

**STUDY OF POSTVULCANISATION OF NATURAL
RUBBER LATEX FILMS**

by

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ABSTRACT

Tensile strength /modulus relationships established for postvulcanised latex films have been found to show characteristics of both prevulcanised latex and dry rubber curves. The curves depend upon the accelerator system used, as with dry rubber. They passed through their maxima after which tensile strength fell, with the down-turn less pronounced than for prevulcanised latex but greater than for dry rubber. The results suggest that postvulcanised latex films remain particulate rather than homogeneous.

Processes known to affect prevulcanised latex films were applied to postvulcanised latex films. These included stirring and maturation of latex, different conditions for drying films and leaching with water and solvents, but only stirring had a significant effect. Stirring was essential to produce homogeneous latices for films with consistent chemical compositions and physical properties.

The structure of films was examined using electron microscopy. Only gross differences could be distinguished using cryo-SEM. On samples which had been swollen and embedded in polystyrene TEM discriminated between prevulcanised and postvulcanised films and showed differences in a series which had been vulcanised for different lengths of time. Upon extended heating the particulate films became homogeneous. However, the modulus and tensile strength of the films did not increase in parallel with the improvement in particle integration, each passing through a maximum before decreasing. This suggests that particle integration proceeds at a much slower rate than crosslinking of rubber molecules in the films. Both techniques showed that even postvulcanised latex films are generally inhomogeneous and remain particulate when well crosslinked and that good particle integration does not result in optimum tensile strength.

The discrepancy between the amount of ZDEC added and the amount which can be extracted from natural rubber latex films was confirmed, as was the finding that the difference is related to the concentration of non-rubbers in the latex. This is believed to be due to a reaction between some of the ZDEC with non-rubbers in the film and not the result of inefficient extraction. This study has indicated that the unextractable material no longer exists as ZDEC in the rubber matrix and that the decomposition of ZDEC continued in the dry film for many weeks in HA latex films but not apparently in DPNR films.

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ABBREVIATIONS

ANOVA	analysis of variance
Antioxidant 2246	2,2'-methylene-bis-(4-methyl-6-tert-butylphenol)
CBS	N-cyclohexylbenzothiazole-2-sulphenamide
cryo-	cryogenic
d.f./D.F.	degrees of freedom
DCM	dichloromethane
DPNR	deproteinised natural rubber
HA	High ammonia (latex)
IPA	isopropyl alcohol
L.I.(G.)	London International (Group)
M.R.P.R.A	Malaysian Rubber Producers' Research Association
NR	natural rubber
phr	parts per hundred of rubber
r.s.d./R.S.D.	relative standard deviation
s.d./S.D.	standard deviation
S300%	stress (modulus) at 300% elongation
SEM	scanning electron microscope/ micrographs
SI	swelling index
TEM	transmission electron microscope/ micrographs
TMTD	tetramethylthiuram disulphide
TS	tensile strength
UV	ultra-violet
w/v	weight/volume
w/w	weight/weight
ZDEC	zinc diethyldithiocarbamate
ZDMC	zinc dimethyldithiocarbamate
ZMBT	zinc benzothioazole-2-thiolate (zinc mercaptobenzthioazole)

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CHAPTER 1: INTRODUCTION

1.1 Objectives

The sulphur vulcanisation of dry natural rubber and prevulcanisation of natural rubber latex have been studied by previous researchers. Much of this attention must be due to their importance in industrial processes. Postvulcanisation of latex films, on the other hand, has received very little attention. Many latex dipping processes make use of partially prevulcanised latex which is dried on a shaped former to make the product. The drying stage usually takes place at elevated temperatures; hence, any unreacted vulcanising ingredients in the film can react to form additional sulphur crosslinks. This process is postvulcanisation. In industrial latex dipping, postvulcanisation is a process which is superimposed upon prevulcanisation of the product.

It is the objective of this investigation to discover more of the basic facts pertaining to the postvulcanisation of natural rubber latex, whilst excluding prevulcanisation from the practical procedure as far as possible. A comparison of the processes for postvulcanisation will be made with those for prevulcanisation.

The study will examine the relationships between physical properties and the effects of changes in processing on those properties. It will also attempt to identify differences in the processes of film formation and to evaluate some of the methods available for examining film structure.

1.2 Natural Rubber Latex

Since this study is concerned with the use of natural rubber latex, a few introductory pages will be devoted to a description of its origin and composition.

Natural rubber latex is a colloidal dispersion of natural rubber hydrocarbon in an aqueous serum and, as the name implies, is of biological origin. It is obtained from the *Hevea brasiliensis* tree by tapping. Tapping involves removing strips of bark from the tree in order to wound the latex vessels and allow latex to exude. The latex collected is known as field latex which contains between 25% and 40% rubber by weight. Field latex requires both preservation and concentration before it is of commercial use¹.

Microbial attack on latex coagulates it within a few hours of collection unless a preservative is added. The ideal preservative enhances the colloidal stability of latex by increasing the charge on the particles and the zeta-potential at the rubber-water interface. Since the protecting proteins of the natural rubber latex are already on the alkaline side of their isoelectric point when the latex leaves the tree, this means that a preservative should increase the pH of the latex and should, therefore, be itself an alkali. A preservative should destroy micro-organisms which cause putrefaction or suppress their activity and growth. It should also deactivate trace metals, particularly heavy metal ions, either by sequestration or by precipitation. This is desirable for two reasons. Firstly, some of these metal ions are necessary for the growth and survival of those micro-organisms which cause spontaneous coagulation. Secondly, some metal ions themselves tend to destabilise the latex, for example magnesium ions. Ammonia fulfils these requirements and is the most widely used preservative. To act as an effective bactericide ammonia must be added at a level of at least 0.1% of the whole latex. Ammonia interacts with the adsorbed proteins on the latex particles to enhance the zeta-potential at the rubber-serum interface; it also promotes the hydrolysis of proteins and phospholipids in the latex. Among the products of hydrolysis of the phospholipids are fatty acids, the fatty acid anions being adsorbed on the surface of the latex particles thereby increasing the particles' negative charge and enhancing stability.

Ammonia has the disadvantage of imparting a strong odour to latex and since it must be handled either as cylinders of the anhydrous liquid or concentrated aqueous solution it is neither convenient nor cheap. There are secondary preservatives in use which allow a reduction in the amount of ammonia required. The preservative systems in use with natural rubber latex concentrate are shown in Table 1¹.

Field latex is not normally used commercially because of its high water content and susceptibility to bacterial attack unless properly preserved. Latex is concentrated to give a dry rubber content of 60% w/w. The concentrate has the advantages of being more economical to transport and being of more uniform quality. There are three main methods of concentration which are: (i) evaporation, (ii) creaming and (iii) centrifugation. Nearly ninety percent of latex concentrate is produced by centrifugation. In evaporation all the non-rubber solids present in field latex remain in the concentrate. In creamed or centrifuged latex only thirty percent of the non-rubbers from the field latex

remain in the concentrate^{1,2}.

Natural rubber latex consists of a dispersion of particles which are composed of 86% rubber hydrocarbon, 10% water, 1% protein and 3% lipids by weight³. The rubber hydrocarbon is cis-1,4-polyisoprene with a molecular weight in the region of one million¹. Unlike most synthetic polymer latices, natural rubber latex has a wide range of particle sizes, with diameter of 0.01 - 5µm and an average between 0.25 and 0.8µm. Although the majority of particles have a diameter of less than 0.2µm it is particles with diameters greater than this which contain the majority of the rubber, over 90%¹.

Since the density of rubber particles (0.93 Mgm⁻³) dispersed in the latex is less than the density of the serum (1.02 Mgm⁻³), particles move upwards over the course of time. The rate is proportional to the square of the particle diameter and is predicted by Stokes' law. To obtain homogeneous preparations, the latex must be agitated before use.

The particles are stabilised by an adsorbed layer of proteins and phospholipids. The composition of fresh latex is shown in Table 2⁴. Preservation with ammonia brings about a number of changes. Fresh latex contains a number of additional structures (e.g. luteoids and Frey-Wyssling particles) which dissolve in the latex serum when latex is ammoniated. Ammonia promotes the hydrolysis of proteins and phospholipids. Proteins are converted to polypeptides and amino acids and phospholipids are converted to a number of products including fatty acid anions. The fatty acid anions are

Table 1 Types of Preservative System Used in Centrifuged Natural Rubber Latex Concentrate

Designation	Abbreviation	Preservative System (% by weight)
High or Full Ammonia	HA	0.7% ammonia
Low ammonia TZ	LA-TZ	0.2% ammonia, 0.025% zinc oxide, 0.025% tetramethylthiuram disulphide
Low ammonia pentachlorophenate	LA-SPP	0.2% ammonia, 0.2% sodium pentachlorophenate
Low ammonia boric acid	LA-BA	0.2% ammonia, 0.24% boric acid

Based on Ref. 1.

Table 2 The Constiuents of Fresh Hevea Latex

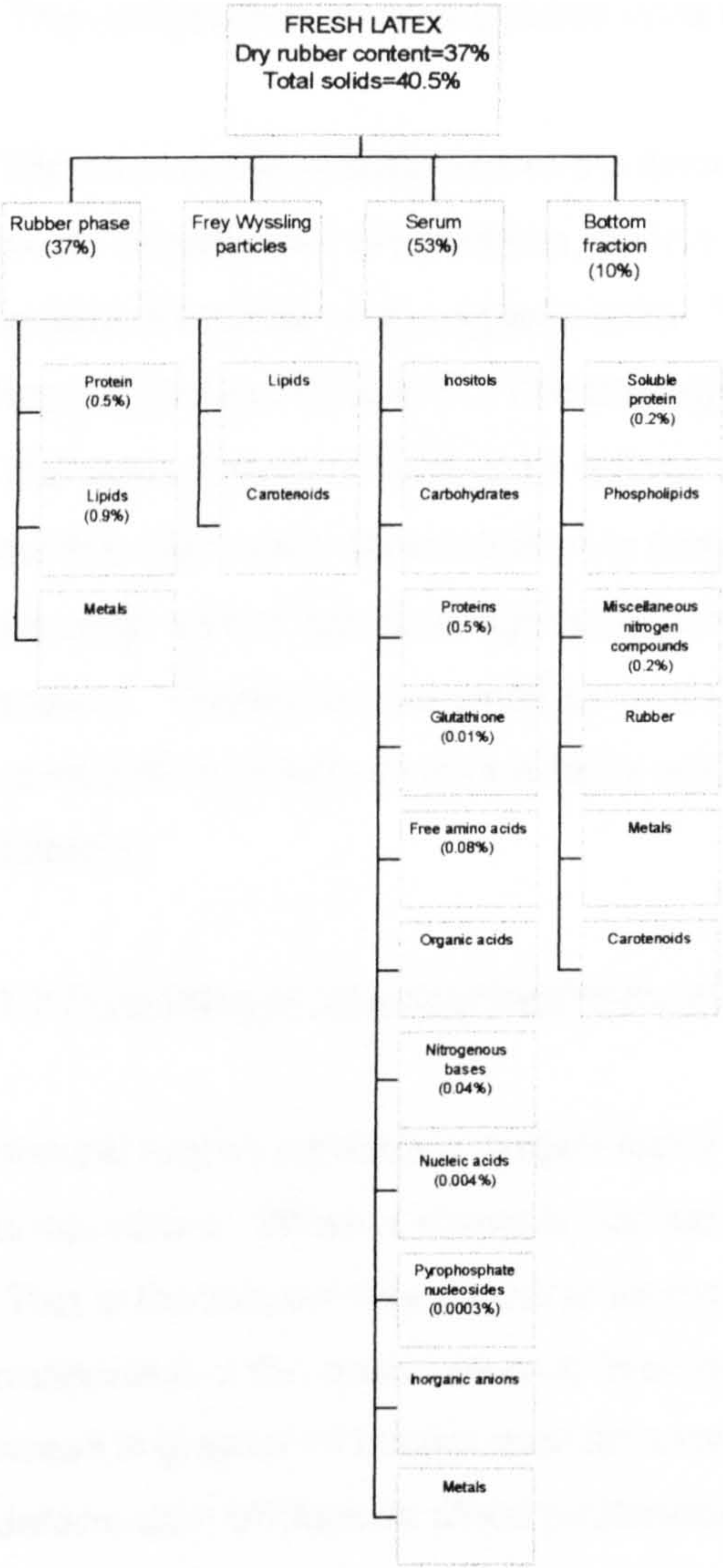
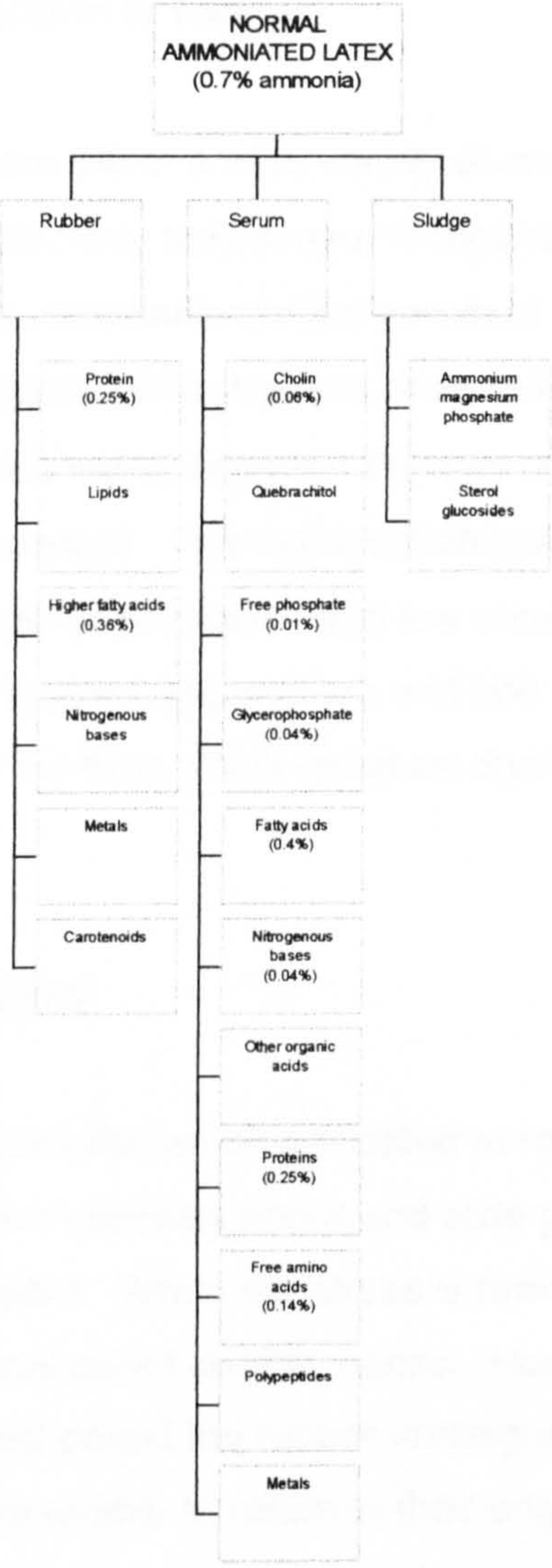


Table 3 The Constiuents of Ammoniated Hevea Latex



Based on Ref. 4

adsorbed on the interfaces of the rubber particles and serve to increase latex stability³. The composition of ammoniated latex is shown in Table 3⁴.

The non-rubber substances in the serum consist of a wide variety of materials. The major constituents are proteins, amino acids, fatty acid soaps, nitrogenous bases and a variety of organic and inorganic salts. The composition of the serum of ammoniated latex is shown in Table 3⁴. The average anion concentrations are shown in Table 4¹. The concentration of individual anions varies widely between batches of concentrates but the total anion concentration is fairly constant. The major cation is ammonium, although serum contains significant amounts of potassium and low concentrations of sodium. There are also small amounts of copper, magnesium and iron. The overall composition of high ammonia latex and of the films which result on drying are shown in Table 5¹.

1.3 Properties of Unvulcanised Natural Rubber

Natural rubber consists of largely linear molecules which are coiled at room temperature. When a stress is applied, the molecules uncoil and slide past each other. This is the reason why rubber is so extensible. When the stress is removed the molecules, in the main, return to their original coiled conformations. However, if the stress is greater or occurs over an extended period the rubber undergoes permanent deformation or fracture since molecules are unable to return to their original positions. Unvulcanised natural rubber has relatively low tensile strength. Unvulcanised rubber is also temperature sensitive, becoming soft and sticky as the temperature rises and brittle as it falls. This temperature sensitivity is a disadvantage. An additional problem with natural rubber is that, being itself a hydrocarbon, it swells considerably and dissolves in a number of hydrocarbon solvents. These problems limit the usefulness of unvulcanised natural rubber. However, these disadvantages can be reduced by a process known as vulcanisation in which neighbouring rubber molecules are joined together by the introduction of crosslinks.

Vulcanisation is a subject which will be discussed in much greater detail in the next chapter. Although it is possible to crosslink rubber molecules in a number of different ways via different crosslink types, the work to be described is concerned only with sulphur vulcanisation.

Table 4 Average Anion Concentrations found in Mature Latex Concentrate Sera

Anion	Latex Type	
	HA	LA-TZ
Carbonate	22.25	22.0
Acetate	12.81	8.74
Malate	9.28	10.14
Succinate	5.45	2.03*
Citrate	5.04	6.94
Formate	4.67	3.13
α-glycerophosphate	2.81	4.24
Glucose-1-phosphate	2.24	0.31*
Phosphate	2.01	2.22
Oxalate	1.16	1.22
Chloride	1.10	2.01
Sulphate	0.58	0.63
Hydroxide	0.51	0.14
Propionate	—	5.34#

HA = high ammonia latex

LA-TZ= low ammonia-TZ latex

*= not always found

#= found only in one latex

(Based on Ref. 1)

Table 5 Overall Composition in Percentage by Weight of Latices and Total Solids Films

	HA		LA-TZ	
	Latex	Film	Latex	Film
Rubber*	59.67	97.61	59.61	97.62
Proteins, etc.\$	1.06	1.73	1.03	1.69
Soaps#	0.23	0.38	0.23	0.38
Salts	0.40	0.28♣	0.38	0.32♣
Ammonia	0.68	—	0.21	—
Water	37.96	—	38.54	—

*=as measured by dry rubber content test⁷⁷

\$=includes carbohydrates, amino acids, sugars

#= calculated as ammonium stearate

♣= assuming carbonate, acetate, and formate are volatilized.

(Based on Ref. 1)

1.4 Compounding

Sulphur vulcanisation involves the reaction of rubber molecules with sulphur aided by an accelerator, and usually zinc oxide is also present. For this to take place, the vulcanising ingredients are mixed with the rubber. The process is termed compounding. Additional materials like antioxidants, fillers, pigments and stabilisers may also be added.

1.4.1 Production and Compounding of Dry Rubber

Latex is converted to dry rubber by means of intentional coagulation. The details vary according to whether sheet, crepe or crumb rubber is to be produced, but the general procedure is the same. Latex is strained into bulking tanks where it is diluted to 15-25 wt. % solids with clean water. It is transferred to coagulation tanks where formic acid is added to reduce its pH to about 4.5 or 4.8. Aluminium partitions are inserted into the tank so that the coagulum is formed in easily handled slabs. The latex coagulates as a result of the drop in pH and when it is sufficiently firm the coagulum is flooded with water to prevent oxidation.

Sheets, 2-3mm thick, are produced by passing the slabs of coagulum through a battery of contrarotating rollers. Crepe is produced by passing the coagulum, under a water spray, through a series of mills; mills with rollers rotating at different speeds which shear and masticate the rubber and where it is washed, intermediate creping mills with grooves on the rollers about 1mm deep and finally, smooth finishing mills which produce a smooth crepe 1-2mm thick. The rubber sheets are dried and smoked, smoke acts as a fungicide. Then they are pressed into blocks for transit. The crepe is dried and packed into bales.

Crumb rubber is produced from coagulum by crumbing. The coagulum is cleaned and homogenised in wash mills. The rubber blanket formed is converted to crumb by milling or granulation, either with or without the use of chemicals. The crumb is dried and pressed into bales.

Rubber must be masticated to reduce its viscosity, so as to incorporate compounding ingredients readily. This is done in a mill or an internal mixer. During mastication, when

the rubber passes between rollers or rotors, the rubber molecules are fragmented by the high shear forces. The free radical chain fragments formed may be terminated to form short chain molecules or may recombine into long chain molecules. During mastication the relative molecular weight of the rubber is reduced, reducing its viscosity and making the incorporation of vulcanising ingredients easier. When vulcanising ingredients are added to the rubber it may be remixed several times in order to incorporate all the ingredients and produce a homogeneous mix.

Dry rubber mixes usually include zinc oxide and a fatty acid as activators. Most dry rubber accelerators do not contain zinc. The "active" accelerator is formed by decomposition of the added accelerator and reaction with zinc oxide at the higher vulcanisation temperatures used for dry rubber vulcanisation, 140°C-200°C. The presence of an "active" accelerator could bring about premature vulcanisation in the mixer or mill. This is termed "scorching". The fatty acid forms a complex with the zinc salt of the accelerator. The complex is believed to be more soluble in rubber than the accelerator salt, thus increasing the efficiency of the accelerator.

1.4.2 Latex Compounding

In prevulcanisation, latex is vulcanised in the dispersed state. In postvulcanisation, the compounded latex is converted to a film and the film is vulcanised.

Compounding latex is a simpler process than compounding dry rubber. However, the problem which occurs with latex but not dry rubber is that its colloidal stability may be altered by the compounding ingredients. In compounding, chemicals are normally added in the form of solutions if they are water soluble; if, as is more commonly the case, they are insoluble in water they are usually added as dispersions in water. The solid is milled to reduce its particle size to a size no greater than that of the largest latex particles, about $5\mu\text{m}^5$. This is important in relation to sedimentation but has been found to have no detectable effects upon vulcanisation rates or vulcanisate properties for prevulcanised latices⁶. The compounding chemicals are usually ground in a mill with water and a dispersing agent to give a dispersion of between 30% and 70% by weight.

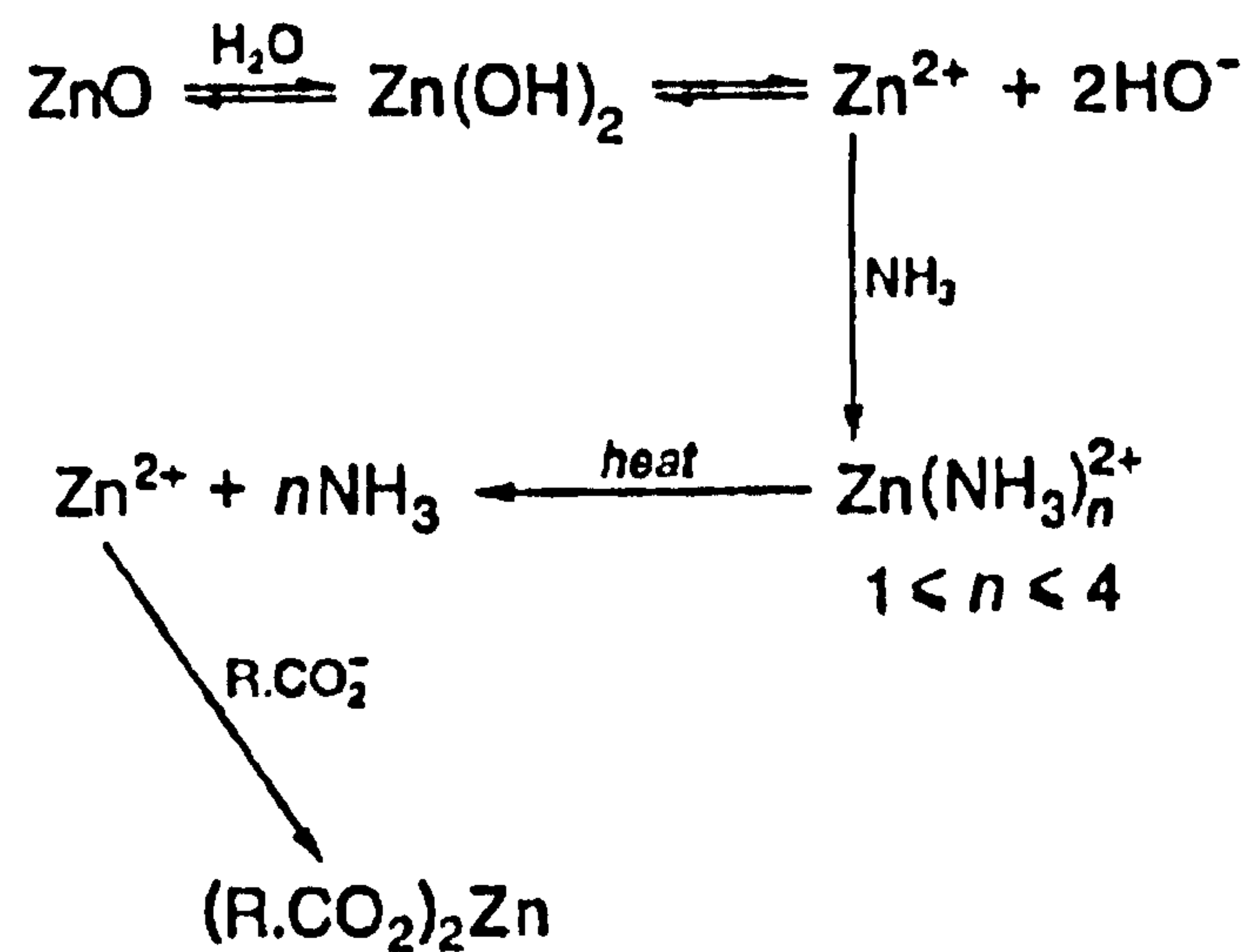
The processing behaviour of unvulcanised and prevulcanised latex is very similar. The particle size is unaffected by vulcanisation and the viscosity remains much the same.

