey and Overbeek (4). They have independently developed a quantitative theory (DLVO theory) in which the stability of colloid particles, especially in relation to added electrolyte, is treated in terms of energy changes which occur when particles approach one another. The theory involves estimations of the energy due to the overlap of electric double layers (usually repulsion, V_R) and the London-van der Waals energy (usually attraction, V_A) in terms of interparticle distance, and their summation to give the total interaction energy, V_T, in terms of interparticle distance. Thus,

$$V_T = V_R + V_A \qquad (8.3)$$

Colloid stability is then interpreted in terms of the nature of the interaction energy-distance curve (Figure 8.2).

8.3.1 London-van der Waals energy, V_A

London dispersion forces account for nearly all the van der Waals attraction which is operative, except for highly polar materials. The London attractive energy between two molecules is very short-range, varying inversely with the sixth power of the intermolecular distance, H, i.e.,

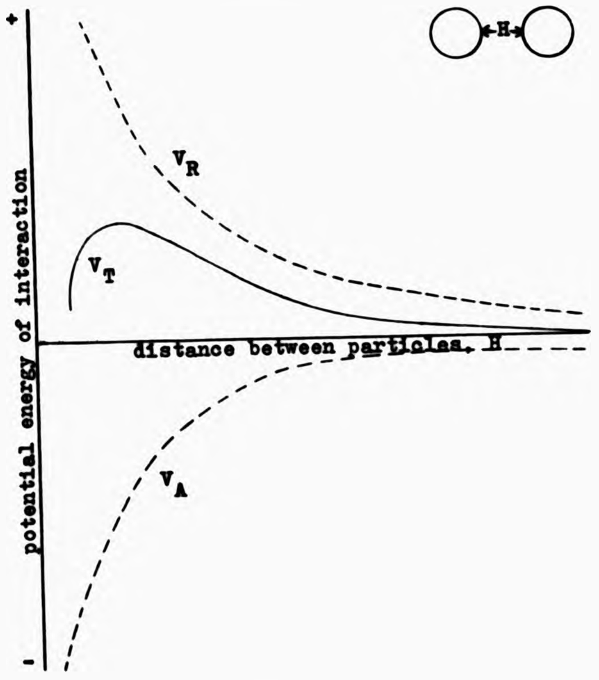


Figure 8.2 Diagrammatic representation of total interaction energy curve, V_T, obtained by summation of potentials associated with attractive forces, represented by curve V_A, and potentials associated with repulsive forces, represented by curve V_R, all potentials being shown as functions of interparticle distance, H

$$V_A \propto 1/H^6 \qquad (8.4)$$

For the case of two spherical particles of radii a_1 and a_2, separated by a shortest distance, H, Hamaker (6) has derived an expression for the London dispersion interaction energy, V_A, which in its simplest form may be written as follows:

$$V_A = \frac{-A}{12} \cdot \frac{1}{2x} \qquad (8.5)$$

where $x = H/(a_1+a_2)$ and $H << a_1$ or a_2, and A is a constant, known as the Hamaker constant. For spheres of equal radius, with $a_1 = a_2 = a$ (i.e., $x = H/2a$), equation 8.5 takes the form

$$V_A = \frac{-Aa}{12H} \qquad (8.6)$$

8.3.2 Double layer interaction energies

The calculation of the interaction energy, V_R, which results from the overlapping of the diffuse parts of the electric double layers around two spherical particles is complex. Before deriving an expression for the interaction energy, V_R, the theory of the electric double layers is discussed.

8.3.3 The electric double layer

8.3.3.1 Introduction

The electric double layer is believed to consist of two regions:

(i) a diffuse region in which ions are distributed according to the influence of electrical forces and random thermal motion (the so-called Gouy-Chapman region); and
(ii) an inner region which includes adsorbed ions (the so-called Stern region).

8.3.3.2 Gouy-Chapman model

The simplest quantitative treatment of the diffuse part of the double layer is that due to Gouy (1910) and Chapman (1913), which is based on the following model:

1. The surface is assumed to be flat, of infinite extent and uniformly charged.
2. The ions in the diffuse part of the double layer are assumed to be point charges which occupy zero volume, and are distributed according to the Boltzmann distribution.
3. The solvent is assumed to influence the double layer only through its dielectric constant, which is assumed to have the same value throughout the diffuse region.
4. A single symmetrical electrolyte of charge-number z is assumed to be present. This assumption facilitates the derivation while loosing little owing to the relative unimportance of co-ion charge number.

Let the electric potential be ψ at a flat surface and at a distance x from the surface in the electrolyte solution. Taking the surface to be positively charged (Figure 8.3) and applying the Boltzmann distribution to the distribution of ions gives

$$\underline{n_{\pm}} = n_o \exp[\mp ze\psi/kT] \qquad (8.7)$$

where $\underline{n_{\pm}}$ is the concentration of z-valent ions of either charge in the diffuse layer at points where the potential is ψ (i.e., where the electrical potential energy is $\mp ze\psi$), n_o is the corresponding bulk concentration of each ionic species, expressed as the number of ions per unit volume, k is the Boltzmann constant, and T is the absolute temperature.

For a symmetrical electrolyte, $z_- = z_+ = z$, the net volume charge density, ρ, at points where potential is ψ, is given by

$$\rho = ze(n_+ - n_-) \qquad (8.8)$$

$$= zen_o\left[\exp\left(\frac{-ze\psi}{kT}\right) - \exp\left(\frac{+ze\psi}{kT}\right)\right] \qquad (8.9)$$

$$= -2\,zen_o \sinh \frac{ze\psi}{kT} \qquad (8.10)$$

ρ is related to ψ by Poisson's equation, which for a flat double layer takes the form

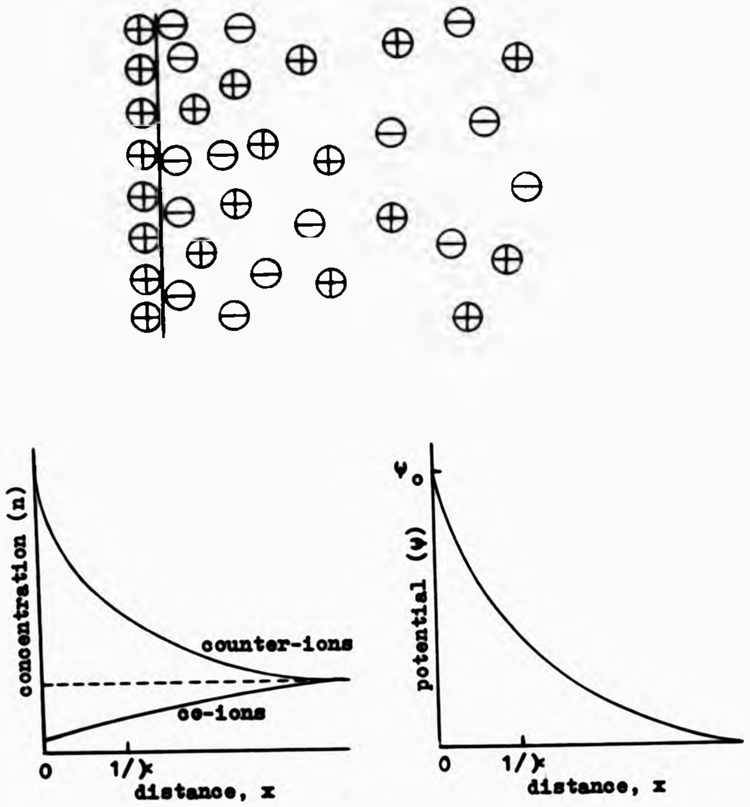


Figure 8.3 Schematic representation of a diffuse electrical double layer according to the Gouy-Chapman theory

$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\epsilon} \qquad (8.11)$$

where ϵ is the permittivity of a material. Combination of equations (8.10) and (8.11) gives

$$\frac{d^2\psi}{dx^2} = \frac{2zen_o}{\epsilon} \sinh \frac{ze\psi}{kT} \qquad (8.12)$$

When $ze\psi/kT \ll 1$, the equation (8.12) becomes

$$\frac{d^2\psi}{dx^2} = \frac{2z^2e^2n_o}{\epsilon kT} . \psi \qquad (8.13)$$

i.e.,

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi$$

where

$$\kappa = \left(\frac{2z^2e^2n_o}{\epsilon kT}\right)^{\frac{1}{2}} \qquad (8.14)$$

The solution (7) of this differential equation with the boundary conditions $\psi = \psi_o$ when $x = 0$ and $\psi = d\psi/dx = 0$ when $x = \infty$ is

$$\psi = \psi_o \exp(-\kappa x) \qquad (8.15)$$

From equation (8.15), it can be seen that, at low potentials, the potential decreases exponentially with distance from the charged surface.

When $ze\psi \ll kT$ cannot be assumed, then the solution of the differential equation (8.12), in terms of hyperbolic tangents is

$$\tanh \xi/4 = (\tanh \xi_o/4)\, e^{-\kappa x} \qquad (8.16)$$

where $\xi = ze\psi/kT$ and $\xi_o = ze\psi_o/kT$, i.e.,

$$\xi = 4 \tanh^{-1}(e^{-\kappa x}. \tanh \xi_o/4) \qquad (8.17)$$

It can be shown that (see Appendix D), equation (8.16) can also be written in the form

$$\psi = \frac{2kT}{ze} \ln \frac{1 + \gamma \exp[-\kappa x]}{1 - \gamma \exp[-\kappa x]} \qquad (8.18)$$

where

$$\gamma = \frac{\exp[ze\psi_0/2kT] - 1}{\exp[ze\psi_0/2kT] + 1} = \tanh \frac{\xi_0}{4} \qquad (8.19)$$

According to equation 8.18, the potential distribution in the diffuse double layer depends upon the surface potential ψ_0, and κ , which in turn depends upon the concentration and nature of the electrolytes present in the aqueous phase. Figure 8.4 illustrates the potential distribution in the diffuse layer for two levels of ionic concentration in the aqueous phase, namely, 10^{-2} and 10^{-3} molar of 1:1 electrolyte. The curves clearly indicate that the diffuse layer is compressed by increasing the ionic strength of the aqueous phase.

The double-layer system as a whole must be electrically neutral. Thus the surface charge on the particles must be equal to the space charge in the diffuse layer. The relationship between the surface charge density, σ_0, and the space charge density, ρ , is

$$\sigma_0 = -\int_0^\infty \rho \, dx \qquad (8.20)$$

Applying the Poisson-Boltzmann distribution, the resulting expression is

$$\sigma_0 = (8n_0 \epsilon kT)^{\frac{1}{2}} \sinh \frac{ze\psi_0}{2kT} \qquad (8.21)$$

At low potentials, this reduces to

$$\sigma_0 = \epsilon \kappa \psi_0 \qquad (8.22)$$

The surface potential ψ_0, therefore, depends upon both the surface charge density σ_0 and (through κ) the ionic composition of the medium.

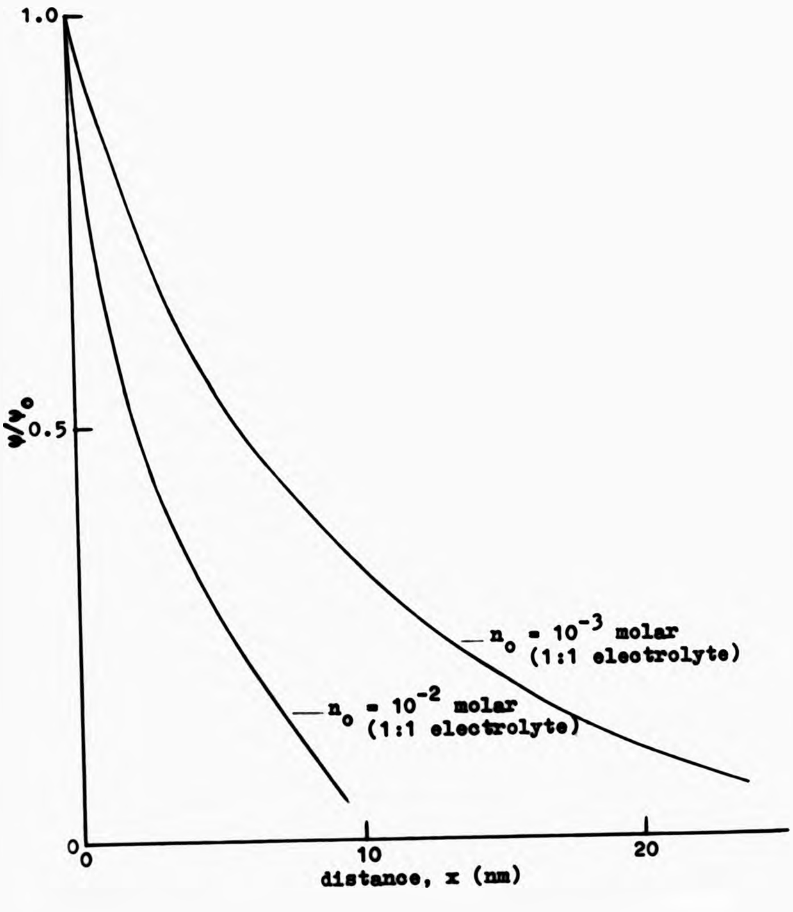


Figure 8.4 Illustrating potential distribution in the diffuse layer for two levels of ionic concentration in the aqueous phase. These curves were drawn according to equation 8.18.

8.3.3.3 Stern model

The Gouy-Chapman model is based upon the assumption of point charges in the electrolyte medium and neglects the finite size of the ions. It is generally satisfactory as a model for the electrical double layer except that an unrealistically high counter-ion concentration is often predicted near to the surface. Stern's model introduces two corrections:

(i) it allows for the finite size of the ions in the layer immediately adjacent to the surface; and
(ii) it considers the possibility of specific ion adsorption at the surface.

The potential changes from ψ_o (the surface potential) to ψ_d (the Stern potential) in the Stern layer, and decays from ψ_d to zero in the diffuse double layer, as illustrated in Figure 8.5. When specific adsorption takes place, counter-ion adsorption usually predominates over co-ion adsorption, and a typical double layer situation would be that depicted in Figure 8.5.

An electrical double layer as a whole is electrically neutral. The surface charge is equivalent to the total of the space charge in the Stern layer and the space charge in the diffuse layer. The total surface charge density, σ_o, is therefore given by

$$\sigma_o = \sigma_s + \sigma_d \qquad (8.23)$$

where σ_d is the surface charge density of the diffuse part of the double layer and is given by equation (8.21) with ψ_o replaced by ψ_d and with the sign reversed, and σ_s is the surface charge density of the Stern layer.

Stern assumed that a Langmuir-type adsorption isotherm could be used to describe the equilibrium between ions adsorbed in the Stern layer and those in the diffuse part of the double layer. Considering only the adsorption of counter-ions, the surface charge density, σ_s, of the Stern layer is given by the expression (8)

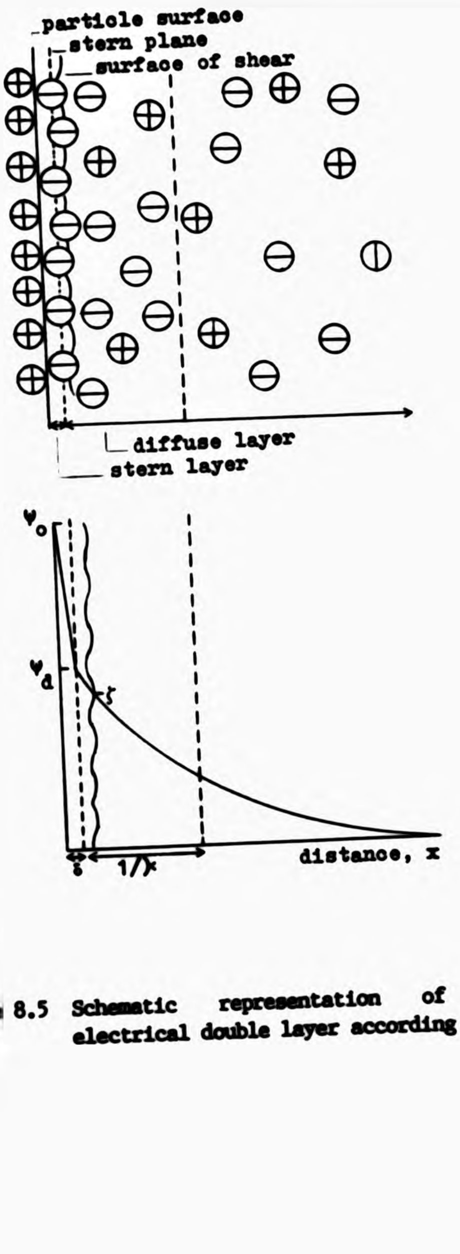


Figure 8.5 Schematic representation of structure of electrical double layer according to Stern theory

$$\sigma_s = \frac{\sigma_m}{1 + \frac{N_A}{n_o V_m} \exp\left(\frac{ze\psi_d + \phi}{kT}\right)} \qquad (8.24)$$

where σ_m is the surface charge density corresponding to a monolayer of counter-ions, V_m is the molar volume of the solvent, ϕ is the specific chemical adsorption potential of a counter-ion adsorbed to the interface.

8.3.4 Derivation of an expression for electrostatic energy, V_R

Langmuir (9) derived an expression for the repulsive force, V_L, based on the concept of osmotic pressure in the space where the diffuse layers overlap. viz

$$V_L = 2n_o kT\,(\cosh \xi_{H/2} - 1) \qquad (8.25)$$

where $\xi_{H/2} = ze\psi_{H/2}/kT$ and $\psi_{H/2}$ is the potential mid-way between the surfaces. The repulsion potential energy, V_R, is evaluated by integrating equation (8.25) with respect to distance H. Hence,

$$V_R = -2\int_{\infty}^{H} V_L dH = -2\int_{\infty}^{H} 2n_o kT\,(\cosh \xi_{H/2} - 1)\, dH \qquad (8.26)$$

By assuming small interaction, i.e., that $\xi_{H/2}$ is small and hence $(\cosh \xi_{H/2} - 1) \approx \xi^2_{H/2}$, equation (8.26) can be rewritten as,

$$V_R = -2\int_{\infty}^{H} 2n_o kT\,(0.5\, \xi^2_{H/2})\, dH \qquad (8.27)$$

The potential distribution between the two overlapping diffuse layers can be obtained by solving the Poisson-Boltzmann equation, i.e., equation (8.12), for the boundary conditions $\psi = \psi_o$ when $x = 0$ and $x = H$ and, $d\psi/dx = 0$ when $x = H/2$. The solution is rather complicated. However, if the interaction is small, i.e., $\kappa H/2 >> 1$, the potential between two plates can be approximated by the summation of the potentials of the two single diffuse layers. The potential midway between the plates $\kappa H/2$ is then given by

$$\psi_{H/2} = \frac{4kT}{ze} \ln \frac{1 + \gamma \exp[-\kappa H/2]}{1 - \gamma \exp[-\kappa H/2]} \qquad (8.28)$$

where

$$\gamma = \frac{\exp[ze\psi_o/2kT] - 1}{\exp[ze\psi_o/2kT] + 1} \qquad (8.29)$$

When $ze\psi_o/kT >> 1$ and $\kappa H/2 >> 2$, equation (8.28) can be approximated to

$$\psi_{H/2} = \frac{8kT}{ze} \gamma \exp[\kappa H/2] \qquad (8.30)$$

Substituting equation (8.30) into equation (8.27) gives

$$V_R = -2 \int_{\infty}^{H} 64 n_o kT \gamma^2 \exp(-\kappa H)\, dH \qquad (8.31)$$

Integrating equation (8.31) gives

$$V_R = 64 n_o kT \gamma^2 \exp(-\kappa H)/\kappa \qquad (8.32)$$

It appears, therefore, that the repulsion potential energy decays exponentially with H, in the case of small interactions between diffuse double layers.

8.3.5 Stability factor, W

For a stabilised colloid (i.e., when there is a repulsive energy barrier), only a proportion of Brownian collisions leads to flocculation. Stability is characterised by so-called 'stability factor', W, which is defined as

$$W = \frac{K}{K'} \qquad (8.33)$$

where K is the rate coefficient for rapid flocculation and K' is the rate coefficient for retarded flocculation.

The following theoretical expression relating the stability factor, W, to the potential energy of interaction has been derived by Fuchs (35):

$$W = 2a \int_{2a}^{\infty} \frac{\exp\,[V/kT]}{r^2}\,dr \qquad (8.34)$$

where r is the distance between the centres of the two particles. The value of W can be evaluated graphically or by numerical integration. Thus, if the potential energy curve for the interaction of two particles is known, i.e., if $V_{(r)}$ is known as a function of r, then W is the area under the curve of $(2a/r^2)\ e^{-V/kT}$ versus r. The Fuchs expression therefore, enables to predict quantitatively the effect of any given potential energy-interparticle separation curve upon colloid stability.

Since, the colloid stability of NR latex is greatly affected by the addition of various ingredients, the results for the effects of added ingredients upon the processing properties of prevulcanised NR latex are primarily interpreted, in subsequent sections, in terms of predicted effects upon colloid stability.

8.4 Results for effect of added potassium laurate upon latex properties

8.4.1 Basic properties

Table 8.1 shows the effect of added potassium laurate upon the basic properties such as TSC, DRC, KOH No., VFA No., alkalinity and pH. As can be seen, there are no distinct changes in these properties. The small decrease in TSC and DRC is due to the progressive dilution of latex with an increase in the added potassium laurate. As expected, since KOH No. is a measure of the amount of the acid anions combined with ammonia, the constancy of KOH No. indicates that no further hydrolytic degradation of lipids, proteins etc. has occurred on increasing the level of added potassium laurate. This is further confirmed by the constancy of the alkalinity results which indicates that the ammonia content in the latex is constant, irrespective of the addition of potassium laurate. Finally, the relative constancy of VFA No. indicates good preservation of latex, in that no further micro-organic activity has occurred. This is hardly surprising since high pH (pH 10) is not conducive to bacterial action.

Table 8.1 Effect of added potassium laurate upon basic properties of prevulcanised NR latex

level of added potassium laurate (moles/ 100g TSC)	TSC (%)	DRC (%)	KOH No.	VFA No.	alkalinity (g ammonia/100g aqueous phase)	pH
0	59.34	58.28	0.56	0.08	1.65	10.22
1.10×10^{-4}	59.18	57.98	0.54	0.07	1.66	10.24
2.95×10^{-4}	59.02	57.65	0.53	0.06	1.62	10.26
4.00×10^{-4}	58.96	57.59	0.55	0.08	1.64	10.24

8.4.2. Mechanical stability, MST

The effect of increasing level of potassium laurate upon the mechanical stability of prevulcanised NR latex is shown in Figure 8.6, curve I. As can be seen, there is a gradual increase in the mechanical stability with an increase in the level of added potassium laurate. The shape of the curve is in general agreement with results reported by other workers (10-13). A possible mechanism which may account for this observation is that the total amount of soap anions adsorbed on the latex particles is increased, thereby increasing the Stern potential and hence the repulsive potential energy. The influence of Stern potential, ψ_d, on the total potential energy of interaction of two identical spherical particles has been demonstrated very well by Tan (13). He showed that small amounts of additional adsorbed anions lead to a large increase in the maximum potential energy.

It is also thought the fatty-acid soap anions may make the indigenous soap more effective stabilisers. Blackley *et al.* (11,14) have postulated that the indigenous soap is aggregated into clusters on the particle surface. The addition of soap which has a different hydrophobe to that of the indigenous soap causes the clusters to be disrupted, and this leads to the increased effectiveness of the indigenous soaps. It is suggested that the laurate is less akin to the indigenous soaps than is, for example, stearate, and therefore has a greater effect in enhancing the mechanical stability.

However, according to the published work (10-13), a large enhancement of the mechanical stability of NR latex can be brought about by small additions of fatty-acid soap. In contrast, the present work shows only a small increment in the mechanical stability of prevulcanised NR latex, on adding small amounts of fatty-acid soaps (Figure 8.6, curve I). The observed difference is thought to be largely a reflection of the difference in the nature of the latex used. The latex used in the present study was NR latex compounded with zinc oxide and other vulcanising ingredients and then prevulcanised. Thus, it is possible that the zinc oxide present in the latex may have been responsible for the reduction in the mechanical stability due to the formation of zinc ammine complexes which reacted with the soaps adsorbed onto the surface of the particles. Hence, it was decided to determine the mechanical

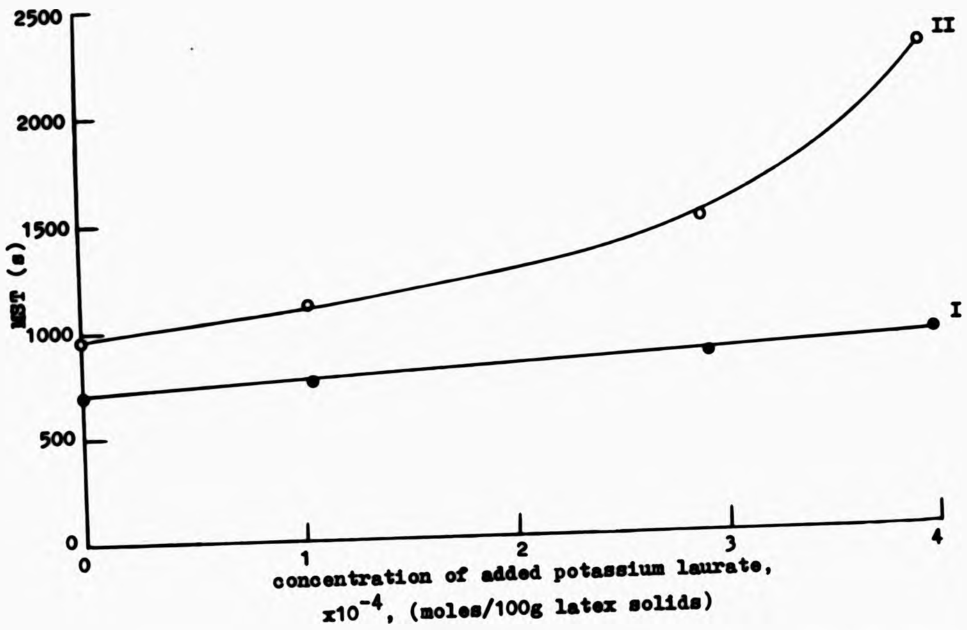


Figure 8.6 Effect of added potassium laurate upon unvulcanised NR latex (II) and upon prevulcanised latex containing zinc oxide (I)

stability of NR latex in the absence of zinc oxide, by adding small quantities of the fatty-acids soaps to the unvulcanised NR latex (Figure 8.6, curve II).

As can be seen from Figure 8.6, curve II, a large enhancement in the mechanical stability was observed when small additions of the fatty-acid soaps were made. The results thus confirm that the zinc oxide causes the destabilisation of latex (Section 8.4.4). However, the rate of destabilisation decreases with increasing concentration of stabilising soap. The results agree satisfactorily with those of Neiman et al. (15,16) and Nithi-Uthai (17).

If the maximum number of added fatty-acid soap anions ($4x10^{-4}$ mole per 100g latex solids) are wholly adsorbed, reasonable calculations show that the total number of soap anions adsorbed onto the latex particles is increased by about 14%. (The concentration of the indigenous higher fatty-acid anions is equivalent to approximately a third of the difference between the KOH and VFA numbers (18)). However, this addition enhanced the mechanical stability by factor of about 3.2 and 1.3 for NR latex and prevulcanised latex respectively. It is thus confirmed that the presence of zinc oxide has a profound effect in reducing the mechanical stability. This agrees well with the reported literature (e.g., 17, 19 and 20) concerning the reduction of stability on addition of zinc oxide to the latex.