Therefore "active" zinc-containing accelerators may be included in the formulation without having a detrimental effect upon the latex processing properties. By contrast the sort of processing operations carried out with dry rubber (mixing, moulding and extruding) are seriously affected by premature vulcanisation. Therefore delayed action accelerators are usually used in dry rubber formulations with zinc oxide. The addition of fatty acids as activators is often unnecessary since natural rubber latex contains naturally occurring fatty acids which have not been removed during processing, as is the case with dry rubber.

The order in which the ingredients are added to latex may affect its colloidal stability. In general, stabilising agents are added first followed by vulcanising ingredients (including sulphur) and antioxidant. If pigments or fillers are required they are added next. Zinc oxide is added towards the end of compounding because it has a destabilising effect upon high-ammonia latex^{5,7}

Latex containing zinc oxide tends to thicken and gel slowly on storage. This widely observed phenomenon occurs when latex contains a source of zinc ions (zinc oxide), free ammonia and ammonium ions and when latex is stabilised by an adsorbed anion which is capable of forming an insoluble zinc soap (see Section 1.2). The rate of gelation increases as the temperature is raised. Although the exact details of the process are not fully understood the main sequence of reactions is shown in Figure 1.

Zinc oxide is the most common source of zinc ions. In the presence of water it undergoes some hydrolysis and behaves as though it were zinc hydroxide. Zinc ions released by the sparingly soluble hydroxide are complexed by free ammonia in the latex to form zinc ammine ions of various compositions. The number of ammonia molecules in the complexes varies from 1 to 4. Under the conditions encountered in latex it is the tetra-ammine complex which predominates, the distribution of zinc between the different amines being shown in Figure 2. The heat-sensitivity of latex containing zinc amines is generally attributed to the thermal lability of zinc tetra- ammine. On heating, these ions tend to lose ammonia to give lower ammine ions and ultimately hydrated zinc ions. McRoberts⁸ proposed that destabilisation of latex was brought about by the lower ammine ions rather than the higher ones interacting with carbonate anions to form insoluble soaps and this had been widely accepted; although more recent work has cast doubt upon this idea^{5,9}.



insoluble zinc carboxylate (e.g. soap or proteinate) precipitated in the surface of the latex particle, with consequent colloidal destabilization

Figure 1 Formation of Zinc Ammines and Insoluble Zinc Soaps
Based on Ref. 3

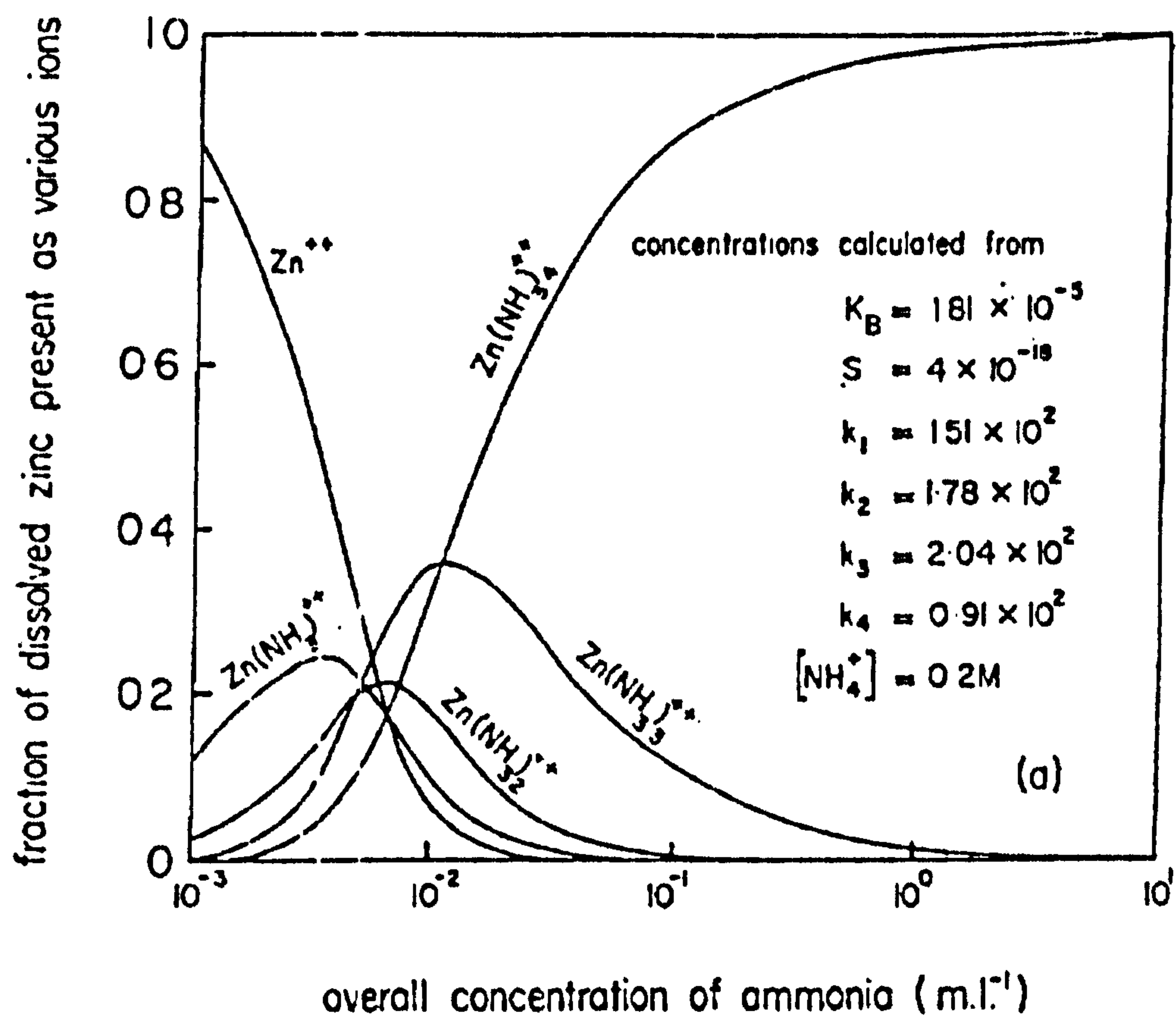


Figure 2 Distribution of Dissolved Zinc Amongst Various Possible Ions

Based on Ref. 3

The ammonium ions present in the system suppress the hydroxide ion concentration, thus enhancing the initial concentration of zinc ions.



Conversely, the heat sensitivity of latex may be reduced by the addition of strong alkali, for example potassium hydroxide. This increases the concentration of hydroxyl ions in the system, displacing the equilibrium between zinc hydroxide and its ions to the left and reducing the concentration of free zinc ions. The addition of excessive amounts of ammonia reduces heat sensitivity by reducing the concentration of free zinc ions present.



The overall solubility of zinc oxide in aqueous solutions of ammonia and ammonium salts depends upon several factors and the situation may be quite complicated since dissolved zinc may exist in five different complexed forms. However, if dissolved zinc exists predominantly in tetra-ammine form the concentration of dissolved zinc is effectively equal to the concentration of zinc tetra-ammine ions and this can be shown to be:

$$[\text{Zn(NH}_3)_4^{2+}] = \frac{KS}{K_B^2} [\text{NH}_3]^2 [\text{NH}_4^+]^2$$

S	=	solubility product for zinc hydroxide
K _B	=	base dissociation constant for ammonia
K	=	overall equilibrium constant for the equilibrium between zinc ions and the zinc tetra-ammine ion

The derivation of this relationship is given by Blackley¹⁰.

The precise mechanism of room temperature zinc oxide thickening is obscure. However, the facts relating to it are known. It is associated with the presence of

ammonium ions and fatty acid soaps in ammonia-preserved natural rubber latex and the tendency to thicken correlates well with the concentration of ammonium ions which slowly develop during the gradual liberation of acidic substances in the latex serum. The mechanism of thickening probably involves the gradual formation of insoluble zinc soaps on the surface of latex particles and leads to a reduction in their surface charge and hence flocculation.

1.4.3 Maturation of Compounded Latex

After latex has been compounded it is usual in industrial processes for it to be left to "mature" for a period of time. This process is said to improve the consistency of finished latex products. Different manufacturers have their own procedures but the latex is usually "matured" for between 1 and 7 days. Slow stirring is maintained to prevent settlement of high density ingredients. During "maturation" a number of processes take place: the surfactants naturally present in latex and those added with the dispersions equilibrate between the aqueous and interfacial phases, there is some dissolution of sulphur and accelerators in the serum and migration of the vulcanising ingredients into the rubber particles. It also allows time for air entrained in the latex during mixing to escape. Some prevulcanisation may also occur during this "maturation" stage, the extent of which depends upon the length of "maturation" and the temperature at which the latex is stored. A maturation period of at least 24 hours is recommended for latex to be used in industrial processes⁵.

As described in Section 1.4.2, most vulcanising ingredients used in latex compounding are sparingly soluble in water and are therefore added in the form of fine dispersions. Vulcanisation of rubber relies upon the vulcanising ingredients being present in the rubber phase. This involves transfer of materials from separate particles of dispersions to rubber in the latex particle and is believed to involve the latex serum (aqueous phase). However, the mechanism by which this transfer takes place is not clear.

Van Gils¹¹ demonstrated the solubility of sulphur in natural rubber latex serum by showing that sulphur could transfer from solid lumps in a muslin bag or a solid deposit on the wall of a container into the rubber particles of the latex. Porter et al.¹² extended this work by showing that not only was sulphur transferred from a solid sulphur deposit to the latex but that this latex could be prevulcanised by heating it in the presence of

accelerator (ZDEC) and zinc oxide dispersions. Similarly the solubility of ZDEC in latex serum was also demonstrated using a solid deposit of ZDEC. The presence of diethylamine in the latex had the effect of considerably shortening the induction period before crosslinking commenced in the compounded latex. This finding supports the suggestion by Loh¹³ that the solubility of dithiocarbamates is due to complexation of the zinc compound by ammonia or other nitrogenous bases in the serum. Porter et al.¹² have shown that in the absence of other vulcanising ingredients both sulphur and ZDEC are soluble in natural rubber latex and are in a form which is available for prevulcanisation. For latex which had been heated in the presence of a sulphur deposit the time elapsed after latex was compounded with other vulcanising ingredients (2 hours or 17 hours) had an effect upon vulcanisate properties.

The findings of Porter et al.¹² support the view that vulcanising ingredients dissolve in latex serum before prevulcanisation occurs. The extent of prevulcanisation was found to depend upon the amount of dissolved sulphur in the latex, because no reserve of solid sulphur was present, and upon the time between compounding and the start of prevulcanisation. The latter conclusion gives support to the practice of "maturing" compounded or prevulcanised latex before use in order to obtain products with superior properties^{3,5,9,14,15}.

In the present work the use of a "maturation" period was investigated with compounded latex which was used to prepare films for postvulcanisation. The findings are described in Section 4.2. Since the films were to be postvulcanised and prevulcanisation was to be eliminated as far as practicable, the "maturation" times investigated were relatively short - a maximum of 40 hours. It is often difficult to distinguish between "maturation" and room-temperature or low-temperature prevulcanisation, particularly at the beginning of the process of prevulcanisation. Room-temperature prevulcanisation of natural rubber latex using dithiocarbamate accelerators has been investigated by a number of workers. Porter reports that there is detectable crosslinking in rubber in less than 12 hours at 27°C if a very active accelerator, zinc dibutyldithiocarbamate (ZDBC), is used¹². Room-temperature prevulcanisation of natural rubber latex by dithiocarbamate accelerators is also described by Loo and Wong^{16,17}. They found that latex could be extensively prevulcanised in just 24 hours at 28-30°C when ZDBC was used as the accelerator. Even a less active accelerator like ZDEC could produce prevulcanised latex in 24 hours at 28°C when the levels of sulphur and accelerators

were 1.0phr each or 1.5phr each¹⁷. Gorton investigated the effect of prevulcanisation at 20°C with ZDEC and ZDBC (ZBUD) as the accelerators⁹. He observed no crosslink development in 1-7 days for the ZDEC formulation but the ZDBC formulation showed appreciable activity even after 1 day. It is perhaps worth noting that the tensile strengths reported by Gorton for films containing ZDEC in which he observed no crosslink development were higher than have been found for any unvulcanised films prepared during the present research programme. The reason for this difference is not clear but leads to the suspicion that some vulcanisation occurred in the films after preparation and before testing. The relaxed modulus values reported by Gorton changed very little and support his conclusions.

1.5 Latex Dipping

Although films prepared in this study have been produced by casting, this is not the most common method of making films from latex. Most latex is used in the manufacture of dipped goods, an area in which London International Group specialises. The process of latex dipping consists of the following stages^{5,14}:-

1.5.1 Dipping

A rigid former is immersed in a compounded latex, a deposit forming on its surface. The former is slowly removed from the latex to ensure a uniform coating and is usually inverted to redisperse the drops which form at the lower extremities.

There are two common methods of dipping: (i) straight dipping, in which a clean, dry former is immersed in latex and (ii) coagulant dipping, in which the former is first immersed in a solution of coacervant (e.g. aqueous calcium nitrate), the former is withdrawn (and may be dried to give a solid coating of coacervant) and finally the former is immersed in latex.

Straight dipping is used to produce very thin films, for example in the production of condoms. It may be repeated a number of times with dry or partially dry films to produce thicker films. After a clean dry former has been dipped into compounded latex it is slowly withdrawn. The former is usually inverted to redistribute excess latex and the deposit formed is dried. It is usual to straight dip more than once since very thin films

from a single dip are prone to pinholes, which arise from grease spots and other imperfections of the surface of the formers. A second dip is very unlikely to have defects which coincide with those in the first deposit unless there is a gross defect on the surface of the former. The thickness of the deposit is approximately proportional to the number of dips. Gorton¹⁸ found that the relationship between deposit thickness and latex viscosity for straight dipping could be described by the following equation:

$$t = a_1 + K_1 \log (\eta_{60})$$

t = deposit thickness

a_1 and K_1 are constants

η_{60} is the apparent viscosity (Brookfield) at 60 rev/min.

This relationship does not apply where porous formers are used or where the compounded latex shows anomalous flow behaviour.

Coagulant dipping produces thicker films and is used in glove, balloon, catheter and feeding teat production. Coagulant dipping is an ionic gelation process in which an increased concentration of ions in natural rubber latex causes partial or total destabilisation by suppressing the electrical double layer surrounding the particles and by interference with the hydration layer.

A clean dry former is dipped into a solution of coagulant, often calcium nitrate in water or water and industrial methylated spirit, and slowly withdrawn. After the former has been partially dried to give a deposit of coagulant it is dipped into the compounded latex and a gel is formed. The former is carefully removed from the latex and the deposit dried.

There are three main variables affecting deposit thickness for coagulant dipped films. They are immersion time of the former, latex viscosity and the nature and concentration of the coagulant. Gorton investigated the factors affecting films formed by coagulant dipping^{18,19}. Figure 3 illustrates the processes occurring during dipping. The diagram shows various regions:

- I a layer of coagulant
- II "first" coagulant deposit
- III "second" coagulant deposit
- IV latex compound

Region II resembles a straight dip deposit. The dissolution and migration of the coagulant to the latex compound through region II occur simultaneously. Upon contact between coagulant ions and latex, region III is formed and the interface between regions III and IV extends away from the former. Two effects hinder the growth of region III. They are the release of serum from the coagulant deposit which results in dilution of the coagulant and an increase in thickness of the deposit through which the coagulant ions have to permeate in order to reach the latex compound.

The relationship between dwell time, viscosity of latex and coagulant deposit thickness is ¹⁹:

$$t_c = A + K\sqrt{D} \log \eta$$

A and K are constants

- η = latex compound viscosity (centipoise)
- D = dwell time(s)
- t_c = coagulant deposit thickness (mm)

The coagulant deposit thickness was also found to depend upon coagulant concentration, the exact relationship varying with coagulant types. For calcium nitrate the relationship was found to be⁵

$$T = 4.01t_s + 0.022 C \sqrt{D}$$

- T = total deposit thickness (mm)
- t_s = thickness of straight dip deposit (mm)
- C = concentration of calcium nitrate solution(%)
- D = dwell time (s)

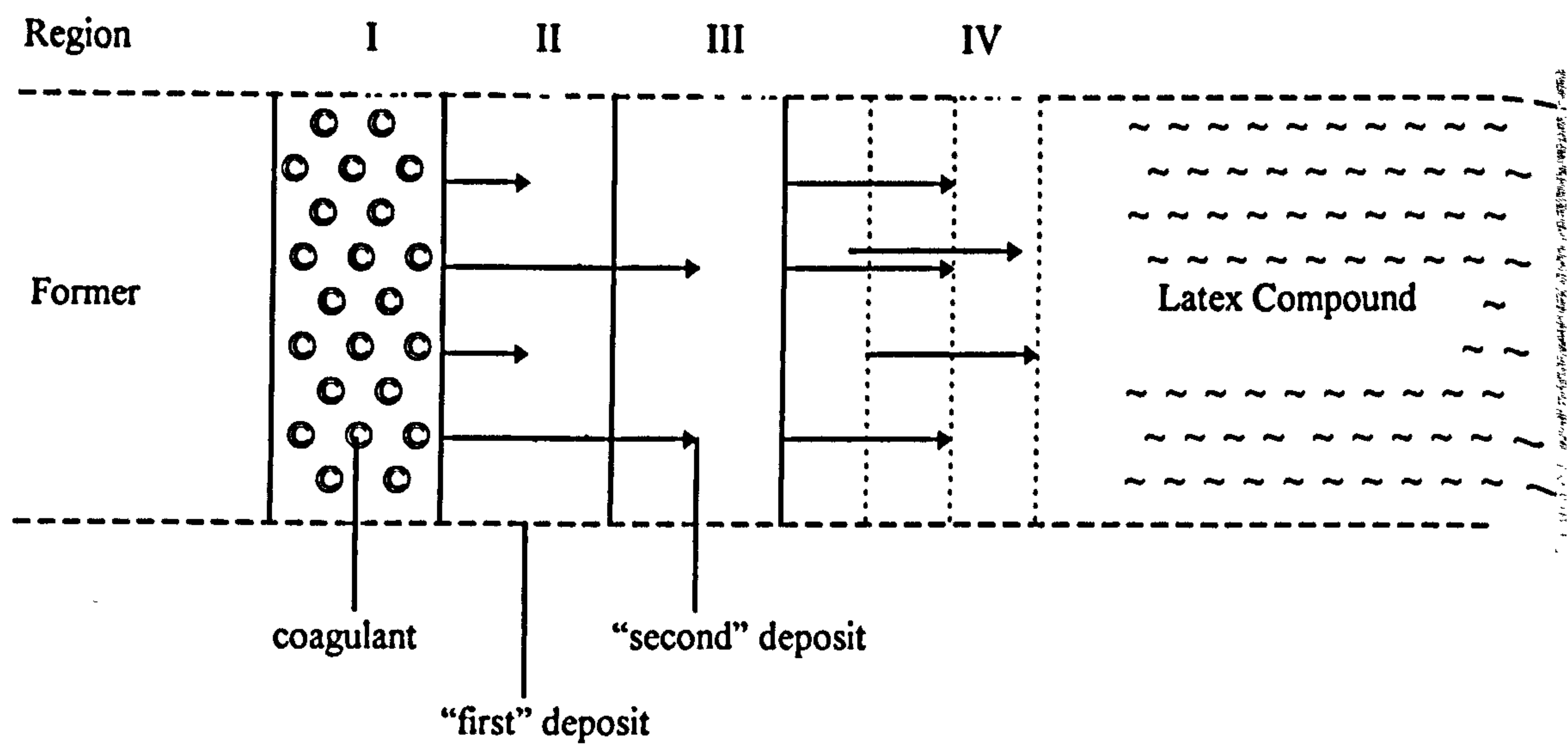


Figure 3 Cross-section of Coagulant Dipping Deposition
Based on Ref.18

1.5.2 Leaching

Leaching is a process carried out on most dipped products in order to remove water-soluble materials from the film. These water-soluble materials may have been derived from the latex serum, coagulant or surfactants. In industrial processes leaching usually makes use of water, often at elevated temperatures.

Leaching is used in industrial processes to improve product properties. It is used to improve the clarity of products, to reduce discoloration and blooming (a process whereby materials present in the bulk of the rubber product diffuse to the surface and may cause the surface to look blotchy or discoloured). In the case of electricians' gloves leaching is used to remove hydrophilic materials which absorb moisture and reduce the electrical resistance of the gloves. Leaching is also used to reduce levels of residual protein in medical devices, for example, surgeons' gloves and catheters. Residual soluble proteins in latex products can give rise to allergic reactions in sensitised people. The reduction of extractable proteins in latex goods, including by leaching, has been described by Subramanian²⁰.

Leaching may be carried out on dried articles after they have been removed from the formers. This is known as dry film leaching. In a description of the process given by Gazeley²¹ the first step is absorption of water through the surface of the film by capillary action. A solution forms in the rubber as soluble material dissolves with the rubber acting as a semi-permeable membrane. A concentration gradient is set up and more water enters the film by osmosis. The swelling of the film is opposed by elastic forces in the rubber and eventually the osmotic forces are balanced by the elastic forces and this is the point where maximum water absorption has been reached. However, since rubber is not a perfect membrane, soluble materials diffuse from the rubber into the water and the osmotic pressure is constantly changing.

Latex films "whiten" when immersed in water due to water absorption by hydrophilic non-rubbers in the films. This absorption is more rapid at the surface which was originally the rubber-air interface than at the surface which was the rubber-substrate interface. The non-rubbers are believed to be transported to the rubber-air surface with water⁵. The film dries as a result of water leaving through the surface and the non-rubbers are left behind. This enrichment of non-rubbers at the surfaces has been

described for synthetic polymer latices and will be discussed in greater detail in Section 1.6.4. The same effect is not observed for coagulant dipped films⁵. In coagulant dipping the serum including non-rubbers, is expelled from the coagulated latex by syneresis into the latex compound.

Gazeley compared the leaching of postvulcanised and prevulcanised latex films prepared from the same formulation²¹. He found that the prevulcanised latex films leach more readily than postvulcanised films. Calcium is leached with reasonable ease. However, leaching of nitrogen-containing compounds was quite poor; the small reduction in nitrogen content of the leached film is thought to be due to loss of nitrate ions rather than any protein or amino acid nitrogen.

In addition to examining the percentage by weight of materials extracted during leaching, Gazeley used the water absorption of leached films as an indicator of leaching efficiency (Figure 4)²¹. He found that the rate of water absorption of postvulcanised films was the same whether they had been leached for 2h or 24h at 25°C and that the curve was effectively the same as that for an unleached postvulcanised film. In the case of prevulcanised latex films under similar conditions, the initial absorption rate is greater than for postvulcanised films but it slows down. For a prevulcanised latex film leached at 100°C for 2h, the initial rate of water absorption is the same as that for postvulcanised films but it levels off after 20-30h.

Gazeley also leached wet gels and found that water absorption was much lower than for dry films, indicating better leaching efficiency (Figure 4). Pendle had also demonstrated this by looking at difference in conductivity of the leach bath (Figure 5).