8.4.3 Calcium stability time, CST

The CST, which is a measure of the stability of latex towards calcium ions, was found to increase with an increase in the level of added potassium laurate (Figure 8.7). It is thought that the introduction of calcium ions (as calcium sulphate) to the latex may either cause a compression of the electric double layer and/or react directly with the stabilising higher fatty-acid anions, thereby forming an insoluble unionised metal soap, according to the reaction:

$$Ca^{++} + 2RCOO^{-} \longrightarrow \underset{\text{(precipitates out)}}{(RCOO)_2Ca \downarrow}$$

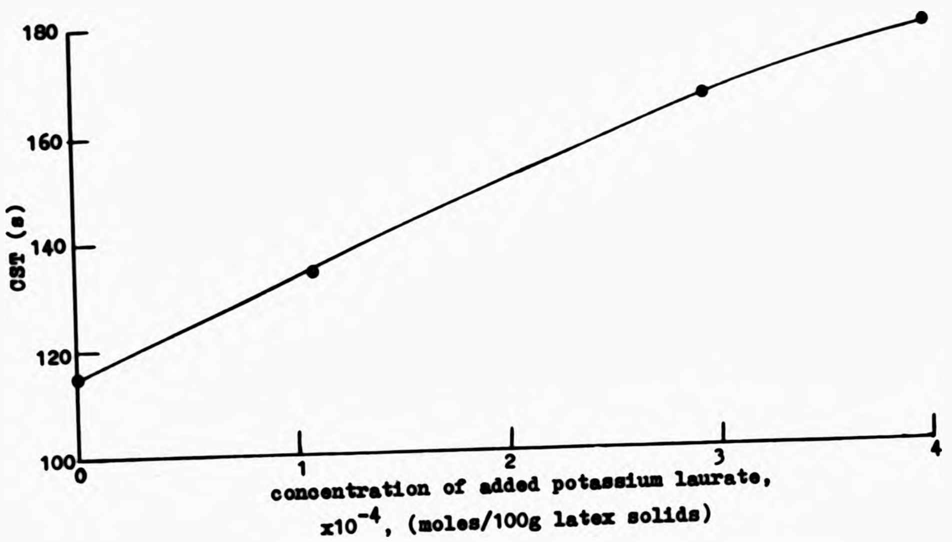


Figure 8.7 Effect of added potassium laurate upon calcium stability time, CST, of prevulcanised latex

Thus the stability of latex reduces. However, when the level of potassium laurate is increased, there is an increase in the surface charge of the particles and hence an increase of the Stern potential. The increase of the Stern potential causes an increase in the maximum potential energy (Figure 8.9), thereby increasing the stability of latex towards destabilisative influences such as added metal salts, e.g., calcium sulphate.

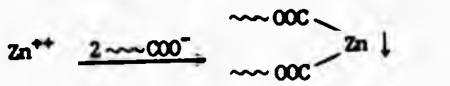
If the amount of added soap is compared with the estimated amount of surface-active fatty-acid anions initially present in the latex, it is found that the added soap is very much less than that initially present. The amount of soap at the highest level of addition (4.00×10^{-4} moles per 100g latex solids) represents only about 11% of the initial amount of surface-active fatty-acid anions (3.75×10^{-3} moles per 100g latex solids). It seems obvious, therefore, that the added potassium laurate is stabilising the latex by making more fatty-acid anions available. However, it is rather surprising that there is a nearly 60% increase in CST for the addition of 4×10^{-4} mole potassium laurate per 100g latex solids, because the amount of added calcium sulphate is approximately 3×10^{3} times greater than the amount of added potassium laurate.

8.4.4. Zinc ammonium acetate viscosity, ZAAV

In general, an increase in viscosity is found on addition of zinc ammonium acetate to the latex (Table 8.2). This is consistent with the reaction mechanism:

$$ZnO + 2NH_4^+OH^- + 2NH_4^+Ac^- \longrightarrow [Zn(NH_3)_4]^{++} + 2Ac^- + 3H_2O$$

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



$$Zn^{++} \xrightarrow{2\sim\sim\sim COO^-} (\sim\sim\sim OOC)_2Zn\downarrow$$

(precipitates out)

The results in Table 8.2, indicate that the rate of destabilisation of latex decreases on increasing the level of added potassium laurate. This may be due to an increase of the Stern potential which arises from an increased concentration of adsorbed soap molecules at the surface of the particle. An increase of the Stern potential accompanying increased soap

Table 8.2 Effect of added potassium laurate upon viscosity, zinc ammonium acetate viscosity, ZAAV, and ZAAV:viscosity ratio of prevulcanised NR latex. The effect upon microgel formation is also shown.

level of added potassium laurate (moles/ 100g TSC)	viscosity (cP)	ZAAV (cP)	ZAAV:viscosity ratio	microgel content
0	47.8	60.4	1.3	s, d
1.10x10^{-4}	47.4	58.9	1.2	s, d
2.95x10^{-4}	46.1	55.4	1.2	s, d
4.00x10^{-4}	45.5	53.1	1.2	s, d

abbreviations used in table: s = singlets and d = doublets

coverage has been found by Green and Saunders (21). The results therefore confirm the previous findings (10-14,17) that the colloid stability of latex increases with an increase in the level of added soap.

8.5 Effect of added ammonia upon latex properties

8.5.1 Basic properties

The effect of added ammonia upon the basic properties of prevulcanised NR latex is shown in Table 8.3. It is observed that all the basic properties remain relatively constant, except the alkalinity. As expected, the increase in alkalinity is equivalent to the amount of added ammonia.

8.5.2 pH and mechanical stability, MST

As expected, the pH of the latex was also increased by increasing the level of added ammonia. The results for mechanical stability are shown in Table 8.3 and Figure 8.8. It is seen that the mechanical stability of prevulcanised NR latex decreased progressively with an increase in the level of added ammonia. However, according to the published literature

Table 8.3 Effect of added ammonia upon basic properties of prevulcanised NR latex

level of added ammonia (g/100g latex)	TSC (%)	DRC (%)	KOH No.	VFA No.	alkalinity (g ammonia/100g aqueous phase)	expected alkalinity (g ammonia/100g aqueous phase)	pH	MST (s)
0	59.34	58.28	0.56	0.08	1.65	1.65	10.22	701
0.3	59.02	58.32	0.58	0.08	2.36	2.39	10.38	608
0.5	60.36	58.42	0.58	0.07	2.90	2.87	10.48	425
0.7	59.17	57.92	0.60	0.07	3.41	3.36	10.52	305

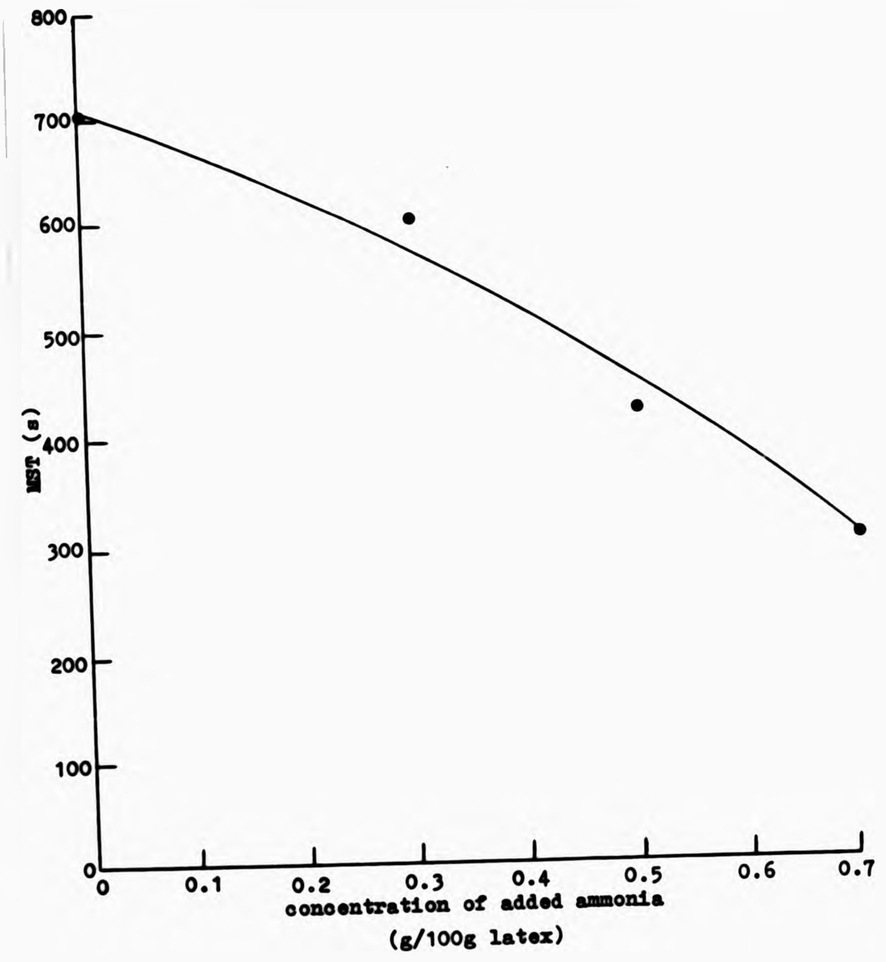


Figure 8.8 Effect of added ammonia upon mechanical stability of prevulcanised NR latex

(13,23,24), the mechanical stability of NR latex increases progressively on increasing the concentration of added ammonia. This difference is thought to be largely a reflection of the differences between unvulcanised and prevulcanised NR latex.

The possible mechanisms which may account for the reduction in the mechanical stability of NR latex compounded with zinc oxide, and other vulcanising ingredients, with an increase in the level of added ammonia are as follows:

(i) effect of increased ionic strength;
(ii) increase in concentration of zinc ammine complexes; and
(iii) reduction of maximum inter-particle potential energy.

These mechanisms are discussed in some detail in the subsequent sections.

8.5.2.1 Effect of ionic strength

The ionic strength, I, of an electrolyte solution is given by the expression

$$I = \tfrac{1}{2}\sum c_i z_i^2 \qquad (8.35)$$

where c_i is the concentration in moles per litre, for a given ionic species i, and z_i is the valency of that ionic species. The electric double layer thickness, which is the inverse of the Gouy-Chapman parameter, κ , (4) is related to the ionic strength as follows:

$$\frac{1}{\kappa} = \left(\frac{\epsilon kT}{2e^2 I}\right)^{\frac{1}{2}} \qquad (8.36)$$

From equation 8.36, it is seen that the electric double layer thickness, $1/\kappa$, is inversely proportional to the square root of the ionic strength. The greater is the thickness of the electrical double layer, the greater will be the repulsive energy, provided that interactions of any other type are absent. Because the attractive potential energy is independent of the ionic strength of the dispersion medium, the interaction potential energy maximum would be expected to decrease with increasing ionic strength, thereby conferring lower colloid stability. The influence of electrolyte concentration on the total potential energy of interaction is shown in Figure 8.13.

However, the effect of ionic strength alone is insufficient to explain the rapid reduction in the mechanical stability when ammonia is added to the latex. Added ammonia will be expected to have little effect upon ionic strength, however much is added, because most of it is present as unionised NH_3, not as $NH_4^+ + OH^-$. The equilibrium constant for the reaction

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

(ammonia is a
a weak base)

is 5.5×10^{-10} mole l^{-1} at 298.15K (36). This suggests that the increase of ionic strength is most unlikely to be the cause of the reduction in MST.

8.5.2.2 Formation of additional zinc ammine complexes

Because zinc oxide was added to the latex as an ingredient of the vulcanisation system, a source of zinc ions was present in the latex. On adding ammonia, further reaction may have taken place between zinc ions and ammonia as follows:

$$\begin{tikzcd}
 & ZnO \arrow[r, rightleftharpoons, "H_2O"] & Zn(OH)_2 \arrow[r, rightleftharpoons] & Zn^{++} + 2OH^- \arrow[d, rightleftharpoons, "NH_3"] \\
(RCO_2)_2Zn & Zn^{++} + nNH_3 \arrow[l, "2RCO_2^-"'] \arrow[rr, rightleftharpoons] & & Zn(NH_3)_n^{++}
\end{tikzcd}$$

$1 \leqslant n \leqslant 4$

insoluble zinc soap
or proteinate precipitated
in the surface of the
particles, with consequent
destabilisation

Thus, the formation of soaps may have resulted in the destabilisation of latex. The results will be discussed further in Section 8.5.4. Also, the ionic strength of the aqueous phase will be increased by the generation of the OH^- and $Zn(NH_3)_n^{++}$ ions, especially the latter for which z is 2. This may well be the main reason for the reduction in MST.

8.5.2.3 Reduction of potential energy maximum

If the negative charge arises from adsorbed fatty-acid anions, then reduction in pH will reduce the charge, and hence the Stern potential. On the basis of the DLVO theory (Section 8.3), an attempt was made to calculate the total potential energy of interaction in terms of distance of separation of two identical spherical particles of latex, at various values of Stern potential, ψ_d. The curves of the type shown in Figure 8.9 were obtained. This author has calculated the total potential energy in terms of interparticle distance, H, using equations 8.5, 8.14 and 8.32. The calculations are based on the following model:

(1) The stability of the latex particles is assumed to be attributable entirely to the presence of adsorbed higher fatty-acid anions at the particle surface, thus ignoring contributions from steric stabilisers. However, these contributions could be important if proteins and protein residues are present, as in NR latex.

(2) The Hamaker constant, A, and the particle radius, a, are assumed to be 1×10^{-20}J and 1×10^{-7}m respectively.

(3) The Stern potential, ψ_d, of the particles is assumed to be 100mV, at full ionisation of the higher fatty acids.

(4) The Stern potential is proportional to the degree of ionisation of the higher fatty acids; thus the Stern potentials at pH 8.50, 9.04, 9.35 and 9.50 are 15, 50, 75 and 100mV respectively (37).

(5) The ionic strength of the latex is equivalent to 10^{-1} moles 1:1 electrolyte.

As can be seen from Figure 8.9, reduction in pH, and hence in Stern potential, reduces the potential energy maximum, thus predicting that the reduction in pH increases the destabilisation of the latex. This is in accordance with the findings of other workers (13,23).

However, in the present investigation, it has been found that the mechanical stability is lowered with an increase in the pH of the latex. In any case, the increase of pH was small, and was in a region where it would not be expected to have much effect upon the extent of ionisation of the fatty-acid soaps.

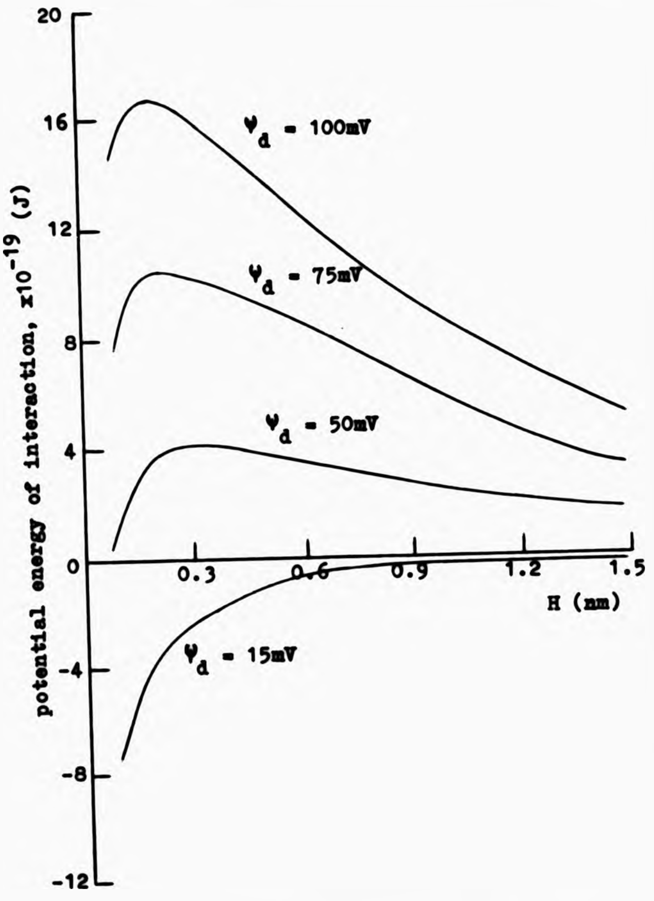


Figure 8.9 Influence of Stern potential, Ψ_d, upon total potential energy of interaction between two identical spherical particles as predicted by DLVO theory: $a = 10^{-7}$m; $T = 298$K; $z = 1$; $A = 1\times10^{-20}$J; $\epsilon_o = 8.85\times10^{-12}C^2N^{-1}m^{-2}$ $(\epsilon/\epsilon_o = 78.5)$; $e = 1.6\times10^{-19}$C; $\kappa = 10^9m^{-1}$. V_A and V_R calculated using equations 8.5, 8.14 and 8.32.

Thus, it is envisaged that the reduction in the mechanical stability with an increase in the level of added ammonia is principally a consequence of the formation of zinc ammine complexes, although increase of ionic strength may play some role in the destabilisation of latex. The main contribution to increase of ionic strength probably comes from the zinc ammine complexes. The discrepancy between the results obtained here and those reported elsewhere (13,23,24) is probably largely attributable to the presence of zinc oxide in the latex used in this work.

8.5.3 Calcium stability time, CST

On increasing concentrations of added ammonia, the stability of prevulcanised latex containing zinc oxide, towards calcium ions decreases (Figure 8.10). Although calcium ions cause a catastrophic effect in the destabilisation of the latex, the further reduction in the destabilisation is brought about by increasing the level of added ammonia. The increased level of ammonia in the latex containing zinc oxide presumably led to the formation of additional zinc ammine complexes, and hence the removal of adsorbed higher fatty-acid anions on the surface of the particles. Thus, the effects of the zinc complex ions and the calcium ions are probably additive in causing destabilisation of the latex.

Indirect evidence for the removal of adsorbed higher fatty-acid anions has been obtained from viscosity measurements. Table 8.4 shows that increasing levels of added ammonia led to the slight increase in the viscosity of latex. It is speculated that the slight increase in viscosity is probably a consequence of increased hydration of the particles with a subsequent decrease of the aqueous phase. The decrease in the aqueous phase, which is acting as the dispersion medium, causes an increase in the effective volume fraction of latex particles and hence viscosity. This view of increase in the degree of hydration, and hence in the effective size of the latex particles has been supported by the microgel studies. From the microgel results in Table 8.4, it is seen that the macroparticles' formation increases with an increased level of added ammonia.

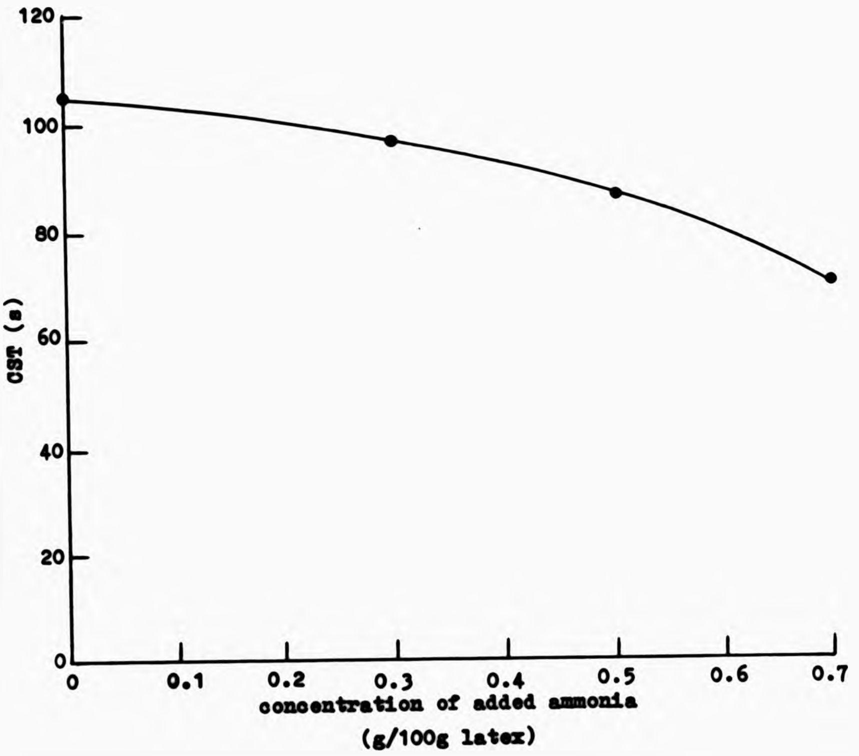


Figure 8.10 Effect of added ammonia upon calcium stability time, CST, of prevulcanised NR latex

Table 8.4 Effect of added ammonia upon viscosity and ZAAV of prevulcanised NR latex. The effect upon microgel formation is also shown.

level of added ammonia (g/100g latex)	viscosity (cP)	ZAAV (cP)	microgel content
0	47.8	60.4	s, d
0.3	48.2	69.3	s, m
0.5	49.5	75.2	m (mostly)
0.7	50.4	80.2	m (mostly)

abbreviations used in table: s = singlets, d = doublets and m = macroparticles

8.5.4 Zinc ammonium acetate viscosity, ZAAV

The results for the effect of added ammonia upon zinc ammonium viscosity are shown in Table 8.4 and Figure 8.11. It is observed that the ZAAV increases on adding the increased concentrations of ammonia. The effect of ammonia concentration on the destabilisation of NR latex has been studied by a number of workers (17,25,26). It is postulated that, for a given system of constant concentration of ammonium salt and of zinc oxide but variable concentration of ammonia, the following equilibria are established:

$$ZnO + H_2O \rightleftharpoons Zn(OH)_2$$

$$Zn(OH)_2 + 6H_2O \rightleftharpoons [Zn(H_2O)_6]^{++} + 2OH^-$$

$$[Zn(H_2O)_6]^{++} + xNH_3 \rightleftharpoons [Zn(H_2O)_{6-x}(NH_3)_x]^{++} + xH_2O$$

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

It is obvious from above equilibria that, on increasing the level of added ammonia, the production of zinc ammine complexes, $[Zn(H_2O)_{6-x}(NH_3)_x]^{++}$, and hence also the formation of the hydroxyl ions $(OH)^-$, is encouraged. In order to maintain the equilibria, therefore, the increased concentration of hydroxyl ions reduces the ammonium ion, (NH_4^+), concentration.

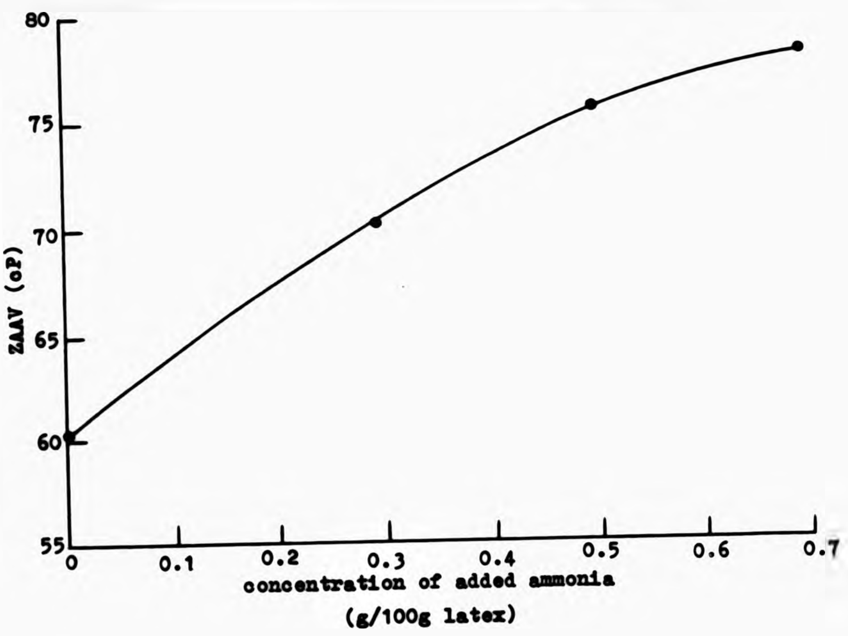


Figure 8.11 Effect of added ammonia upon zinc ammonium acetate viscosity, ZAAV, of prevulcanised NR latex

Thus, the destabilisation of latex on increasing the level of added ammonia is thought to be a consequence of the balance of two opposing effects:

(i) A coagulating effect: The increased levels of added ammonia increase the concentration of the zinc ammine complexes which brings about a decrease in the Stern potential of latex particles (17). The decrease in the Stern potential reduces the stability of the latex, (Figure 8.9).

(ii) A stabilising effect: The increased concentration of zinc ammine complexes discourages the formation of ammonium ions. Thus, the reduction of ammonium ions reduces the effect of compression of the electrical double layer which surrounds the latex particles, thereby conferring higher stability to the latex.

From Figure 8.11, it is observed that the ZAAV increases with an increase in the concentration of ammonia. The reason for this is that, as expected, the mechanism (i) is probably more pronounced compared with the mechanism (ii). Hence the resultant effect is a reduction of the stability of latex on increasing the concentration of added ammonia. The observed results agree in a generally satisfactory way with those reported by other workers (17,25,26).

8.6 Effect of added potassium hydroxide upon latex properties

8.6.1 Basic properties

The effect of added potassium hydroxide upon the basic properties like TSC, DRC, KOH No., VFA No. and alkalinity of prevulcanised NR latex is shown in Table 8.5. As expected, the TSC, DRC and VFA No. are relatively constant on the addition of potassium hydroxide. However, again as expected, on increasing the level of added potassium hydroxide, there is an increase in the alkalinity and a decrease in the KOH No. The proportional increase in the alkalinity and decrease in the KOH No. is almost in accordance with the expected values (Table 8.5). The small variations probably arise from experimental errors in determining these quantities.

Table 8.5 **Effect of added potassium hydroxide upon basic properties of prevulcanised NR latex**

level of added potassium hydroxide (g/100g TSC)	TSC (%)	DRC (%)	KOH No.	expected KOH No.	VFA No.	alkalinity (g ammonia/100g aqueous phase)	expected alkalinity (g ammonia/100g aqueous phase)
0	59.34	58.28	0.56	0.56	0.08	1.65	1.65
0.3	59.01	57.65	0.23	0.26	0.08	2.78	3.02
0.5	59.33	57.90	0.07	0.06	0.07	3.81	3.93
0.7	59.31	57.56	-	-0.14*	0.08	4.68	4.84

* negative value indicates the presence of excess potassium hydroxide.

8.6.2 pH. ionic strength and mechanical stability, MST

The pH of the latex was increased by the addition of increasing amounts of potassium hydroxide (Table 8.6). The results for mechanical stability are presented in Table 8.6 and Figure 8.12. From Figure 8.12, it can be seen that on increasing the level of added potassium hydroxide, the mechanical stability of prevulcanised NR latex increased at first until it reached a maximum, then it decreased. The manner in which the mechanical stability varies with added potassium hydroxide is in agreement with the previous workers (22-23).

The initial increase is presumably a consequence of the conversion of any residual free fatty acid and ammonium salts of fatty acids to the corresponding potassium soaps. The latter are probably more effective stabilisers for NR latex than are ammonium salts. In addition, there may be protein residues adsorbed at the particle interfaces which ionise further when the pH is raised by potassium hydroxide. The decrease in the mechanical stability on further addition of potassium hydroxide may be due to the potassium hydroxide now acting as a strong electrolyte. The latter increases the ionic strength of the aqueous phase (Table 8.6) with a consequent reduction in the MST (Section 8.5.2.1).

Possible quantitative explanations for these observations can be offered on the basis of the DLVO theory (Section 8.3). Figure 8.13 shows the calculated potential energy-separation curves for interaction between two identical spherical latex particles, in relation to added electrolyte. Again, this author has calculated the total interaction potential energy in terms of interparticle distance, H, using equations 8.5, 8.14 and 8.32. As before, the calculations are performed by making the following assumptions:

1. The latex particles are stabilised by adsorbed higher fatty-acid anions only.
2. The Hamaker constant, A, is $1\text{x}10^{-20}$J.
3. The particle radius, a, is $1\text{x}10^{-7}$m.
4. A single symmetrical electrolyte of charge number, z, is assumed.
5. The ionic strength derived entirely from the potassium hydroxide is assumed.

6. The Stern potential, ψ_d, of the particles is assumed to be 100mV, at full ionisation of the higher fatty acids.

Table 8.6 Effect of pH upon ionic strength, I, and mechanical stability, MST, of prevulcanised NR latex. The effect upon microgel formation is also shown.

level of added potassium hydroxide (g/100g TSC)	pH	ionic strength of aqueous phase (moles litre^{-1})	MST (s)	microgel content
0	10.22	0.019	701	s, d
0.3	10.40	0.102	855	s, d
0.5	10.48	0.153	410	m (mostly)
0.7	10.63	0.210	100	m (mostly)

abbreviations used in table: s = singlets, d = doublets and
m = macroparticles

The potential energy-separation curves shown in Figure 8.13 confirm a substantial reduction of the potential energy barrier with increasing concentration of an added electrolyte. However, this reduction is not sudden and sharp (Figure 8.14), as might be suggested by the mechanical stability results (Figure 8.12). In fact, the maximum potential energy value corresponding to the maximum amount of potassium hydroxide added, suggests that the latex should still be very stable at room temperature. This may partly be true, but according to the mechanical stability results, the latex at the maximum concentration of added electrolyte has low colloid stability, and may be in a critical condition of incipient gelation. It may be that the effect of added potassium hydroxide upon steric and hydration stabilisation is overlooked.

The sudden reduction in the mechanical stability is further confirmed by the microgel studies (Table 8.6). It is observed from Table 8.6 that, as the mechanical stability decreases, so the aggregation size of particles or microgel formation increases, for a given concentration of added potassium hydroxide. Furthermore, Loha (23) tested the hypothesis that increased ionic strength explains the reduction in the

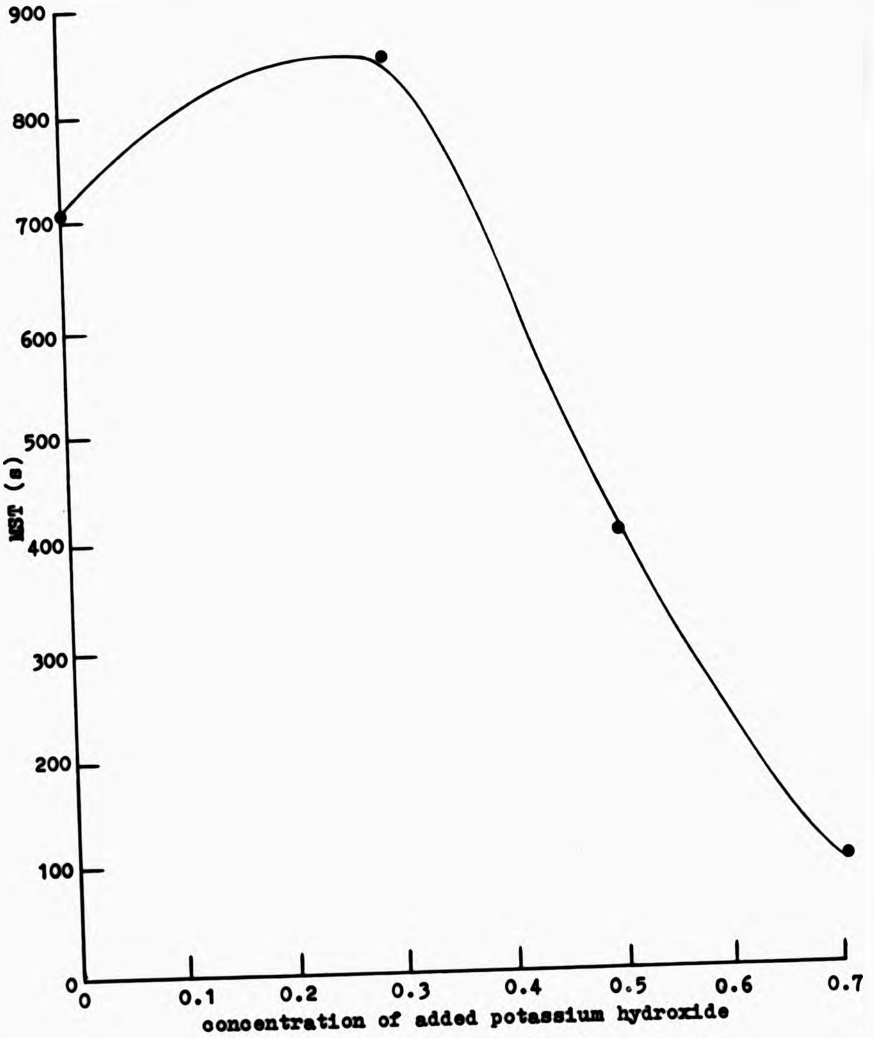


Figure 8.12 Effect of added potassium hydroxide upon mechanical stability of prevulcanised NR latex

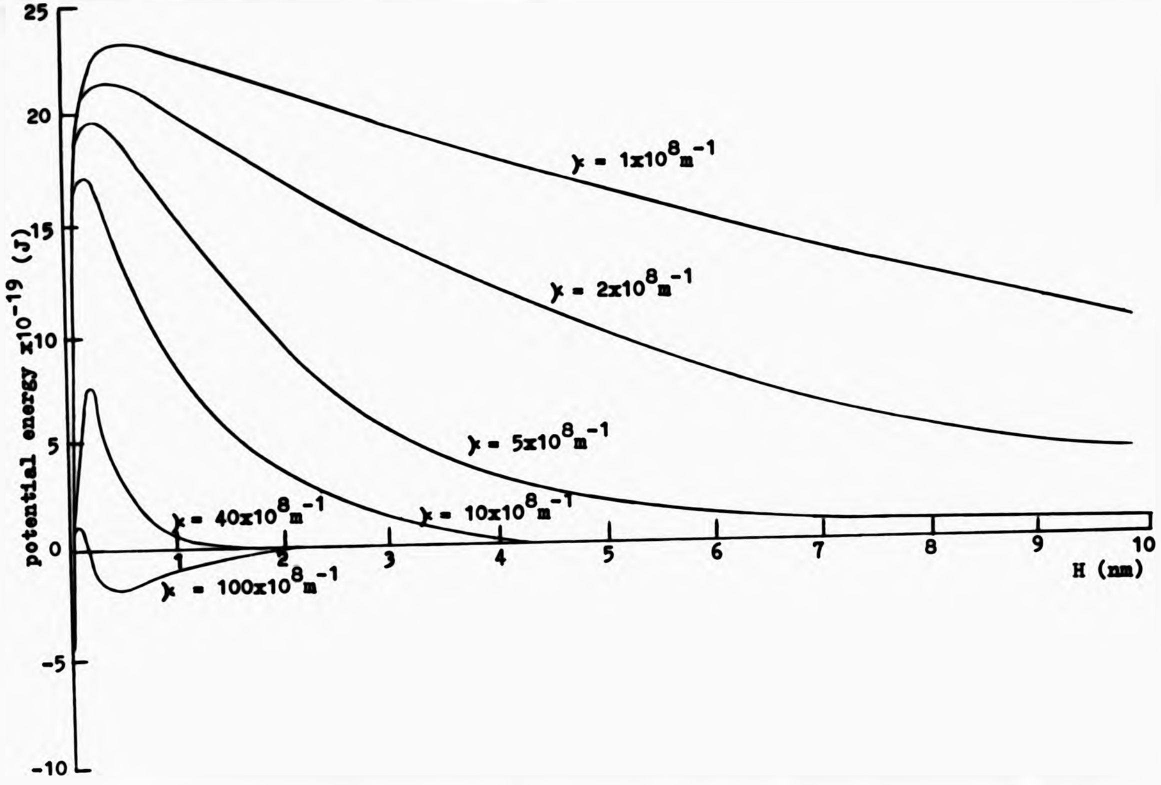


Figure 8.13 Influence of electrolyte concentration, κ, upon total potential energy of interaction between two identical spherical particles as predicted by DLVO theory: $a = 10^{-7}$m; $T = 298$K; $z = 1$; $A = 1x10^{-20}$J; $\epsilon_o = 8.85x10^{-12}C^2N^{-1}m^{-2}$, $(\epsilon/\epsilon_o = 78.5)$; $e = 1.6x10^{-19}$C; $\psi_d = 100$mV. V_A and V_R calculated using equations 8.5, 8.14 and 8.32.

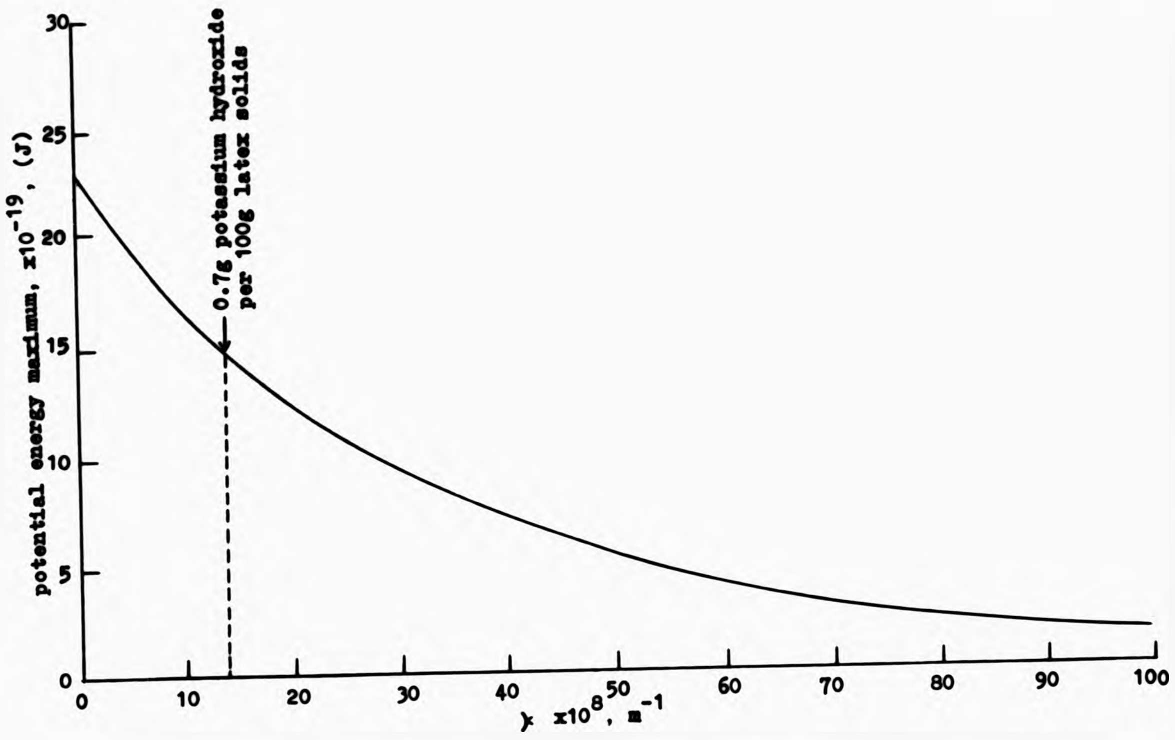


Figure 8.14 Plot of potential energy maximum versus electolyte concentration, κ

stability of latex when excess potassium hydroxide is added by comparing the results for the effect of added potassium hydroxide upon mechanical stability with the effects of added potassium chloride. He found that on increasing the ionic strength by 0.1mole l^{-1}, the mechanical stability reduced by a factor of about 13 for potassium hydroxide and about 2 for potassium chloride. This confirms that the ionic strength alone cannot be responsible for the rapid decrease in the mechanical stability. The results obtained here are comparable with those of Loha. It is found that the mechanical stability reduced by a factor of 14 on increasing the ionic strength by 0.1mole l^{-1}.

It is thus possible that at high pH, excessive potassium hydroxide interferes with the ability of electric charges to promote hydration of the particles, and therefore cause a sudden decrease in the mechanical stability. Indirect evidence for this possibility has been obtained from the viscosity measurements. Table 8.7 shows that increasing levels of added potassium hydroxide lead to a sudden reduction in the latex viscosity. It is thought that the reduction in viscosity is a consequence of loss of hydration layer around the particles with a subsequent increase of the aqueous phase. The increase in the aqueous phase, which is acting as the dispersion medium, results in reduction of the effective volume fraction of latex particles and hence viscosity. Additionally, the collapse of adsorbed steric stabilisers might also contribute to the effects upon both MST and viscosity.

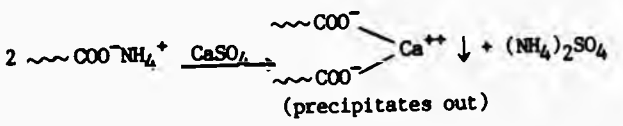
Table 8.7 Effect of added potassium hydroxide upon viscosity, ZAAV and CST of prevulcanised NR latex

level of added potassium hydroxide (g/100g TSC)	viscosity (cP)	ZAAV (cP)	CST (s)
0	47.8	60.4	115
0.3	44.5	48.4	110
0.5	26.1	27.8	109
0.7	25.2	26.0	113

8.6.3 Calcium stability, CST

The stability of prevulcanised NR latex towards calcium ions appears to be approximately constant on increasing the level of added potassium hydroxide, as shown in Table 8.7. The most plausible reason for this phenomenon becomes evident by considering the overall rate of coagulation. It is proposed that the addition of calcium sulphate most probably has a catastrophic effect in causing the coagulation of the latex such that the effect of added potassium hydroxide upon the overall coagulation rate remains insignificant. Thus, the main mechanism governing the coagulation rate in the presence of calcium sulphate is as follows:

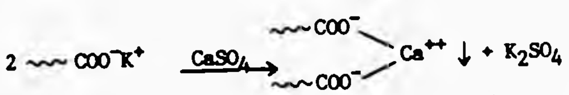
(a) in the absence of potassium hydroxide



$$2 \sim COO^-NH_4^+ \xrightarrow{CaSO_4} \begin{matrix} \sim COO^- \\ \sim COO^- \end{matrix} \Big\rangle Ca^{++} \downarrow + (NH_4)_2SO_4$$

(precipitates out)

(b) in the presence of potassium hydroxide



$$2 \sim COO^-K^+ \xrightarrow{CaSO_4} \begin{matrix} \sim COO^- \\ \sim COO^- \end{matrix} \Big\rangle Ca^{++} \downarrow + K_2SO_4$$

(precipitates out)

It appears therefore, that the CST is not a suitable test to measure the considerable changes in the colloid stability of NR latex, which may occur when potassium hydroxide is added.

8.6.4 Zinc ammonium acetate viscosity, ZAAV

The results for the effect of added potassium hydroxide upon ZAAV are presented in Table 8.7. As can be seen, there is a reduction in ZAAV on increasing the level of added potassium hydroxide.

It is generally accepted that the addition of potassium hydroxide to ammonia-preserved NR latex reduces the destabilising effect of zinc ions (whether added as zinc oxide or as zinc salts), and this is precisely what has been observed. In cases where zinc oxide is present, the explanation usually given is that the equilibrium

$$Zn(OH)_2\ (s) \rightleftharpoons Zn^{++} + 2OH^-$$

is shifted to the left by the added OH^- ions, thereby reducing the Zn^{++} concentration. In cases where water-soluble zinc salts are present, zinc ions are thought to be removed by precipitation as zinc hydroxide. Thus, the explanations for reduction in the ZAAV on increasing the concentration of added potassium hydroxide (Table 8.7) may be offered as follows:

(a) $Zn(NH_3)_4^{++}$ ions were ionised by the reaction

$$Zn(NH_3)_4^{++} + 2OH^- \rightleftharpoons Zn(OH)_2 \downarrow + 4NH_3$$

(b) the added potassium hydroxide tended to enhance the chemical stability of the latex.

If the amount of potassium hydroxide added is compared with the amount of zinc added in the ZAAV test, it is found that the amount of zinc oxide added is about 6 times greater than the amount of potassium hydroxide added at the lowest level of addition, and about 2 times greater than the amount of potassium hydroxide added at the highest level of addition. This supports mechanisms (a) and (b) in explaining the results presented in Table 8.7, i.e.,

(i) why there is an increase in the viscosity for the latex containing zinc ammonium acetate and zinc oxide (i.e., ZAAV results) compared with the viscosity for the latex containing zinc oxide only (i.e., viscosity results), for a given concentration of added potassium hydroxide; and

(ii) why there is a reduction in ZAAV on increasing the level of added potassium hydroxide.

8.7 Effect of added ammonium acetate upon latex properties

8.7.1 Basic properties

As expected, addition of ammonium acetate had a negligible effect upon the TSC, DRC and alkalinity of prevulcanised NR latex. The results are presented in Table 8.8. However, an increase in the VFA and KOH numbers was observed (Table 8.8). The observed increase in VFA No. and in KOH No. on increasing the level of added ammonium acetate is, more or less, in agreement with the expected increase, as shown in Table 8.8. Furthermore, the difference in KOH and VFA numbers is approximately constant, and this is consistent with the HFA content being unaffected by the addition of ammonium acetate (Table 8.9).

8.7.2 Mechanical and chemical stability of latex

Figure 8.15 shows the effect of added ammonium acetate upon the mechanical stability of the latex. As can be seen, there is a rapid decrease in the mechanical stability on increasing the level of added ammonium acetate. There are two possible mechanisms which may account for this:

(1) The addition of ammonium acetate has a direct effect in increasing the ionic strength of the aqueous phase of the latex (Table 8.10), and hence reduces the thickness of the electrical double layer surrounding the particles, thus causing a reduction in the stability of the latex.

(2) Since the latex contains zinc oxide, the addition of ammonium acetate suppresses the concentration of hydroxyl ions. According to the principle of the solubility product, suppression of the hydroxyl ions enhances the initial concentration of zinc ions and thus leads to the formation of a higher concentration of zinc ammine complexes.

This effect is also observed in Figure 8.16, which shows the enhancement of the zinc ammonium acetate viscosity on adding increased concentrations of ammonium acetate. It appears, therefore, that destabilisation of latex by the addition of ammonium acetate is due to the operation of both these mechanisms. It is also possible that there may be specific effect of the acetate anions, which have been found to be more destabilising in latices containing zinc oxide than are many other anions (17).

Additionally, indirect evidence for the destabilisation of latex has been obtained from both the microgel studies and the

Table 8.8 Effect of added ammonium acetate upon basic properties of prevulcanised NR latex

level of added ammonium acetate (g/100g latex)	TSC (%)	DRC (%)	KOH No.	expected KOH No.	VFA No.	expected VFA No.	alkalinity (g ammonia/ 100g aqueous phase)
0	59.34	58.28	0.56	0.56	0.08	0.08	1.65
0.1	58.61	56.97	0.66	0.65	0.10	0.12	1.57
0.2	58.10	56.67	0.72	0.74	0.23	0.24	1.59
0.3	57.20	55.98	0.75	0.82	0.34	0.36	1.60

Table 8.9 Effect of added ammonium acetate upon high fatty acids number, HFA No. of prevulcanised NR latex

level of added ammonium acetate (g/100g latex)	KOH No.	VFA No.	HFA No.*
0	0.56	0.08	0.16
0.1	0.66	0.10	0.19
0.2	0.72	0.23	0.16
0.3	0.75	0.34	0.14

* 1/3[KOH No.- VFA No.](18)

Table 8.10 Effect of added ammonium acetate upon ionic strength of prevulcanised NR latex

level of added ammonium acetate (g/100g latex)	pH	VFA No.	ionic strength (moles litre^{-1})
0	10.22	0.08	0.021
0.1	10.19	0.10	0.027
0.2	10.05	0.23	0.062
0.3	10.01	0.34	0.091

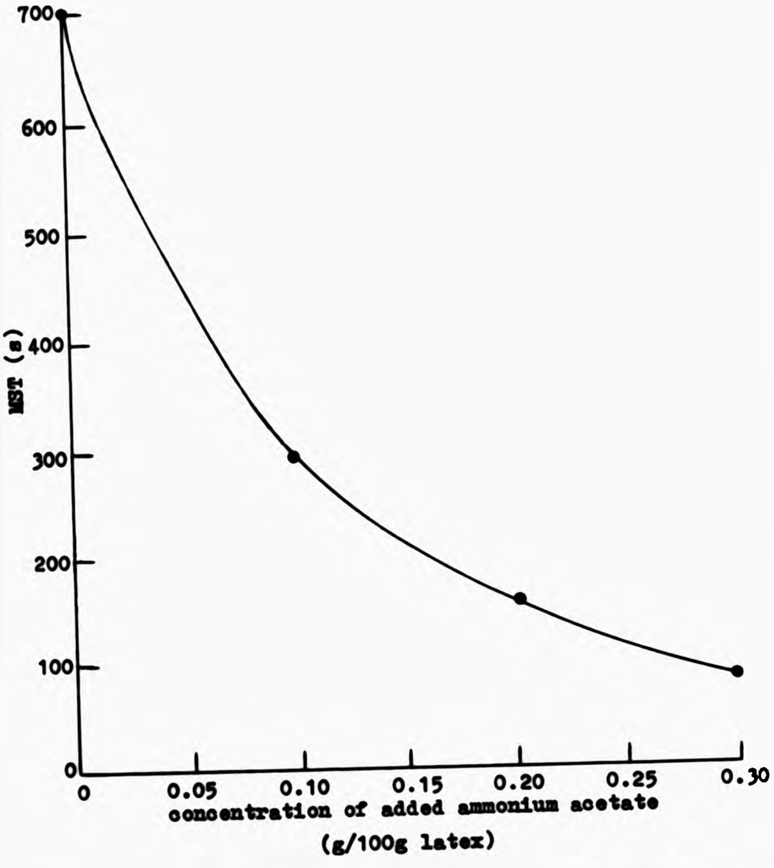


Figure 8.15 Effect of added ammonium acetate upon mechanical stability of prevulcanised NR latex

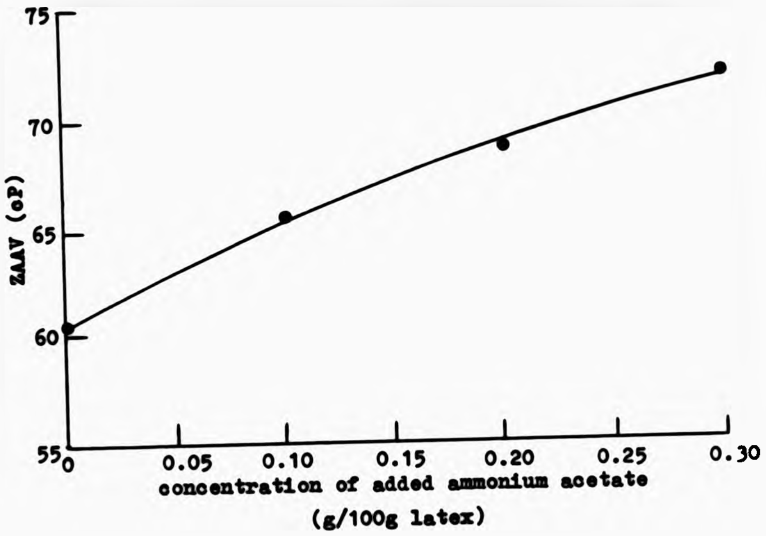


Figure 8.16 Effect of added ammonium acetate upon zinc ammonium acetate viscosity, ZAAV, of prevulcanised NR latex

viscosity measurements (Table 8.11). It has been well-known for many years that the addition of ammonium salts to NR latex containing zinc oxide leads to an increase in viscosity. Normally, it is said to be a consequence of particle aggregation, water being trapped within the spaces of these aggregates. In so doing, the effective volume of the dispersion medium decreases, and consequently the viscosity increases. The observations on microgel formation are consistent with this increase in viscosity.

The results of destabilisation of latex with increasing levels of added ammonium acetate agree in a generally satisfactory way with those reported by other workers (e.g., 17).

8.7.3 Calcium stability, CST

The stability of prevulcanised latex containing zinc oxide decreases towards calcium ions, on increasing the concentration of added ammonium acetate (Figure 8.17). After the initial rapid decrease in the stability of latex due to the catastrophic effect of calcium ions, the further reduction is thought to be a consequence of:

(a) an increase in the ionic strength of the aqueous phase; and
(b) formation of zinc ammine complexes.

These results further support the view that the reduction in the mechanical and chemical stability of latex containing zinc oxide is principally due to both of the above effects.

8.8 Effect of added magnesium chloride upon latex properties

8.8.1 Introduction

In order to minimise coagulum formation a very low concentration of the solution of magnesium chloride was added to the latex. However, the low concentration of this solution also reduced the TSC of the latex. Thus, the balance of the two was important; the concentrations of the magnesium chloride solution selected and the amounts added are shown in Table 8.12.

Table 8.11 Results for viscosity and microgel formation upon adding ammonium acetate

level of added ammonium acetate (g/100g latex)	viscosity (cP)	microgel content
0	47.8	s, d
0.1	49.5	t, m
0.2	52.3	m (mostly)
0.3	55.7	m (mostly)

abbreviations used in table: s = singlets, d = doublets, t = triplets and m = macroparticles

Table 8.12 Concentration of magnesium chloride solution selected and amount added to NR latex

concentration of magnesium chloride solution (%) w/w	weight of magnesium chloride (g/100g latex) (wet weight)	weight of magnesium chloride (g/100g latex) (dry weight)
0.1	10	0.01
0.2	10	0.02
0.4	10	0.04

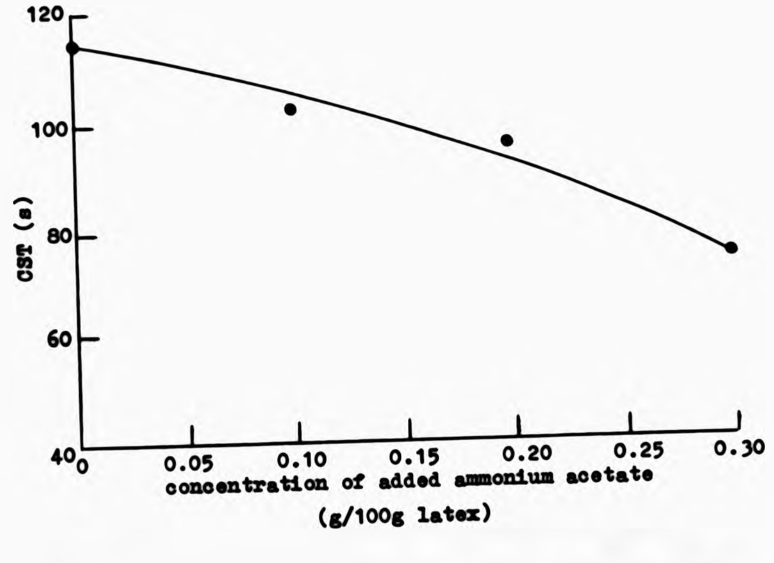


Figure 8.17 Effect of added ammonium acetate upon calcium stability time, CST, of prevulcanised NR latex

8.8.2 Basic properties

As expected, the basic properties, namely, TSC, DRC, alkalinity, KOH No., VFA No. and pH, remained relatively constant on adding small quantities of magnesium chloride. The results are presented in Table 8.13.

8.8.3 Mechanical stability, MST

Figure 8.18 shows that the addition of small quantities of magnesium chloride to NR latex containing zinc oxide drastically reduces the mechanical stability. This observation is in agreement with the results reported by other workers (13,23). There are three possible explanations to account for the destabilisation of latex in the presence of added magnesium chloride.