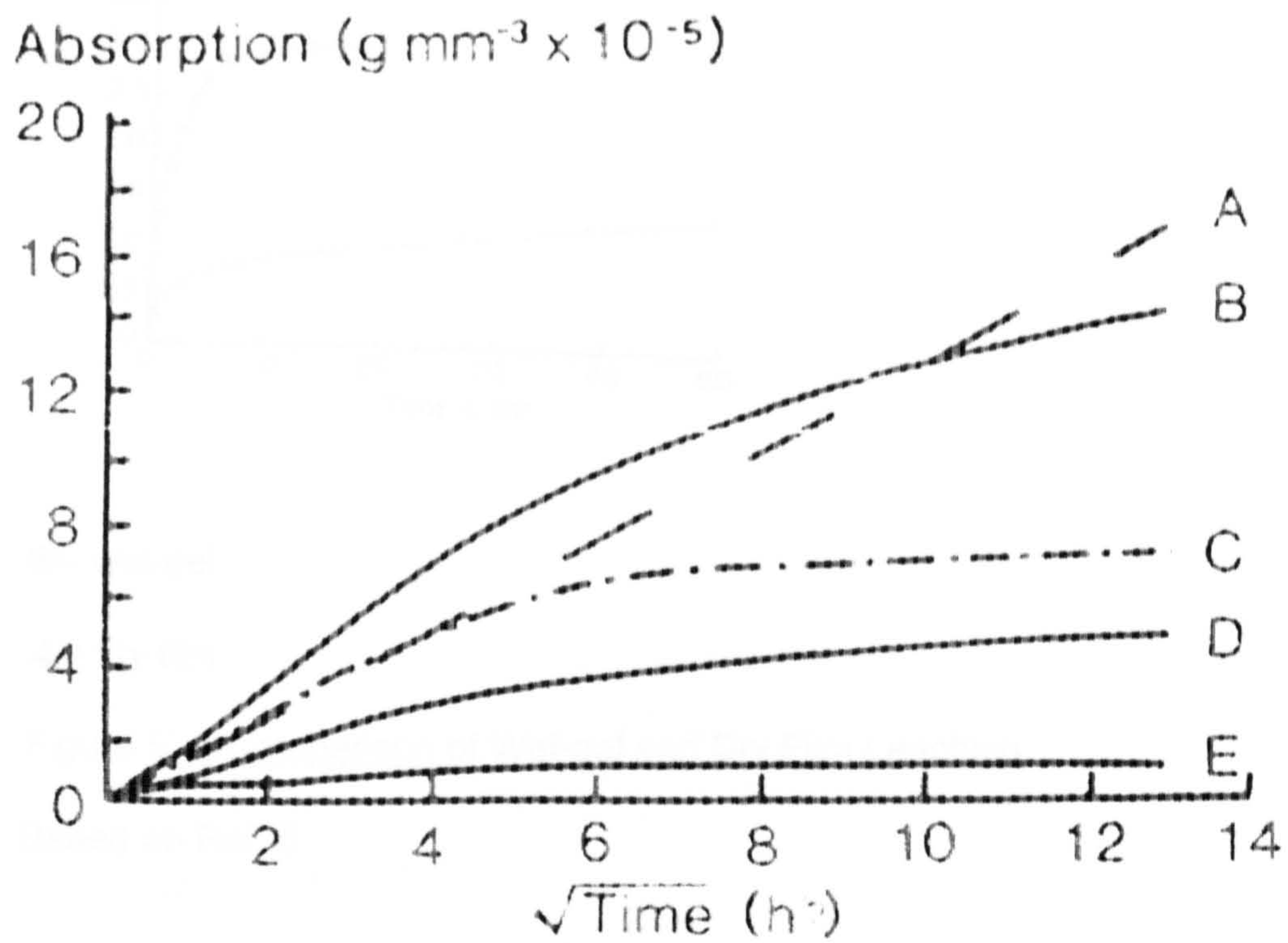
Gazeley also carried out leaching experiments with prevulcanised latex films of different moduli, subjecting the films to various drying temperatures and leach bath temperatures²¹. The percentage weight loss versus time was examined for films leached at 25°C. For the low modulus latex the initial rate of extraction was very similar for the different film drying temperatures; the initial rate being slow and increasing rapidly for a leach time in the region of 16-24h (Figure 6(A)). The initial rate was slightly affected by drying temperature. For the medium modulus latex the 50°C and 70°C curves are similar to those for the low modulus latex, but the 25°C curve is different. It climbs steadily initially then flattens off as the removal of soluble materials reaches

equilibrium (Figure 6(B)). For the high modulus latex all the curves are steep initially then flatten off (Figure 6(C)). The 25°C curve has the steepest initial section, becoming less steep after approximately 100 min. The 50°C and 70°C are similar to each other, with a less steep initial curve forming a plateau between 1000 and 10,000 min.

Films dried at 70°C were leached at different temperatures (Figure 7(A-C))²¹. For the low and medium modulus latex films, curve for leaching at 25°C and 50°C coincide. There is slow extraction for approximately 2h after which the rate increases (Figure 7(A and B)). For leaching at 100°C the initial slow stage is greatly reduced or eliminated. For the high modulus latex there is no initial slow stage and the rate of extraction is increased by raising the leach bath temperature from 25°C to 50°C. However, little further increase in rate results from raising the leaching temperature to 100°C (Figure 7(C)).

Gazeley concluded that the differences in extraction rates of soluble materials from films and gels and the differences in water absorption by leached films and gels were due to differences in their structure. He explained the differences in extraction rate for prevulcanised latex films of different moduli in terms of the capillary structure of the films. The extent of capillary structure was expected to be relatively small in a low modulus prevulcanised film; since the smaller extent of crosslinking within latex particles would not constrain particle-particle integration. Therefore, coalescence would be well advanced in films dried at 25°C and increasing the drying temperature would only cause a small increase in coalescence and, hence, a small decrease in extraction rate. In the case of the high modulus latex film the rapid extraction rates could be explained in terms of retarded particle integration which produced films with a more open and extensive capillary structure. Increasing the drying temperature is believed to increase particle coalescence and, therefore, decrease the extent of the capillaries. The medium modulus latex films were believed to have an intermediate structure which could be altered by changing the drying or leach bath temperatures.

The sudden change in the extraction rate for low modulus films (Figure (7(A))) is thought to be due to the size of the capillaries reaching a critical value. Extraction does not occur until a capillary reaches a certain minimum cross-sectional area. They may already exist in films where particle integration has been retarded but in other cases the capillaries must be swollen to the required size under the influence of osmotic pressure.



A, postvulcanised, leached 24h at 25°C or 2h at 100°C;

B, prevulcanised, leached 24h at 25°;

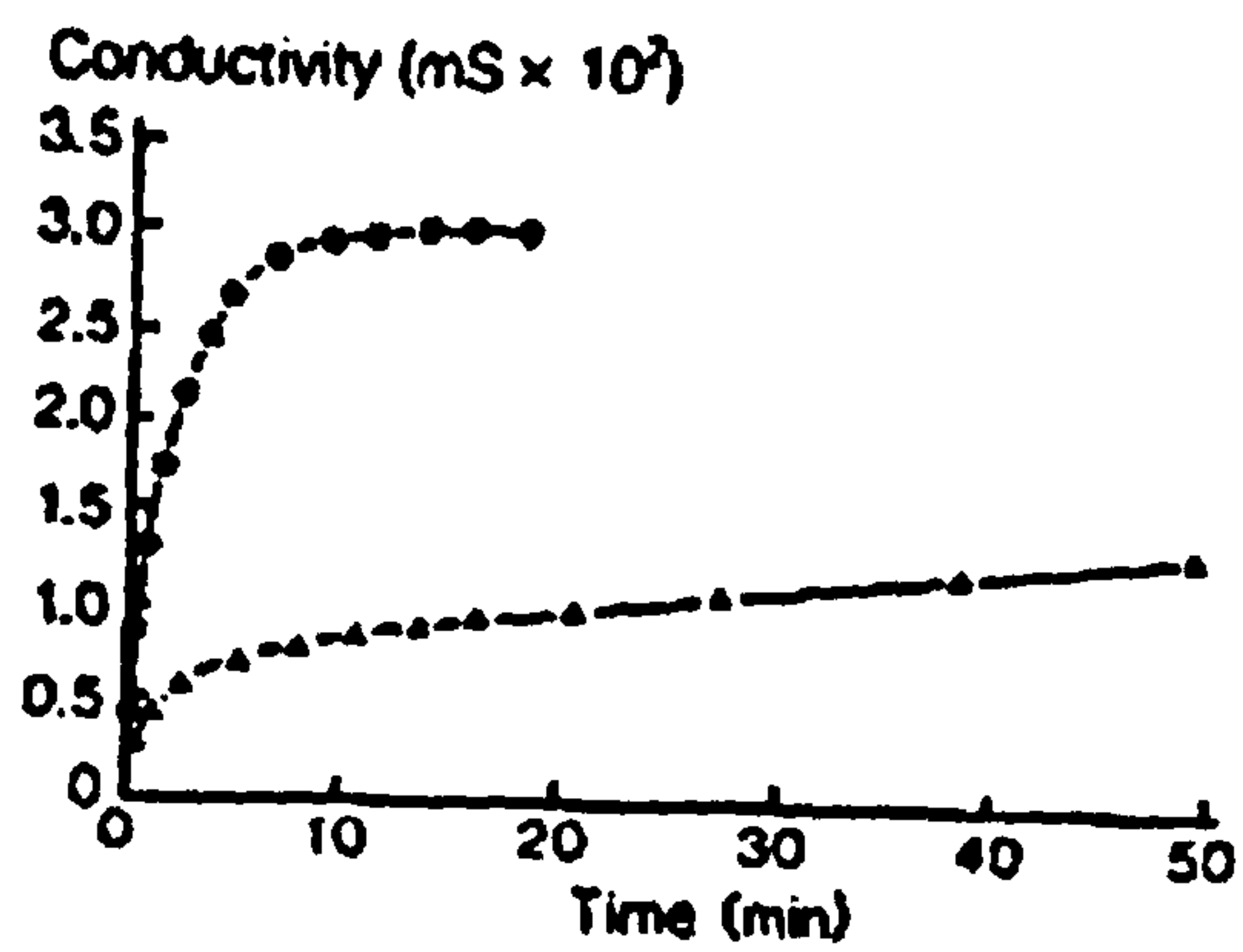
C, prevulcanised, leached 2h at 100°C;

D, wet-gel leached 300s at 80°C;

E, wet-gel leached 2h at 80°C.

Figure 4 Water Absorption of Leached Films

Based on Ref. 5

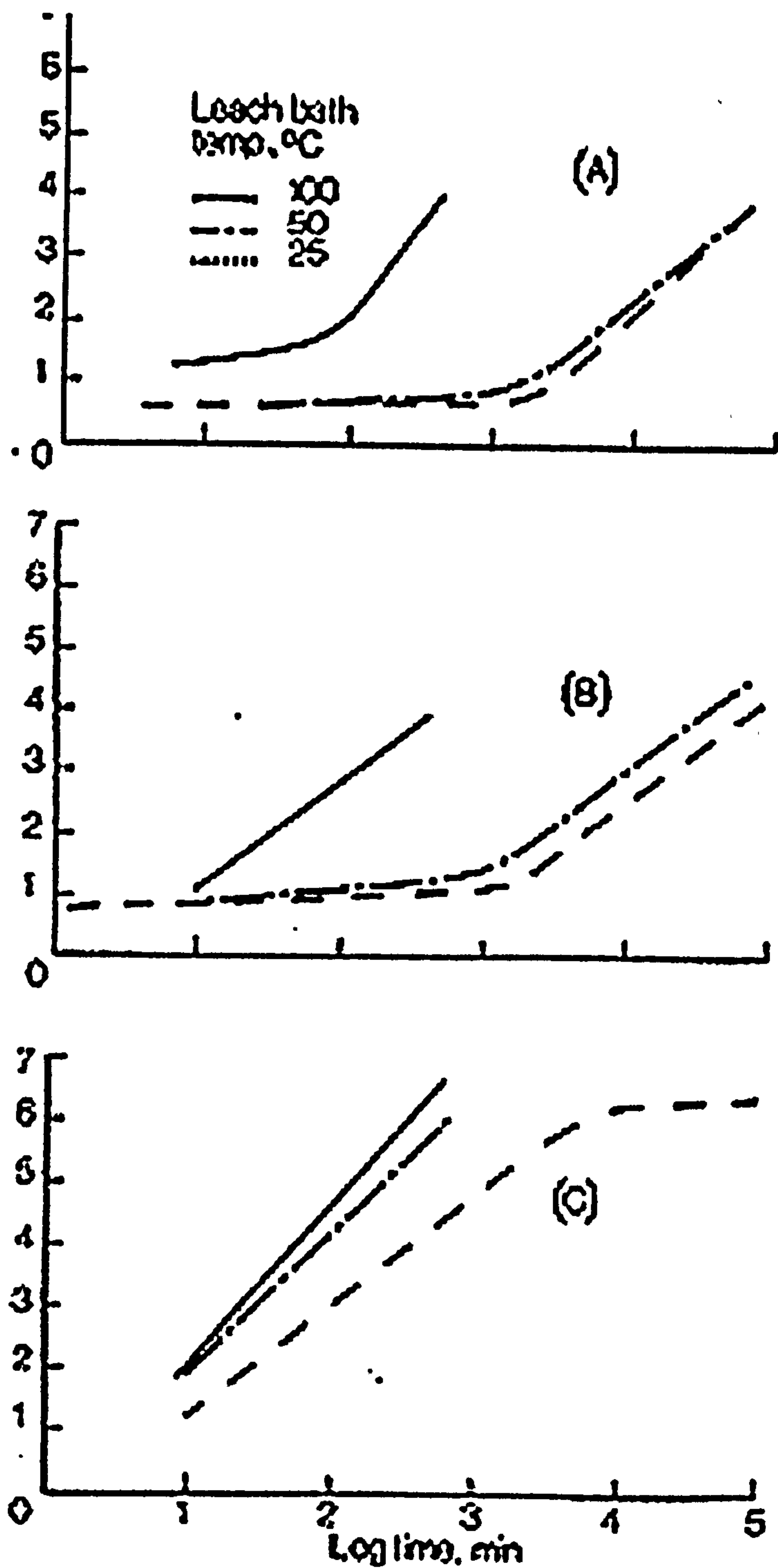


● = wet-gel

▲ = dry film

Figure 5 A Comparison of Wet-gel and Dry Film Leaching

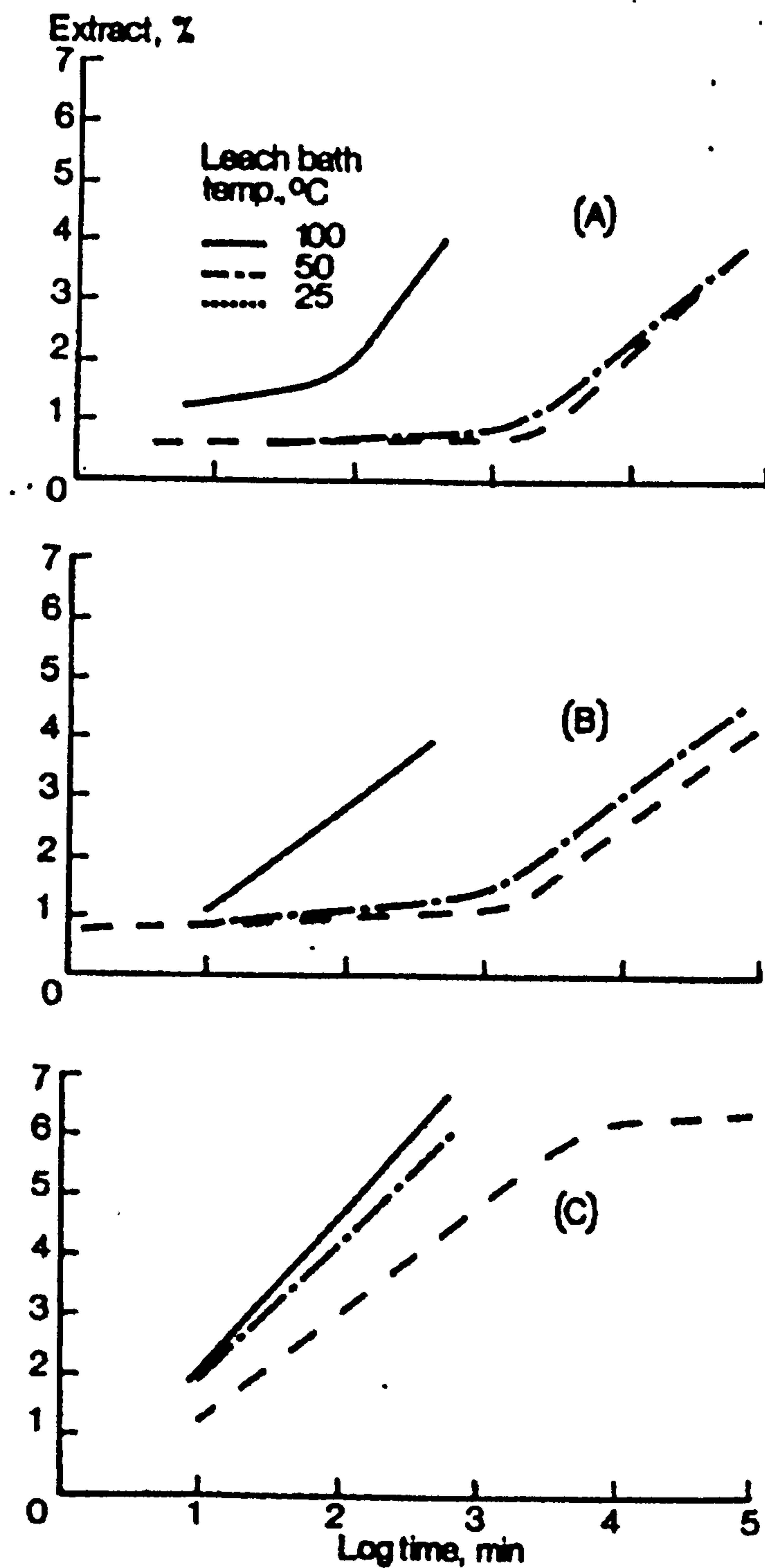
Based on Ref. 5



A= low-modulus latex, B= medium-modulus latex, C= high-modulus latex

Figure 6 The Effect of Drying Temperature on Leaching Prevulcanised Latex Films
(leached at 25°C)

Based on Ref.21



A= low-modulus latex, B= medium-modulus latex, C= high-modulus latex

Figure 7 The Effect of Bath Temperature on Leaching of Prevulcanised Latex Films (dried at 70°C)
Based on Ref.21

In the case of wet gel leaching, particle coalescence is retarded by the presence of water between the particles . This provides rapid access to water soluble materials during leaching.

Postvulcanised latex films proved more difficult to leach than prevulcanised latex films. This could perhaps be explained in terms of good particle integration in the film before vulcanisation, which would lead to few capillaries through which extraction could occur. Thoughts about the structure of postvulcanised latex films in the light of results reported in this thesis are discussed in Section 6.8.

The effect of leaching upon the physical properties of latex films has been investigated for prevulcanised films by a number of workers²²⁻²⁵. It is generally found to increase tensile strength and modulus, as illustrated in Figures 8 and 9. The effect of leaching is often greater than heating the dried film, see Table 6. Merrill^{23,24} also investigated leaching prevulcanised latex films with acetone and found their tensile strength to be further enhanced. His results are shown in Figure 10. Leaching is believed to improve physical properties of latex films by removing non-rubbers from the particle interfaces, thus facilitating particle coalescence. The subject of film formation will be discussed in later Sections 1.6.1 - 1.6.4. Much less attention has been paid to postvulcanised latex films. Porter and Wong²⁵ observed increases in tensile strength and modulus for postvulcanised films. The increases in tensile strength on leaching were found to be smaller than for prevulcanised latex films (see, e.g. Fig. 8). Further investigations into the effect of leaching upon postvulcanised latex films have been carried out during the present research programme and the effect has been found to be less clear-cut than it at first appeared. The results of leaching experiments are described later (Section 4.5).

The choice of whether to leach the wet gel or dry film is dependent not only upon how efficient the process needs to be but also upon the length of time available for leaching. If leaching is part of a continuous process, its duration is generally limited in order that production is not unduly curtailed. Continuous processes generally make use of wet gel leaching which is efficient and rapid. The leach tanks are usually also maintained at an elevated temperature. Wet gel leaching is most suitable for thin products. In the case of electricians' gloves, where leaching needs to be very extensive, the leaching is carried out on the dried stripped product because the long leach times required would introduce an unacceptable delay into a continuous manufacturing operation. Again,

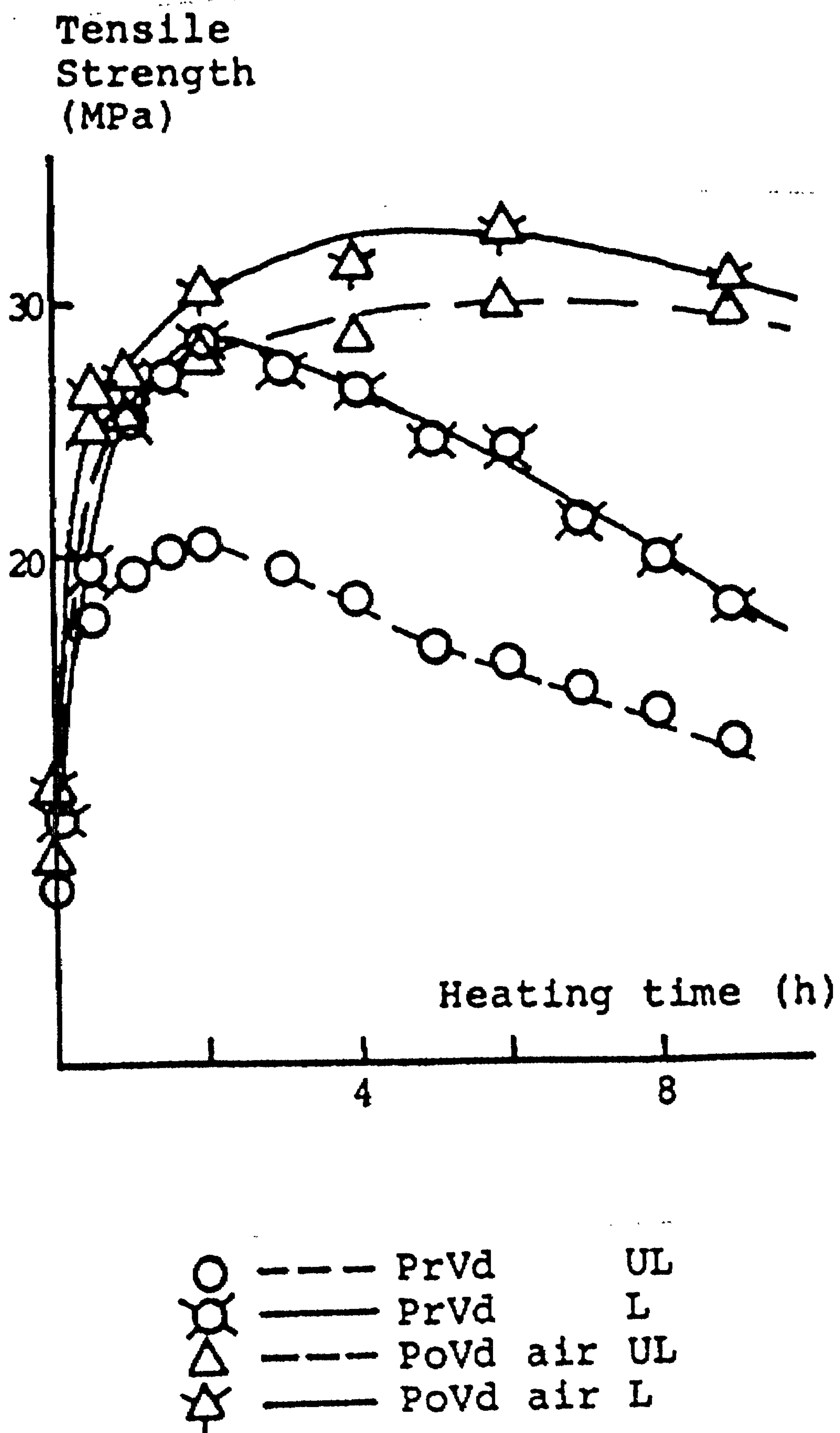


Figure 8 Prevulcanisation : Strength of Unleached and Leached Films

Based on Ref. 25

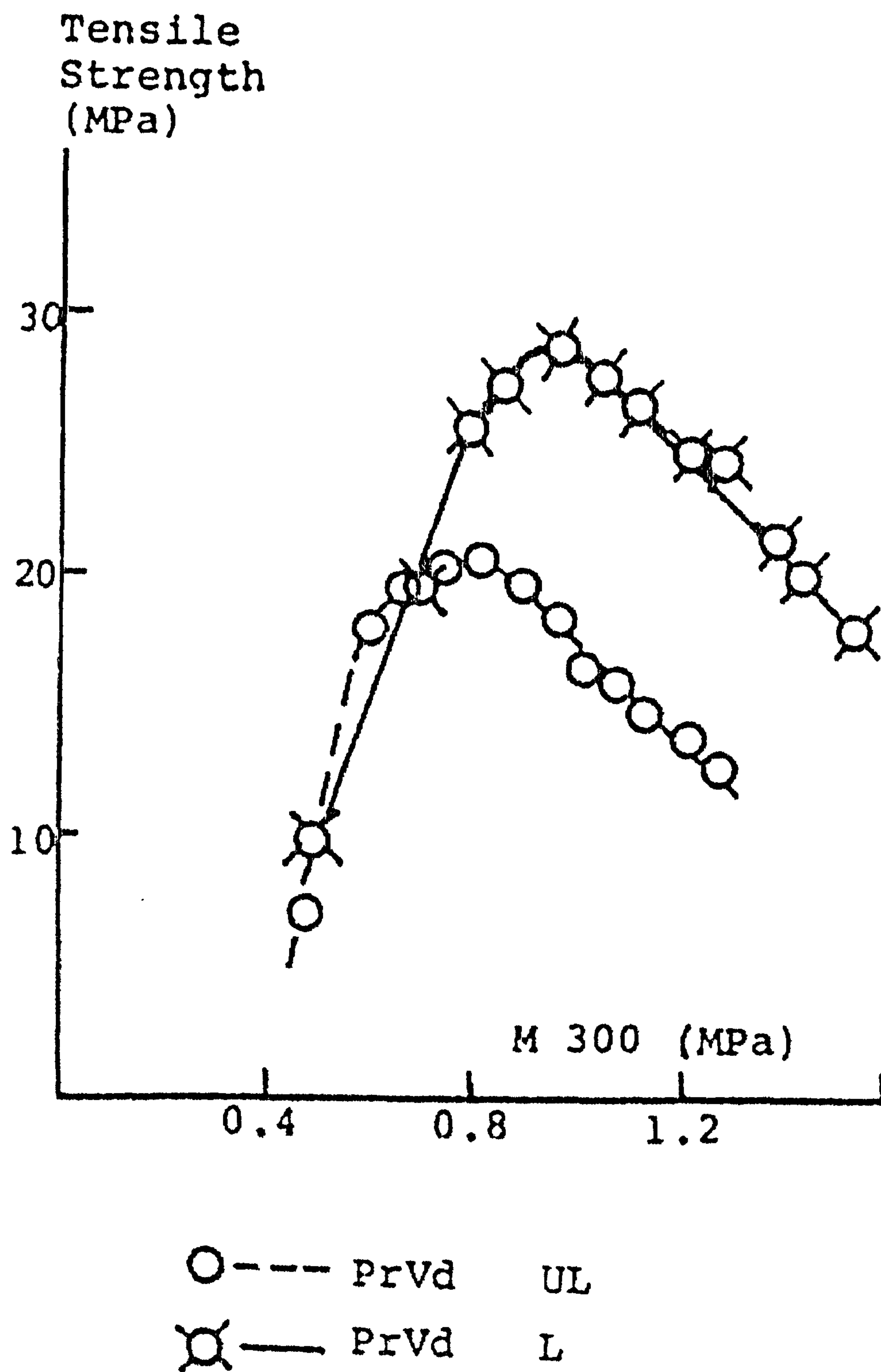


Figure 9 Prevulcanisation : Relationship Between Strength and Modulus

Based on Ref. 25

Table 6 The Effect of Leaching and Heating Dried Films of Prevulcanised Latex

Formulation	Treatment	Tensile Strength (MPa)	Elongation-at- break (%)	Modulus (MPa)	
				300%	500%
1	none	20.6	960	0.78	1.25
1	leach 16h /20°C	30.0	1015	0.85	1.39
1	heat 30 min /100°C	25.9	1010	0.84	1.25
1	leach 16h /20°C, heat 30 min /100°C	29.7	980	0.95	1.48
2	none	17.8	820	1.08	1.98
2	leach 16h /20°C	35.0	873	1.52	2.98
2	heat 30 min /100°C	28.6	880	1.25	1.91
2	leach 16h /20°C, heat 30 min /100°C	33.2	860	1.52	2.86

Based on Refs. 1 and 9

leaching may be carried out at elevated temperatures.

1.5.3 Drying and Vulcanisation

These steps are often simultaneous and are usually carried out in hot-air ovens. Drying is a physical process which removes water from the films whereas vulcanisation is a chemical reaction producing crosslinks between rubber molecules in the films. The temperature for final drying and vulcanisation is usually 100-110°C. Intermediate drying steps are usually at lower temperatures.

Vulcanisation will not be discussed further here; it is discussed in detail in Chapter 2.

Drying of latex films and processes of film formation have been studied mainly for synthetic polymer latices, although some have been carried out using natural rubber latex. The literature relating to film formation in general and the drying of latex films in particular will be described in Section 1.6.5.

1.5.4 Stripping

Stripping is the process of removing vulcanised articles from formers. Dry stripping involves the application of dusting powder to prevent rubber surfaces from sticking together. After this the product is removed from the former by rotating brushes and is then graded and packed. Wet stripping uses water as part of the process of removing articles from formers. In the case of condoms they are first loosened by immersing the formers in a leach tank. Then the condoms can be flushed off by passing the formers through water jets. Gloves are usually removed by pulling cuffs down towards the finger-tips so that they are turned inside out. A slurry of water and starch, or just water, is applied continuously to the former to assist glove removal. A dusting powder (e.g. starch or talc) is usually applied to the wet product to prevent rubber surfaces from sticking together. This stage is unnecessary for powder-free gloves where alternative surface treatments are used. Wet stripping requires a drying step before products can be graded or packed.

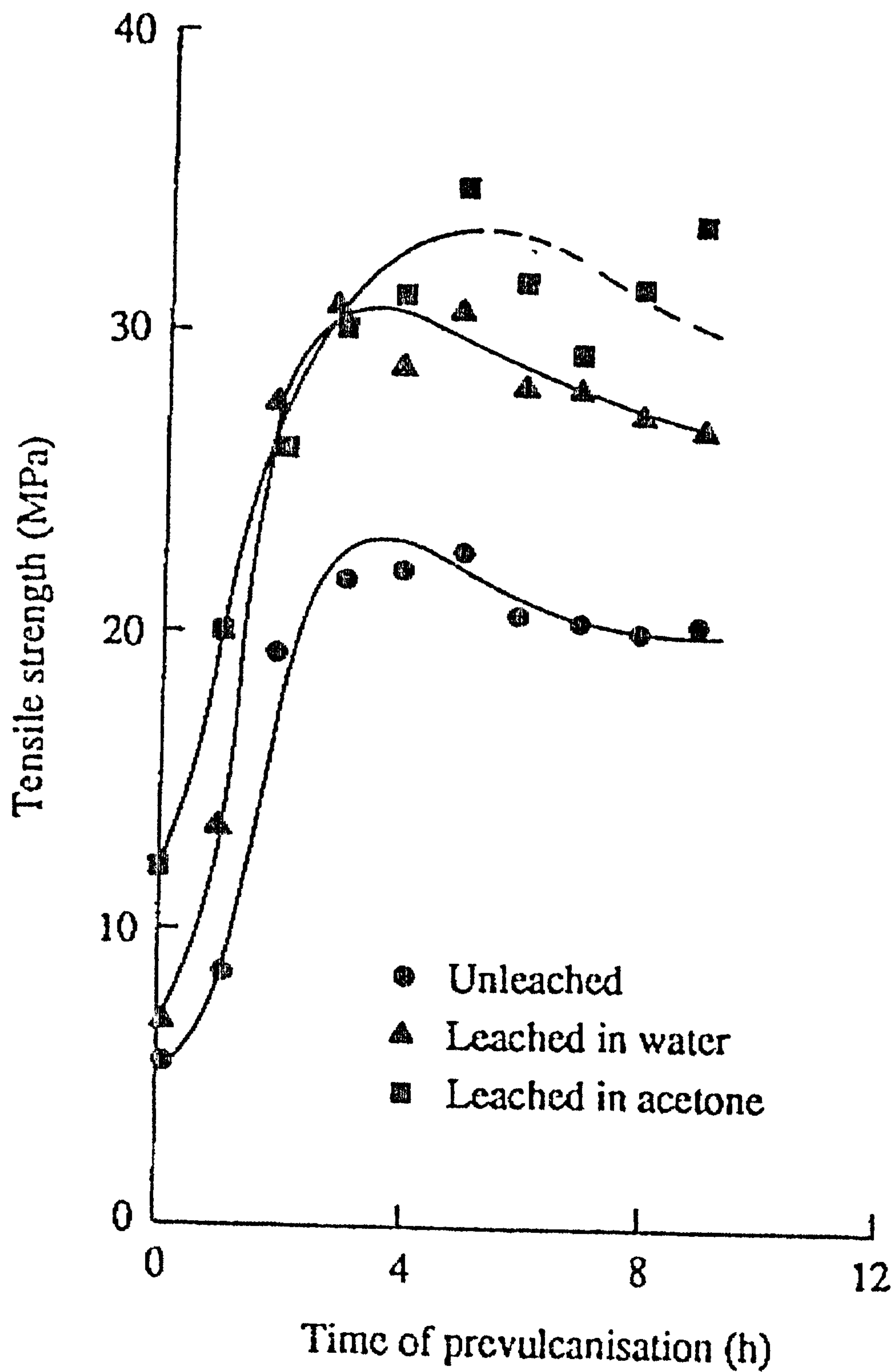


Figure 10 Effect of Leaching in Water and in Acetone on Tensile Strength of Films derived from Pre vulcanised Natural Rubber Latex

Based on Ref. 24

1.6 Mechanism of Film Formation

The formation of coherent films from polymer latex particles is of considerable industrial importance, for example in the paint, paper and adhesives industries. It is also crucial in the production of dipped goods from rubber latices. Since natural rubber latex forms films so readily, little work has been conducted using polyisoprene; most has concentrated upon the film-forming abilities of synthetic polymers used in the paint industry which are generally monodisperse in terms of particle size and have much higher glass-transition temperatures than natural rubber, which has a glass transition temperature of about -72°C. Natural rubber latex is very polydisperse (in terms of particle size), it has a much lower glass transition temperature than the synthetic polymers investigated and the latex contains a far more complex mixture of non-rubbers. However, the general principles found to apply to film formation for synthetic polymer latices are expected to apply to natural rubber latex. A number of theories have been proposed for the mechanism by which spherical particles of a polymer, dispersed in a liquid phase are brought together, deform and form a continuous film. They have been summarised and reviewed in several papers²⁶⁻³⁰. However, none of them has satisfactorily explained all the observations.

1.6.1 The Forces Acting Upon Polymer Particles and the Role of Water in Film Formation

The "dry sintering" mechanism was suggested by Dillon et al.³¹. This process occurs after the water has evaporated from the emulsion. Energy for the process is provided by the polymer-air interfacial tension. The particles undergo viscous flow and coalesce. The progress of the fusion follows an equation developed by Frenkel³².(see also Figure 11)

$$\theta^2 = \frac{3\gamma t_r}{2\pi r \eta}$$

θ	=	half angle of coalescence
γ	=	surface tension
t_r	=	time
r	=	particle radius
η	=	particle viscosity

This model was criticised by Brown³³ who made the following points:

- (i) Film formation and water evaporation proceed simultaneously for many emulsion systems.
- (ii) The rate of water loss is a determining factor for coalescence of polymers which have "borderline" film-forming ability.
- (iii) If the temperature is maintained below a certain critical value during water evaporation then porous incompletely fused films may be formed. The temperature at which coalesced films may be formed from emulsions as the water evaporates may not be adequate to produce coalescence if applied to a porous polymer film which was formed at a lower temperature. Water plays a very important role in the film-forming process.
- (iv) Lightly crosslinked polymer particles may form continuous films. This cannot be due purely to viscous flow since interpenetration by self-diffusion is hindered.

Brown³³ proposed a mechanism based upon capillary action where the capillary forces that arise from the water-air interfacial tension are responsible for film coalescence. In the first stage of film formation water evaporates from an unbroken surface film and the concentration of the dispersion increases until the particles are unable to move. Once the particles are immobile the second stage of film formation occurs. In the second stage there are two possibilities:

- (i) Water evaporates completely from the channels between the particles leaving an array of undistorted, unfused polymer spheres.
- (ii) The particles deform and form a coalesced film.

During this second stage there are two main forces acting upon the particles. The first is the capillary pressure resulting from the interfacial tension of a concave water surface in the polymer interstices, designated F_c . This force promotes coalescence and only begins to operate after the solids are increased to a certain critical level. The second is

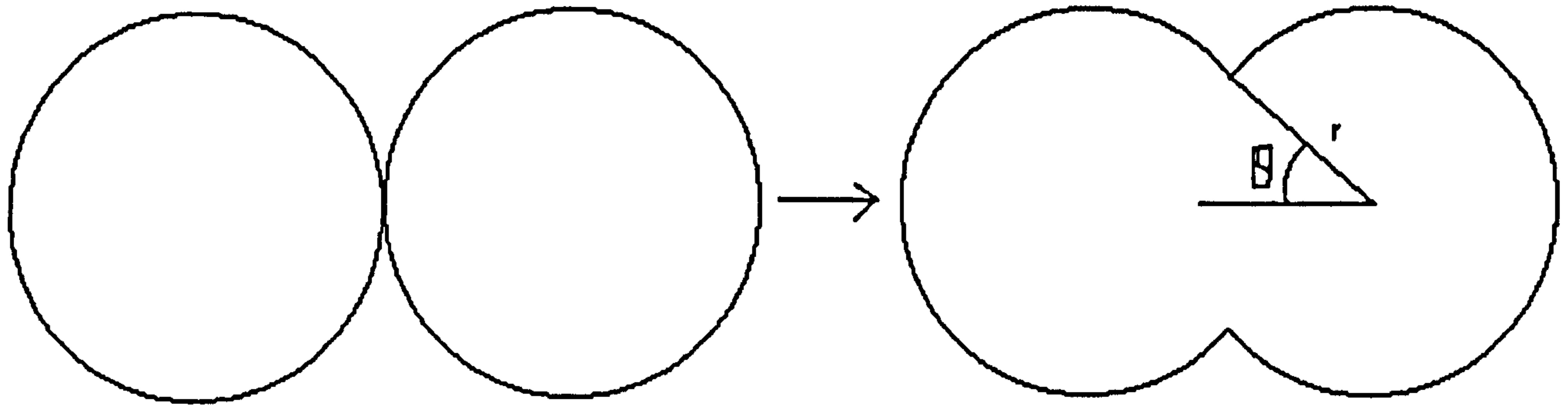


Figure 11 Fusion of Contiguous Particles by Viscous Flow
(Based on Refs. 32 and 33)

the resistance of the spherical polymer particle to deformation, this is designated F_G .

The condition for film formation is that

$$F_c > F_G$$

Brown related F_G to the time-dependent elastic modulus of the polymer, G_t , and was able to redefine the condition of film formation as

$$G_t < 35\sigma/r$$

σ = polymer-water interfacial tension

r = particle radius

Mason³⁴ in examining Brown's model pointed out that capillary pressure and contact pressure do not act over the same area and he derived a criterion for film formation based upon the corrected area for the interstitial capillary. Mason also commented that capillary pressure should not be assumed to be constant throughout the second stage of drying and he derived an equation for capillary pressure as a function of particle deformation. The resulting condition for film formation is:

$$G_t < 266\sigma/r$$

This differs from Brown's criterion by a factor of more than 7.

Other comments made by Mason are that there is an assumption that a thin film of liquid is present between the contacting spheres and that without it the capillary force between the particles will be reduced; also that Frenkel's elastic deformation equation applies only to small displacements and assumes that the areas of contact are circular; with the large deformations involved in film formation this cannot be the case.

Vanderhoff et al.³⁰ proposed another mechanism for film formation. The model for the mechanism consisted of polymer spheres suspended in a water droplet which are brought together as the water evaporates. The stabilising layers are brought into contact and the forces from the water-air interfacial tension provide additional pressure on the particles. The mathematical relationships derived show that the pressure promoting fusion is independent of latex particle size and they were able to observe coalescence even for large particle sizes. Dillon's³¹ and Brown's³³ equations indicate that coalescence is inversely proportional to particle radius. Mason³⁴ observed that Vanderhoff did not distinguish between force and pressure and that this makes a

considerable difference to the analysis.

Mason³⁴ stated that the physical nature of the polymer, indicated by the glass-transition temperature, is the most important factor in film formation rather than the stabilising layer or the particle size. When a polymer is above its glass-transition temperature it will behave as a viscous liquid and as such meets all the requirements for film formation independent of particle size. Below the glass-transition temperature the polymer will act as an elastic solid and hence will not fulfil the film-formation requirements.

Sheetz³⁵ proposed a mechanism for film formation which had two essential features:

1. The heat of the surroundings provides the major source of energy for film formation. It does useful work in evaporating the water.
 2. The evaporation of the water does useful work, since the water diffusing through the polymer particles produces a compressive force normal to the surface.
- He found that the contribution of capillarity³³ and the change of free energy of the polymer-water interface³⁰ (referred to by Sheetz as wet sintering) are most important in the first half of film formation.

Vanderhoff et al.³⁶ proposed three stages for the evaporation of water from a latex film. They are :

1. An initial stage during which the particles are free to move about in Brownian motion and the water evaporates at approximately the same rate as in pure water or dilute emulsifier solution. This rate persists until the concentration is reduced to about 25-40% by volume of water.
2. The intermediate stage when the drying rate diminishes rapidly. This stage begins once the particles are in irreversible contact, with water filling the interstices. The water evaporates, reducing the area of the water-air interface as the water contracts between the spheres and reducing the rate of evaporation. The intermediate stage ends when the particles coalesce under the combined interfacial tensions of the water-air and water-polymer surfaces.

3. In the final stage, the rate of drying is nearly constant but is 10-20 times smaller than in the first stage.

The remaining water escapes by diffusion through capillary channels in the film or through the polymer itself. The rate of evaporation decreases throughout the final stage, asymptotically approaching that through the pure polymer. This model was found to apply to the drying of natural rubber latex films³⁷, see Section 1.6.5.

Kendall and Padget²⁸ discuss a model for latex coalescence called the Johnson, Kendall and Roberts³⁸ (JKR) theory. The theory describes the equilibrium between two elastic spheres which are brought together through a combination of body and surface forces. The area of contact is influenced by three factors: external loads; surface attractions; and elastic forces. The theory gives a better description of the coalescence observations, particularly the time-dependent behaviour and the dependence upon particle size. However, it does not describe multi-particle coalescence and applies only to purely elastic spheres. This means that it can be applied to high molecular weight polymers which are well away from their glass-transition temperature. Many latex materials are viscoelastic and the theory does not cover the viscoelastic problem.

Eckersley and Rudin²⁶ found that the degree of fusion of films was greater than predicted by earlier theories and they proposed that the interfacial tension forces act in tandem with the capillary force.

El-Aasser and Robertson³⁹ used an ultracentrifugation technique to determine the minimum pressure required to cause the coalescence of styrene-butadiene latex particles and found it to be two orders of magnitude lower than that calculated by Brown³³ and Vanderhoff et al.³⁰.

Hwa⁴⁰ measured the flocculation point for a model acrylic latex. It was found to occur between 50-60% volume polymer depending upon the type of soap present. This indicates that, initially, the network formed is a loose, random arrangement.

Coalescence of polymer latices was examined by Cansell et al.⁴¹ by simultaneously following weight losses and dielectric constants during water evaporation from a latex. It was possible to differentiate between film-forming and non-film-forming latices. The

flocculation point of film-forming latices could be clearly determined. Both flocculation point and maximum packing point could be shown for non-film-forming latices.

Dielectric measurements appear to be reliable for examining the film-formation process of latices with different colloidal characteristics, since they can readily detect the influence of particle diameter, surface charge density and ionic strength, which are all parameters which reflect latex stability. Cansell et al.⁴² examined film-forming and non-film-forming latices by differential scanning calorimetry. They found that film-forming latices contained a fraction of water trapped in disconnected microdomains created by the deformation of latex particles during film formation.

1.6.2 The Effect of Polymer Particle Size

The evidence for the dependence of coalescence upon particle size is contradictory. According to Brown³³ there is a maximum latex particle size for coalescence at a given temperature. For polymer particles with a radius greater than this critical value it is necessary to reduce the polymer modulus. This can be done by raising the temperature or by plasticising the polymer. The temperature below which latex will not form a coherent film is called the minimum film formation temperature (MFFT). Brodnyan and Konen⁴³ found that MFFT was independent of particle size whilst Eckersley and Rudin²⁶ and Jensen and Morgan⁴⁴ found that MFFT did increase with increasing particle size.

1.6.3 Changes in Film Structure After Initial Film Formation

Voyutskii^{45,46} commented that surface tension and capillary forces alone could not account for the properties exhibited by latex films. These theories did not account for the irreversibility of film formation or the time dependence of film properties nor did they consider the fate of emulsifiers. After the polymer particles had formed a close-packed network and begun to distort, Voyutskii proposed a stage during which the free polymer chain ends diffused across the polymer boundaries to form a strong link between the particles. This was termed "autohesion" and it is able to account for the observation of "gradual further coalescence"^{47,48} upon ageing the cast films. Support for the interdiffusion of polymer chains comes from work by Hahn et al.^{49,50} using small angle neutron scattering measurements (SANS) with deuterated polymers which shows

massive interdiffusion of material from different latex particles which is not confined simply to free chain ends but also involves larger polymer chains. Linné et al.⁵¹ studied interdiffusion as a function of annealing time also using SANS measurements for deuterated polystyrene films and also found evidence of diffusion as a function of time. Zhao et al.⁵² used a fluorescence technique to obtain evidence of polymer interdiffusion.

Chainey et al.⁵³ attributed the decrease in gas permeability of homopolymer films to the process of gradual interdiffusion of polymer chain ends. Their work indicated that although films from latex became less gas permeable with time they remained more permeable than films cast from solutions of polymer, suggesting that they are less homogeneous.

Distler and Kanig^{54,55} asserted that latex films do not become completely homogeneous and were able to show particle boundaries delineated by hydrophilic surface groups even in surfactant-free latices.

1.6.4 The Fate of Surfactants

Voyutskii^{45,46} addressed the fate of emulsifiers during the water evaporation stage of film formation and suggested that they either remained in the film as an independent network, forming aggregates as they moved away from the polymer-liquid interface, or that they dissolved in the polymer and in this way were removed from the surface of the particles. In both cases the surface of the polymer particles becomes uncovered and this allows polymer-polymer contact between particles which is a prerequisite for "autohesion". In the case where the emulsifier is insoluble in the polymer, heterogeneous films are formed.

Zhao et al.⁵⁶ have found that the distribution of surfactant throughout the film is not uniform. There is enrichment at the film interfaces, greater at the film-air interface than at the film-substrate interface. The concentration of surfactant increases with time and varies with the type of surfactant. Enrichment has two causes:

- (i) a continuous surfactant layer is formed at each interface in order to minimise interfacial surface tensions;

(ii) because of its incompatibility with the polymer, surfactant is expelled from the bulk of the film during the drying and maturation process.

Urban and Evanson⁵⁷ also found surfactant enrichment at the polymer-air interface. They believe that the surfactant was carried to the surface by the water flux during film formation for the reasons given above. This effect was also discussed with reference to natural rubber latex in Section 1.5.2. They found that the situation at the polymer-substrate interface was more complex: the accumulation of surfactant appeared to depend upon the surface energy of the substrate relative to the latex or dry polymer. Two other observations were that if the polymer film was stretched, surfactant diffused to the increased surface area to raise the surface concentration and reduce the surface tension. Roulstone et al.⁵⁸ studied the effect of added surfactants upon the water-vapour permeability of latex films and noted that there was a difference between the surfaces of the film which they explained in terms of surface roughness and surfactant enrichment.

Vanderhoff et al.^{30,36} observed the development of blister-like eruptions on the surface of films as they aged. These were believed to be the incompatible stabiliser, which was expelled as the latex particles underwent further coalescence.

Khodzhaeva et al.⁵⁹ discussed the structure of films prepared from polyisoprene latices. They found that polyisoprene films containing an anionic emulsifier rapidly lose their globular structure upon drying. This contrasts with the case for natural rubber latex films which retain particulate structure at all stages of drying and even after prolonged storage. This is believed to be due to the presence of protein surfactant upon the particle surfaces. The type of emulsifier has an important effect upon film structure: a film of polyisoprene latex containing a non-ionic emulsifier retained its particulate structure upon drying.

In films evaporated from natural rubber latex the protein which stabilises the particles in the latex phase appears to form hard domains which behave like particulate fillers, affecting stress-strain behaviour and enhancing modulus⁶⁰. The effect disappears if the protein is removed enzymatically, hydrolytically or if it is disrupted and dispersed by mechanical working.

1.6.5 Drying of Natural Rubber Latex Films

Gazeley and Swinyard³⁷ studied the drying of natural rubber latex films. The drying curves were similar in form to those of Vanderhoff³⁶. They found no significant difference between the results for coagulant-dipped and cast films. This indicates that Brownian motion of the particles makes no significant contribution to water loss since this cannot occur in a gel. In the first stage of drying, the water can pass through the gel or the wet latex at the same rate as it is removed from the surface. For wet gels the water passes through capillaries between the partially coalesced rubber particles. As water is lost there is further coalescence and the capillary structure is reduced. In a cast film a coherent film forms at the surface at an early stage of drying. A local drop in pH resulting from loss of ammonia causes this gelation.

The drying of prevulcanised latex films are found to be greater than for unvulcanised latex under similar conditions. Prevalcanised latex shows some increase in the first stage of drying but the main difference is the faster rate during the final stage of drying, which is diffusion-controlled. This is believed to be due to the retarded particle coalescence of prevulcanised latex particles which gives a capillary network with an extended lifetime. Crosslinking between rubber molecules in the prevulcanised latex particles reduces the molecules' mobility and hence reduces their ability to move across particle boundaries and intermingle once the particles are in contact in the drying film.

For cast natural rubber latex, under good drying conditions, water is likely to evaporate from the surface faster than it can be transported through the bulk of the film. This would favour coalescence of particles in the surface layer by bringing particles at the surface into contact and would introduce diffusion control at an early stage because the remaining water would have to diffuse through the rubber rather than through the capillaries between latex particles. Since prevulcanised latex particles coalesce less readily, films of these latices would be expected to dry more rapidly than unvulcanised films.