1. Effect of ionic strength

The ionic strength of the aqueous phase increases progressively with the addition of magnesium chloride. From Figure 8.14, it can be seen that the increased concentration of electrolyte, and the concomitant increase in the ionic strength of the aqueous phase, reduces the maximum height of the potential energy barrier. It follows that the increased ionic strength of the aqueous phase causes the compression of the electrical double layer surrounding the latex particles. The reduction in the thickness of the double layer lowers the repulsive forces. The van der Waals forces, therefore, become significant, thus leading to the destabilisation of the latex. However, because only very small quantities of magnesium chloride were added in these experiments, the effect of increased ionic strength upon the mechanical stability is negligible.

2. Interaction between added magnesium ions and higher fatty-acid anions

It is reasonable to suppose that chemical interaction between the added magnesium ions and the higher fatty-acid anions to form insoluble magnesium salts is the main reason for the massive reduction in the mechanical stability. Thus, according to the reaction,

Table 8.13 Effect of added magnesium chloride upon basic properties of prevulcanised NR latex

level of added magnesium chloride (g/100g latex)	TSC (%)	DRC (%)	KOH No.	VFA No.	alkalinity (g ammonia/100g aqueous phase)	pH
0	59.34	58.28	0.56	0.08	1.65	10.22
0.01	55.37	54.07	0.58	0.07	1.65	10.20
0.02	55.69	54.30	0.60	0.06	1.65	10.21
0.04	55.47	54.10	0.59	0.07	1.66	10.22

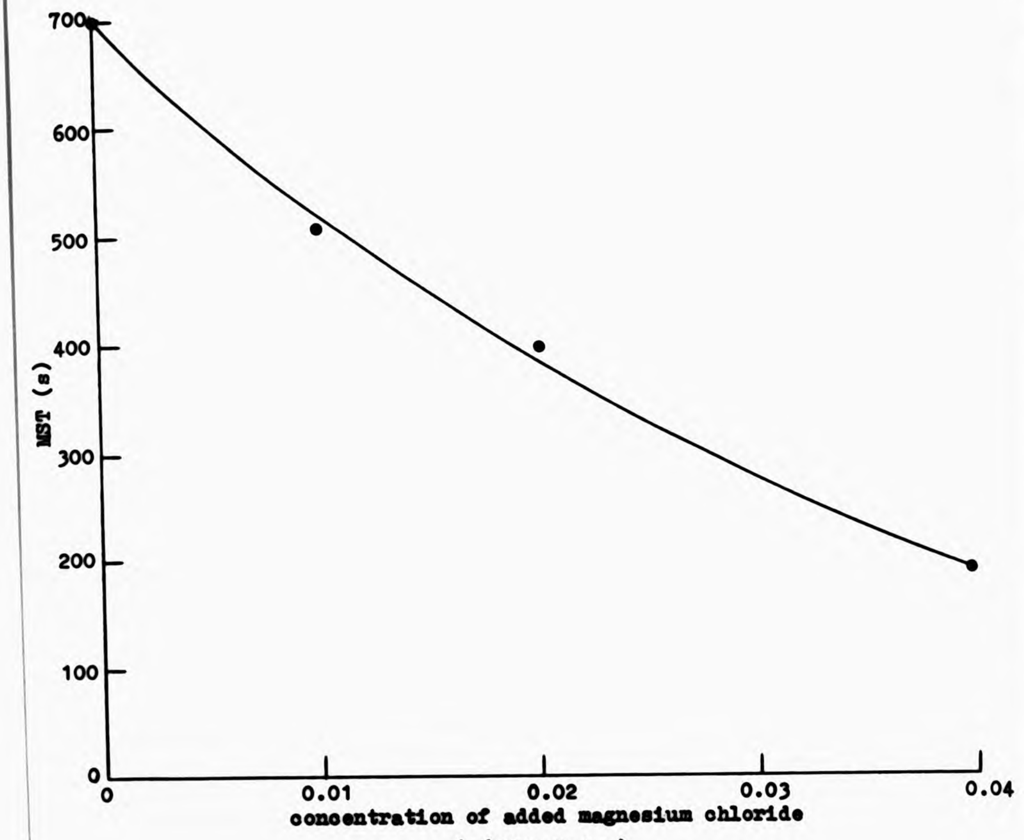


Figure 8.18 Effect of added magnesium chloride upon mechanical stability of prevulcanised NR latex

$$Mg^{++} + 2RCOO^{-} \longrightarrow (RCOO)_2Mg$$

it is expected that each magnesium ion reacts with two adsorbed higher fatty-acid anions. This allows the amount of higher fatty-acid anions reacted to be calculated. Figure 8.19 shows these same results re-plotted on the assumption that the reduction in MST is a consequence of removal of higher fatty-acid anions by reaction with magnesium ions according to the above reaction. Extrapolation of the curve to zero mechanical stability suggests that the removal of about 2.46×10^{-3} mole adsorbed higher fatty-acid anions per 100g latex solids would reduce the mechanical stability to zero. The initial level of fatty-acid soap anions was probably about 2.86×10^{-3} mole per 100g latex solids, as estimated from the following equation:

$$\begin{array}{c}\text{concentration of adsorbed}\\ \text{higher fatty-acid anions}\\ \text{(mole per 100g latex solids)}\end{array} = \frac{\text{KOH No.} - \text{VFA No.}}{3 \times 56} \qquad (8.37)$$

Thus, the proportion of the total amount of fatty-acid anions which is required to confer minimum colloid stability upon the NR latex at room temperature is:

$$\frac{2.86 \times 10^{-3} - 2.46 \times 10^{-3}}{2.86 \times 10^{-3}} \times 100 \approx 24\%$$

This value agrees fairly well with that reported elsewhere (13).

3. Specific adsorption effect

Specific adsorption of cations into the Stern layer would cause a reduction in the Stern potential. The reduced Stern potential would lower the potential energy maximum, thereby making the latex more susceptible to coagulation. This effect has been clearly demonstrated in Figure 8.9. However, this effect is unlikely to be important in this case, relative to chemical interaction with the fatty-acid anions.

8.8.4 Calcium stability, CST

The increased level of added magnesium chloride seems to have no significant effect upon the stability of latex towards calcium ions (Figure 8.20). A plausible reason for this is

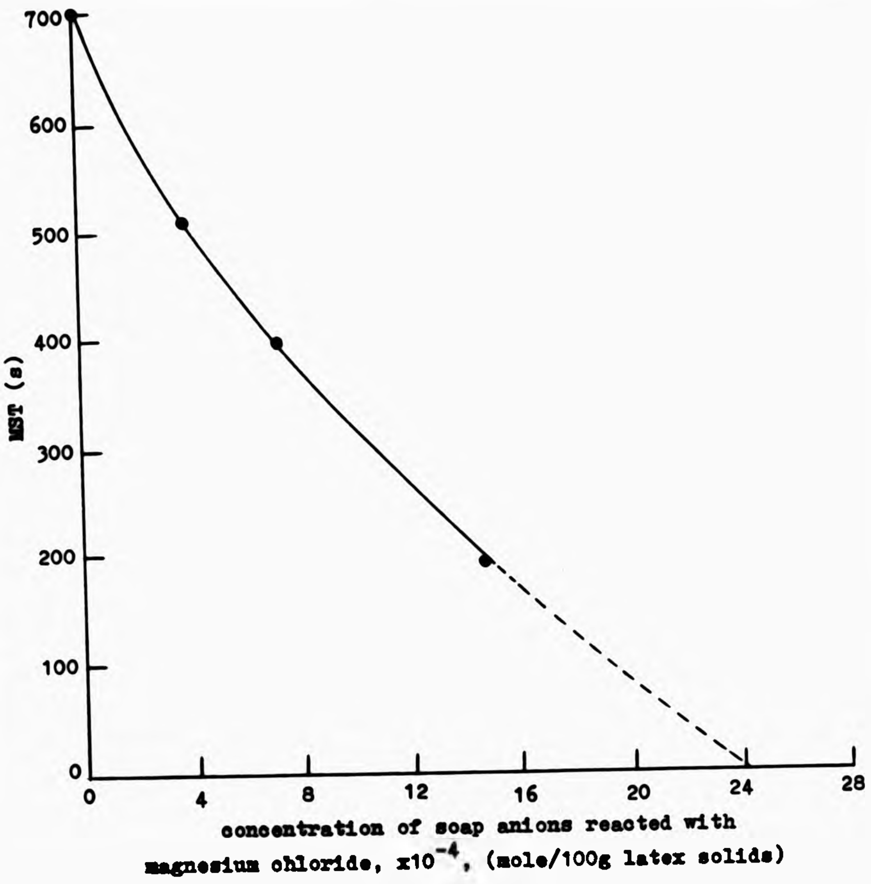


Figure 8.19 Re-plot of MST results on the assumption that the reduction in mechanical stability is a consequence of removal higher fatty-acid anions by reaction with magnesium ions

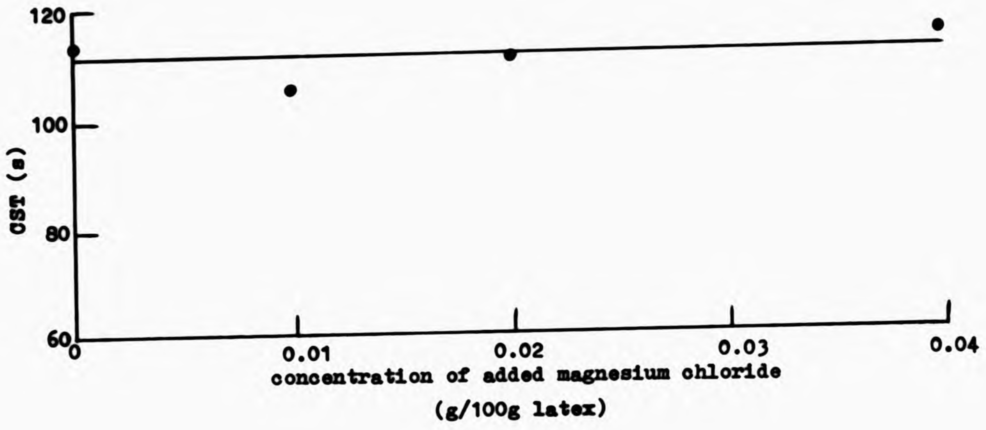


Figure 8.20 Effect of added magnesium chloride upon calcium stability time, CST, of prevulcanised NR latex

that the addition of calcium sulphate has a catastrophic effect upon the destabilisation of the latex such that the effect of small additions of magnesium chloride upon the overall coagulation rate becomes negligible.

8.8.5 Zinc ammonium acetate viscosity, ZAAV

Table 8.14 shows that addition of magnesium chloride causes the ZAAV to increase dramatically. It increases to such an extent that the latex gels in two cases. This is entirely as expected, because the magnesium chloride has reduced the colloid stability of the latex by reacting with fatty-acid anions (as discussed above), and so the latex is sensitised to the destabilisation effect of the zinc ammonium acetate.

The observations on microgel formation (Table 8.15) are consistent with this interpretation.

8.9 Correlation between mechanical stability, MST, and calcium stability

In the study of the effects of heating upon the properties of NR latex (Chapter 5), a linear relationship was obtained between the mechanical stability, MST, and the calcium stability, CST, (Figure 5.5). This was rather surprising, and hence more results were desirable before drawing any definite conclusions. Thus, the mechanical stability results obtained in this part of the investigation are correlated with the calcium stability results as shown in Figure 8.21. When linear regression analysis was performed on these results, a regression coefficient, r, of value 0.70 was obtained. Clearly, this suggests lack of correlation between the mechanical stability and the calcium stability. This is probably not surprising when consideration is given to the various changes arising in the measurements of mechanical stability and of calcium stability, upon the addition of various ingredients. For instance, the mechanical stability test is sensitive towards various additives like metal salts and alkalis. In contrast, however, the calcium stability test shows hardly any variation on adding such ingredients, probably due to the catastrophic effect of calcium ions towards the stability of the latex. In some cases, however, the calcium stability test offers a rough indication to the

Table 8.14 **Effect of added magnesium chloride upon viscosity and ZAAV of prevulcanised NR latex**

level of added magnesium chloride (g/100g latex)	viscosity (cP)	ZAAV (cP)
0	39.2	55.4
0.01	40.4	74.2
0.02	41.8	latex gelled
0.04	43.1	latex gelled

Table 8.15 **Effect of added magnesium chloride upon microgel content of prevulcanised NR latex with and without zinc ammonium acetate**

level of added magnesium chloride (g/100g latex)	microgel content of latex without zinc ammonium acetate	microgel content of latex with zinc ammonium acetate
0	s, d and t	m (aggregation of 5-10 particles)
0.01	m (aggregation of 5-6 particles)	f (extensive aggregation)
0.02	m (aggregation of 10-20 particles)	latex gels
0.04	m (aggregation of 10-25 particles)	latex gels

abbreviations used in table: s = singlets, d = doublets, t = triplets, m = macroparticles and f = flocculation

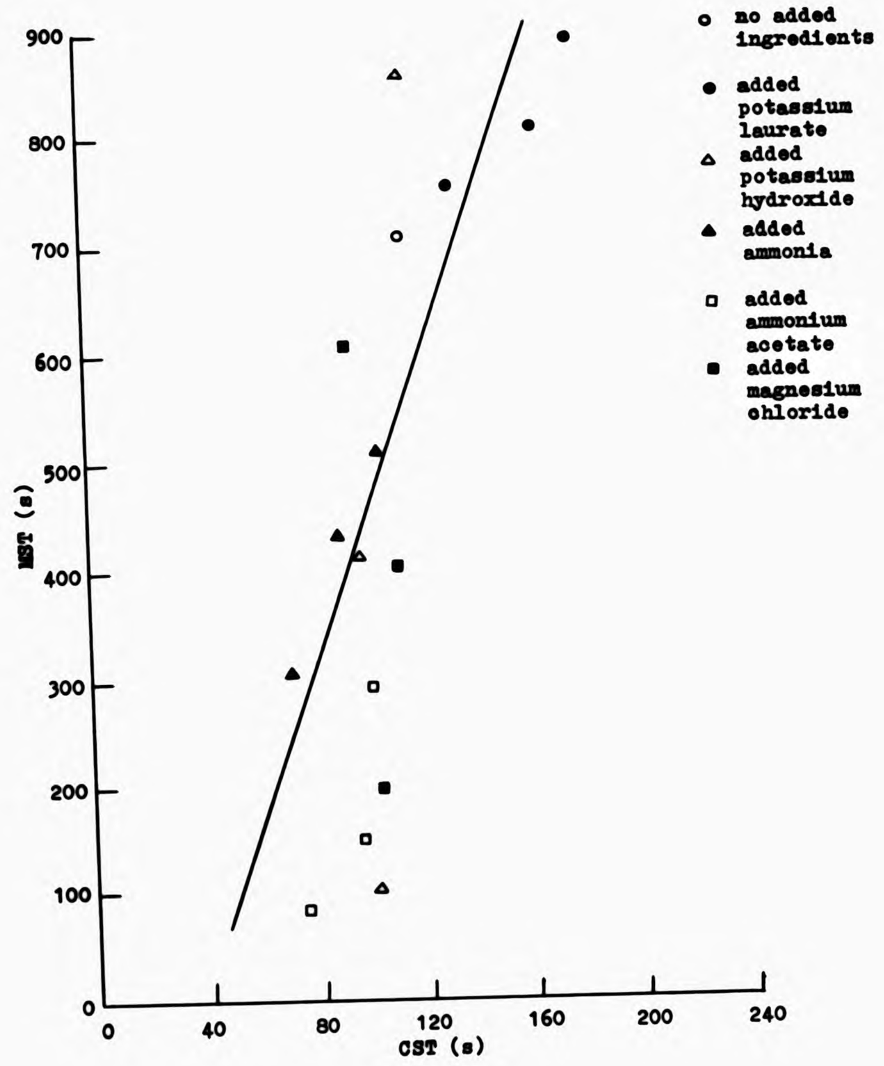


Figure 8.21 Correlation between mechanical stability time, MST, and calcium stability time, CST

changes in the stability of latex brought about by, for example, potassium laurate, ammonium acetate and ammonia.

It is clear from the above that no conclusions can be drawn from the limited data available so far. Thus, further work is required, perhaps in respect of modifying the calcium stability test, in order to extend its use as a test for assessing the colloid stability of the latex like the mechanical stability test. It must be borne in mind that the basis of the development of the calcium stability test was to gain an understanding of the effect of calcium ions upon the stability of latex during coagulant dipping and, to some extent, this objective has been achieved (see Section 4.4).

8.10 Summary

In general, it has been found that the basic properties, in particular, TSC and DRC, remain relatively unaffected by increasing the concentration of the added ingredients. However, the stability of latex, as measured by either MST or ZAAV, or in some cases CST, is greatly affected by the nature and amount of an added ingredient.

An increase in the stability of the latex brought about by increasing the level of added soap is largely due to increasing adsorption of soap anions, which increase the Stern potential and hence the stability of the latex. An enhancement in the rate of destabilisation upon increasing the concentration of added ingredients may possibly occur due to one or more of the following mechanisms:

1. effect of ionic strength
2. zinc ammine complexes formation
3. interaction between the added ingredient and the adsorbed fatty-acid soaps
4. interference with the ability of the electric charges to promote hydration of the particles
5. effects of steric stabilisation

On adding electrolyte to the latex, the ionic strength of the aqueous phase increases, thereby causing a compression of the electrical double layer. Thus the stability of the latex decreases. However, the effect of ionic strength alone is insufficient to explain the substantial drop in the stability of the latex. In the case of the addition of ammonia or ammonium acetate to prevulcanised NR latex containing zinc oxide, the formation of zinc ammine complexes is thought to be the main factor responsible for reducing the colloid stability. The destabilisation of latex brought about by the addition of metal salts is thought to be a consequence of interaction of the metal ions with adsorbed fatty-acid anions to form insoluble salts.

On increasing the level of added potassium hydroxide the stability of latex increases initially, followed by a rapid reduction in the stability. The initial increase is attributed to the conversion of any residual free fatty-acid and ammonium salt of fatty acid to the corresponding potassium soaps. The latter are probably more effective stabilisers for NR latex than are ammonium salts. Also, there may be protein residues adsorbed at the particle interfaces which ionise further when the pH is raised by potassium hydroxide. However, since the ammonia-preserved NR latex containing zinc oxide was used, it is most probable that the addition of potassium hydroxide reduced the destabilising effect of zinc ions. With further additions of potassium hydroxide, the stability of the latex is drastically reduced without apparently greatly affecting the charge on the particles. It is thus proposed that the excess potassium hydroxide probably interferes with the ability of the bound electric charges to promote hydration of the particles. The collapse of adsorbed steric stabilisers might also contribute to the effects upon both the mechanical stability and the viscosity.

The above findings are in accordance with the results of both the viscosity and the microgel formation.

8.11 Processing properties

8.11.1 Introduction

Several workers have attempted to study the processing properties of NR latex, particularly the drying behaviour of NR latex films (27,28). However, no published investigations of the effects of added ingredients upon these properties have been located. This may be a consequence of lack of knowledge on the subject itself. The purpose of this section is thus to apply collectively the knowledge of the various aspects of processing behaviour of both the straight- and the coagulant-dipped films (Chapters 6 and 7 respectively), and thereby to attempt to gain some insight to the problems dealt with herein. The procedures used for investigating the effects of added ingredients upon the processing properties, namely, drying rate, ammonia loss, set time and curtaining effect are described in Chapter 3.

8.11.2 Drying rate of straight-dipped films

8.11.2.1 Effect of added potassium laurate

The effect of added potassium laurate upon the drying rate of straight-dipped films is shown in Figure 8.22. As can be seen, increasing the concentration of added potassium laurate has no effect upon rate of drying of films. This is consistent with the results of the viscosity measurements. From Table 8.2, it is observed that the viscosity increase is negligible on increasing the level of added potassium laurate. This suggests that the volume fraction of disperse phase in the latex is approximately constant. Thus, assuming the rate of evaporation of water from the film to be proportional to the surface area of water at the surface, and hence the aggregate size of the capillaries at the surface (Section 6.7.5), the loss of water is constant. These results further confirm the small changes arising in the stability of the latex with added potassium laurate at various concentrations (Section 8.4). That is to say, in the early stages of drying of a straight-dipped film prepared from ammoniated NR latex, the loss of water is thought to depend upon the formation of a coherent film on the surface (Chapter 6). The formation of this film is mainly a consequence of gelation caused by the local drop in pH resulting from loss of ammonia at the surface (27). Thus, the factors affecting the stability of the latex, and hence the surface film formation, would also be expected to affect the rate of drying of films.

8.11.2.2 Effect of added potassium hydroxide

Figure 8.23 shows the effect of added potassium hydroxide upon the drying behaviour of straight-dipped films. It is seen that on increasing the concentration of added potassium hydroxide, the rate of loss of water is retarded slightly initially, and then increases. The initial decrease is attributed to an

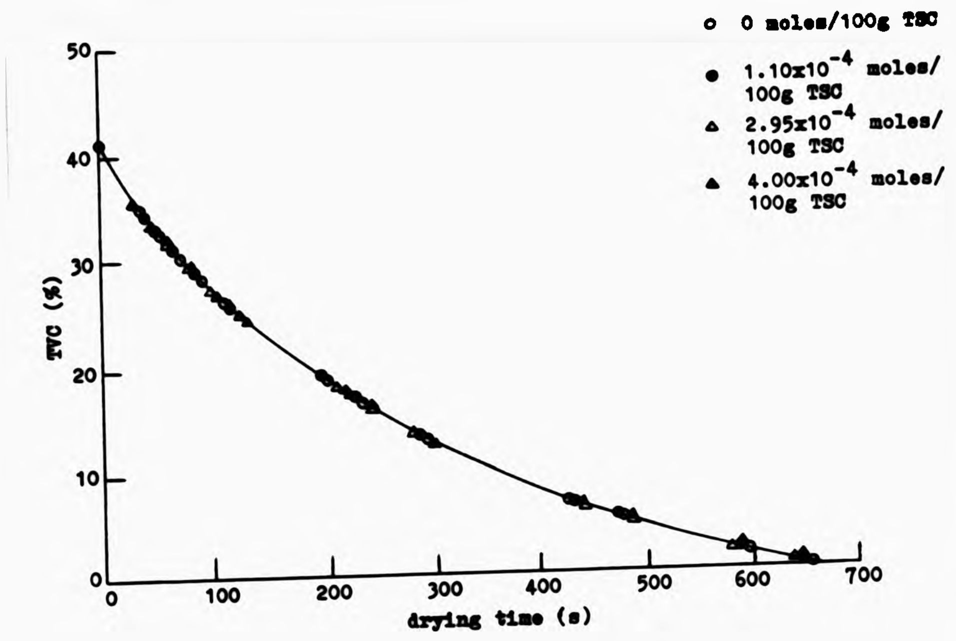


Figure 8.22 Effect of added potassium laurate upon drying rate of straight-dipped films from prevulcanised NR latex. The drying temperature was 30°C and relative humidity 25%.

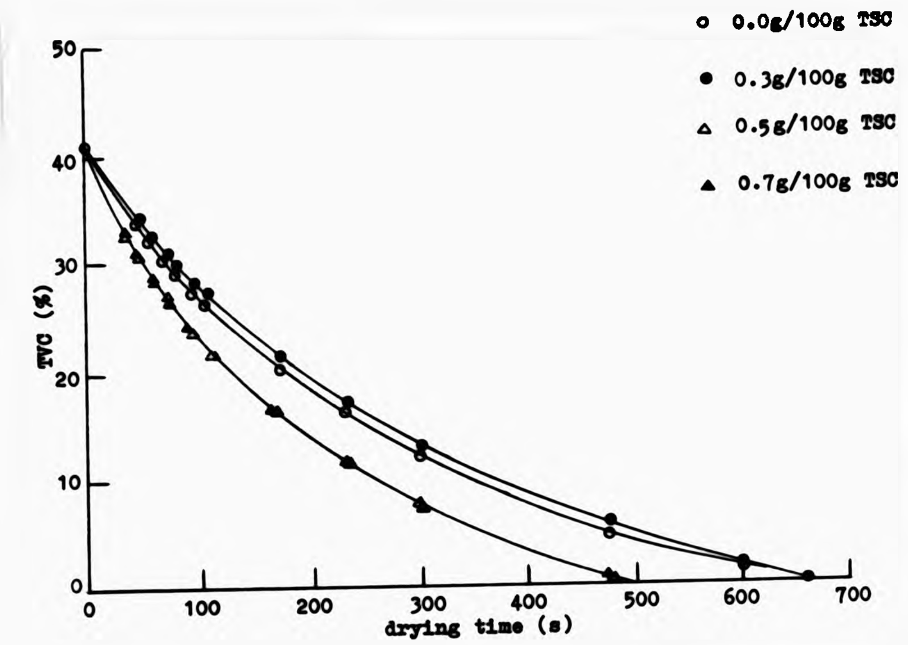


Figure 8.23 Effect of added potassium hydroxide upon drying rate of straight-dipped films from prevulcanised NR latex. The drying temperature was 30°C and relative humidity 25%.

enhancement in the stability of the latex. The addition of potassium hydroxide probably converts the free fatty acid and ammonium salt of fatty acid to the corresponding potassium soaps. These soaps are probably more effective stabilisers for NR latex than are ammonium salts and hence encourage the hydration of the particles. Also, there may be protein residues adsorbed at the particle interfaces which ionise further when the pH is raised by potassium hydroxide. However, because zinc oxide was added to the latex as a vulcanising ingredient, the addition of potassium hydroxide has most probably reduced the destabilising effect of the zinc ions, thereby increasing the stability of the latex. Thus, an enhancement in the stability of the latex prevents the reduction in the interfacial area of water-air which otherwise would reduce the rate of evaporation of water. Hence, the initial retardation in rate of evaporation of water is probably a consequence of the increased hydrophilic nature of the stabiliser. The decrease in the rate of evaporation of water on further addition of potassium hydroxide is directly comparable with the substantial reduction in the viscosity of the latex (Table 8.7), and also with the reduction in MST (Figure 8.12). The reduction in viscosity indicates that the effective volume of the latex particles is reduced considerably, thereby increasing the surface area for evaporation of water. This further supports the view that the excess potassium hydroxide interferes with the ability of the bound electric charges to promote hydration of the particles.