CHAPTER 2: VULCANISATION CHEMISTRY

2.1 Historical Introduction

Until the discovery of sulphur vulcanisation in the last century natural rubber was of limited use owing to changes in its properties with changes in temperature. The discovery of sulphur vulcanisation is credited to two individuals, Goodyear in the United States of America and Hancock in Great Britain. They both obtained patents in which they described rubber which had been cured using sulphur. Goodyear's patent of 1844 describes a solution of rubber dissolved in turpentine combined with white lead (basic lead carbonate) and sulphur, each ground separately in turpentine. The three components were spread on a smooth surface to form a sheet and then heated to form the desired product. The typical composition of the mixture was 20 parts sulphur, 28 parts white lead and 100 parts rubber. In 1843 Hancock obtained a patent in which he described vulcanisation by the migration of sulphur through a rubber sheet when the sheet was placed in molten sulphur. He found that the samples did not stiffen when put on ice. Unvulcanised rubber is stiff at low temperatures because of the formation of crystallites. The ability of rubber to form crystallites is reduced by the formation of crosslinks during vulcanisation. The term vulcanisation, was coined by Brockedon from Vulcan the Roman God of fire and smiths. Although the process of vulcanisation has been much refined over the intervening years the use of sulphur, in combination with other chemicals, is still paramount.

It was early this century that the possibility of vulcanising natural rubber latex was investigated. In 1921 Schidrowitz obtained a patent in which he described the prevulcanisation of latex by heating with sodium polysulphide, sulphur and zinc oxide in steam at 145°C for some 30 to 45 minutes. Later, the use of water-soluble accelerators allowed the temperature of vulcanisation to be reduced to 70-80°C¹⁵. The introduction of ultra-accelerators has allowed the vulcanisation temperature to be reduced still further if desired.

2.2 Sulphur Vulcanisation of Dry Natural Rubber

2.2.1 Unaccelerated Sulphur Vulcanisation⁶¹

Much of the early work on sulphur vulcanisation was carried out at BRPRA (now MRPRA), and is recorded in "The Chemistry and Physics of Rubber-like Substances"⁶¹. Investigation of vulcanisate structure was hampered by the difficulty in carrying out instructive chemical investigation on vulcanised rubber because of its insolubility. The use of low molecular weight olefins as models for natural rubber allowed the types of structure formed to be determined.

It was initially believed that the products of the reaction between olefins and sulphur alone would be less complex and more easily analysed than those formed by a reaction between olefins and sulphur in the presence of accelerators and activators. This was not in fact the case and the chemistry of the unaccelerated system was very complex⁶².

Progress in the identification of products was closely allied to developments in instrumental methods for the separation and identification of multicomponent mixtures of thermally sensitive compounds. Gas-liquid chromatography played an important role in this process. The compounds identified enabled the main sequence of vulcanisation reactions to be worked out.

Although the research to be reported in this thesis involves only accelerated sulphur vulcanisation, unaccelerated sulphur vulcanisation will also be described in order to give some indication of the complexity of the reactions and to highlight the advantages derived from the use of accelerators.

In order to assist in the understanding of the course of unaccelerated sulphur vulcanisation, low molecular weight alkenes were used as "model" compounds for natural rubber. 2-Methylpent-2-ene has become the most commonly used "model" compound since its boiling point is such that it can be conveniently separated from the product sulphides. 2-Methylpent-2-ene models the α -methylic and one of the two α -methylenic sites found in polyisoprene. These sites represent the positions of attachment by sulphur to the polyisoprene backbone. All three sites found on cis-1,4-

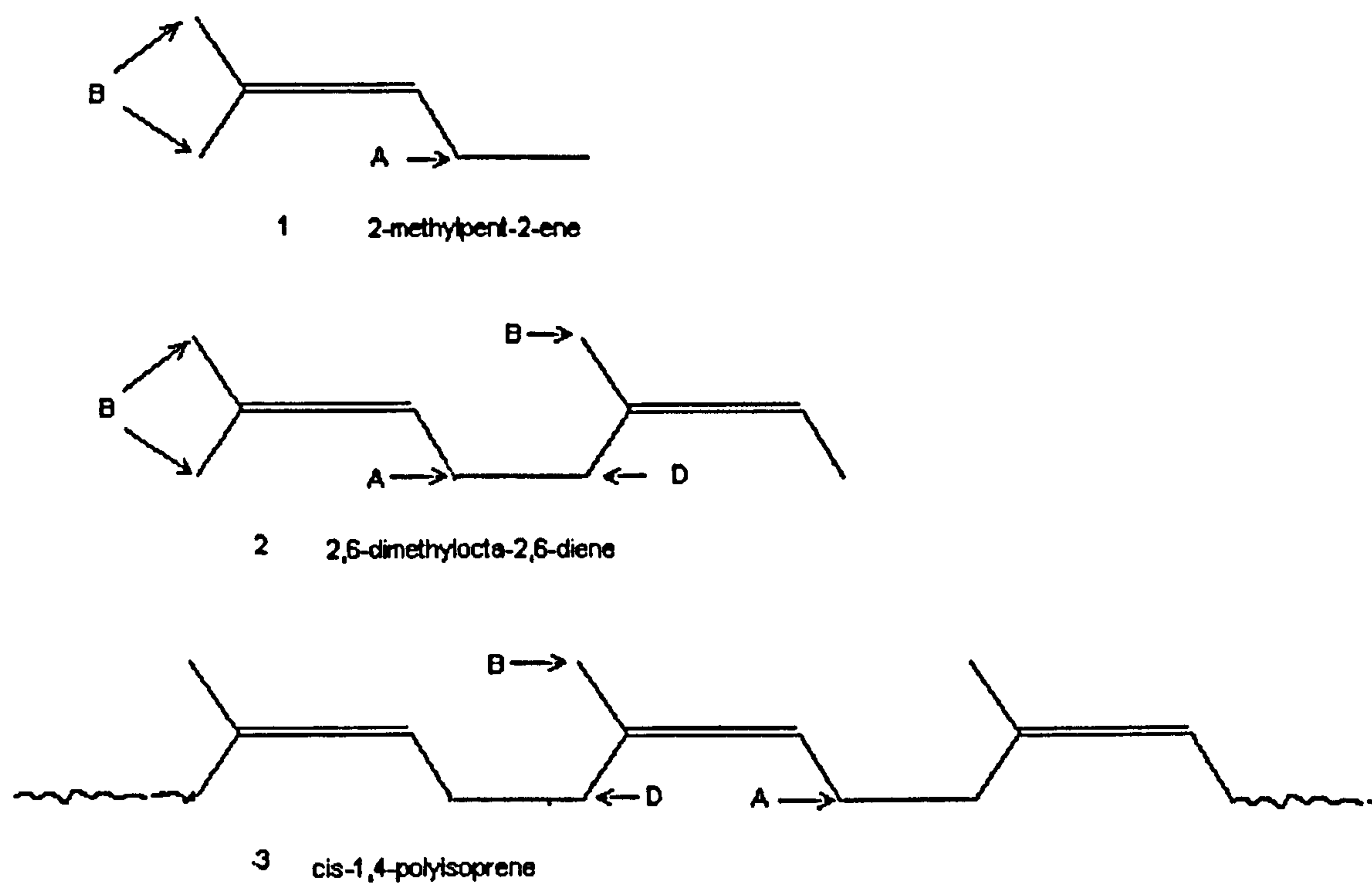
polyisoprene are found on the 1,5-diene, 2,6-dimethylocta-2,6-diene. The structures and sites of sulphur attachment are shown as 1, 2 and 3 in Scheme 1⁶¹.

The interaction between mono-olefins and sulphur at temperatures up to 140°C gave rise to products which were principally polysulphides in which two hydrocarbon groups were linked by polysulphidic groups ⁶¹. On extensive heating, the number of sulphur atoms in the crosslink decreased with reaction time to 1-2. When higher temperatures and extended reaction times were avoided, no hydrogen sulphide, thiols or other sulphurated functional groups were formed. Therefore, the polysulphide was formed without dehydrogenation of the monoolefin. Three main types of polysulphide were formed. They are shown in Scheme 2⁶¹. The relative proportions of each type and the structures of the alkenyl and alkyl groups in I were dependent upon the olefin used. 2-Methylpent-2-ene, an olefin having a structure closely resembling the structural unit of polyisoprene, formed a higher proportion of 4 and less of 5 and 6. The alkenyl alkyl polysulphides were mainly of the structures 7 and 8.

When 1,5-dienes were used to investigate sulphuration the analogous crosslinked polysulphides were formed but, in addition, a substantial amount of the sulphur was combined in cyclic monosulphides. 2,6-Dimethylocta-2,6-diene was used as a simple analogue of natural rubber. The cyclic monosulphides 9-12 (see Scheme 3) were formed and a conjugated triene (2,6-dimethylocta-2,4,6-triene) was formed concurrently. These were shown to be secondary products. The initial polysulphides formed from reactions of dienes were found to be more complex than those formed by monoolefins and to undergo secondary reactions with neighbouring olefin centres to form structures containing cyclic monosulphide groups. The structures are shown in Scheme 4, 13-17. The proportion of total sulphur combined in the free cyclic monosulphides increased progressively with reaction time.

The network formed by heating natural rubber with sulphur alone, without accelerators, consists of a very complex structure associated with poor crosslinking efficiency; 40-55 sulphur atoms were combined for each chemical crosslink formed. From the reactions of "model" compounds, the poor crosslinking efficiency was attributable to the incorporation of sulphur into long polysulphide crosslinks, vicinal crosslinks like 15, shown in Scheme 4, which act as a single crosslink, and large numbers of cyclic

Scheme 1 The Structure of "Model" Olefins and Cis-1,4- Polyisoprene

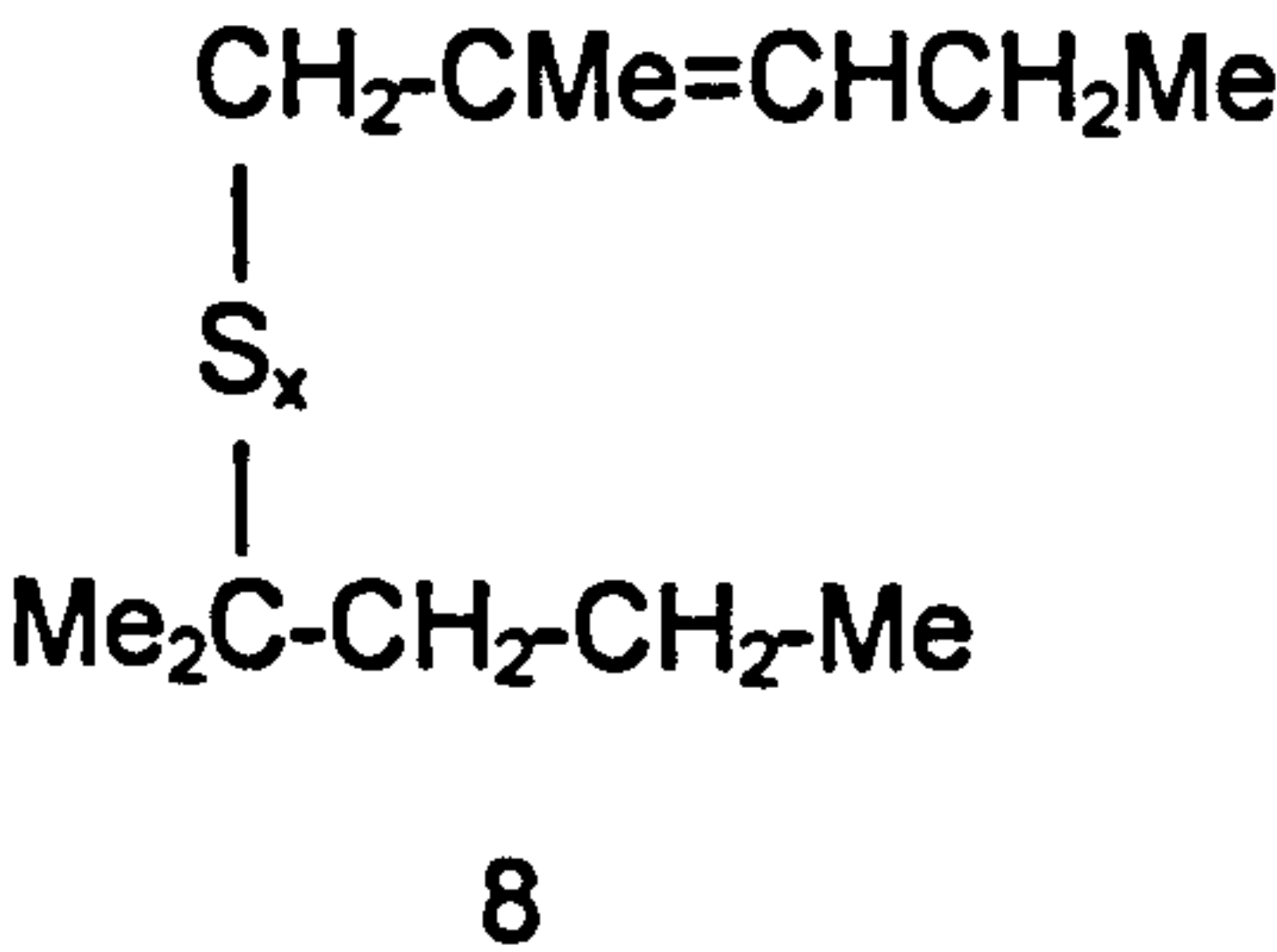
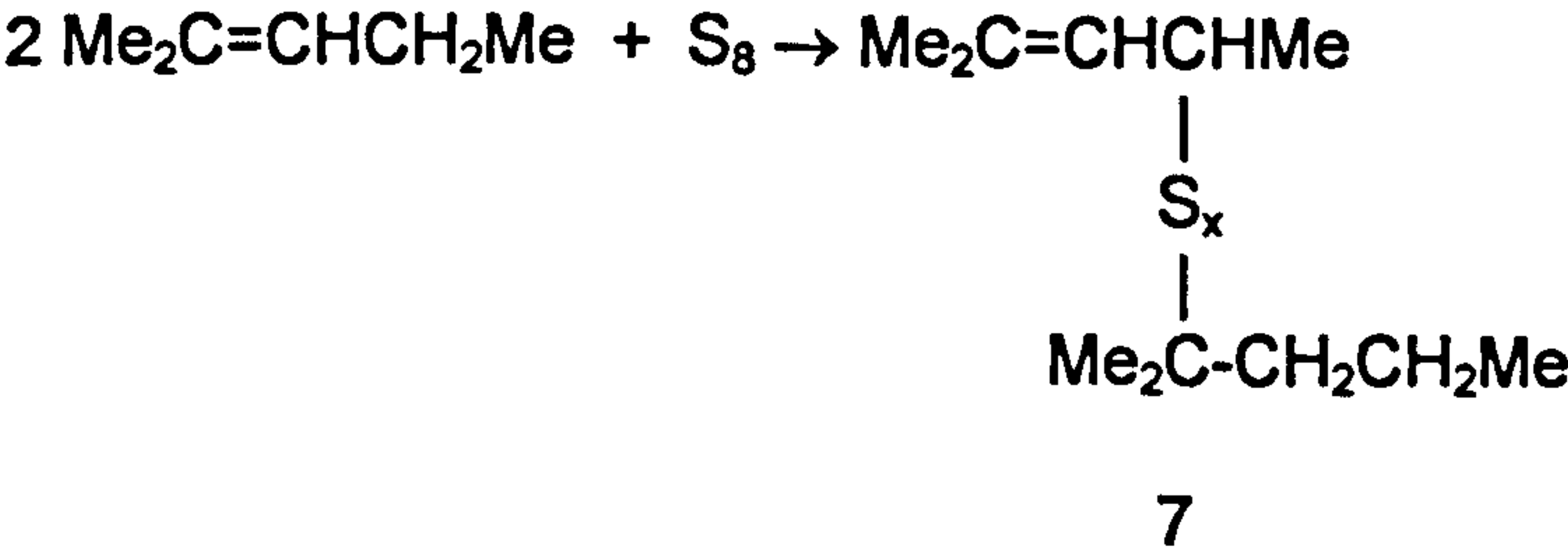
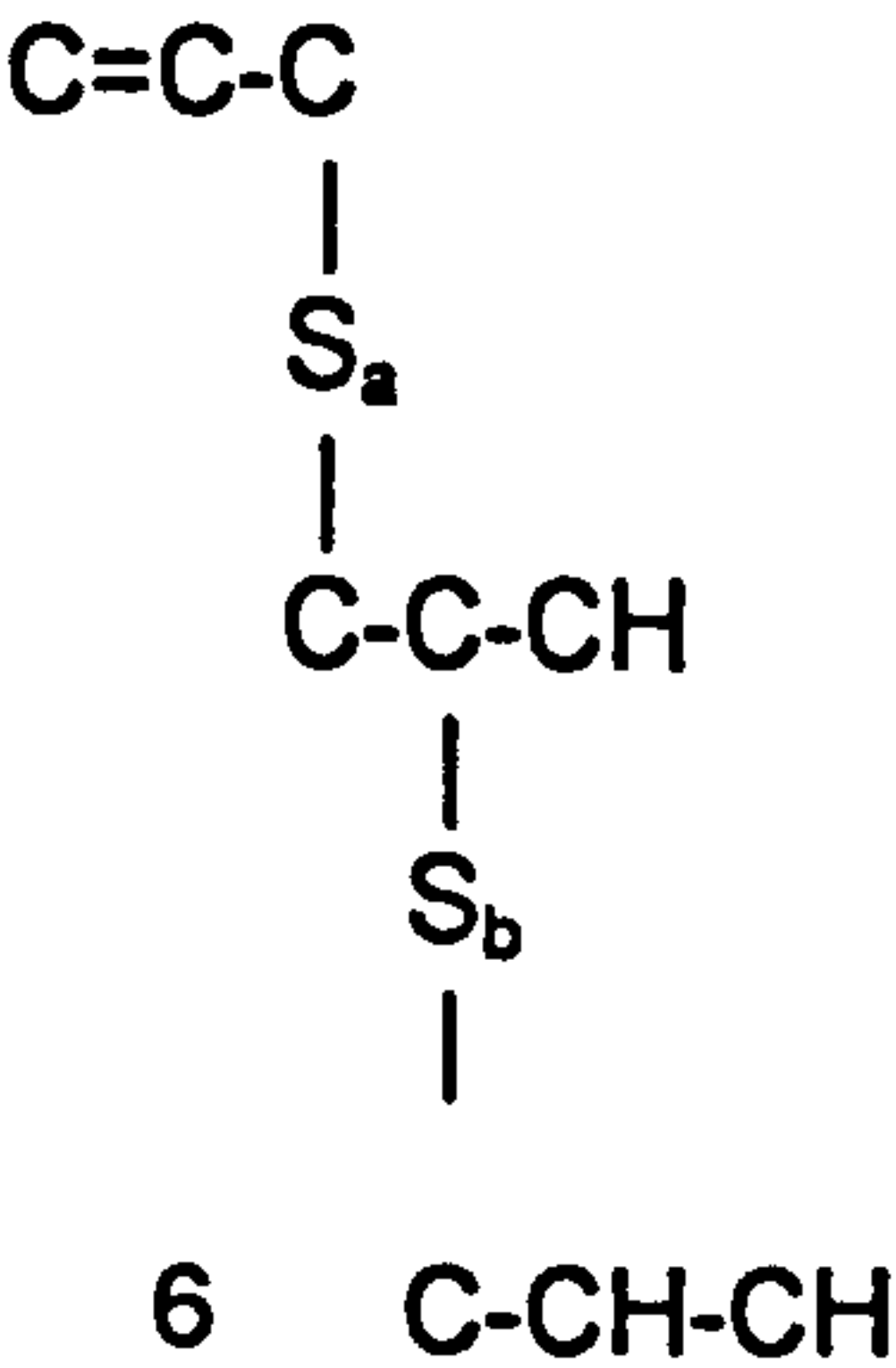
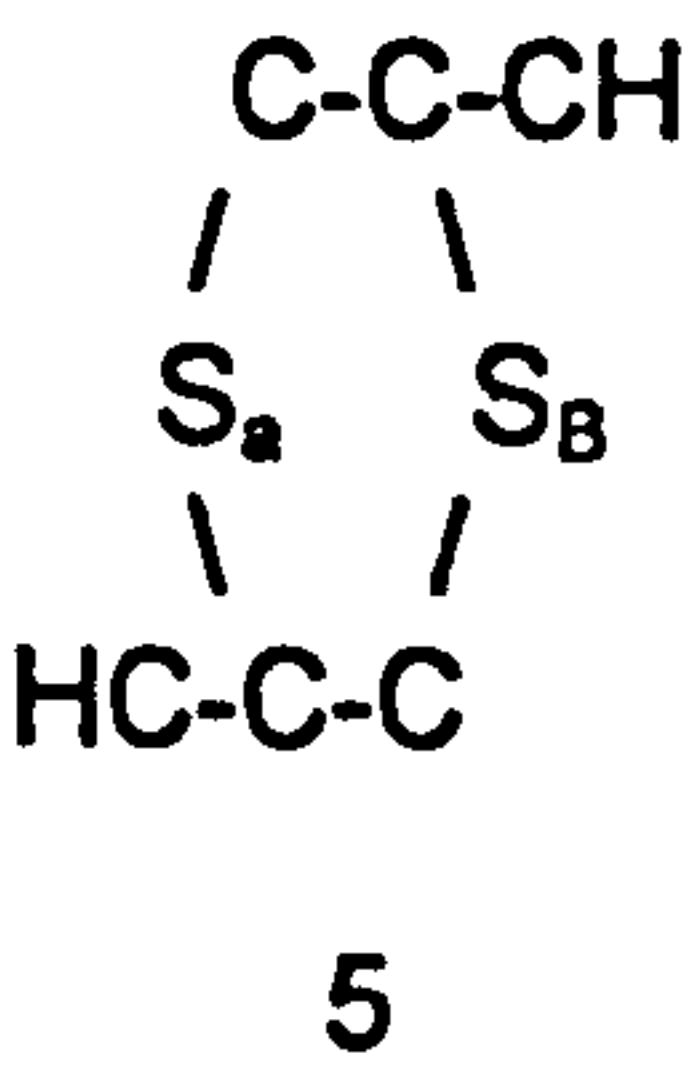
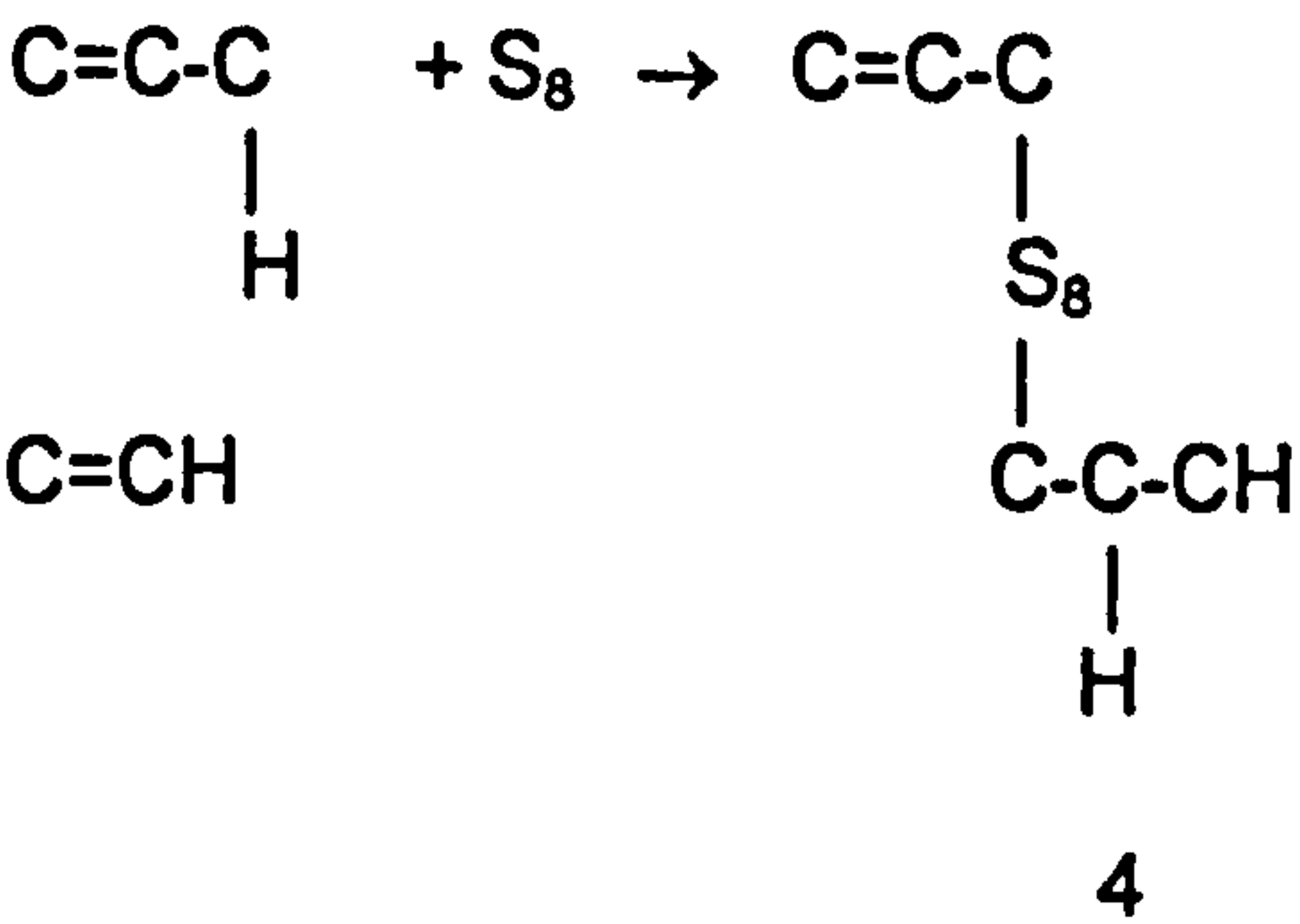


B = α -methylic sites

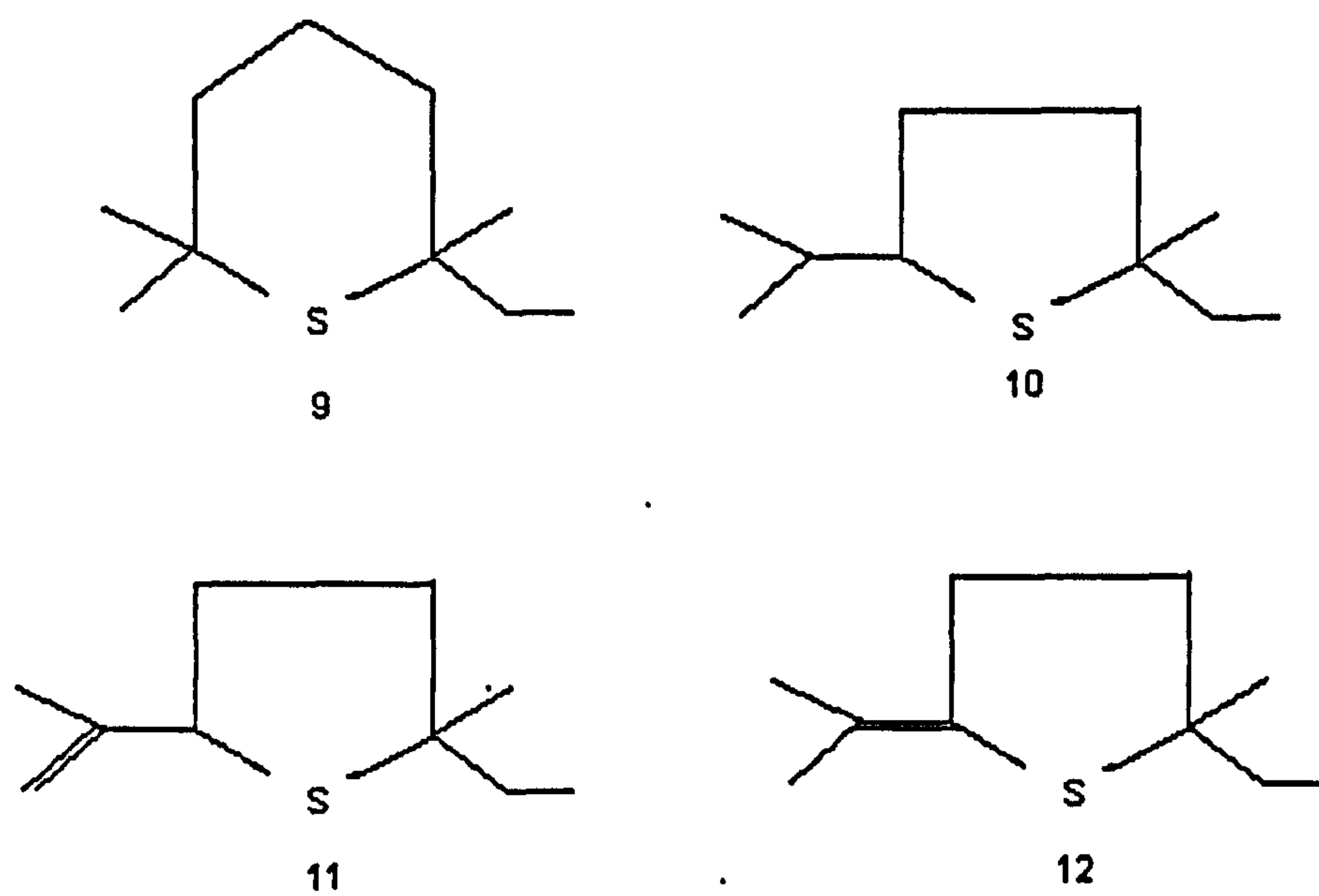
A and D = α -methylenic sites

Based on Ref. 61

Scheme 2 Types of Polysulphides Formed by the Reaction of Mono-olefins with Sulphur

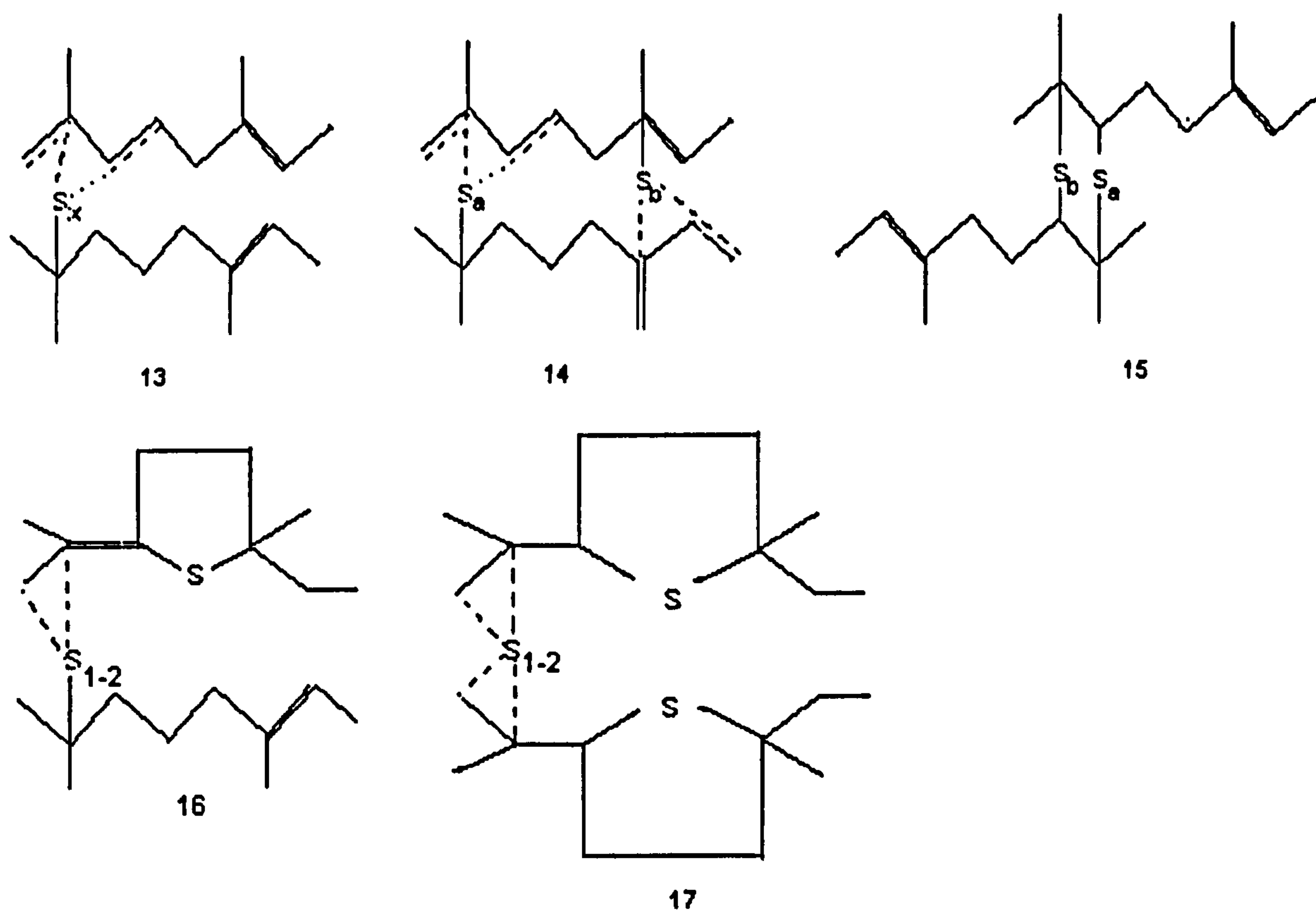


Scheme 3 Cyclic Monosulphides Formed by the Reaction of 2,6-dimethylocta-
2,6-diene with Sulphur



Based on Ref. 61

Scheme 4 Polysulphides Formed During the Reaction of 2,6-dimethylocta-2,6-
diene with Sulphur



Based on Ref. 61

monosulphides which represent a major modification of the main chains. Other main chain modifications which occurred were scission and the formation of conjugated trienes. A representation of the structural features of an unaccelerated sulphur-natural rubber vulcanisate network is shown in Figure 12.

2.2.2 Accelerated Sulphur Vulcanisation^{61,62,63}

Accelerated sulphur vulcanisation involves the use of an organic accelerator with sulphur. In dry rubber vulcanisation most accelerators in commercial use do not contain zinc, instead zinc oxide and a fatty acid are added to the accelerator to form an active accelerator system. The process of milling and mixing dry rubber and the vulcanising ingredients inevitably causes some heating of the mix. If an "active" accelerator were included, i.e. one which contains zinc, it would lead to vulcanisation during the mixing process. This premature vulcanisation is known as "scorching". It is disadvantageous to have a partially vulcanised rubber mix when carrying out other processing operations, e.g. injection moulding. Therefore, the accelerators used in dry rubber vulcanisation are generally "delayed action" accelerators which react with zinc oxide at, or close to, the vulcanisation temperature (140-200°C) to form the "active" accelerator which facilitates the combination of sulphur and natural rubber.

During the coagulation of latex and washing of the coagulum to produce dry rubber most of the non-rubbers are removed; unlike latex where approximately 30% of the non-rubbers remain, see Section 1.2. The solubility in rubber of "active" accelerators, e.g. ZMBT and ZDEC, is enhanced by complexation with carboxylic acids (e.g. fatty acids) or nitrogenous bases^{64,65}. Natural rubber latex contains these substances and therefore the addition of fatty acids is not strictly necessary. The addition of fatty acids to dry rubber mixes increases the efficiency of the "active" accelerator by increasing its solubility in rubber⁶⁴.

Zinc-containing accelerators are included in latex compounds, since compounding of latex does not involve any heating. Therefore, zinc oxide does not fulfil the same function as in dry rubber vulcanisation. It may in some cases be omitted from the formulation. In the vulcanisation of latex, zinc oxide is used to ensure the regeneration of the accelerator. Merrill^{23,24} observed the depletion of the accelerator ZDEC during

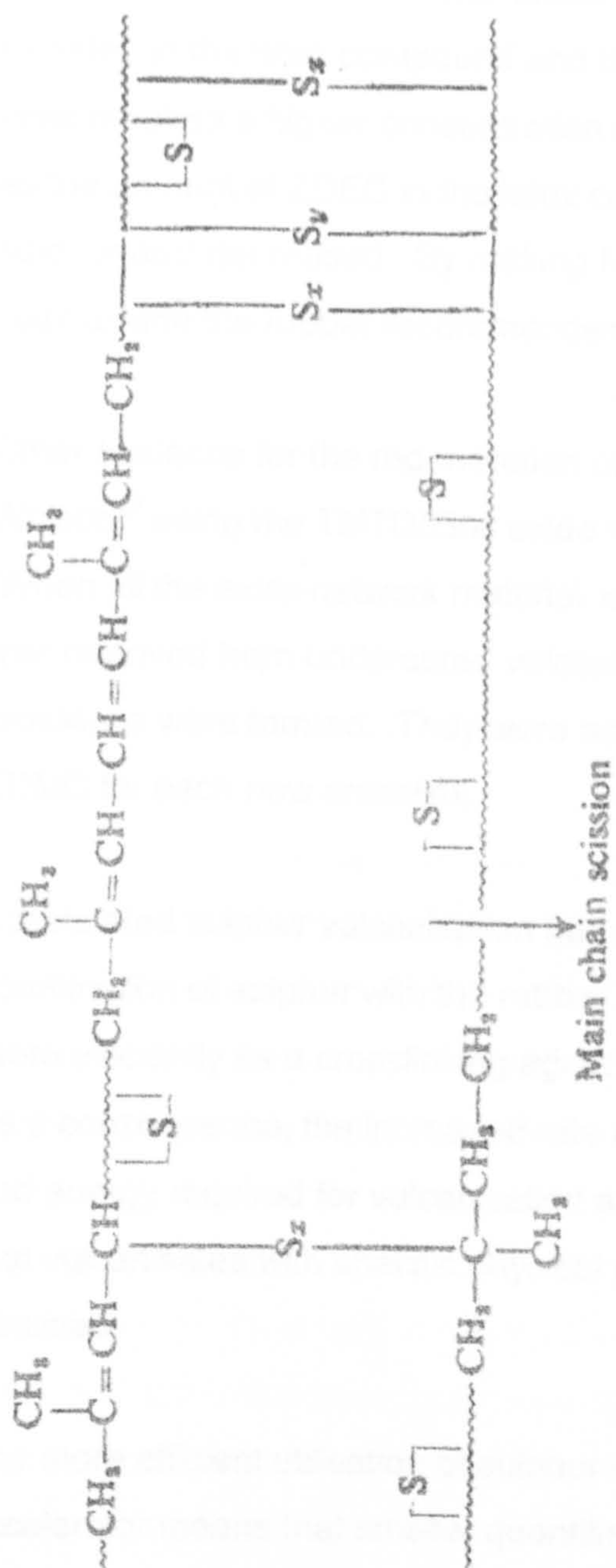


Figure 12 Structural Features of an Unaccelerated Sulphur-Natural Rubber
Vulcanisate

Based on Ref. 61

prevulcanisation of latex. This effect was considerably reduced when zinc oxide was included in the latex compound and the resulting films prepared from the prevulcanised latex reached a higher concentration of chemical crosslinks. Merrill also showed that as the amount of ZDEC in the latex compound decreased, the disappearance of free sulphur also decreased. By making further additions of ZDEC the combination of sulphur with the rubber recommenced.

Other evidence for the regeneration of accelerator comes from the work of Moore and Watson⁶² using the TMTD/Zinc oxide vulcanising system and cis-1,4-polyisoprene^{61,62}. When all the extra-network material, except zinc oxide and traces of zinc sulphide, was removed from undercured vulcanisates and the materials reheated, new crosslinks were formed. They were accompanied by the formation of a molecule of ZDMC for each new crosslink.

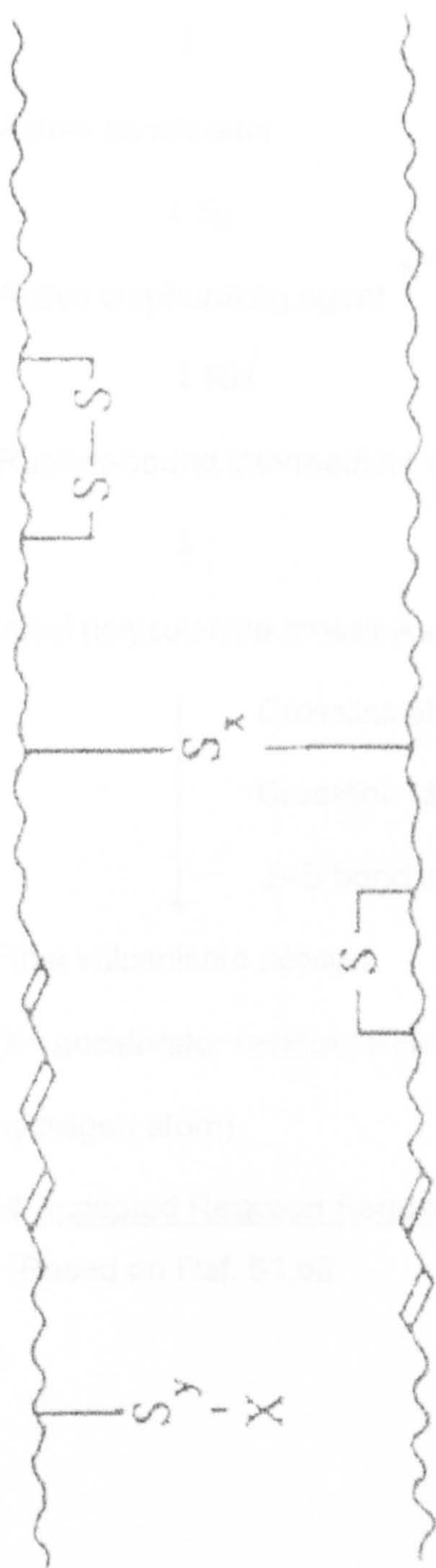
Accelerated sulphur vulcanisation has a number of advantages. The rate of combination of sulphur with the rubber is greatly increased, the sulphur is combined more efficiently as a crosslinking agent and produces a simpler vulcanisate structure. As a consequence, the increased rate of crosslinking leads to reductions in the time and energy required for vulcanisation and allows greater control over the process so that vulcanisates with specific physical properties and ageing characteristics can be obtained.

The more efficient utilisation of sulphur in the vulcanisation of rubber containing an accelerator means that smaller quantities of sulphur are required than in an unaccelerated rubber mix in order to produce vulcanisates with similar concentrations of effective sulphur crosslinks. This results in savings on materials. The more predictable combination of sulphur in accelerated vulcanisation leads to less uncombined sulphur remaining in the final vulcanisate. If the concentration of uncombined (free) sulphur in the vulcanisate is greater than the solubility of sulphur in rubber it will crystallise out and migrate to the surface, making the surface look patchy or discoloured. This phenomenon is known as "blooming". The problem of blooming is likely to be less severe with accelerated vulcanisates, where the amount of free sulphur can be minimised, than in unaccelerated vulcanisates. By varying rubber formulations, cure times and cure temperatures for the more predictable accelerated rubber systems, greater control over the process is possible, producing vulcanisates

with specific properties and ageing characteristics. By careful control of formulation, cure temperature and cure time it is possible to minimise the variation between different rubber mixes. The general structural features of an accelerated sulphur-NR vulcanisate network are shown in Figure 13.

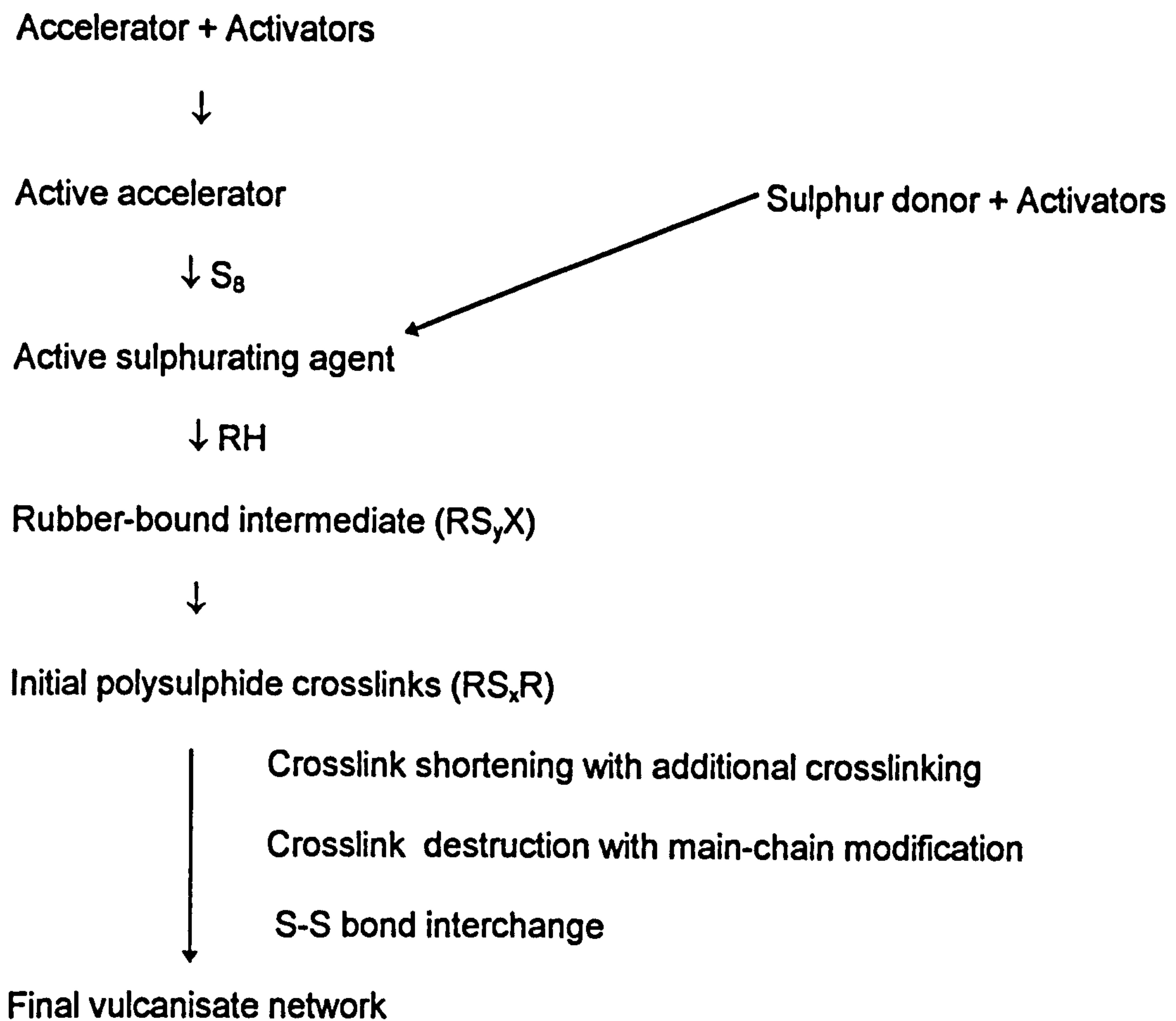
The generally accepted sequence for accelerated sulphur vulcanisation is shown in Figure 14. The "active sulphurating agent" is a species which reacts with the rubber to form carbon-sulphur bonds. The "rubber-bound" intermediate contains a fragment derived from the accelerator and is linked to the rubber chain via two or more sulphur atoms. These pendent groups are the precursors to crosslinks, the crosslinks being formed either by direct reaction of the pendent group with another rubber molecule or by disproportionation with a second pendent group on a neighbouring rubber chain. The initial polysulphidic crosslinks undergo a number of reactions, described below to form the final vulcanisate network. The reaction sequence shown in Figure 14 is a simplified outline scheme. Some of the reactions take place consecutively whilst others compete with each other. The individual reactions have their own responses to temperature, to time and to catalysts. With such a complex combination of reactions it is clear that the final vulcanisate structure will be critically dependent upon the vulcanisation conditions and composition of the vulcanising mixture.

The formation of the "active sulphurating agent" involves a number of steps. Zinc oxide and activators such as nitrogen bases and carboxylic acids are usually used in conjunction with the accelerator and are believed to be involved in the formation of the "active sulphurating agent". Zinc is thought to be involved in the formation of the "actual accelerator" which is a precursor to the "active sulphurating agent". As was mentioned earlier in connection with the role of zinc oxide, the zinc accelerator thiolates are rendered soluble in the rubber hydrocarbon by the co-ordination of the zinc by carboxylate ions or nitrogenous bases, see Figure 15. The proposed main pathway is the formation of crosslinks in accelerated sulphur vulcanisation is shown in Figure 16. The mechanism by which the active sulphurating agent is formed and whether its reaction with rubber is by a free radical or polar pathway are the subjects of much speculation amongst a number of groups of workers. The mechanisms have been reviewed by Chapman and Porter⁶².



(X= accelerator residue; x,y= 1-6)

Figure 13 Generalised Structure of a Sulphur Vulcanisate of Natural Rubber
Based on Ref. 63



(X= accelerator residue; RH= rubber hydrocarbon, where H is an allylic hydrogen atom).