8.11.2.3 Effect of added ammonia

The rate of evaporation of water is found to be retarded slightly on increasing the level of added ammonia, as is shown in Figure 8.24. Again, this effect can be compared with the effect upon viscosity (Table 8.4). A small increase in the viscosity on increasing the concentration of added ammonia, is thought to arise from the progressive increase in the degree of hydration of the particles with a subsequent decrease of the aqueous phase. The decrease of the aqueous phase, which acts as the dispersion medium, causes an increase in the effective volume fraction of latex particles. Thus the effective surface area for evaporation of water is reduced, thereby reducing the drying rate of films. The slight viscosity increase is consistent with the results for the rate of drying of films. However, it is surprising that the massive

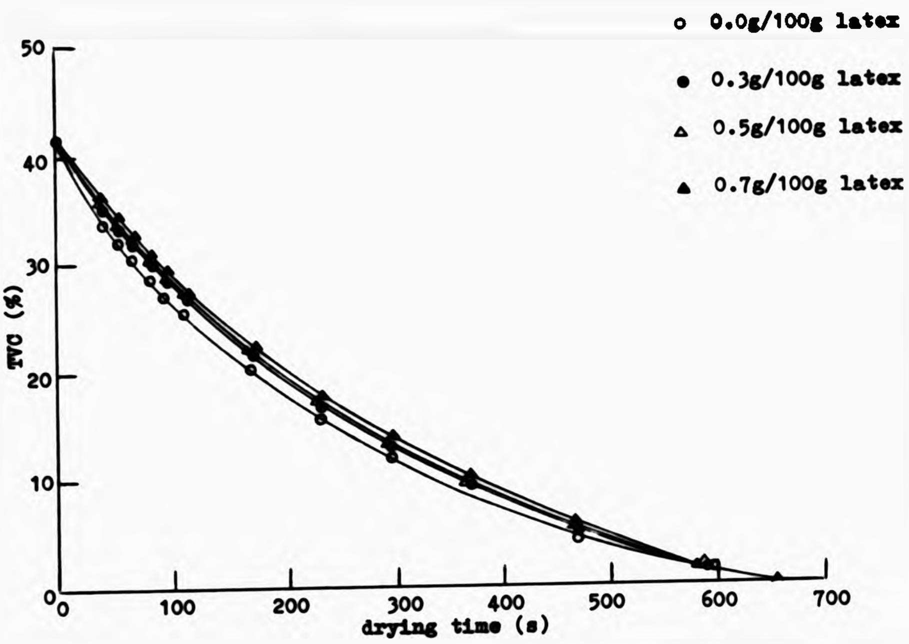


Figure 8.24 Effect of added ammonia upon drying rate of straight-dipped films from prevulcanised NR latex. The drying temperature was 30°C and relative humidity 25%.

reduction in the stability of latex (Figure 8.8) does not seem to have very much effect upon the loss of water from the film produced from that latex. From the mechanisms discussed for straight-dipped films in Chapter 6, it would be anticipated that the reduced stability of latex would offer some resistance to passage of water through the bulk to near the surface of the film, thereby lowering the rate of evaporation of water. Additionally, the reduction in the stability of latex would be expected to encourage the reduction in the interfacial area of water-air. In so doing, the rate of loss of water from the film would be reduced. The stability results are therefore consistent with the results for the rate of drying of films, i.e., the reduced stability of latex does cause retardation of the rate of loss of water from films produced from that latex. However, it is not clear why the massive reduction in the stability of latex produces only small changes in the drying rate of films formed from it, on increasing the levels of added ammonia. It is likely that the excess ammonia probably inhibits the formation of a coherent film on the surface at the early stages of drying. The formation of this film is thought to arise due mainly to the gelation caused by the local drop in pH resulting from loss of ammonia (27). Thus, the rate of loss of water from latex films would not be affected appreciably on increasing the levels of added ammonia, provided this added ammonia is always in excess. This is thought to be a likely explanation, because one of the most important conclusions reached so far in this investigation is that the factors which are responsible for the formation of a surface film, also control the overall drying rate of straight-dipped films from NR latex (see Chapter 6).

8.11.2.4 Effect of added ammonium acetate

The results shown in Figure 8.25, indicate that the rate of evaporation of water is progressively retarded by increasing the levels of added ammonium acetate. Like ammonia, this effect is directly comparable with the effect upon viscosity (Section 8.7). The increase in viscosity is thought to be a consequence of the increase in the aggregation size of the particles which encapsulate the water region. Thus the effective surface area for evaporation of water is reduced, thereby reducing the drying rate of films. However, unlike ammonia, the stability results of ammonium acetate appear to

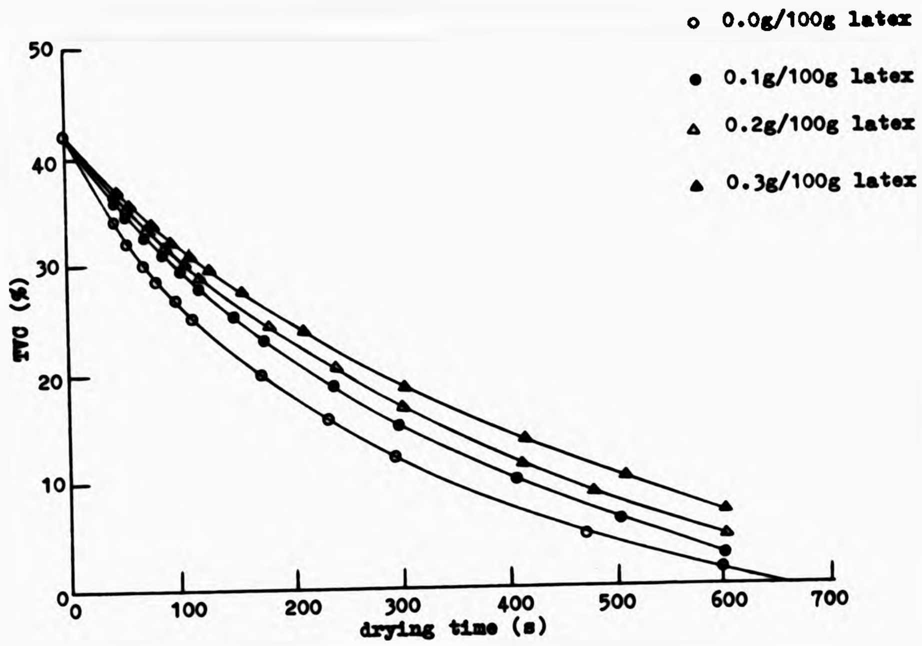


Figure 8.25 Effect of added ammonium acetate upon drying rate of straight-dipped films from prevulcanised NR latex. The drying temperature was 30°C and relative humidity 25%.

be consistent with the rate of evaporation results. As expected, it is observed that on increasing the concentration of added ammonium acetate, not only the stability of latex reduces considerably (Figure 8.15), but also the rate of evaporation of water from films produced from that latex (Figure 8.25). This observation further supports the hypothesis that the excess ammonia prevents the formation of a surface film, as discussed in preceding section. There are two possible reasons to account the reduction in rate of evaporation of water with reduced stability:

(a) reduction in the stability of latex probably causes an enhancement in the reduction of the interfacial area of water-air, thereby reducing the rate of evaporation of water from a film formed from that latex.
(b) reduced stability of latex probably hinders the passage of water through the bulk to near the surface of the film, thus retarding the loss of water from a film produced from that latex.

8.11.2.5 Effect of added magnesium chloride

The effect of added magnesium chloride upon the drying behaviour of latex films, produced from latex of 55% TSC, is shown in Figure 8.26. It is seen that the drying rate of films decreases on increasing the level of added magnesium chloride. A possible explanation for the observed phenomenon may be offered by considering the microgel formation results (Table 8.15) in conjuction with the viscosity results (Table 8.14). On addition of magnesium chloride, the aggregation size of the particles is increased with a subsequent increase in the viscosity. This increases the effective volume of the disperse phase of latex particles and hence reduces the surface area for evaporation of water. Thus, the rate of evaporation of water reduces on increasing the level of added magnesium chloride. The stability results are also found to be consistent with the rate of drying of films.

8.11.2.6 Summary of results

The principal conclusion which has emerged from the results of the effect of added ingredients upon the drying behaviour of the latex films is that the rate of evaporation of water correlates with the viscosity changes brought about by adding

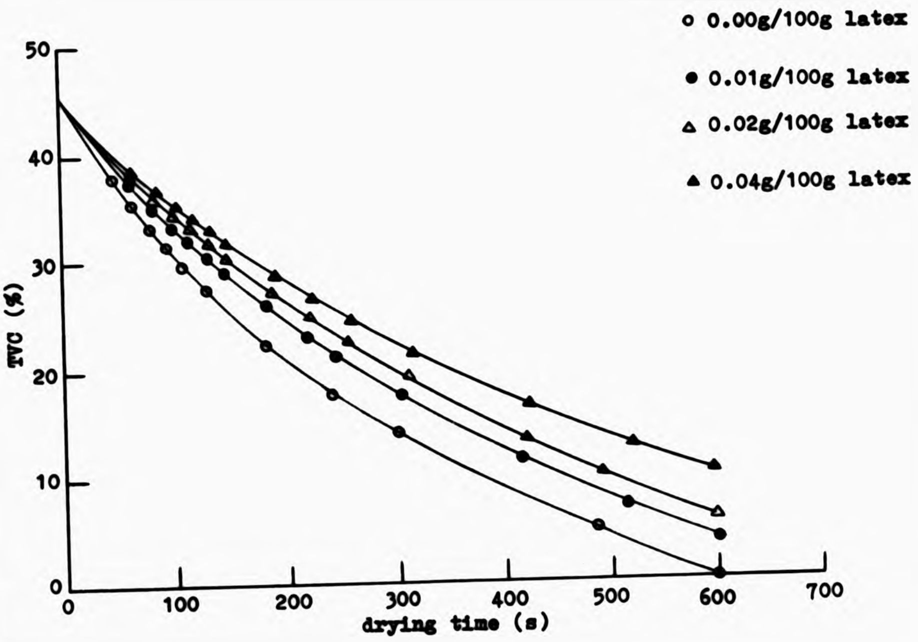


Figure 8.26 Effect of added magnesium chloride upon drying rate of straight-dipped films from prevulcanised NR latex. The drying temperature was 30°C and relative humidity 25%.

various ingredients. This correlation is evident when the viscosity results are plotted against evaporation coefficient, K, as shown in Figure 8.27. The evaporation coefficient, K, was obtained by the procedure described in Section 6.7.5. Linear regression analysis was performed on the results of viscosity and evaporation coefficient, as shown in Figure 8.27. A regression coefficient, r, of value −0.97 was obtained, thus suggesting a very good correlation between the viscosity and the evaporation coefficient, K. However, because a negative value of r is obtained, it suggests that there is an inverse relationship between the viscosity of the latex and rate of evaporation (characterised by K) of the film formed from that latex. This is very interesting. Possible reasons to account the reduction in K with increasing viscosity are as follows:

1. The increased viscosity of the latex probably hinders the diffusion of water from the bulk to near the surface of a dipped film formed from that latex, and hence reduces the rate of evaporation of water from the surface of this film.
2. The increased viscosity of latex is thought to be a consequence of an increase in the effective volume fraction of the dispersed phase. This mechanism probably lowers the interfacial area of water-air and hence the evaporation coefficient. K.

The stability results are in accordance with the results of rate of drying of films, for all the latices containing various added ingredients at various concentrations except the latex containing added ammonia at various concentrations. For ammonia, it is thought that the excess ammonia probably inhibits the formation of surface film, which otherwise arises due to the local drop in pH resulting from loss of ammonia at the surface. In so doing, the reduction in interfacial area of water-air is prevented.

8.11.3 Ammonia loss from straight-dipped films

The ammonia loss from a straight-dipped film was measured by the procedure given in Section 3.7.2. In general, when TAC was plotted as a function of drying time, at various concentrations of an added ingredient, a typical curve of the type shown in Figure 8.28 was obtained. As can be seen, there

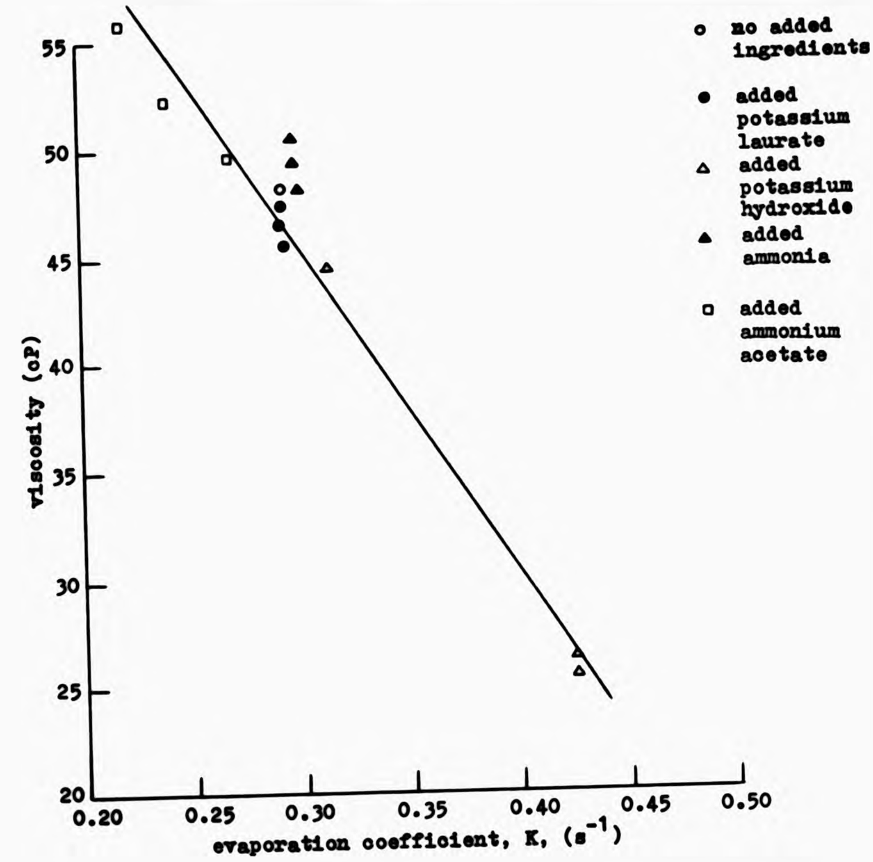


Figure 8.27 Correlation between viscosity and evaporation coefficient, K

was an initial rapid loss of ammonia. This was followed by a gradual loss of ammonia as the drying process continued. These results are consistent with the previous observations (Section 6.8). Additionally, it is observed that the curves for TAC versus drying time are similar in nature and in magnitude, for all the latices containing various added ingredients at various concentrations, irrespective of the total amount of ammonia present in the latex originally. In other words, after the initial rapid loss of ammonia within the first 30s the further loss of ammonia is the same in all cases, provided that the drying conditions such as temperature and relative humidity remain constant. Typical results for the effect of added ammonia upon the rate of loss of ammonia from a straight-dipped film, at constant drying temperature of 30°C and relative humidity 25%, are shown in Figure 8.28. The effect of other added ingredients at various concentrations followed more or less the same pattern. This seems a little surprising at first, since it was thought that according to the mechanisms illustrated schematically in Figure 6.19, the nature of these curves should vary, especially in relation to added ingredients. This is because the latter are believed to control the rate and the type of reactions occurring with ammonia. With the limited data available, however, it is difficult to offer any explanations for the observed findings. Nevertheless, one possibility may be that since there are other major changes which occur in the latex, as discussed in preceding sections, the effect upon rate of loss of ammonia is probably negligible. This is particularly true, when consideration is given to the overall drying process of the film. It has been found that a very large percentage of the total ammonia is lost from the film in a very short time compared to the percentage of the total water lost from the same film (Section 6.8.7). Bearing this in mind, it is envisaged that a more clear picture may be obtained if the experiment is repeated using NR latex which does not contain compounded ingredients, especially zinc oxide, as this interferes with the reactions which may otherwise take place with ammonia.

8.11.4 Set time

Set time is defined as the time taken for a known weight (hence thickness, since area is constant) of latex to set completely under controlled conditions of temperature and

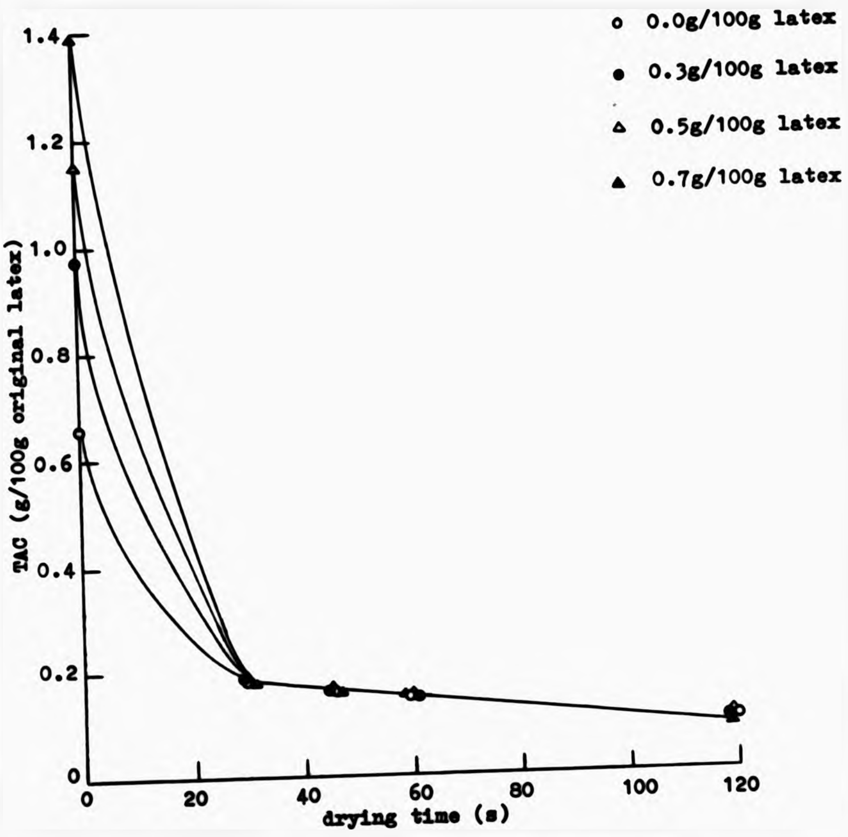


Figure 8.28 Typical results showing effect of added ammonia upon rate of loss of ammonia of a straight-dipped film from prevulcanised NR latex, at constant drying temperature of 30°C and relative humidity 25%

relative humidity. The effect of added ingredients upon set time was investigated by the procedure given in Section 3.7.3. The results are shown in Figure 8.29. Essentially, the set time is found to increase slightly on increasing the concentration of added potassium laurate, and to decrease on increasing the level of added ammonia, added ammonium acetate, and added magnesium chloride. In the case of added potassium hydroxide, however, the set time increases at first and then decreases. These observations are best explained on the basis of the stability of the latex.

The set time is expected to increase with an increase in the stability of the latex, since the former is a measure of the time taken for the latex particles to attain irreversible contact with one another. Thus, an attempt was made to correlate the stability, namely, mechanical stability and calcium stability, with the set time. These correlations are shown in Figures 8.30 and 8.31 respectively. It is interesting to note in Figure 8.30, that there is surprisingly a linear relationship between the set time and the mechanical stability. When linear regression analysis was performed on these results, a regression coefficient, r, of value 0.99 was obtained. This suggests that there is strong correlation between MST and set time. This leads to the conclusion that the factors which affect the stability of the latex upon increasing the concentrations of added ingredients are also responsible for the changes in the set time. These factors have already been discussed in detail in preceding sections. However, lack of correlation (regression coefficient, r, was found to be 0.71) between the calcium stability and set time for addition of added ingredients (Figure 8.31) is probably not surprising when the various changes arising during the calcium stability test are considered. The calcium stability test measures the sensitivity of latex to destabilisation by calcium ions. Since a sudden massive reduction in stability is brought about by addition of calcium ions (Section 8.4.3), this test is regarded as being rather insensitive to small changes which may otherwise be detected by, for example, the mechanical stability test and/or set time. Also, the addition of calcium sulphate may cause the formation of local coagulum which reduces the stability of latex drastically, thus producing the CST values which are somewhat erroneous.

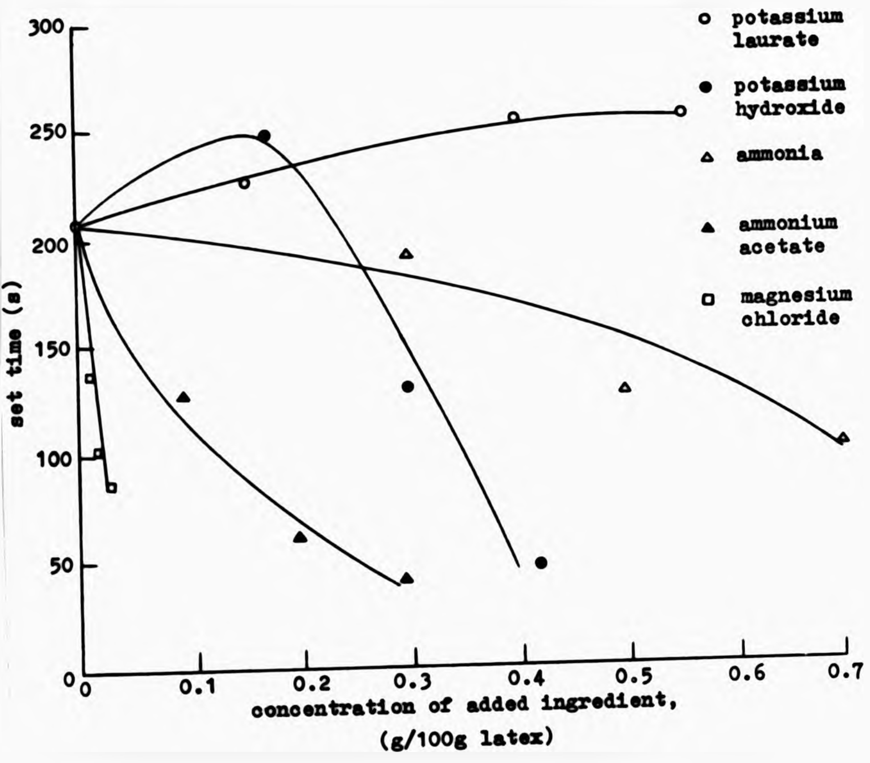


Figure 8.29 Effect of added ingredients upon set time

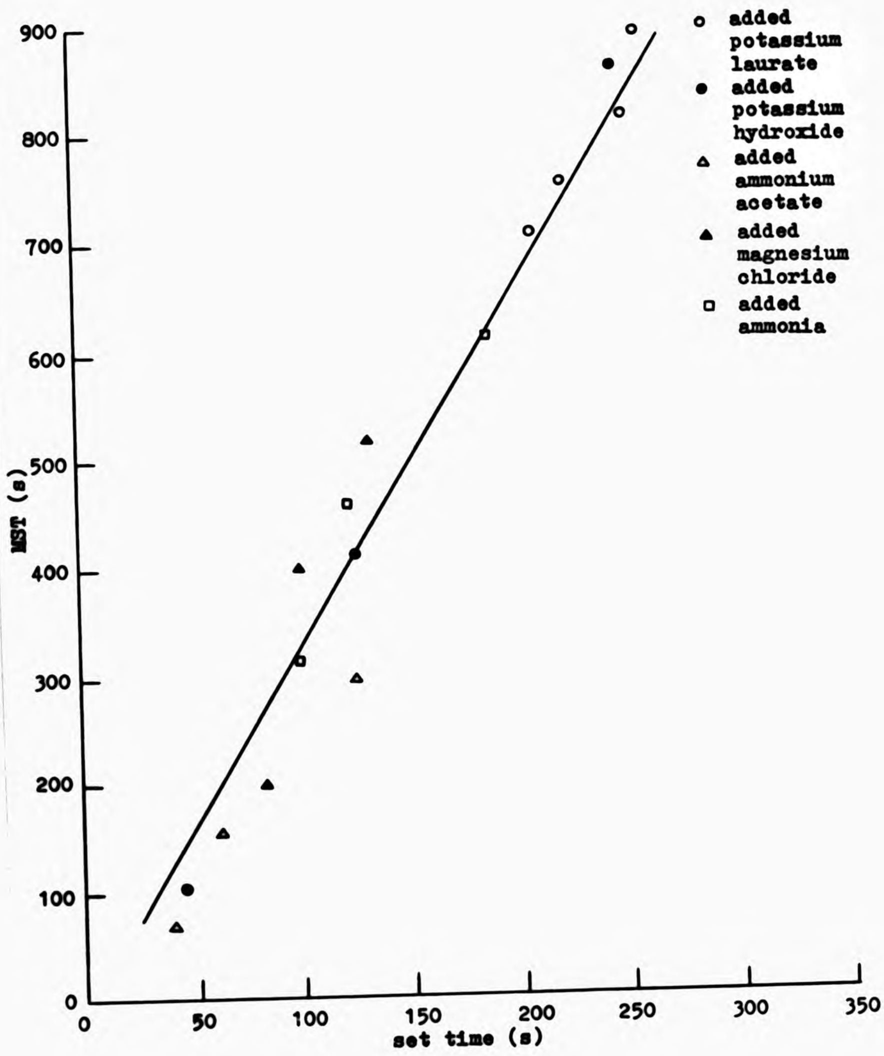


Figure 8.30 Correlation between mechanical stability time, MST, and set time, t_S, for latices containing various amounts of various ingredients

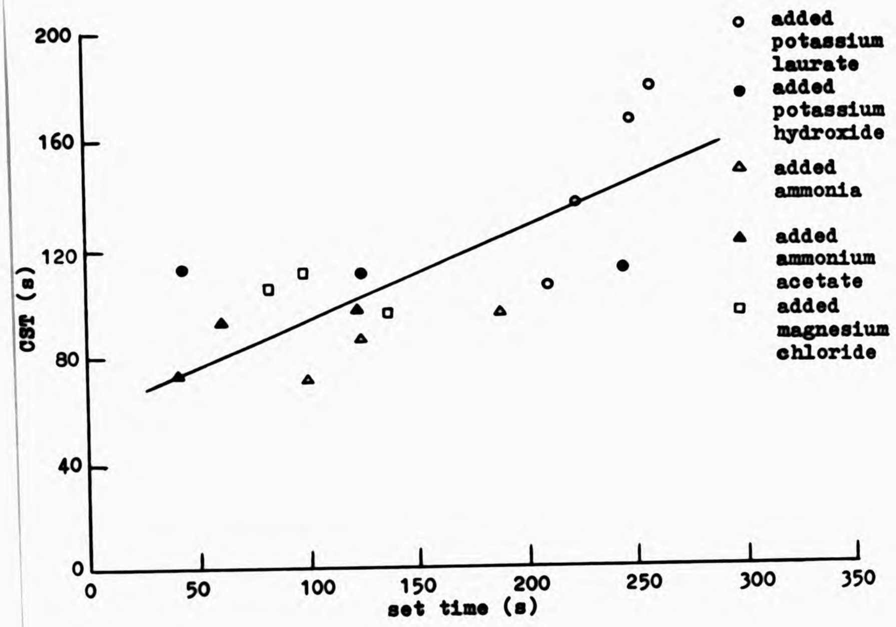


Figure 8.31 Correlation between calcium stability time, CST, and set time, t_S, for latices containing various amounts of various ingredients

8.11.5 Relationship between set time and TVC

In an attempt to acquire an understanding of the effect of the added ingredients upon the coalescence of the rubber particles, the set time has been correlated with TVC. The results are shown in Table 8.16. As can be seen, on the one hand, the coalescence of rubber particles occurs at about 80% TSC or above, for latices containing added potassium laurate or added potassium hydroxide. It is reported that volume fractions of rubber particles excess of 0.8 are possible before the particles are forced into irreversible contact (27). On the other hand, irreversible contact of particles occurs at about 65% TSC or above for latices containing added ammonia, added ammonium acetate, or added magnesium chloride. This discrepancy is largely a reflection of the low set time.

It is postulated that the reduction in set time upon increasing the concentration of certain added ingredients, is a consequence of particle aggregation and the subsequent increase in effective volume of the disperse phase because water is trapped within the spaces of the latex aggregates. This leads to a reduction in the aqueous phase which is acting as a dispersion medium, and thus results in reduced set time. Furthermore, the results support the postulate that the viscosity of latex increases on adding increased levels of ammonia, ammonium acetate, or magnesium chloride. This is an interesting observation. When an attempt was made to correlate set time with viscosity (Figure 8.32), a very poor correlation of regression coefficient, r, of 0.14 was obtained. It is not clear why there is hardly any correlation between the two.

8.11.6 'Curtaining effect', CE

The curtaining effect for a film obtained by latex dipping is defined as the irregularities arising as a consequence of non-uniform flow of the latex down the former prior to its setting. The procedure for measuring the 'curtaining effect' is given in Section 3.7.4. The results for the effect of added ingredients upon the 'curtaining effect', at a given withdrawal rate of 1.3mm s^{-1} are given in Table 8.17. Because a CE value of $2.5x10^{-4}$g is taken as a reference value (Section 6.12), values of CE equal to or more than $2.5x10^{-4}$g give an indication of the presence of a 'curtaining effect'. Thus it is seen from Table 8.17, that the 'curtaining effect' is

Table 8.16 Effect of added ingredients upon volume fraction of rubber, V_r

concentration (g/100g latex)	set time (s)	TVC (%)	TSC (%)	V_r
for latices containing added potassium laurate				
0	210	18.0	82.0	0.83
0.02	225	17.5	82.5	0.84
0.04	252	16.0	84.0	0.85
0.06	260	15.0	85.0	0.86
for latices containing added potassium hydroxide				
0	210	18.0	82.0	0.83
0.18	248	17.5	82.5	0.84
0.30	127	21.5	78.5	0.80
0.42	45	30.0	70.0	0.72
for latices containing added ammonia				
0	210	18.0	82.0	0.83
0.30	188	21.0	79.0	0.80
0.50	125	26.0	74.0	0.76
0.70	100	29.0	71.0	0.73
for latices containing added ammonium acetate				
0	210	18.0	82.0	0.83
0.10	75	32.0	68.0	0.70
0.20	62	33.0	67.0	0.69
0.30	40	37.0	63.0	0.65
for latices containing added magnesium chloride				
0	210	18.0	82.0	0.83
0.01	135	30.0	70.0	0.72
0.02	100	33.0	67.0	0.69
0.04	82	37.0	63.0	0.65

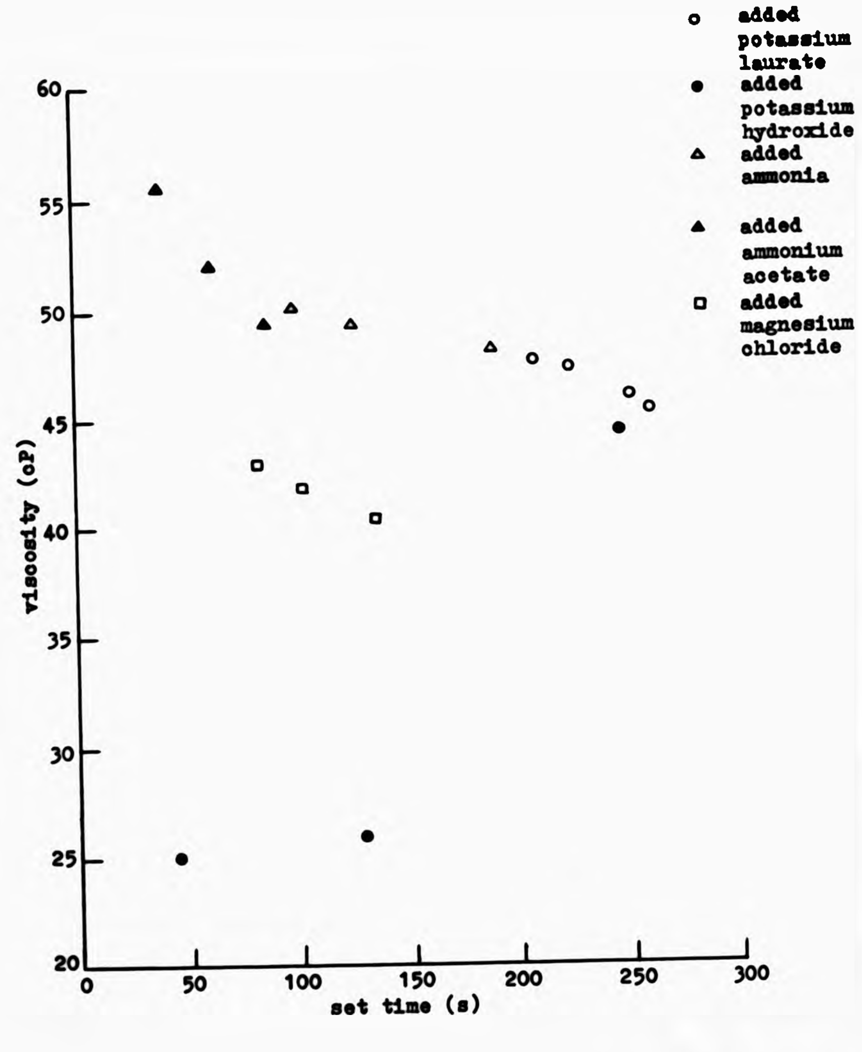


Figure 8.32 Correlation between viscosity and set time, t_S, for latices containing various amounts of various ingredients

Table 8.17 Effect of added ingredients upon curtaining effect CE, both across and down the former for films formed at a withdrawal rate of 1.3mm s^{-1}

concentration (g/100g latex)	CE values across former (g)	CE values down former (g)
for latices containing added potassium laurate		
0	1.5×10^{-4}	2.2×10^{-4}
0.02	1.3×10^{-4}	2.5×10^{-4}
0.04	1.7×10^{-4}	2.6×10^{-4}
0.06	1.4×10^{-4}	2.4×10^{-4}
for latices containing added potassium hydroxide		
0	1.5×10^{-4}	2.2×10^{-4}
0.18	1.4×10^{-4}	2.1×10^{-4}
0.30	1.4×10^{-4}	2.3×10^{-4}
0.42	1.8×10^{-4}	2.5×10^{-4}
for latices containing added ammonia		
0	1.5×10^{-4}	2.2×10^{-4}
0.30	2.4×10^{-4}	3.1×10^{-4}
0.50	2.0×10^{-4}	3.0×10^{-4}
0.70	2.2×10^{-4}	3.4×10^{-4}
for latices containing added ammonium acetate		
0	1.5×10^{-4}	2.2×10^{-4}
0.10	1.8×10^{-4}	2.7×10^{-4}
0.20	2.1×10^{-4}	2.9×10^{-4}
0.30	1.9×10^{-4}	3.6×10^{-4}
for latices containing added magnesium chloride		
0	1.5×10^{-4}	2.2×10^{-4}
0.01	1.4×10^{-4}	2.5×10^{-4}
0.02	1.9×10^{-4}	3.0×10^{-4}
0.04	2.2×10^{-4}	3.8×10^{-4}

absent both across and down the former for films obtained from latices containing increasing levels of added potassium laurate or added potassium hydroxide. However, on increasing the level of either added ammonia, or added ammonium acetate or added magnesium chloride, a certain degree of CE is detected down the former, although it is absent across the former. This is not surprising, when consideration is given to the stability of the latex, and hence to its set time.

The investigation which has been carried out so far in measuring the stability and set time of latex, suggests that on increasing the concentration of added ingredients, particularly, ammonia, ammonium acetate and magnesium chloride, the set time reduces (Table 8.16). It is therefore reasonable to suppose that the non-uniform flow of latex down the former, prior to its setting, is high at a low set time. Thus, the latex possessing low stability and hence low set time gives rise to a significant curtaining effect, especially, down the former as it suffers some degree of flowing effects. Generally speaking, these results appear to agree satisfactorily with the visual examinations made of the test samples.

8.12 Physical properties of coagulant-dipped films

8.12.1 Introduction

This section is concerned with the effect of added ingredients upon the tensile properties, namely, tensile strength and elongation at break, of latex deposits in both the wet and dry state, prepared by coagulant dipping. The procedures for measuring these properties are described in Section 3.8.

8.12.2 Reproducibility of values of tensile strength and elongation at break

There are a number of factors which will obviously have a profound effect upon the reproducibility of the elongation at break and particularly tensile strength of latex deposits. These include the presence of foreign bodies and air bubbles in the deposit, the condition of the former, and also the variation of the thickness throughout the deposit. The latter seems to be the main problem for deposits formed by coagulant dipping. However, this problem was easily overcome by obtaining the deposit at a reasonable withdrawal rate of 1.3mm s^{-1}, followed by its immediate reversion (i.e., the deposit on its former was inverted immediately after withdrawal from the latex). If severe variation of thickness was evident in any deposit, then that deposit was rejected.

In order to demonstrate the reproducibility of tensile strength and elongation at break values, individual results of replicate determinations on test-pieces cut from the same wet latex deposit and from the same dry deposit are given in Tables 8.18 and 8.19 respectively. These results clearly show that it is reasonable to take an average of the four determinations on the same deposit.

8.12.3 Effect of various added ingredients

The results for the effect of added ingredients, namely, potassium laurate, potassium hydroxide, ammonia and ammonium acetate, upon the tensile strength and elongation at break of dry rubber deposits are shown in Figures 8.33 and 8.34 respectively. The effect of added magnesium chloride upon tensile properties will be discussed in Section 8.12.4. Generally, the values of both the tensile strength and elongation at break are relatively insensitive to the increased concentration of these added ingredients.

A similar absence of trend in tensile strength (Figure 8.35) and in elongation at break (Figure 8.36) of the wet-gel deposits is observed on increasing the level of added either potassium laurate or potassium hydroxide or ammonia or ammonium acetate. In this case, as expected, the tensile strength and elongation at break have much lower values. The tensile strength of the wet gel is approximately 5% that of the dry film. Shukri (29) found that the tensile strength of the wet-gel deposit is approximately 10% that of the dry deposit. The discrepancy is probably mainly a consequence of differences in the techniques used to determine the wet-gel strength. For example, Shukri determined the tensile strength of the wet rubber deposit at a standard rate of jaw separation of 500cm per minute, as compared to 20cm per minute in the present work. Due to the greater sensitivity of the latter, a more precise and accurate value is thought to be obtained.

Table 8.18 Replicate values of tensile strength and elongation at break of test-pieces cut from the same wet-gel deposit

sample number	tensile strength (MPa)	elongation at break (%)
1	1.4	170
2	1.5	190
3	1.3	160
4	1.4	170
mean (SD*)	1.4 (0.08)	173 (12.58)

* SD = standard deviation

Table 8.19 Replicate values of tensile strength and elongation at break of test-pieces cut from the same dry deposit

sample number	tensile strength (MPa)	elongation at break (%)
1	27.1	660
2	27.8	670
3	26.4	680
4	28.1	660
mean (SD*)	27.4 (0.76)	668 (9.57)

* SD = standard deviation

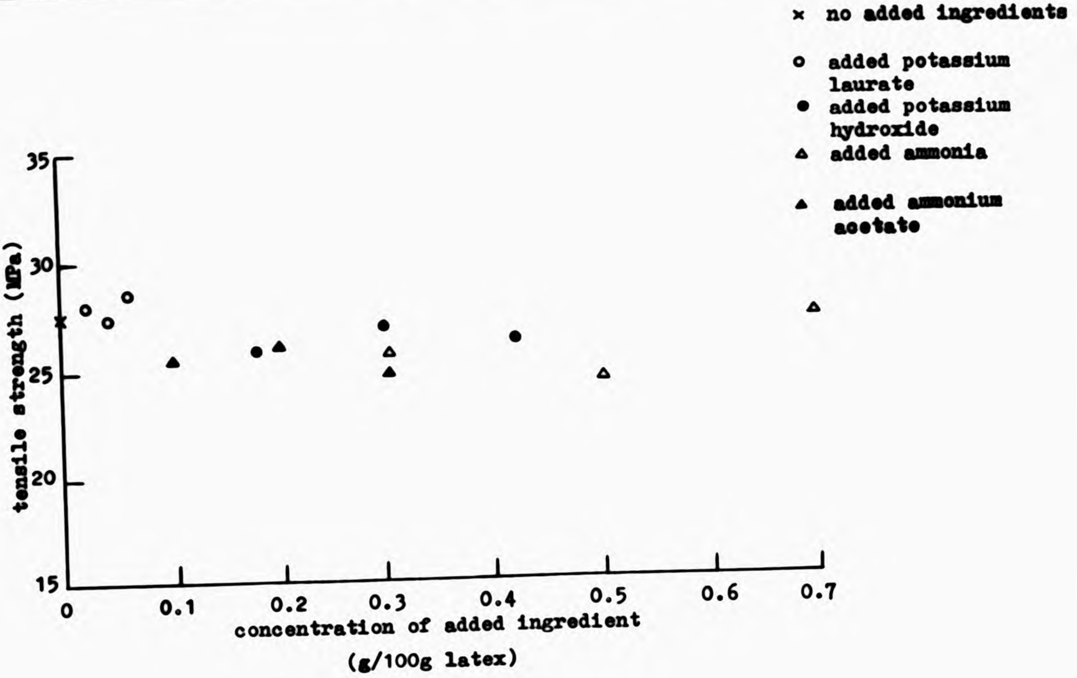


Figure 8.33 Effect of various added ingredients upon tensile strength of dry deposits

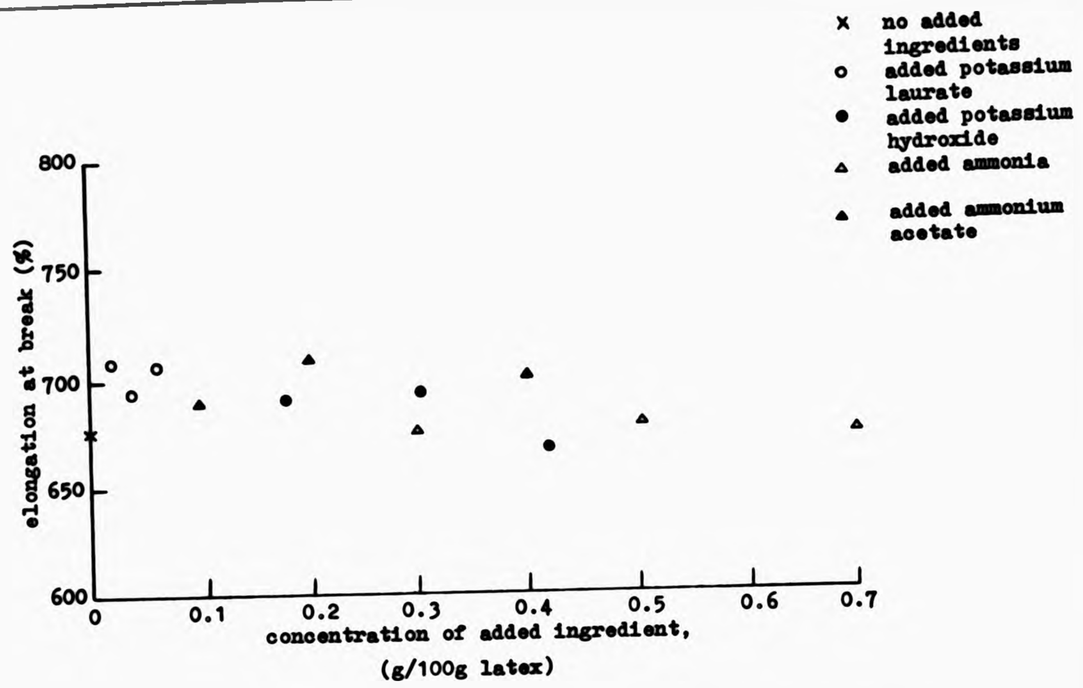


Figure 8.34 Effect of added ingredients upon elongation at break of dry deposits

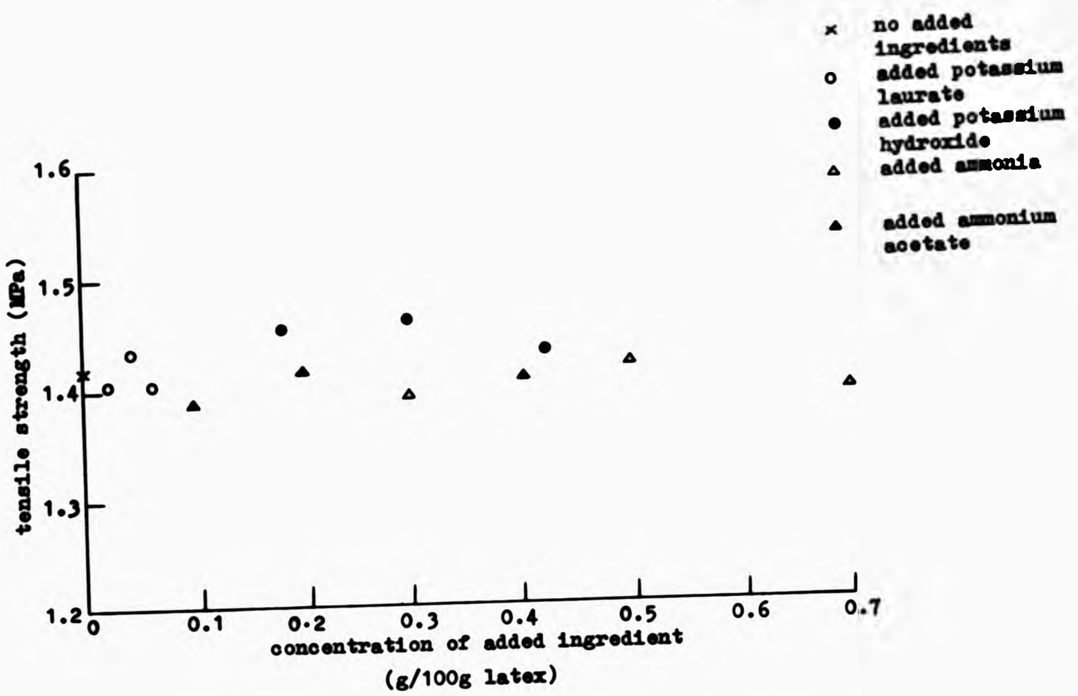


Figure 8.35 Effect of various added ingredients upon tensile strength of wet latex deposits

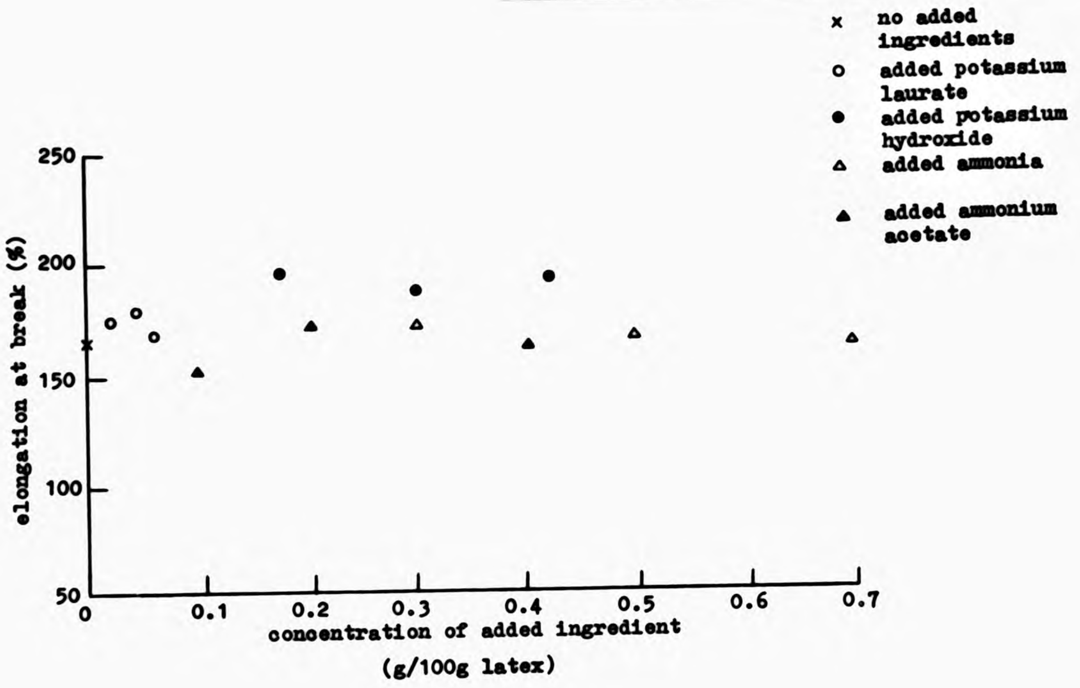


Figure 8.36 Effect of various added ingredients upon elongation at break of wet latex deposits

The effect of addition of soap upon the wet-gel strength is apparently inconsistent with the results reported by Shukri (29) and by Voyutskii et al. (30). These workers have shown that both the tensile strength and the elongation at break of the wet gels decrease with an increase in the soap content. This was explained as being a consequence of the increase in the degree of coverage of the particle surface by the stabiliser, thus affecting the ability of the latex particles to coalesce. However, the discrepancy between the present results and those reported previously may be attributable to the effect of leaching. Leaching removes a large proportion of the non-rubber constituents such as surface-active agents and other additives, and so facilitates inter-particle integration and the formation of a more homogenous film. This view is supported by the lower tensile strength of the unleached dry deposits compared with the higher tensile strength of the leached dry deposits, from the same latex compound. This effect is demonstrated in Figure 8.37 for films from latex compounds containing increased levels of added potassium laurate. From Figure 8.37, it is observed that the tensile strength of the unleached films is significantly lower than the tensile strength of the corresponding leached films. Also, the tensile strength of the unleached film decreases progressively with increased level of added potassium laurate.

8.12.4 Effect of added magnesium chloride

The results show that, on increasing the level of added magnesium chloride, the tensile strength, elongation at break and modulus at 100%, 300% and 500% elongations of a dry deposit, decrease progressively (Figures 8.38 and 8.39). Additionally, as expected, the tensile strength of the wet-gel deposit is much lower than that of the dry deposit (Figure 8.40). Also, the wet-gel strength is found to decrease progressively on increasing the level of added magnesium chloride. There are two possible explanations for these observations:

(i) The presence of added magnesium chloride, and also of other non-rubber constituents in the latex, may hinder the formation of a homogenous film, thereby producing lower strength films. However, since both the dry and the wet deposits were leached, the effect of these non-rubber constituents can be eliminated.

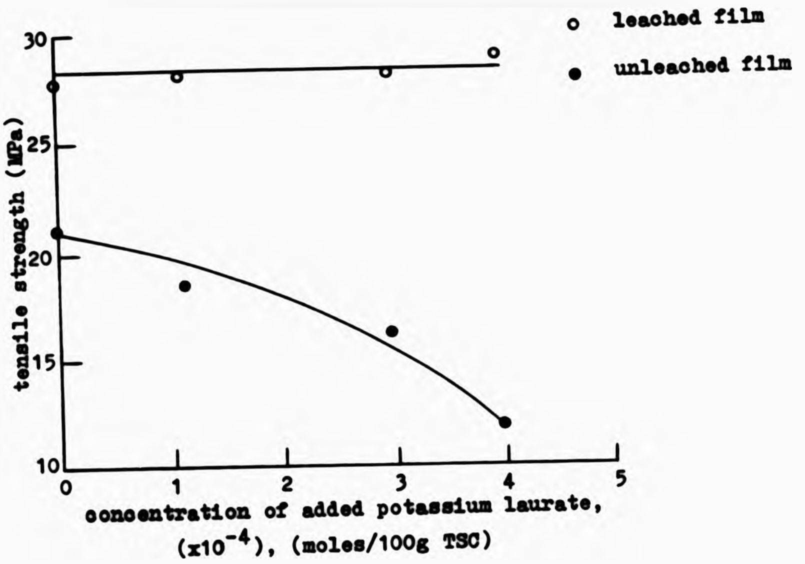


Figure 8.37 Comparison of tensile strength of leached and unleached dry deposits for films obtained from latex compounds containing increased levels of added potassium laurate

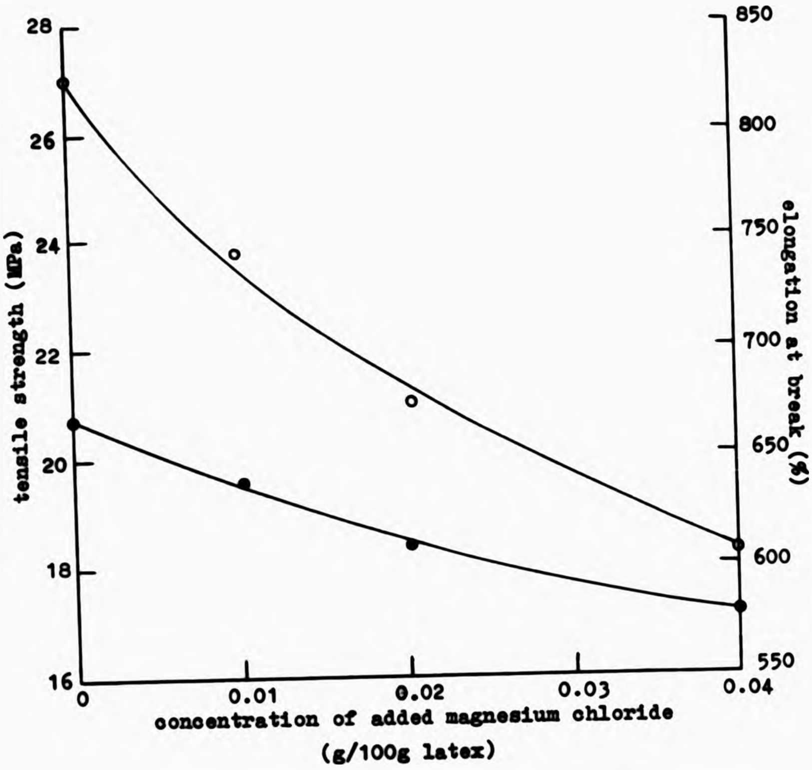


Figure 8.38 Effect of added magnesium chloride upon tensile strength, (o), and elongation at break, (●), of dry latex deposits

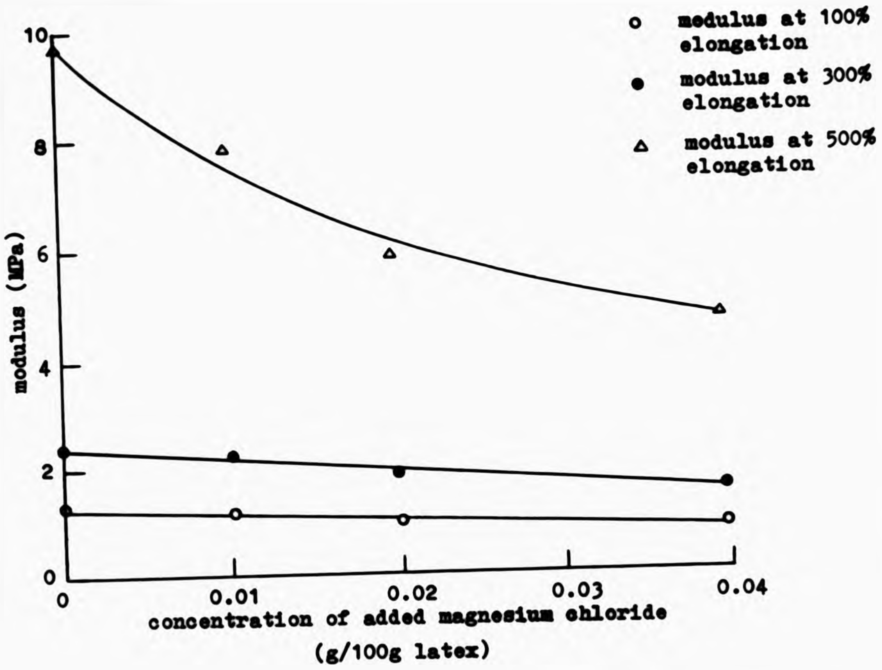


Figure 8.39 Effect of added magnesium chloride upon modulus at various elongations, of dry latex deposits

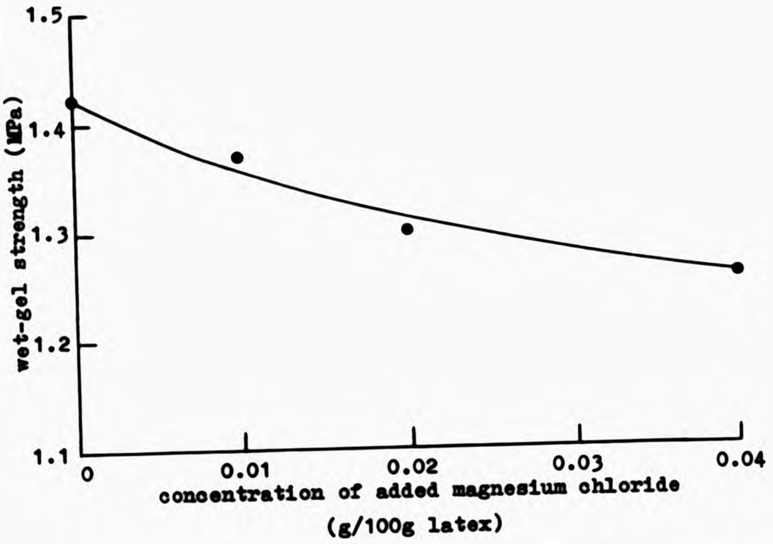


Figure 8.40 Effect of added magnesium chloride upon tensile strength of wet latex deposits

(ii) The addition of magnesium chloride may cause the formation of local coagulum. Thus, the increased degree of local coagulum formation by an increased level of added magnesium chloride may prevent the formation of a coherent film, thereby lowering the strength of the film. It may also interfere with the prevulcanisation reaction, and this might be the reason for the low modulus values.