Figure 14 Accepted Reaction Sequence for Sulphur Vulcanisation

Based on Ref. 61,62

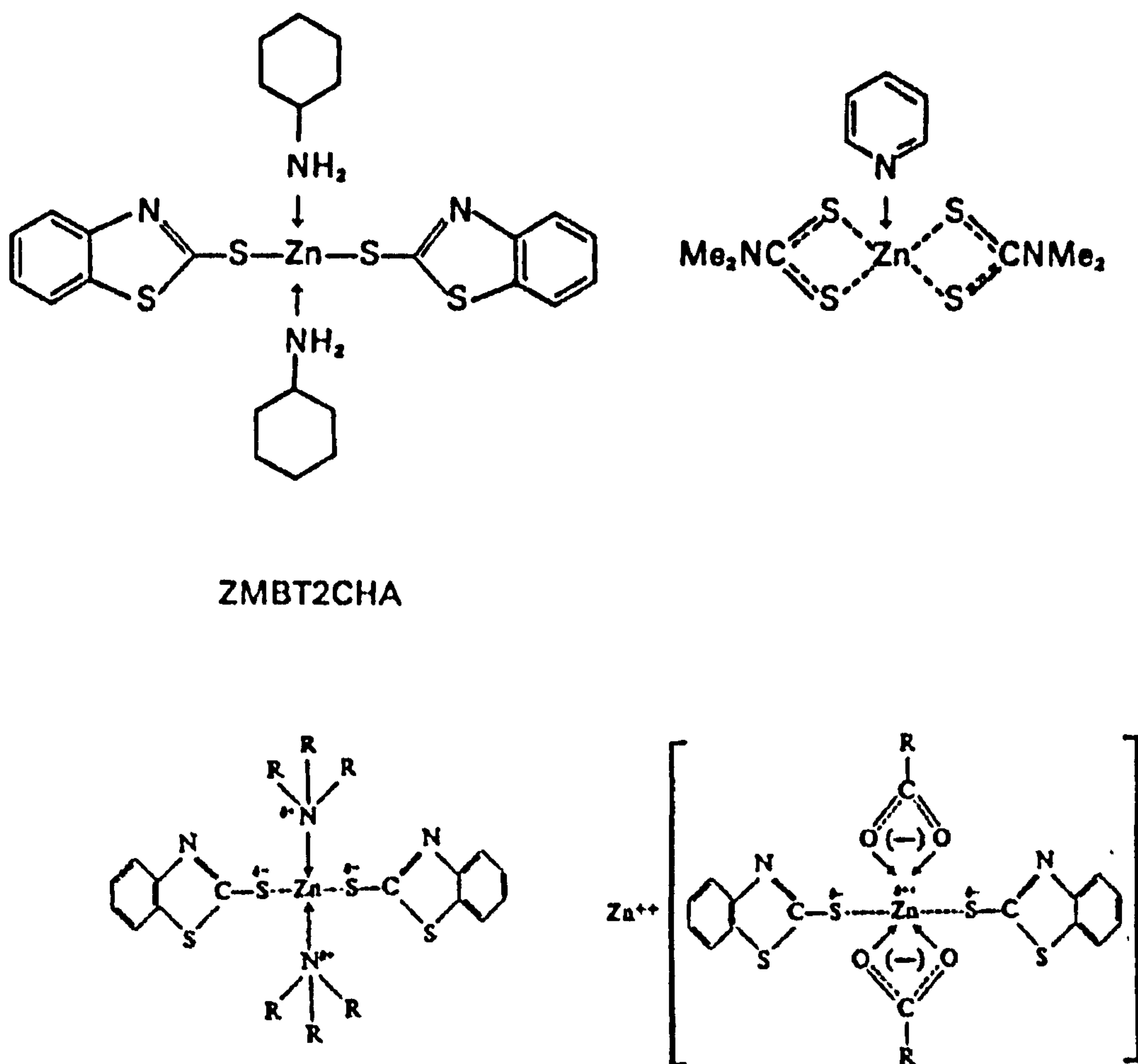


Figure 15 Zinc Thiolate Complexes
Based on Refs. 61 and 62.

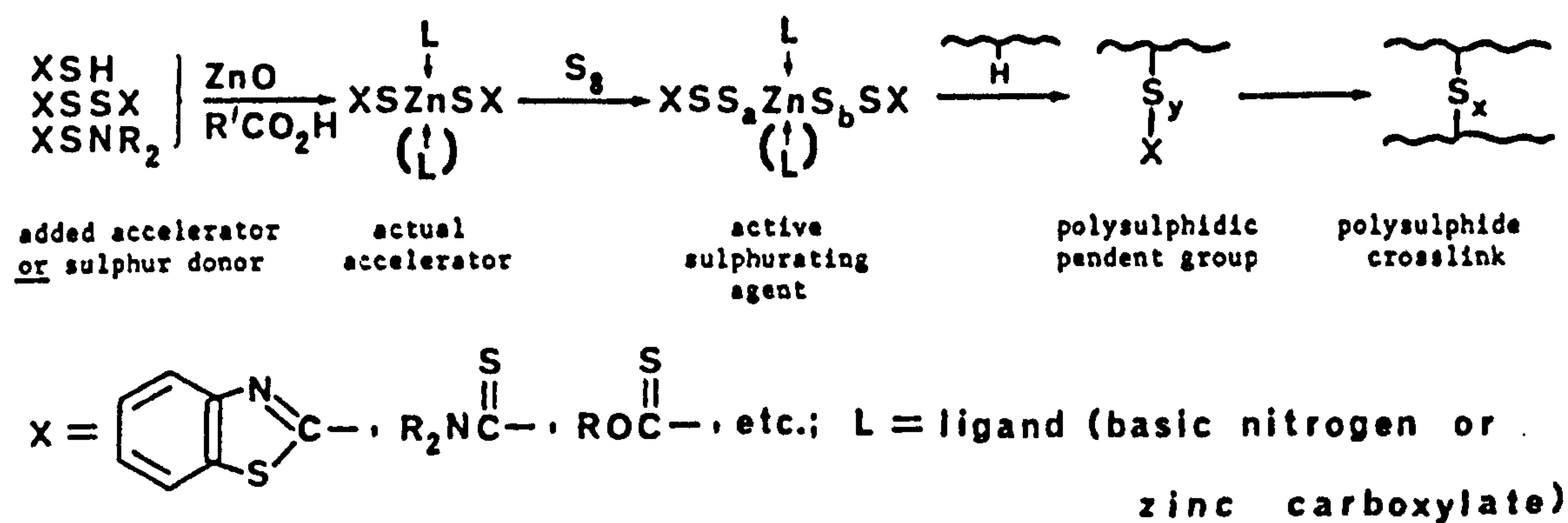


Figure 16 Postulated Main Pathway to Crosslinks in Accelerated Sulphur Vulcanisation of Natural Rubber

Based on Ref. 63

The rubber-bound intermediates form crosslinks by two routes. The first route is by disproportionation between two rubber-bound intermediates and the second is by reaction of a rubber-bound intermediate with a second rubber hydrocarbon molecule⁶².

The initial polysulphidic network which is formed undergoes a number of further reactions known as "network maturing reactions" which result in a final vulcanisate network, see Figure 14. The final composition of the vulcanisate network is dependent upon a number of different factors. The ratios of accelerator to sulphur in the formulation and the concentrations of activators like nitrogenous bases or carboxylic acids (which increase the solubility of the zinc thiolate in rubber) have an effect upon type of final crosslink formed. In systems where the ratio of accelerator to sulphur is high or the concentration of soluble zinc is high the polysulphidic crosslinks which are formed initially are converted to monosulphide crosslinks and the sulphur removed from the polysulphidic crosslinks is recycled in forming additional crosslinks as cure time progresses. This is known as desulphuration, shown in Figure 17. In situations where the ratio of accelerator to sulphur is low or the concentration of soluble zinc is low a more complex vulcanisate network which is largely polysulphide remains even at long cure times. There is some conversion of polysulphides to di- and monosulphides but this is relatively slow. There are also modifications to the rubber backbone and cyclic sulphides are formed, see Figure 17. The situation is more like that for an unaccelerated cure. The rubber formulation and cure times are not the only factors affecting the final vulcanisate structure, cure temperature is also very important in determining the types of crosslinks which are finally formed^{65,66}. The different sulphur crosslinks have different thermal labilities. Thermal decomposition of crosslinks is a process which is in competition with desulphuration. The relative rates of the reaction are temperature dependent, see Figure 17. Below 50°C it is the formation of polysulphidic pendent groups and their reaction to forming polysulphide crosslinks which predominate and other reactions depicted on Figure 18 do not play an important part.

At 100°C desulphuration of the polysulphide crosslinks is sufficiently rapid for mixtures of mono-, di- and polysulphides to be formed; an example of the change in crosslink

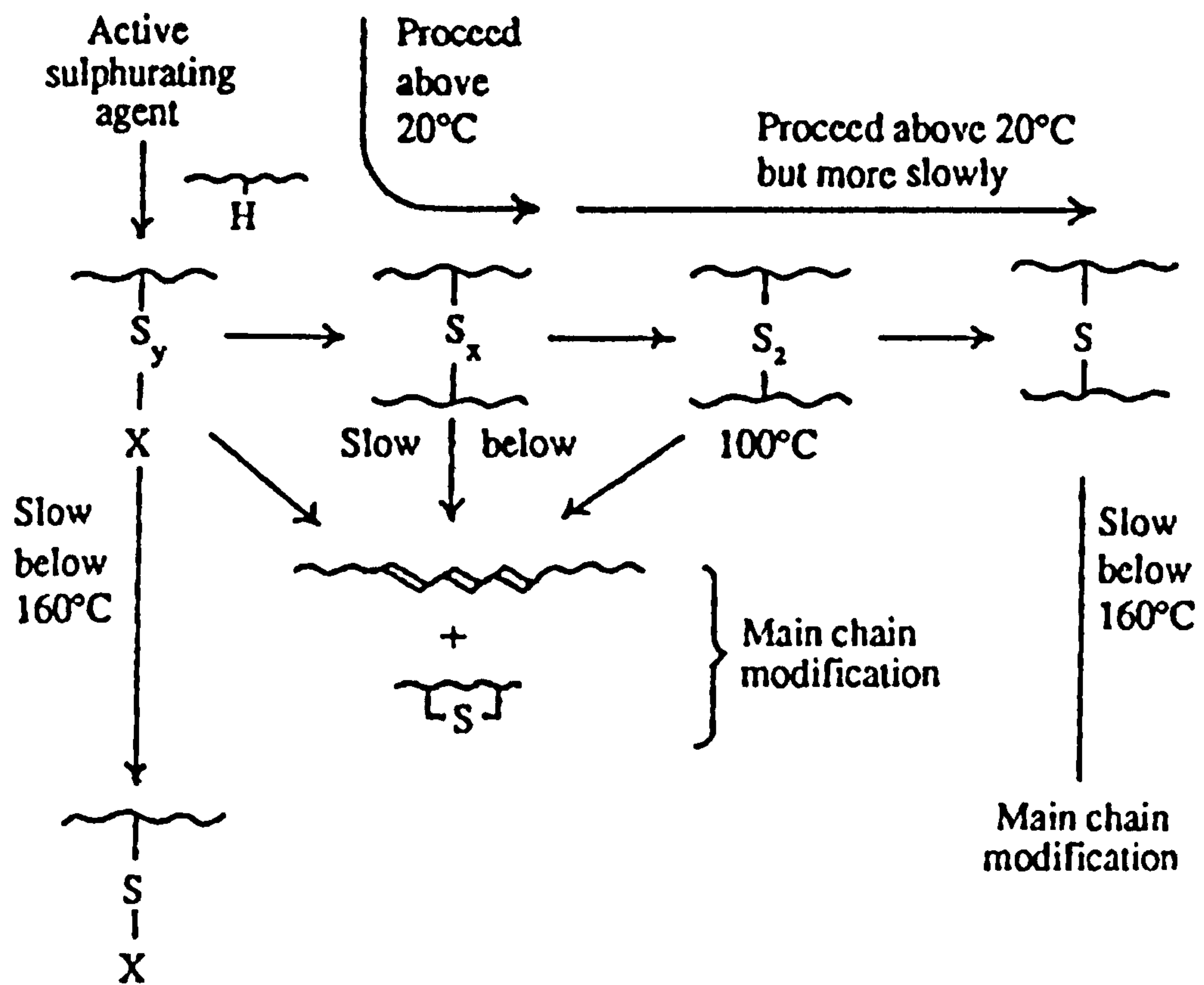


Figure 17 The Effect of Temperature of Vulcanisation upon Vulcanisation Reactions

Based on Ref. 63

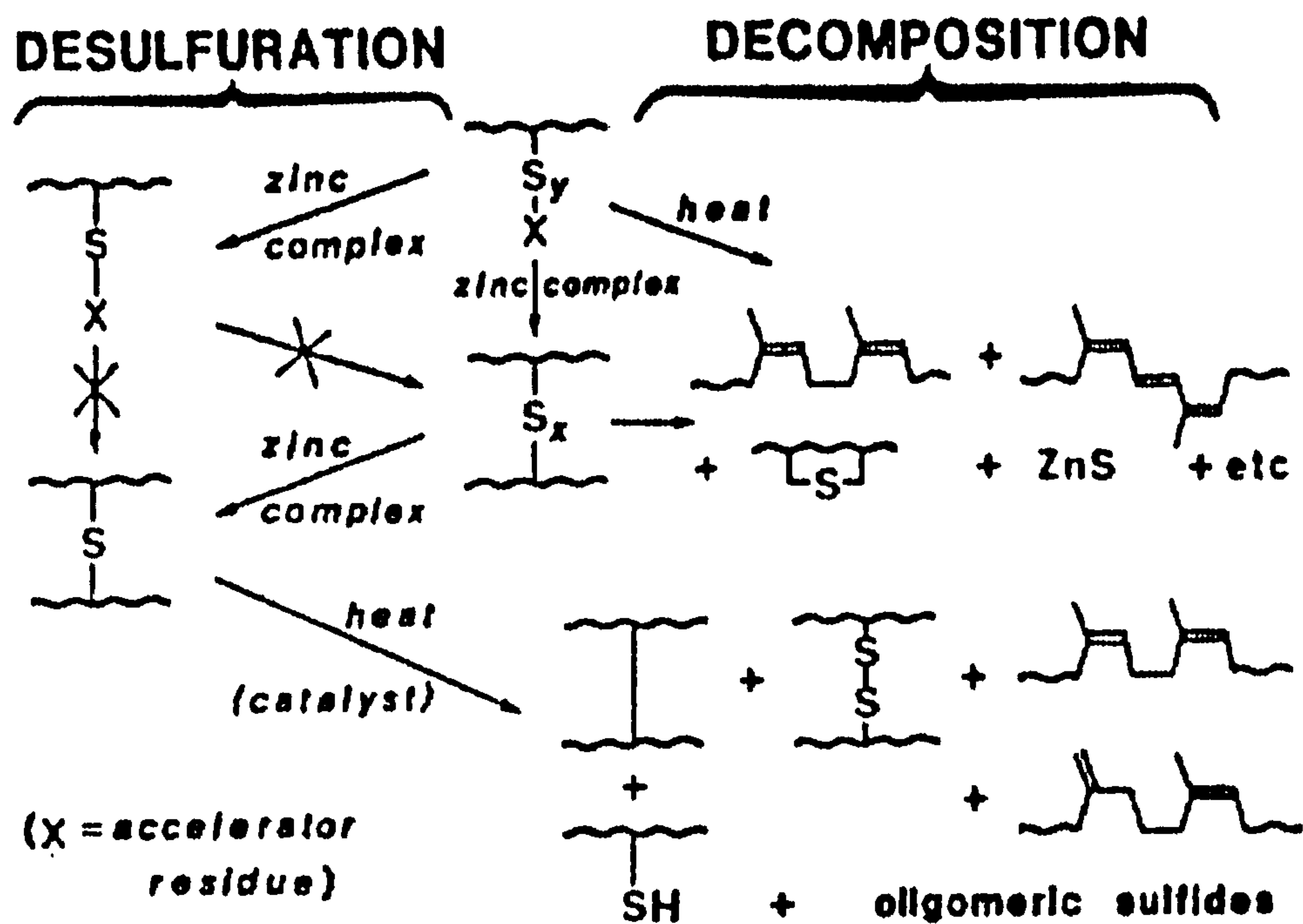


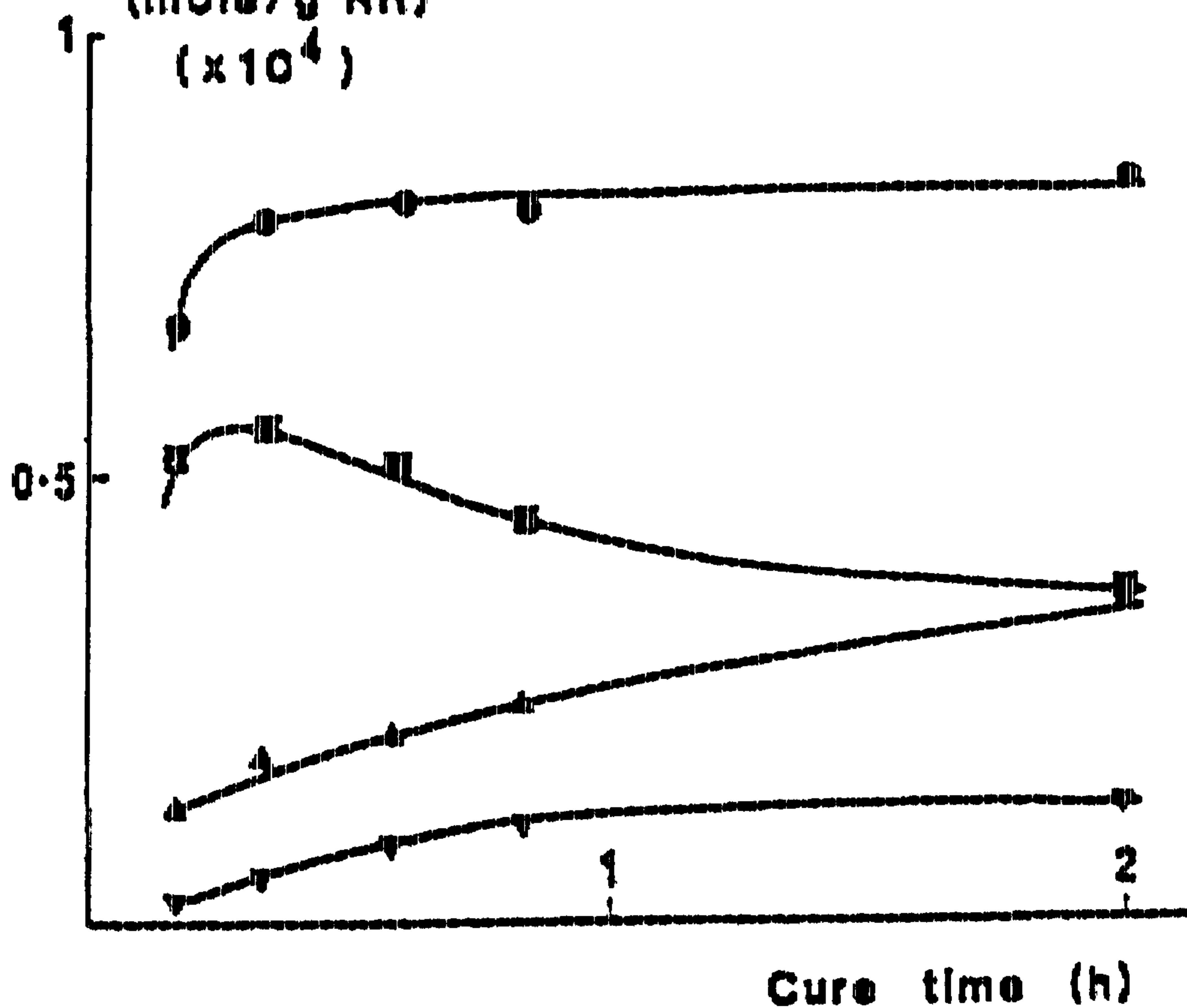
Figure 18 Desulphuration and Decomposition of Pendent Groups and Crosslinks in Polyisoprenes

Based on Refs. 62 and 63

composition is shown in Figure 19. It is also assumed that pendent groups will also undergo desulphuration at this temperature. Decomposition reactions leading to net crosslink loss are only apparent above 100°C. The rates of desulphuration and decomposition increase relative to sulphuration and crosslink formation up to 150-160°C. At 140°C the rate of decomposition of polysulphide crosslinks is rapid whereas that of the monosulphide is relatively slow. It is between 150-160°C that the least stable of the monosulphide crosslinks begin to decompose and desulphuration of the pendent groups affects crosslinking efficiency. The rates of these reactions increase with increases in vulcanisation temperature; at 200°C the half-life of even monosulphide crosslinks is only minutes long. At 210°C the weakest carbon-carbon bonds in the polyisoprene backbone begin to decompose, albeit slowly.

By careful control of cure temperature, cure time and the use of formulations containing the appropriate concentration of zinc accelerator - thiolate complexes, it is possible to produce vulcanisates which contain predominantly polysulphidic crosslinks, predominantly monosulphidic or a mixture of these and disulphidic crosslink types. The physical properties of vulcanisates are influenced by the composition of the crosslinks and this will be discussed in Section 2.5.1. For vulcanisates, containing a high proportion of polysulphide crosslinks, which are used at temperatures up to 100°C it is possible to maintain the degree of crosslinking and network structure and hence physical properties, over moderate periods of time. At 180°C, in order to sustain the degree of crosslinking in the network for a substantial amount of time the crosslinks must be mainly monosulphidic. The conditions under which a vulcanisate will be used are an important consideration when planning the formulation and vulcanising conditions for it.

Degree of
chemical crosslinking
(mole/g RH)
($\times 10^4$)



Cure system in parts by weight per hundred of rubber: Sulfur, 2.5; zinc oxide, 3.0; zinc diethyldithiocarbamate, 1.0; zinc benzothiazole-2-thiolate, 1.0 ●, total crosslinks; ■, polysulphide; Δ, disulphide; ∇, monosulphide crosslinks.

Figure 19 Distribution of Mono-, Di- and Polysulphide Crosslinks as a Function of Reaction Time for Natural Rubber Latex Vulcanised at 100°C

Based on Ref. 66

2.3 Prevulcanisation of Latex

In prevulcanisation of natural rubber latex an uncrosslinked colloidal dispersion of natural rubber particles is transformed into a colloidally-stable dispersion of crosslinked rubber particles by heating the latex in the presence of sulphur, an organic accelerator and, usually, zinc oxide. In view of the fact that the rubber particles and the vulcanising ingredients are initially physically separate and that they are largely insoluble in the aqueous phase of the latex it is indeed remarkable that the vulcanising ingredients are able to transfer to the rubber particles and to participate in the formation of crosslinks within them.

There is no reason to believe that reaction sequences proposed for sulphur vulcanisation of dry rubber should not apply also to prevulcanisation of latex. Since the temperatures used to prevulcanise latex, typically 50-80°C, are much lower than the vulcanisation temperatures for dry rubber, many of the "network-maturing" reactions described in Section 2.2 will not occur. Decomposition of crosslinks is insignificant at temperatures below 100°C and conversion of polysulphidic crosslinks to di- and monosulphides is slow, as shown in Figure 17. Loh examined the types of crosslink present in films prepared from prevulcanised latex and found them to be predominantly polysulphidic, the concentration of monosulphidic crosslinks being so low that they were difficult to measure.^{1,13}.

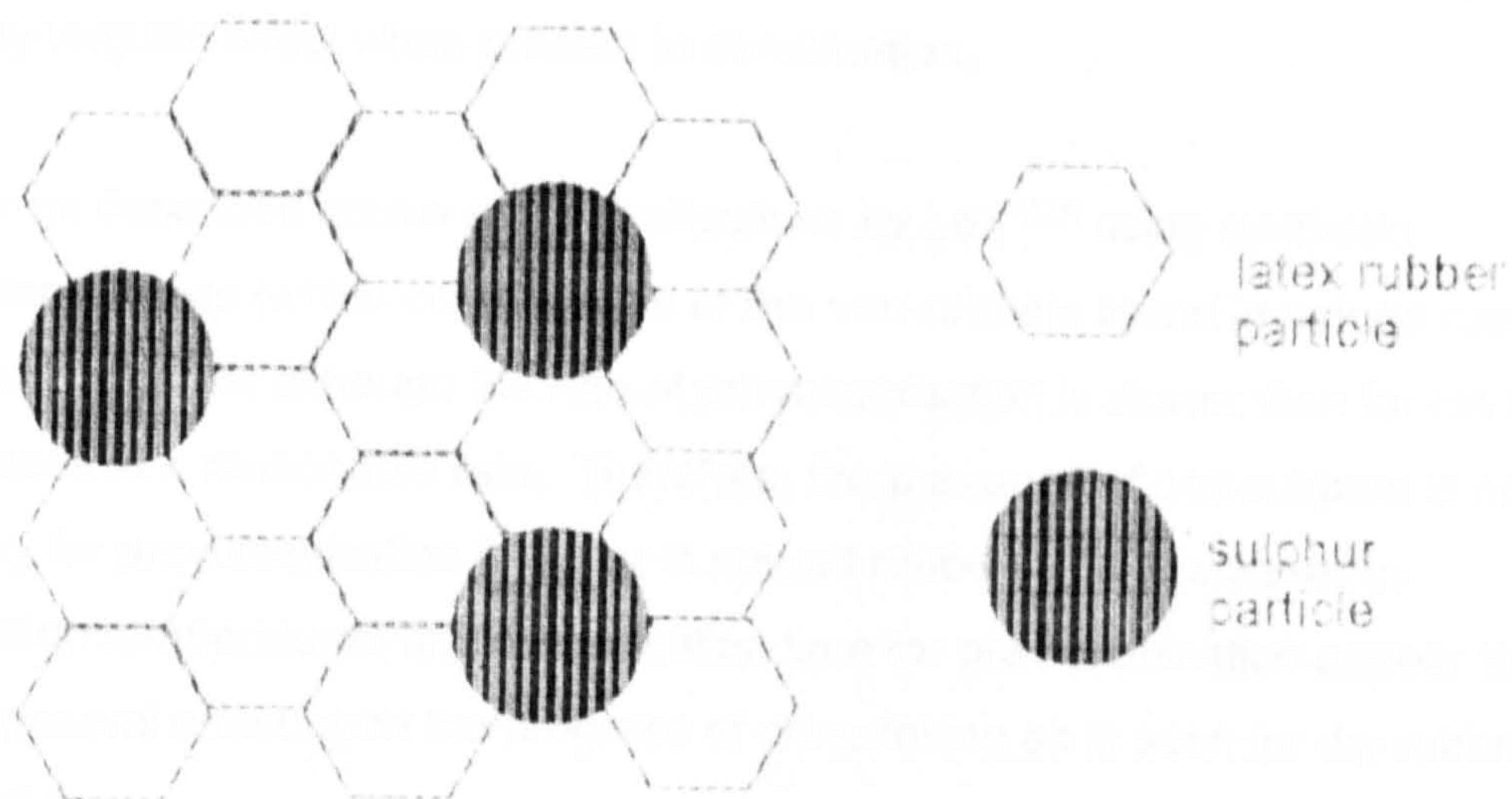
Prevulcanisation is believed to occur only if the "active sulphurating agent" is present in the rubber particles²⁴. Whether the "active sulphurating agent" is formed in the aqueous phase (latex serum), at the surface of the latex particle or within the latex particle is not known. However, there have been a number of investigations which have thrown light upon the transfer of vulcanising ingredients from their solid phases into the latex (see Sections 1.4.2 and 1.4.3 and Refs. 6,11 and 12).