This hypothesis of formation of local coagulum interfering with the prevulcanisation reaction has been tested further by determining the concentration of crosslinks present in the latex deposits, by swelling measurements. The procedure is described in Section 3.9 and the results are given in Figure 8.41. The results show that there is a progressive reduction in the concentration of crosslinks upon increasing the level of added magnesium chloride. Thus the swelling results are in accordance with the modulus results. It is proposed that the reduction in the concentration of crosslinks on increasing the level of added magnesium chloride may be a consequence of, possibly the formation of local coagulum which may have interfered with the ability of the latex particles to crosslink during the prevulcanisation reaction. This is thought to be a likely explanation, because magnesium chloride and other compounding ingredients were added to the latex before prevulcanisation. It is possible that the formation of local coagulum resulting from the addition of magnesium chloride may have entrapped these vulcanising ingredients. The effective concentration of these ingredients is therefore lowered, thereby reducing the crosslinks inserted during the prevulcanisation reaction.

Indirect evidence that the formation of local coagulum may be partly responsible for the reduced concentration of crosslinks during the prevulcanisation reaction, is obtained by considering the destabilising effects of various added ingredients. Despite using very low concentrations of solution of magnesium chloride, the destabilising effect of these divalent salts appears to be high. This would be expected. It may be argued, however, that added ammonium acetate and/or ammonia should also show similar effects upon tensile properties as magnesium chloride, as suggested earlier by the stability results. However, although the zinc oxide/ammonia/ammonium acetate system destabilises latex in a similar way to

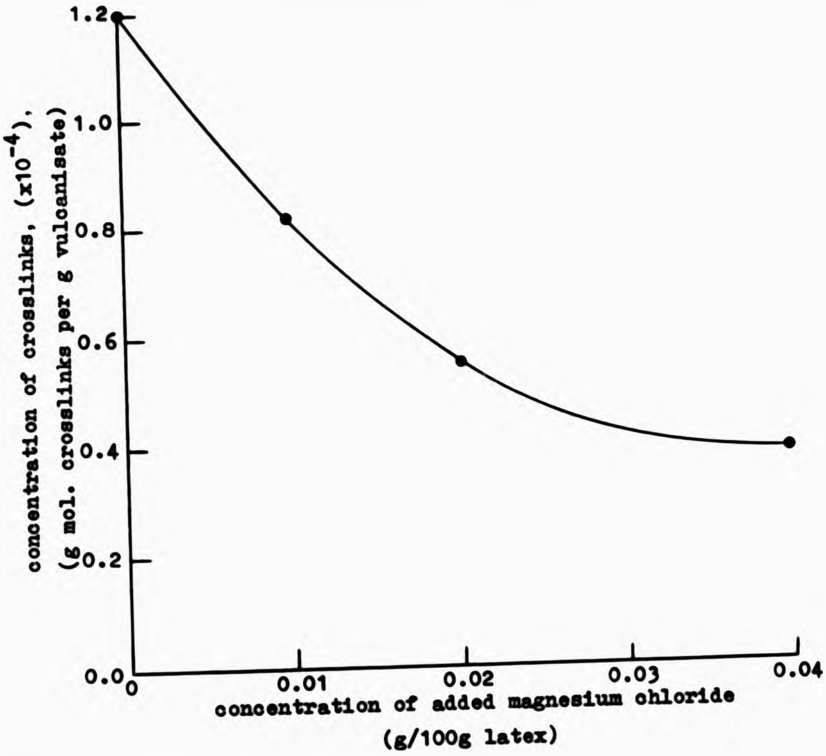


Figure 8.41 Effect of added magnesium chloride upon concentration of crosslinks, as determined by swelling experiment

divalent ions such as calcium and magnesium, there are some significant differences. Zinc ions in latex react with ammonia to give complex ammine cations. These cations form insoluble salts with all fatty-acid soaps having 12 or more carbon atoms, but do not appear to react in the same way with protein. It has been demonstrated that ammoniacal solutions of lactic casein are not affected by the addition of large amounts of zinc ammine salt solutions at any temperature below 60°C (31). This selective reaction of the ammoniated zinc ions may explain why salts tend to have a lesser destabilising effect upon NR latex compared with the extent of the destabilisation produced by, for example, magnesium ions. Thus, because the formation of local coagulum occurred only when magnesium chloride was added, this may well be the reason for the reduced concentration of crosslinks.

8.13 Summary

The study of the effect of certain added ingredients upon certain of the properties of latex throws light upon some aspects of the observed processibility variations. Principally, it has been found that the non-rubber materials which interfere with the stabilisation of latex also cause changes in the process properties and to a lesser extent, the physical properties of films from latex. For example, the rate of drying of films, set time and, to a small extent, the curtaining effect, all are affected by additions which bring about changes in the stability of the latex. There are one or more of the following factors which participate in the mechanism of the destabilisation of latex, depending upon the nature and amount of added ingredient. These include

1. effect of ionic strength
2. variation of surface charge of latex particles and hence of the Stern potential
3. interaction between an adsorbed surface active agent and an additive
4. interference with the ability of electric charges to promote hydration of the particles
5. formation of zinc ammine complexes
6. effects of steric stabilisation

The physical properties of coagulant-dipped films from prevulcanised latex, however, are found to be affected to a lesser extent, by the nature and amount of added ingredients. The added magnesium chloride appears to be an exception, probably due to its ability to cause an immediate coagulation. However, this aspect of this area of investigation is perhaps rather misleading, because leached films were used. It is thought that leaching extracts most of the non-rubber materials which may otherwise reduce the strength of the film. Thus, it would be desirable to repeat this aspect of the investigation using unleached films in order to ascertain the true effects of the added ingredients during the course of prevulcanisation and hence the quality of the finished dipped product.

Finally, indications have been obtained that the new test methods, namely, calcium stability test, microgel test, set time and curtaining effect, which were developed to gain a deeper understanding of the factors responsible for the stability of NR latex and hence for the quality of the finished dipped product, may prove to be useful.

CHAPTER 9 : CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

9.1 New test methods

9.1.1 Introduction

In the present study, various new test methods have been devised which may be useful to the latex industry. These test methods were developed in an attempt to gain a deeper understanding of the factors which are responsible for the colloid stability of NR latex, and which may hence have a bearing upon the quality of a finished product. The test methods are listed in subsequent sections.

9.1.2 Microgel test

Microgel may be defined as agglomerates of two or more rubber particles to form larger particles. At this stage, the original interface between the particles may or may not still exist. The microgel test was developed by performing both microscopic studies and nanosizer measurements. The former allowed a measure of size of microgel and its structural determination, and the latter allowed a quantitative measure of microgel.

9.1.3 Calcium stability test

Basically, the calcium stability test involves the measurement of coagulation time (or calcium stability time, CST). The CST is defined as the time taken for the latex containing 100g total solids to coagulate completely after the addition of a known weight of calcium sulphate in the form of an aqueous dispersion. The intention underlying the development of this test was to attempt to acquire some knowledge of the effect of calcium ions upon the stability of latex during repeated coagulant dipping. As expected, a reduction in the CST of the latex was found with repeated coagulant dipping. This is attributed to repeated coagulant dipping causing an increase in the calcium content of the latex through diffusion of calcium ions from the former into the bulk of the latex, thereby reducing the stability of this latex.

9.1.4 Set-time test

The set time of a dipped film is defined as the time taken for a known thickness of latex to set completely under controlled conditions of temperature and relative humidity. A linear relationship has been found between the set time and the weight (hence thickness since the area of the film was constant) of a dipped latex film. The set time increased with increasing weight of dipped latex film under the same conditions of temperature and relative humidity. It is postulated that when the initial thickness (or weight) of a drying dipped latex film is increased, there is a reduction in the tendency of the rubber particles to coalesce after a given time. This is mainly due to the average distance of separation between the particles after any given drying time, being greater for thicker films than for thinner films. As expected, as the temperature of a dipped film is increased, the set time decreases. This is attributed to the increase in the rate of evaporation of water. This enables the critical total solids content for setting to be attained more rapidly, thereby reducing the set time. In general, the coalescence of rubber particles is found to take place at about 83% total solids content.

9.1.5 'Curtaining effect' test

The 'curtaining effect' of a film obtained by latex dipping may be defined as the irregularities arising due to the non-uniform flow of latex down the former prior to its setting. It was found that when forming a film by straight dipping, factors such as the presence of grease on the former, creaming of the latex, disturbance of the former whilst being withdrawn from the latex, all give rise to the 'curtaining effect'. These observations confirm what has been known for many years, namely, that it is necessary to clean the formers thoroughly if satisfactory dipped products are to be obtained.

9.1.6 Effect of heating upon properties of NR latex

This investigation was carried out in order to acquire a deeper understanding of the effect of heating upon the properties of NR latex. Also, the effect upon properties of compounded latex was investigated. Principally, the latex was compounded with sulphur, zinc oxide and accelerator. It was found that some of the common properties like TSC, DRC and VFA No. are virtually unaffected upon heating both the uncompounded and compounded NR latex. However, properties like alkalinity and pH are reduced upon heating these latices. The reduced alkalinity is thought to be a consequence of reduced ammonia content in the latex due to a combination of evaporation of ammonia and the reaction of ammonia with fatty acids and amino acids formed by the hydrolysis of phospholipids and proteins respectively. This would also account for the reduction in pH. The hydroxyl ions are removed as a result of the reduction of acid anions, thus lowering the pH value.

An increase in KOH No., MST and CST is observed upon heating the latex, with and without the compounding ingredients. This increase is attributed to the further hydrolysis of lipids and proteins, such hydrolysis having been accelerated by heating the latex, thus yielding an increase in acid anions and a subsequent increase in KOH No. The adsorption of ammonium salts of the acid anions at the particle interface produces a higher surface charge and therefore, higher repulsive forces between approaching particles, thereby leading to an increase in both the MST and CST. Also, the viscosity and zinc ammonium acetate, ZAAV, are found to increase upon heating the uncompounded and compounded NR latex. The most probable cause for this increase is an increased degree of loose, reversible agglomeration of the particles, probably attributable to the denaturation of the proteins on heating. In the case of compounded latex, an additional factor responsible for the increase in ZAAV is thought to be that at increased temperatures the concentrations of zinc diammine and lower ammines is increased, and hence the reaction of the adsorbed stabiliser with an enhanced concentration of lower zinc ammine complexes increases. Thus the destabilisation of latex containing zinc ammine ions increases with an increase in temperature.

9.3 Rate of drying of dipped latex films

9.3.1 Introduction

In present work, a detailed investigation has been carried out into the rate of drying of both straight- and coagulant-dipped films formed from prevulcanised NR latex. Considerable progress has been made towards understanding of the mechanisms associated with the drying behaviour of these films. The principal findings are summarised in subsequent sections.

9.3.2 Straight-dipped films

A straight-dipped film prepared from prevulcanised NR latex was found to form a coherent film on the surface at an early stage of drying. This was thought to be mainly a consequence of gelation caused by the local drop in pH resulting from loss of ammonia at the surface, as is evidenced by the results of ammonia loss. It was found that there was an initial sharp drop in the ammonia content in less than 30s. The principal feature of this stage of drying is that the water passes through the surface by diffusion at a rate equal to that at which it is removed from the surface by evaporation. This conclusion is further supported by the linear relationship between the diffusion coefficient, D, and the evaporation coefficient, K. The rate of evaporation of water, R_E, from the surface depends upon the effective surface area, A_S, of the aqueous phase, and hence upon the aggregate size of the capillaries present in the surface, as follows:

$$R_E = KA_S$$

The diffusion coefficient for the diffusion of water through latex film was found to be of the order of $10^{-6}cm^2s^{-1}$, and the activation energy to be $1.4kJ\ mol^{-1}$. This suggests that the diffusion of water is not through the rubber itself, but through the capillaries formed on the surface during the early stages of drying of dipped latex films.

9.3.3 Coagulant-dipped films

An investigation of the drying behaviour in the later stages for coagulant-dipped films has not been carried out, but is believed to be a very slow process of diffusion. However, the early stages of the drying of wet latex gels formed by coagulant dipping can be divided into two regions. In Region I, which is an initial region of constant rate, the loss of water is principally by syneresis. Hence,

$$R_E = K$$

This region persists until the volume fraction of rubber has increased to 70–90%. The Region II begins when the rate of drying drops off rapidly to a value 15-25 times smaller than that in Region I. The main feature of this stage of drying is that the water passes through a capillary network formed by partial coalescence of the rubber particles, at a rate equal to that at which it is removed from the surface. Thus,

$$R_E = KA_S$$

The rate of loss of water is found to be strongly dependent upon the gel structure, as is evidenced by the results for gels produced at various dwell times under the conditions which favour the formation of a strong gel, for example, at short dwell times some water is forced out by syneresis. Other process variables such as the TSC of the latex and the concentration of the coagulant solution appear to have a negligible effect upon the gel structure, as is evidenced by effect upon the rate of evaporation of water.

A rather unexpected relationship between the diffusion coefficient, D, and the evaporation coefficient, K, (Figures 7.21 and 7.22) has been observed. This indicates that the drying behaviour of coagulant-dipped films can be divided into three distinct sections, labelled A, B and C respectively. In summary,

(a) in Section A, i.e., for gels produced at high dwell times (>60s):

$$\begin{matrix}\text{rate of}\\ \text{evaporation}\end{matrix} = \begin{matrix}\text{rate of}\\ \text{diffusion}\end{matrix} > \begin{matrix}\text{rate of}\\ \text{syneresis}\end{matrix}\ ;$$

(b) in Section B, i.e., for gels produced at mid-dwell times (45–60s):

$$\begin{matrix}\text{rate of}\\ \text{evaporation}\end{matrix} = \begin{matrix}\text{rate of}\\ \text{diffusion}\end{matrix} \gtrless \begin{matrix}\text{rate of}\\ \text{syneresis}\end{matrix}\ ;\ \text{and}$$

(c) in Section C, i.e., for gels produced at low dwell times (<45s):

$$\begin{matrix}\text{rate of}\\ \text{evaporation}\end{matrix} = \begin{matrix}\text{rate of}\\ \text{diffusion}\end{matrix} < \begin{matrix}\text{rate of}\\ \text{syneresis}\end{matrix}\ .$$

9.3.4 Comparison of drying behaviour of straight- and coagulant-dipped films

When a comparison of the drying behaviour of straight- and coagulant-dipped films was made, it was found that the expected syneresis occurred in the early stages of drying of coagulant-dipped films only. In addition, the rate of loss of water in terms of drying time per unit thickness for a coagulant-dipped film was considerably higher than that for a straight-dipped film. This is thought to be a consequence of syneresis which promotes drying in the case of coagulant-dipped films.

9.4 Effect of added ingredients upon processing properties of prevulcanised NR latex

9.4.1 Introduction

A systematic and comprehensive investigation was made of the effects of added ingredients upon the latex, process and physical properties of prevulcanised NR latex. The ingredients were added before prevulcanising the latex; thus it is possible that the added ingredients affected the prevulcanisation behaviour of the latex. A brief summary of the results and conclusions from this investigation is given in subsequent sections.

9.4.2 Latex properties

As expected, properties such as TSC and DRC remained relatively unaffected by increasing the level of added ingredients. However, the colloid stability of the latex, which was measured by either MST or ZAAV (or in some cases CST), was affected considerably by the nature and the amount of added ingredients. One or more of the following factors may participate in the mechanism of the colloidal destabilisation of latex, depending upon the nature and amount of added ingredient:

1. ionic strength effects
2. zinc ammine complexes formation
3. interaction between the added ingredient and the adsorbed fatty-acid soaps
4. interference with the ability of the electric charges

to promote hydration of the particles

5. steric stabilisation effects

An increase in the stability of the latex brought about by increasing the level of added soap is largely due to increased adsorption of soap anions at the rubber-aqueous phase interface, which increases the Stern potential and hence the stability of the latex. In the case of the addition of ammonia or ammonium acetate to prevulcanised NR latex containing zinc oxide, the formation of zinc ammine complexes is thought to be the main factor responsible for reducing the colloid stability. The destabilisation of latex brought about by the addition of metal salts is thought to be a consequence of interaction of the metal ions with adsorbed fatty-acid anions to form insoluble soaps. On increasing the level of added potassium hydroxide, the initial increase in the stability of latex containing zinc oxide, is most probably due to the reduced destabilising effect of zinc ions by potassium hydroxide. With further additions of potassium hydroxide, the stability of the latex is drastically reduced without apparently greatly affecting the charge on the particles. The reduction in colloid stability at high levels of potassium hydroxide addition is greater than can be accounted for merely by increased ionic strength. It is thus postulated that the excess potassium hydroxide probably interferes with the ability of the bound electric charges to promote hydration of the particles. The collapse of adsorbed steric stabilisers might also contribute to the effects upon both the MST and the viscosity.

The above findings are consistent with both the results of viscosity determinations and observations concerning microgel formation.

9.4.3 <u>Processing properties</u>

Principally, it has been found that the non-rubber substances which interfere with the colloid stabilisation of the latex also cause changes in the process properties of films from prevulcanised NR latex. The rate of drying of films, set time and, to small extent, the curtaining effect, are all affected by additions which bring about changes in the stability of the latex.

9.4.4 Physical properties

The physical properties of coagulant-dipped films from prevulcanised NR latex in both its wet and dry states have been found to be affected to a lesser extent, by the nature and amount of added ingredients. However, added magnesium chloride may cause the formation of local coagulum. Thus, the increased degree of local coagulum formation by an increased level of added magnesium chloride may prevent the formation of a coherent film, thereby lowering the strength of the film. Also, it is possible that the formation of local coagulum resulting from the addition of magnesium chloride may have entrapped the vulcanising ingredients, thus lowering the effective concentration of these ingredients. In so doing, the crosslinks inserted during the prevulcanisation reaction are lowered, thus giving rise to films of lower modulus. The swelling measurements are consistent with this hypothesis of formation of local coagulum interfering with the prevulcanisation reaction.

9.5 Suggestions for further work

This investigation of the relationships between latex properties, processing behaviour and product properties has increased our knowledge of the fundamental science underlying dipping processes. However, this investigation must be regarded as but a preliminary study of very complex processes. It has high-lighted some areas of study which are worthy of further work that may eventually provide quantitative explanations for some aspects of the processing behaviour of NR latex and may also enable decisions to be taken concerning the relative importances of the various effects.

9.5.1 Modification of calcium stability test

It appears that the new test methods may be useful. Particularly is this so far the calcium stability test, because it gives a rough indication to the changes in the stability of NR latex brought about by various added ingredients. In some cases, however, this test shows hardly any variation on adding certain ingredients, perhaps due to the catastrophic effect of calcium ions upon the colloid stability of the latex. Further work might usefully be undertaken to attempt to modify this test to extend its usefulness as a test for the colloid stability of latex like the mechanical stability test. Whereas the MST test endeavours to assess mechanical stability, the calcium stability test endeavours to assess chemical stability. Thus, it would be most useful to have a good test of this type. This could possibly be achieved by using calcium compounds of lower stability than the sulphate, or calcium complexes which release calcium ions at very low concentrations. The latter might be very useful if they were soluble in water.

9.5.2 Possible use of low-ammonia NR latex

To establish whether the formation of a coherent film on the surface at the early stages of drying, is an important factor in the overall drying process of straight-dipped films, further work should undertaken, perhaps using low-ammonia NR latex. It is expected that the use of low-ammonia latex would probably assist the formation of surface film which was thought to be mainly a consequence of gelation caused by the local drop in pH resulting from loss of ammonia at the surface. The outcome of this investigation might help to confirm the proposed mechanisms.

9.5.3 Measurement of the relative importances of processes which affect the overall drying behaviour of coagulant-dipped films

One major problem in this work was to distinguish between the processes of syneresis, diffusion and evaporation, because all three are believed to be interrelated in a complex manner. Although this work has gone some way to clarifying the relative contributions which these processes make to drying behaviour, further work is required to decide on the relative importances of these processes. If the nature and conditions under which these processes occur are varied, the relative contributions of rate of syneresis, rate of diffusion and rate of evaporation to the overall drying behaviour of coagulant-dipped films could be more accurately delineated.

9.5.4 Effect of added ingredients upon physical properties of unleached coagulant-dipped films

The physical properties of coagulant-dipped leached films from prevulcanised NR latex were found to be virtually unaffected by the natures and amounts of added ingredients. However, this aspect of this area of investigation is rather misleading. It is thought that leaching extracts most of the non-rubber materials which might otherwise affect the strength of the film. Thus, it would be desirable to repeat this aspect of the investigation using unleached films in order to ascertain the true effects of the added ingredients, present during the prevulcanisation, upon the properties of the final dipped film.

9.5.5 Effect of added ingredients upon processing properties of NR latex

A systematic and comprehensive investigation should be undertaken on the effects of added ingredients upon the processing properties using NR latex which does not contain compounded ingredients, especially zinc oxide. This is because, zinc oxide probably interferes with many of the reactions which may otherwise take place with certain added ingredients.

9.5.6 Use of model rubber latices

Because of the highly polydisperse nature of the rubber particles, and the complexity of the non-rubber constituents, NR latex is a very difficult substance to study. For these reasons, an investigation using well-defined model rubber latices might be helpful because the use of such latices would be expected to simplify the interpretation and analysis of the results. Model polyisoprene latices can be prepared by the emulsion polymerisation of isoprene under appropriate conditions. Control can be exercised especially over the non-rubber substances present in such latices. Investigations using these latices might provide additional information concerning the relationships between latex properties, processing behaviour and product properties, as well as clarifying certain ambiguous areas which have become evident from the present investigation.

APPENDIX A

Derivation of equation:

$$\% \text{ TAC} = \frac{17V}{10^5} \times \frac{50 + W_1}{W_2} \times \frac{100}{W_1}$$

where V is the titre volume of 0.01N sulphuric acid in ml, W_1 is the weight of latex on slide in grams, and W_2 is the weight of diluted latex in grams. Basically, the titration procedure was as follows:

weight of latex on slide, W_1, (g) —— add 50g water ——> total weight of diluted sample, $W_1 + 50$, (g)

weight of sample of diluted latex for titration, W_2, (g)

titration with 0.01N sulphuric acid

V = volume of acid required for titration

According to the above procedure, the argument runs as follows:

mass of NH_3 in titration sample, W_2, g $= (0.01V/1000) \times 17$ g

$$\therefore \text{ mass of } NH_3 \text{ in } 50+W_1 \text{ g of diluted latex} = \frac{17V}{10^5} \times \frac{50+W_1}{W_2} \text{ g}$$

$\therefore$ mass of NH_3 in W_1 g of undiluted latex $= \dfrac{17V}{10^5} \times \dfrac{50+W_1}{W_2}$ g

$\therefore$ mass of NH_3 in 100 g of undiluted latex $= \dfrac{17V}{10^5} \times \dfrac{50+W_1}{W_2} \times \dfrac{100}{W_1}$ g

$=$ % TAC by definition

APPENDIX B

Loss of ammonia calculation

It has been been hypothesised that the total loss of ammonia is made up of two components as follows:

total loss of ammonia = loss of ammonia by evaporation + loss of ammonia by reaction with extra acids formed during hydrolysis of lipids and proteins

1. Loss of ammonia by evaporation

The loss of ammonia by evaporation was determined to be 0.11g NH_3/100g aqueous phase by heating latex sample A and 0.17g NH_3/100g aqueous phase by heating latex sample C.

2. Loss of ammonia by reaction with extra acids

TSC of latex is 62% and DRC of latex is 60%. This means that 38% is water and this is where alkalinity is located.

100g solids = 100 x (38/62) = 61.3g aqueous phase

(i) Samples A and B

For sample A:

KOH No. = 0.62g KOH/100g latex solids
= 0.31g NH_3/100g aqueous phase

For sample B:

KOH No. = 0.79g KOH/100g latex solids
= 0.39g NH_3/100g aqueous phase

Thus, the amount of ammonia which reacted with the additional acids formed during the hydrolysis of lipids/proteins on heating the latex is,

0.39 - 0.31 = 0.08g NH_3/100g aqueous phase

(ii) Samples C and D

For sample C:

$$\text{KOH No.} = 0.65\text{g KOH/100g latex solids}$$
$$\equiv 0.32\text{g } NH_3\text{/100g aqueous phase}$$

For sample D:

$$\text{KOH No.} = 0.71\text{g KOH/100g latex solids}$$
$$\equiv 0.35\text{g } NH_3\text{/100g aqueous phase}$$

Thus, the amount of ammonia which reacted with the additional acids formed during the hydrolysis of lipids/proteins on heating the latex is,

$$0.35 - 0.32 = 0.03\text{g } NH_3\text{/100g aqueous phase}$$

3. Loss of ammonia by reaction with hydroxyl ions

$$pH = -\log_{10} [H^+]$$
$$\text{and } [H^+]\,[OH^-] = 1\text{x}10^{-14}\text{mol dm}^{-3}$$

Thus,

sample	pH	$[H^+]$ (mol dm^{-3})	$[OH^-]$ (mol dm^{-3})
A	11.41	$3.89\text{x}10^{-12}$	$2.57\text{x}10^{-3}$
B	10.32	$4.79\text{x}10^{-11}$	$2.09\text{x}10^{-4}$
C	10.70	$2.00\text{x}10^{-11}$	$5.00\text{x}10^{-4}$
D	10.50	$3.16\text{x}10^{-11}$	$3.16\text{x}10^{-4}$

The reduction of $[OH^-]$ (i.e., reduction of pH) is a result of H^+ reacting with OH^-.

$$H^+ + OH^- \rightleftharpoons H_2O$$

The H^+ is derived from the formation of acids by hydrolysis.

$$\begin{array}{l} -\text{COO}^{-}\text{H}^{+} \\ \text{NH}_4^{+}\text{OH}^{-} \end{array} \longrightarrow \begin{array}{l} -\text{COO}^{-}\ \text{NH}_4^{+} \\ +\ \text{H}_2\text{O} \end{array}$$

$$\begin{array}{l} 2\text{H}^{+}\text{PO}_4^{--} \\ 2\text{NH}_4^{+}2\text{OH}^{-} \end{array} \longrightarrow \begin{array}{l} (\text{NH}_4)_2\text{PO}_4 \\ +\ \text{H}_2\text{O} \end{array}$$

Every —COOH formed reacts with one OH^- ion and every PO_4^{--} formed reacts with two OH^- ions. Thus, on heating sample A, the amount of lipids hydrolysed (if no polypeptides are hydrolysed) is

$(2.57\text{x}10^{-3}-2.09\text{x}10^{-4})$ x 1/4 x 837 x 40/1000 g lipid/100g latex

i.e., the reduction of ammonia content by reaction with OH^- ions is therefore consistent with the further hydrolysis of 0.02g lipid/100g latex. However, in the case of samples C and D, potassium hydroxide was added to the latex. This will suppress the ionisation of NH_4OH.

APPENDIX C

Theoretical relative humidity calculation

Relative humidity, RH, is defined in two equivalent ways as follows:

- (a) as the ratio of the quantity of water vapour present in the atmosphere to the quantity which would saturate that atmosphere at the same temperature, expressed as a percentage;
- (b) as the ratio of the pressure of water vapour present in the atmosphere to the vapour pressure of water at the same temperature, expressed as a percentage.

The theoretical relative humidity, RH_T, at any temperature can be calculated, if experimental relative humidity, RH_E, at one temperature is known. For the purpose of this exercise, it was decided to take a temperature of 35°C at which RH_E was 25% as the base value.

1. Calculation of water vapour pressure at this temperature, $(P_1)_{35}$

At this temperature, saturated water vapour pressure, $(P_S)_{35}$, is 5627Nm^{-2}, and relative humidity, $(RH_E)_{35}$, is given by,

$$(RH_E)_{35} = \frac{(P_1)_{35}}{(P_S)_{35}} \times 100$$

or

$$(P_1)_{35} = \frac{(RH_E)_{35}(P_S)_{35}}{100}$$

$$= 1407\text{Nm}^{-2}$$

2. Calculation of number of moles, x, of water in the drying cabinet

It is thus possible to calculate number of moles of water in the drying cabinet required to produce the pressure $(P_1)_{35}$. Thence,

$$(P_1)_{35} = x.RT_{35}/V$$

where x is the number of moles, R is the gas constant (8.314J $mol^{-1}K^{-1}$), T_{35} is the absolute temperature and V is the volume of drying cabinet ($0.1435m^3$). From this equation, it is found that

$$x = \frac{(P_1)_{35}V}{RT_{35}} = 0.079 \text{ moles}$$

3. Calculation of water vapour pressure at any other temperature T'

If there are x moles of water always in the drying cabinet, then the water vapour pressure at any other temperature T', P_2', can be calculated as follows:

$$P_2' = \frac{x.RT'}{V}$$

or $$P_2' = [(RH_E)_{35}(P_S)_{35}/100]\ T'/T_{35}$$

4. Calculation of theoretical relative humidity, RH_T', at any other temperature T'

Having calculated the water vapour pressure at any temperature T', i.e., P_2', the relative humidity at that temperature can be calculated as follows:

$$RH_T' = \frac{P_2'}{P_S'} \times 100 = \left[\frac{(RH_E)_{35}(P_S)_{35}}{100}\ \frac{T'}{T_{35}} \times \frac{100}{P_S'}\right]$$

where P_S' is the saturated vapour pressure at temperature T'. This equation gives

$$RH_T' = 457 \times \frac{T'}{P_S'}$$

APPENDIX D

By definition:

$$\tanh u = \frac{\sinh u}{\cosh u} = \frac{(e^{u} - e^{-u})/2}{(e^{u} + e^{-u})/2} = \frac{e^{2u} - 1}{e^{2u} + 1} \qquad (1)$$

The equation

$$\tanh \frac{\xi}{4} = \tanh \frac{\xi_o}{4} . e^{-\lambda x}$$

can be written in the form

$$\xi = 4 \tanh^{-1} \left| \tanh \frac{\xi_o}{4} . e^{-\lambda x} \right| = 4 \tanh^{-1} (\gamma e^{-\lambda x}) \qquad (2)$$

where $\gamma = \tanh \frac{\xi_o}{4} = \frac{e^{\xi_o/2} - 1}{e^{\xi_o/2} + 1}$ by equation (1).

Now suppose that $x = \tanh u$. Then by equation (1)

$$x = \frac{e^{2u} - 1}{e^{2u} + 1}$$

$$\therefore \quad x(e^{2u} + 1) = e^{2u} - 1$$

$$\therefore \quad e^{2u}(x - 1) = - 1 - x$$

$$\therefore \quad e^{2u} = \frac{1 + x}{1 - x}$$

$$\therefore \quad u = \frac{1}{2} \ln \frac{1 + x}{1 - x} \qquad (3)$$

But if $x = \tanh u$, then it follows that $u = \tanh^{-1} x$. Hence equation (3) gives

$$\tanh^{-1} x = \frac{1}{2} \ln \frac{1 + x}{1 - x} \qquad (4)$$

Applying equation (4) to equation (2) gives

$$\xi = 2 \ln \frac{1 + \gamma e^{-\kappa x}}{1 - \gamma e^{-\kappa x}} \text{, i.e., } \psi = \frac{2kT}{ze} \ln \frac{1 + \gamma e^{-\kappa x}}{1 - \gamma e^{-\kappa x}}$$

because $\xi = ze\psi/kT$

REFERENCES

CHAPTER 1

1. Gorton, A.D.T. and Pendle, T.D., J. Nat. Rubb. Res., I, 122, (1986).
2. Bateman, L., Ed., "The Chemistry and Physics of Rubber-like Substances", Chapter 3, John Wiley, New York, (1963).
3. Chen, S.F. and Ng, C.S., Rubb. Chem. Technol., 57 (2), 243, (1984).
4. Archer, B.L. and Cockbain, E.G., Biochem. J., 75, 236 (1960).
5. Altman, R.F.A., Archief Voor de Rubbercultuur in de Nederlandsch, Indies, 25, 1-13, (1941).
6. Bateman, L., Ed., "The Chemistry and Physics of Rubber-like Substances", Chapter 4, John Wiley, New York, (1963).
7. Gorton, A.D.T. and Pendle, T.D., Rubb. Chem. Technol., 51, 986, (1978).
8. Blackley, D.C., Burgar, W.F.H., Shukri, B.A.W., Mechanisms of Formation of Latex Deposits by Coagulant Dipping, Ph.D. Thesis, (1982).
9. Medalia, A.I., Townsend, H.B. and Grover, H.N., Anal. Chem., 26, 697, (1954).
10. Philpott, M.W., Activation of Sulphur Bearing Vulcanisation Accelerators and Curing Agents, Proc. 4th Rubb. Technol. Conf., London, p.470, (1962).
11. Pendle, T.D. and Gorton, A.D.T., Rubb. Chem. Technol., 51, 986, (1978).
12. Schidrowitz, P., US Pat., 1, 443 149, (1923).
13. Schidrowitz, P., J. Soc. Chem. Ind., 42, 7234, (1923).
14. Schidrowitz, P., India Rubber World, 73, 140, (1925).
15. Schidrowitz, P., Ind. Eng. Chem., 18, 1147, (1926).
16. Arora, B.R., M.Sc. Project Thesis, LSPT, London, (1986).
17. Gazeley, K.F., Plast. and Rubb. Inst., Emulsion Polymers Conf., London, 16-17 June, (1982).
18. Pendle, T.D. and Weiss, G.H., Proc. Int. Rubb. Conf., Kuala Lumpur, 5, 135, (1975).
19. Gorton, A.D.T., Latex Dipping 1, J.R.R.I., Malaysia, 20, 27, (1968).
20. Roberts, A.D., Ed., "Natural Rubber Science and

Technology", Oxford Sci. Publications, MRPRA, Chapters 3 and 4, (1988).
21. Gorton, A.D.T. and Iyer, G.C., J. Rubb. Inst., Malaysia, 23 (4), 263, (1973).
22. Sandomirskii, D.M. and Korrsunskii, B.L., Sov. Rubb. Technol., 20 (5), 15, (1961).
23. Gorton A.D.T., J. Rubb. Res. Inst., Malaysia, 20 (1), 27, (1967).
24. Gorton, A.D.T. and Pendle, T.D., Proceed. Int. Rubb. Conf., Kuala Lumpur, (1985).
25. Gorton, A.D.T. and Pendle, T.D., J. Nat. Rubb. Res., 1 (2), 122-134, (1986).
26. Jurado, C.W. and Mayan, K.G., Rubb. Chem. Technol., 59, 84-102, (1986).
27. Chong, K.L. and Porter, M., Int. Polym. Latex Conf., London, Preprint No.16, (1978).
28. Gorton, A.D.T., Int. Rubb. Conf., Kiev, (1978).
29. Loh, A.C-P., Ph.D. Thesis, CNAA, (1982).
30. Mahr, T.G., J. Phys. Chem., 74, 2160, (1970).
31. Shukri, B.A.W., Ph.D. Thesis, CNAA, (1982).
32. Gouw, K.A., B.Sc. Project Thesis, NCRT, London, (1970).
33. Teoh, S.C., B.Sc. Project Thesis, NCRT, London, (1971).

Chapter 2

1. Medalia, A.I., Townsend, H.B. and Grover, H.N., Analy. Chem. 26 (4), 697, (1954).
2. Savinkova, A.M., Voyutskii, S.S., Chernaya, V.V. and Arinkina, K.L., Sov. Rubb. Technol., 18 (3), 19, (1959).
3. Golberg, I.I., et al., Authors Certificate No. 126638 from I/III/1960, Byull. Izobret., 5, 43, (1960).
4. Shukri, B.A.W., Ph.D. Thesis, CNAA, (1982).
5. Shepelev, M.I., Sandomirskii, D.M., Chernaya, V.V. and Trefimovich, D.P., Sov. Rubb. Technol., 21 (1), 17, (1962).
6. Savinkova, A.M., Voyutskii, S.S., Chernaya, V.V. and Arinkina, K.L., Sov. Rubb. Technol., 18 (3), 19, (1959).
7. Shepelev, M.I., Trofimovich, D.P., Sandomirskii, D.M. and Maizelis, B.A., Sov. Rubb. Technol., 22 (8), 23, (1963).
8. Voyutskii, S.S., Savinkova, A.M. and Chernaya, V.V., Sov. Rubb. Technol., 21 (8), 7, (1962).
9. Sandomirskii, D.M. and Chernaya, V.V., Trans. Inst. Rubb. Ind., 1, 29, (1954).
10. Vdovchenkova, M.K. and Chernaya, V.V., Sov. Rubb.

Technol., 21 (5), 5, (1962).
11. Thorsrud, A., Rubb. Chem. Technol., 28, 1175, (1955).
12. Grubman, Y.V., Trofimovich, D.P. and Chernaya, V.V., Sov. Rubb. Technol., 27 (5), 24, (1968).
13. Gorton, A.D.T., Int. Rubb. Conf., Kiev, (1978).
14. Flint, C.F., "The Chemistry and Technology of Rubber Latex", London, 387, (1938).
15. De Vries, A.J., "Report on the Symposium on Rubber", Delft, p.22-27, (1936).
16. Noble, R.J., "Latex in Industry", New York, p.158-246, (1936).
17. Kirchhof, F., Kautschuk, 3, 239-245, 256-261, (1927).
18. Rao, N.V.C., Winn, H. and Shelton, J.R., Ind. Eng. Chem., 44, 576, (1952).
19. Martinon, M.N., Rev. Gen. Caout., 28, 109, (1951).
20. Gorton, A.D.T., NR Technol., 6 (3), 52, (1975).
21. Gorton, A.D.T., NR Technol., 10 (1), 9, (1979).
22. Humphreys, N.C.H. and Wake, W.C., Trans. Inst. Rubb. Ind., 25, 334, (1950).
23. Sutton, S.D., Trans. Inst. Rubb. Ind., 27 (4), 193, (1951).
24. Philpott, M.W., J. Rubb. Res. Inst., Malaya, 22 (5), 441, (1969).
25. Carl, J.C., "Neoprene Latex", 14, (1962).
26. Bradford, E.B., J. Appl. Physics, 23, 609, (1952).
27. Guzman, J.A.M., Ph.D. Thesis, NCRT, London, (1977).
28. Roberts, A.D., Ed., "Natural Rubber Science and Technology", Oxford Sci. Publications, MRPRA, p.79, (1988).
29. Humphreys, N.C.H. and Wake, W.C., Inst. Rubb. Ind., 25, 334, (1950).
30. Blackley, D.C., "High Polymer Latices", Applied Science Publishers Ltd., London, p.386-399, (1966).
31. Loh, A., Ph.D. Thesis, PNCRT, (1982).
32. Merrill, R.W.T., M.Phil. Thesis, CNAA, (1988).
33. Brodnyan, J.G. and Konen, T., J. Appl. Polym. Sci., 8, 687-697, (1961).
34. Sheetz, D.P., J. Appl. Polym. Sci., 9, 3759-3773, (1965).
35. Willhoit, D.L., TAPPI, 51, 25-33, (1968).
36. De La Court, F.H., Xth FATIPEC Congr., 293, (1970).
37. Mahr, T.G., J. Phys. Chem., 74, 2160, (1970).
38. Bertha, S.L. and Ikeda, R.M., J. Appl. Polym. Sci., 15 (1), 105, (1971).
39. Vanderhoff, J.W., Bradford, E.B. and Carrington, W.K., J.

Polym. Sci., Symposium No. 41, 155-174, (1973).

40. Gazeley, K.F. and Swinyard, P.E., NR Technol., 18 (1200), 4, (1987).
41. Dillon, R.E., Matheson, L.A., and Bradford, E.B., J. Colloid Sci., 6, 108, (1951).
42. Brown, G.L., J. Polym. Sci., 22, 423, (1956).
43. Schuller, H., Farbe Lack, 6 (74), 561, (1968).
44. Sukhareva, L.A., Kiselev, M.R. and Zubov, Kolloid Zh., 29, 206, (1967).
45. Voyutskii, S.S., J. Polym. Sci., 32, 528, (1958).
46. Voyutskii, S.S., Polymer Reviews, Interscience, New York, Vol. 4, Chapter I-IV, (1963).
47. Vanderhoff, J.W. and Bradford, E.B., J. Macromol. Chem. 1, 335, (1966).
48. Hansen, C.M., Ind. Eng. Chem., Prod. Res. and Dev., 13, 150-152, (1974).
49. Andrews, M.D., J. Paint Technol., 46 (598), 40-48, (1974).
50. Sullivan, D.A., J. Paint Technol., 47 (610), 60-67, (1975).
51. Blackley, D.C., "High Polymer Latices", Vol. 1, Applied Science Publishers Ltd., London, (1966).
52. Bateman, L., Ed., "The Chemistry and Physics of Rubber-like Substances", Chapter 4, John Wiley, New York, (1963).
53. Blackley, D.C., Salleh, B.M. and Twaits, R., Plastics and Rubber: Materials and Applications, 4, 77, (1979).
54. Blackley, D.C., Loha, S. and Twaits, R., Proc. Int. Polym. Latex Conf., London, (1978).
55. Feigin, R.I. and Napper, D.H., J. Colloid Interface Sci., 75 (2), 567, (1980).
56. Feigin, R.I. and Napper, D.H., J. Colloid Interface Sci., 74 (2), 567, (1980).
57. Verhaar, G., Rubb. Chem. Technol., 32, 1627, (1959).
58. Blackley, D.C. and Ong, E.K., J. Inst. Rubb. Ind., 4, 17-20, (1970).
59. Gorton, A.D.T. and Pendle, T.D., Int. Rubb. Conf., Kuala Lumpur, Preprint, (1985).
60. Gorton, A.D.T. and Pendle, T.D., J. Nat. Rubb. Res., 1 (2), 122-134, (1986).
61. Bjerrum, J., "Metal Ammine Formation in Aqueous Solution", Hasse and Son, Copenhagen, (1941).
62. Kray, G.M. and Van den Tempel, M., Trans. Inst. Rubb. Ind., 28, 144, (1952).

63. Flint, C.F., Rubb. Chem. Technol., 23, 691, (1950).
64. Madge, E.W., Collier, H.M. and Newnham, J.L.M., Proc. Third Rubb. Technol. Conf., p.67, (1954).
65. Newnham, J.L.M., Trans Inst. Rubb. Ind., 29, 160, (1953).
66. McRoberts, T.S., Proc. Third Rubb. Technol. Conf., p.38, (1954).
67. Gorton, A.D.T. and Pendle, T.D., Rubb. Chem. Technol., 51, 986, (1978).
68. Madge, E.W., Collier, H.M. and Duckworth, I.H., Trans. Inst. Rubb. Ind., 28, 15, (1952).
69. Blackley, D.C., Nor Aisah, bt. A.A. and Twaits, R., Plastics and Rubber: Materials and Applications, 4, 77, (1979).
70. Blackley, D.C. and Azas, M., Plastics and Rubber: Materials and Applications, 2, 57, (1980).
71. Blackley, D.C. and Haynes, A.C., Plastics and Rubber: Materials and Applications, 1 (1), 73, (1981).
72. Loha, S., M.Phil. Thesis, CNAA, (1975).
73. Tan, K.Y., Ph.D. Thesis, CNAA, (1982).
74. Dawson, H.G., Analyt. Chem., 21, 1066, (1949).
75. Minoura, Y., Kautschuk Und. Gummi. Kunststoffe, 19, 688, (1966).
76. Blackley, D.C., "High Polymer Latices", Applied Science Publishers Ltd., London, p.454, (1966).
77. Martin, G., "Proc. 2nd Rubb. Technol. Conf.", London, p.319, (1948).
78. Madge, E.W., Trans. Inst. Rubb. Ind., 28, 207, (1962).
79. Deryagin, B.V. and Landau, L., Acta Phys. Chem., 14, 633, (1941).
80. Verwey, E.J.W. and Overbeek, J.Th.G., "Theory of the Stability of Lyophobic Colloids", Elsevier, (1948).
81. Novotny, C.K. and Jordon, W.F., Ind. Engng. Chem., Anal. Edition, 13, 189, (1941).
82. Van Dalfsen, J.W., Rubb. Chem. Technol., 14, 315, (1941).
83. Lepetit, F., Trans. Inst. Rubb. Ind., 23, 104, (1947).
84. Murphy, E.A., Proc. Rubb. Technol. Conf., p.151, (1938).
85. Kidder, G.A., India Rubber World, 124, 563, (1951).
86. Gorton, A.D.T., Rubb. Chem. Technol., 45, 1202, (1972).
87. Wren, W.G., Trans. Inst. Rubb. Ind., 18, 91, (1942).
88. Van Gils, G.E., Rubb. Chem. Technol., 25, 641, (1952).
89. Cassagne, P., Rubb. Chem. Technol., 25, 303, (1952).
90. Nithi-Uthai, B., Ph.D. Thesis, FNCRT, London, (1977).
91. Van Gils, G.E., India Rubber World, 125, 317, (1951).
92. McRoberts, T.S., Rubb. Chem. Technol., 30, 254, (1957).

93. Wechsberg, H.E., Ph.D. Thesis, University of London, (1955).

Chapter 3

1. Flory, P.J. and Rehner, J., J. Chem. Phys., 11, 512, (1943).
2. Flory, P.J., "Principles of Polymer Chemistry", Cornell University Press, New York, (1953).
3. Sheehan, C.J. and Bisio, A.L., Rubb. Chem. Technol., 39 (1), 149, (1966).

Chapter 4

1. Calvert, K.O., Plastics and Rubber: Materials and Applications, 2, 59, (1977).
2. Weast, R.C., "Handbook of Chemistry and Physics", The Chemical Rubber Co., 51st Ed., Ohio, (1970-1971).

Chapter 5

1. Martosugito, I.H., M.Sc. Project Thesis, CNAA, (1987).
2. Nithi-Uthai, B., Ph.D. Thesis, FNCRT, London, (1977).
3. Gorton, A.D.T. and Pendle, T.D., Proceed. Int. Rubb. Conf., Kuala Lumpur, (1985).
4. Gorton, A.D.T. and Pendle, T.D., J. Nat. Rubb. Res., 1 (2), 122-134, (1986).
5. Verhaar, G., Rubb. Chem. Technol., 29, 1484, (1956).
6. Bachle, B., Rubb. Chem. Technol., 10, 675, (1937).
7. Bateman, L., Ed., "Chemistry and Physics of Rubber-like Substances", John Wiley, New York, p.73, (1963).
8. Krray, G.M. and Van Den Tempel, M., Trans. Inst. Rubb. Ind., 28, 144, (1952).
9. Thong, C., NCRT Project Thesis, (1973).
10. Schidrowitz, P., Brit. Pat., 208, 235, (1920); US Pat. 1, 440, 371 (1923).
11. Blackley, D.C., Nor Aisah, bt A.A. and Twaits, R., Plastics and Rubber: Materials and Applications, 4, 77, (1979).
12. Tan, K.Y., Ph.D. Thesis, CNAA, (1982).
13. Jurado, C.W. and Mayhan, K.G., Rubb. Chem. Technol., 59, 84-102, (1986).

Chapter 6

1. Weast, R.C., "Handbook of Chemistry and Physics", The Chemical Rubber Co., 51st Ed., Ohio, (1970-1971).
2. Fick, A., Ann. Phys., 94, 59, (1855).
3. Gazeley, K.F., Int. Conf., The Plastics and Rubber Institute, Session C, No.18, London, 21-22 May, (1985).
4. Gick, M.M.S., Ph.D. Thesis, PLSPT, London, (1988).
5. Vanderhoff, J.W., Polymer News, 3 (4), 194, (1977).
6. Vanderhoff, J.W., Bradford, E.B. and Carrington, W.K., J. Polym. Sci., Symposium No. 41, 155, (1973).
7. Gazeley, K.E. and Swinyard, P.E., NR Technol., 18 (4), 1200, (1987).
8. Frensdorff, H.K., J. Polym. Sci., 2A, 341, (1964).
9. Prehlein, G.W., Vanderhoff, J.W. and Witmeyer, R.J., ACS Polymer Preprints, Philadelphia, 16 (1), 268, (1975).

Chapter 7

1. Sheetz, D.P., J. Appl. Polym. Sci., 9, 3759, (1965).
2. Vanderhoff, J.W., Bradford, E.B. and Carrington, W.K., J. Polym. Sci., Symposium No. 41, 155, (1973).
3. Gazeley, K.F. and Swinyard, P.E., NR Technol., 18 (4), 1200, 81, (1987).
4. Shukri, B.A.W., Ph.D. Thesis, CNAA, (1982).
5. Gorton, A.D.T., J. Rubb. Res. Inst. Malaysia, 20 (1), 27, (1967).
6. Sandomirskii, D.M. and Korsunskii, B.L., Sov. Rubb. Technol., 20 (5), 15, (1961).
7. Shepelev, M.I., Sandomirskii, D.M., Chernaya, V.V. and Trefimovich, D.P., Sov. Rubb. Technol., 21 (1), 17, (1962).
8. Savinkova, A.M., Voyutskii, S.S., Chernaya, V.V. and Arinkina, K.L., Sov. Rubb. Technol., 18 (3), 19, (1959).
9. Shepelev, M.I., Trofimovich, D.P., Sandomirskii, D.M. and Maizelis, B.A., Sov. Rubb. Technol., 22 (8), 23, (1963).
10. Voyutskii, S.S., Savinkova, A.M. and Chernaya, V.V., Sov. Rubb. Technol., 21 (8), 7, (1962).
11. Sandomirskii, D.M. and Chernaya, V.V., Trans. Inst. Rubb. Ind., 1, 29, (1954).

Chapter 8

1. Napper, D.H., J. Colloid Interface Sci., 32, 106, (1970).
2. Napper, D.H., Ind. Eng. Chem. Prod. Res. Develop., 9 (4), 467, (1970).
3. Napper, D.H., J. Colloid Interface Sci., 58 (2), 390, (1977).
4. Verwey, E.J.W. and Overbeek, J.Th.G., "Theory of the Stability of Lyophobic Colloids", Elsevier, (1948).
5. Deryagin, D.V. and Landau, L., Acta Phys. Chim. URSS, 14, 633, (1941).
6. Hamaker, H.C., Physica, 4, 1058, (1937).
7. Kruyt, H.R., Colloid Science, Elsevier: "Irreversible Systems", Vol. 1, p.115-193, (1952).
8. Stern, O., Elektrochem., 30, 508, (1924).
9. Langmuir, I., J. Chem. Phys., 6, 893, (1938).
10. Madge, E.W., Collier, H.M. and Duckworth, I.H., Trans. Inst. Rubb. Ind., 28, 15, (1952).
11. Blackley, D.C., Nor Aisah, bt A.A. and Twaits, R., Plastics and Rubber: Materials and Applications, 4, 77, (1979).
12. Bateman, L., Ed., "The Chemistry and Physics of Rubber-like Substances", John Wiley, New York, Chapter 4, (1963).
13. Tan, K.Y., Ph.D. Thesis, CNAA, (1982).
14. Blackley, D.C., "Emulsion Polymers and Emulsion Polymerisation", Ed. Bassett and Hamielec, ACS Symposium Series 165, p.171, (1981).
15. Neiman, R.E. and Lyashenko, O.A., Kolloid. Zh., 24, 494, (1962).
16. Neiman, R.E. and Verezhnikov, V.N., Kolloid. Zh., 24, 599, (1962).
17. Nithi-Uthai, B., Ph.D. Thesis, FNCRT, (1977).
18. Calvert, K.O., Plastics and Rubber: Materials and Applications, 2, 59, (1977).
19. Gorton, A.D.T. and Pendle, T.D., Proceed. Int. Rubb. Conf., Kuala Lumpur, (1985).
20. Gorton, A.D.T. and Pendle, T.D., J. Nat. Rubb. Res., 1 (2), 122-134, (1986).
21. Greene, B.W. and Saunders, F.L., J. Coll. Int. Sci., 33, 393, (1970).
22. Minoura, Y., Kautschuk Und. Gummi., Kunstoffe, 19, 688, (1966).
23. Loha, S., M.Phil. Thesis, CNAA, (1977).

24. Dawson, H.G., Analyt. Chem., 21, 1066, (1949).
25. Dawson, H.G., Rubber World, 135, 239, (1956).
26. Ahmed Zamani, B.A., NCRT Project Thesis, (1973).
27. Gazeley, K.E. and Swinyard, P.E., NR Technol., 18 (4), 1200, (1987).
28. Vanderhoff, J.W., Bradford, E.B. and Carrington, W.K., J. Polym. Sci., Symposium No. 41, 155, (1973).
29. Shukri, B.A.W., Ph.D. Thesis, CNAA, (1982).
30. Voyutskii, S.S., Savinkova, A.M. and Chernaya, V.V., Sov. Rubb. Technol., 21 (8), 7, (1962).
31. Roberts, A.D., Ed., "Natural Rubber Science and Technology", Oxford Sci. Publications, MRPRA, p.78, (1988).
32. Heller, W. and Pugh, T.L., J. Chem. Phys., 22, 1778, (1954).
33. Fischer, E.W., Kolloid Z., 160, 120, (1958).
34. Bagchi, P., J. Colloid Interface Sci., 47, 86, (1974).
35. Fuchs, N., Z. Phys., 89, 736, (1934).
36. Weast, R.C., "Handbook of Chemistry and Physics", The Chemical Rubber Co., 51st Ed., Ohio, (1970-1971).
37. Turley, D., M.Phil. Thesis, CNAA, (1979).

TITLE .... PROCESSING BEHAVIOUR OF NR LATEX WITH SPECIAL REFERENCE TO DIPPING

AUTHOR .... Bholan Ruby Arora,.....

DEGREE ....

AWARDING BODY The Polytechnic of North London, CNAA 1990
DATE ....

THESIS
NUMBER ....

cms 1 2 3 4 5 6

REDUCTION X 20
CAMERA 4
No. of pages