Loh^{13,24} carried out experiments where the solubility of the vulcanising ingredients was assessed from the opacity of films prepared from compounded latex. He found that latex containing 1phr sulphur stored at ambient conditions for one month produced opaque films indicating that the sulphur had not dissolved completely in the rubber particles. However, when a film prepared immediately from the latex containing 1phr

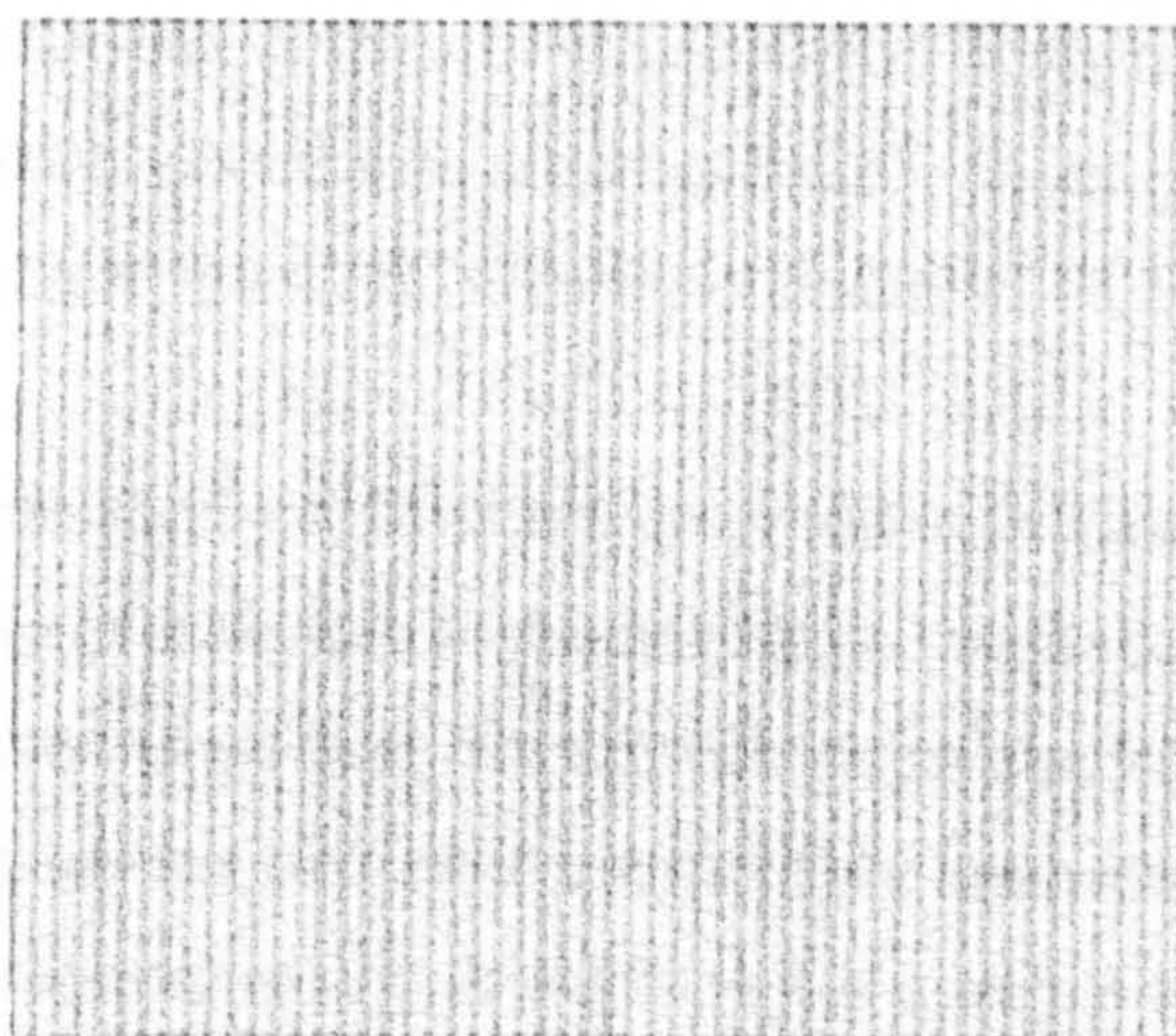
sulphur was stored in ambient conditions for one month the film became clear, suggesting that the sulphur had dissolved in the rubber particles. The physical separation of rubber particles and sulphur particles by the serum in latex and the comparatively low solubility of sulphur in serum make the transfer of sulphur from the dispersion to the rubber much slower than when rubber and sulphur particles are in close contact as is the case in a dry film. This is illustrated in Figure 20. When latex and the sulphur dispersion were heated to 50°C for 30 minutes the film prepared from this latex was also clear, indicating that the process of dissolution of sulphur in the rubber is faster at slightly elevated temperatures.

Latex and a dispersion of zinc dibutyldithiocarbamate (ZDBC) produced opaque films even after heating for 10 hours at 70°C. When latex, a sulphur dispersion and ZDBC dispersion were heated at 50°C, opaque films were produced from the latex for the first four hours and clear films from the fifth hour onwards. These results suggest that sulphur is more soluble in the latex aqueous phase and subsequently in the rubber particles than ZDBC and that solubility of ZDBC is enhanced by the presence of sulphur. However, Porter¹² has shown with ZDEC that the presence of sulphur is not essential for ZDEC to dissolve in the latex.

The non-rubbers present in natural rubber latex are a complex mixture, as shown in Table 3 (Section 1.2). They have been found to increase the rate of prevulcanisation. For natural rubber latex which had been purified by deproteinisation and centrifugation the rate of crosslinking during prevulcanisation was found to be slower than for unpurified HA latex under equivalent conditions⁶⁷. The purified latex was also found to have an induction period before crosslinking commenced. When materials typical of those normally present in unpurified latex were added separately to purified latex, ammonia was found to have a negligible effect upon the rate of prevulcanisation; the rate was increased by sodium hydroxide, potassium hydroxide, ammonium linoleate, ammonium carbonate and ammonium dihydrogen phosphate. The rate of crosslinking increased to a greater extent with the addition of β -alanine, which is representative of the amino acids present in HA latex, and with the addition of HA serum. None of the materials added to the purified latex increased the rate of crosslinking to the rate seen for HA latex. When free linoleic acid was added to purified latex it was found to retard the rate of crosslinking. It has not been possible so far to identify which non-rubbers



cast rubber latex sheet showing dispersed sulphur embedded in the rubber matrix



rubber latex sheet in which sulphur is dissolved

Based on Ref.13

Figure 20 Change in an Opaque Cast Sheet of Compounded HA Latex Left Standing for One Month at Ambient Conditions

are most important in facilitating prevulcanisation and it appears likely that they may have a synergistic effect when present in combination.

The findings described above and investigations by Loh^{13,24} using synthetic polyisoprene latices (which contain none of the non-rubbers found in natural rubber latex) both show that although the rate of prevulcanisation is slower than for HA latex, it still proceeds at a reasonable rate. Therefore, the presence of non-rubbers is not necessary for prevulcanisation to occur in natural rubber latex. Increases in vulcanisation temperatures and vulcanisation time for prevulcanisation appear to have a similar general effect upon the progress of crosslinking as is seen for dry rubber vulcanisation.

2.4 Postvulcanisation of Latex Films

Postvulcanisation of latex films has received very little attention. This is probably because in terms of industrial processes it is less widely utilised than either prevulcanisation of latex or vulcanisation of dry rubber. Postvulcanisation of latex films almost always occurs as a part of the drying stage for articles manufactured from prevulcanised latex and is rarely considered as a separate process.

Postvulcanised latex films are prepared from latex which has been compounded in the same way as latex for prevulcanisation, see Section 1.4.2. After compounding, the latex is used to prepare films by casting or dipping on an inert substrate. The films are dried and it is not until after this that they are heated. By careful choice of accelerators, drying temperature and drying time it is possible to minimise the vulcanisation which occurs before the film is heated. In postvulcanisation, crosslinking occurs in the rubber after the film has been formed.

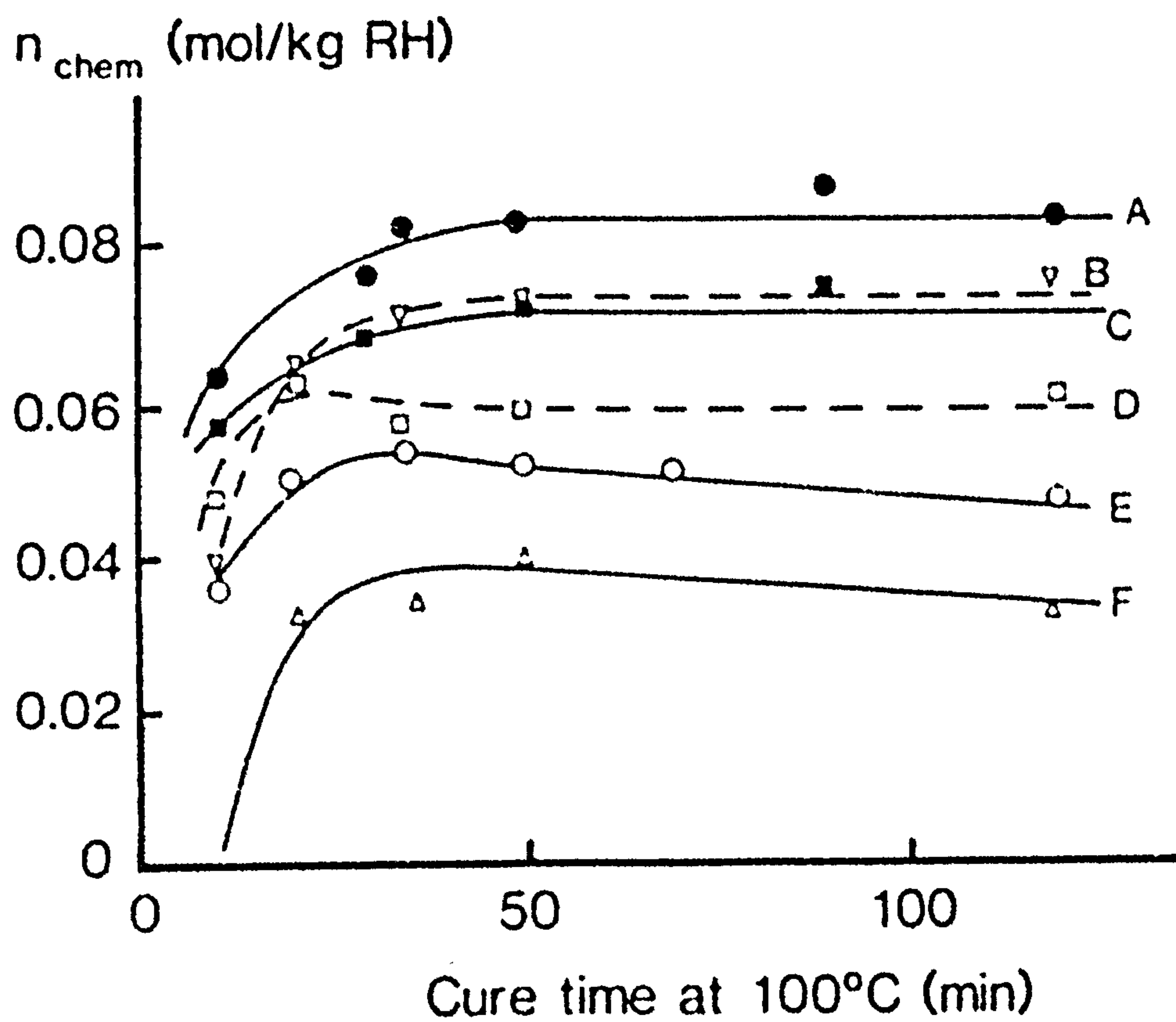
The process for postvulcanisation of latex films is essentially the same as for dry rubber vulcanisation. One difference is that there is no mastication step for latex postvulcanisation, thus retaining the original higher molecular weight of rubber. Secondly, the non-volatile non-rubbers present in latex are present in the film. The general reaction sequence for postvulcanisation is expected to be the same as for dry

rubber vulcanisation. The formation of the "active sulphurating agent" in the rubber depends upon the sulphur and accelerator dissolving from the dispersion particles into the rubber and diffusing through the film. The dissolution of sulphur in rubber occurs even at room temperature, albeit slowly¹³, see Figure 20.

The information relating to examination of crosslink type for postvulcanised latex films is far from extensive and has been limited to modest vulcanisation temperatures. Postvulcanised latex films examined are similar to prevulcanised latex films in being largely polysulphidic⁶². This accords with the general scheme for dry rubber at similar temperatures, see Figure 17.

Chong and Porter compared the postvulcanisation of latex films at 100°C with that of dry rubber vulcanisates using the same vulcanising temperature and formulation^{60,62}. The latex film vulcanised more efficiently than the dry-rubber film. This was attributed to the presence of non-rubbers in the latex film which act as activators, see Figure 21 and Table 7. This suggestion was supported by the behaviour of other rubbers which contain differing amounts of non-rubbers, see Figure 21 and Table 7. Chong found that polysulphide crosslinks predominated in both the latex and dry-rubber films cured at 100°C as shown in Figure 22. The destruction of polysulphides on extended cure was counterbalanced by the increase in di- and monosulphides^{60,62}. This was not seen to the same extent for the dry rubber vulcanisate, leading to some reversion in total crosslinking^{60,62}. Calver investigated crosslink type for latex films postvulcanised at 90°C for between 1 and 16 hours⁶⁸. He obtained films which were 99% polysulphidic over the whole vulcanisation period.

The rate of prevulcanisation of latex is generally believed to be faster than that for postvulcanisation. The work of Loh^{13,24} in which the prevulcanisation and postvulcanisation were carried out using latex with the same formulation and the same vulcanisation temperature showed the rate of postvulcanisation to be very slow when compared with prevulcanisation, see Figure 23. The vulcanisations were carried out using 1phr sulphur and 1.31phr ZDBC at 50°C. Porter and Wong²⁵ carried out similar experiments using a formulation containing 1.5phr sulphur, 1.5phr ZDEC, zinc oxide and potassium hydroxide vulcanised at 70°C. They found that the rate of postvulcanisation was similar to that of prevulcanisation for the first 2-4 hours. After



A, HA latex; B, DPNR latex; C, whole latex rubber; D, block DPNR; E, SMR 5; F, synthetic IR.

Based on Ref. 62

Figure 21. Response in terms of concentration of chemical crosslinks, n_{chem} , of six polyisoprene rubbers to the latex vulcanizing system given in Table 7.

Table 7. Vulcanization characteristics of dry and latex rubbers using a latex vulcanizing system at 100°C

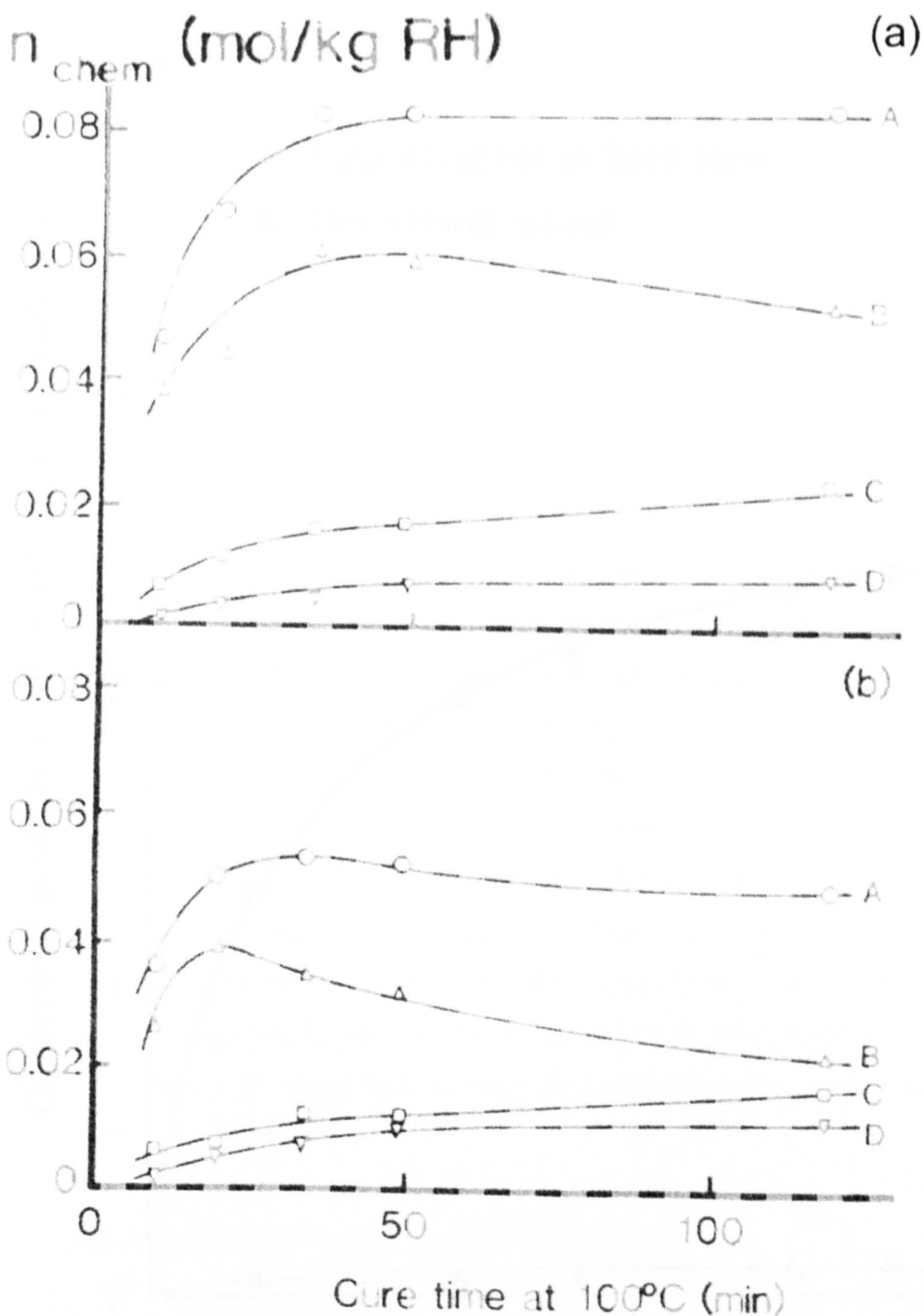
Type of rubber used	Max. n_{chem} (mol kg ⁻¹ RH)	Time to max. n_{chem} (min)	[S _x] at max. n_{chem} (%)
SMR 5	0.0510	40	77
HA latex	0.0855	50	73
Whole latex rubber	0.0760	35	70
DPNR latex	0.0730	40	-
Block DPNR	0.0605	20	-
Synthetic cis- IR	0.0385	40	-

Formulation

Zinc oxide
Sulphur
ZDEC
ZMBT
polymerised 2,2,4-trimethyldihydroquinoline

3.0 phr
2.5 phr
1.0 phr
1.0 phr
1.0 phr

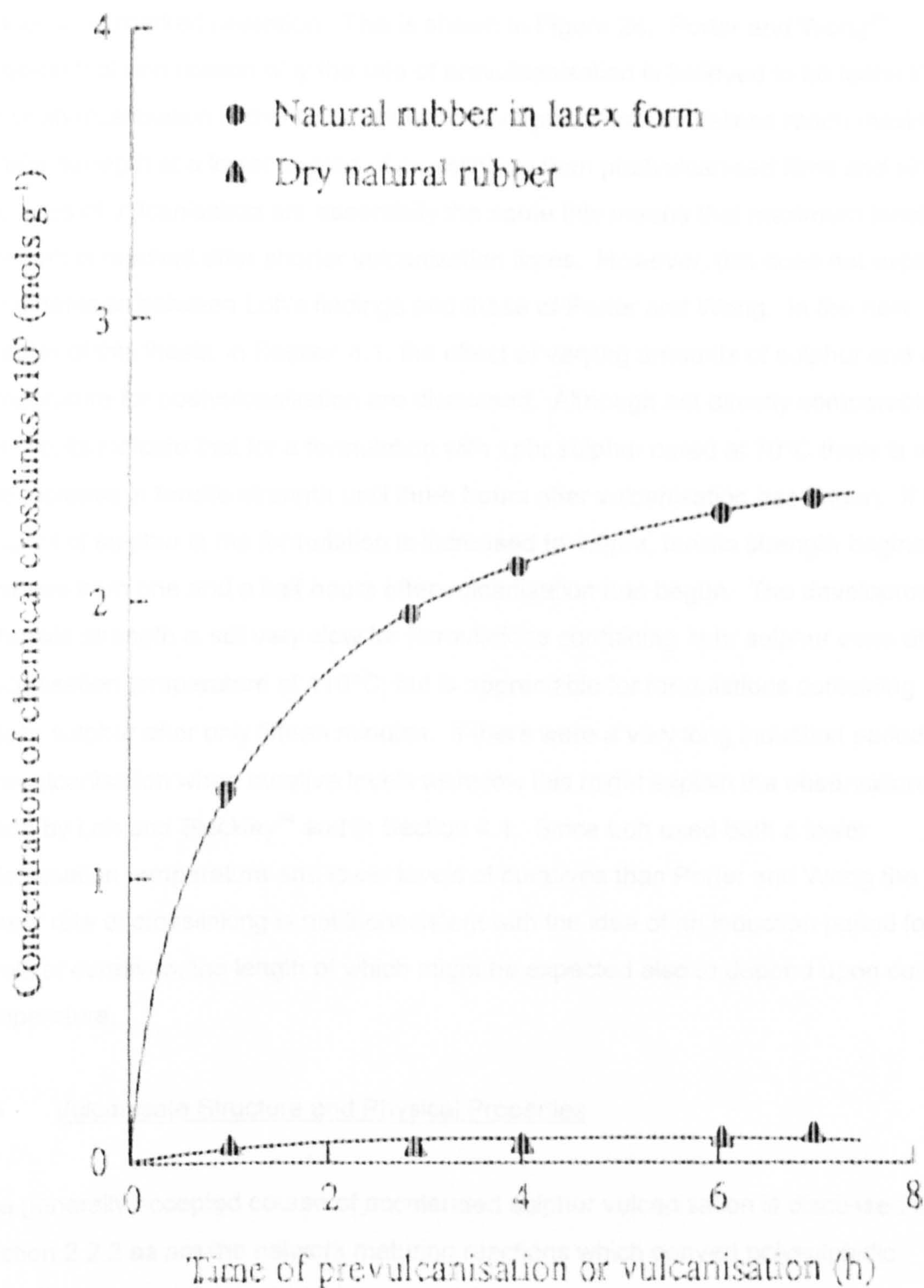
Based on Ref. 62



A, total; B, polysulphides; C, disulphides; D, monosulphides. (a) Cast films from HA latex, (b) dry rubber (SMR 5).

Based on Ref. 62

Figure 22 The formation of the various types of sulphur crosslinks during vulcanisation
(the vulcanising system is as in Table 7):



Reaction system: rubber 100, sulphur 1, zinc dibutyldithiocarbamate 1.31.

Based on Ref. 24

Figure 23 Variation of concentration of chemical crosslinks in rubber with time of vulcanisation at 50°C for natural rubber in latex form and dry natural rubber.

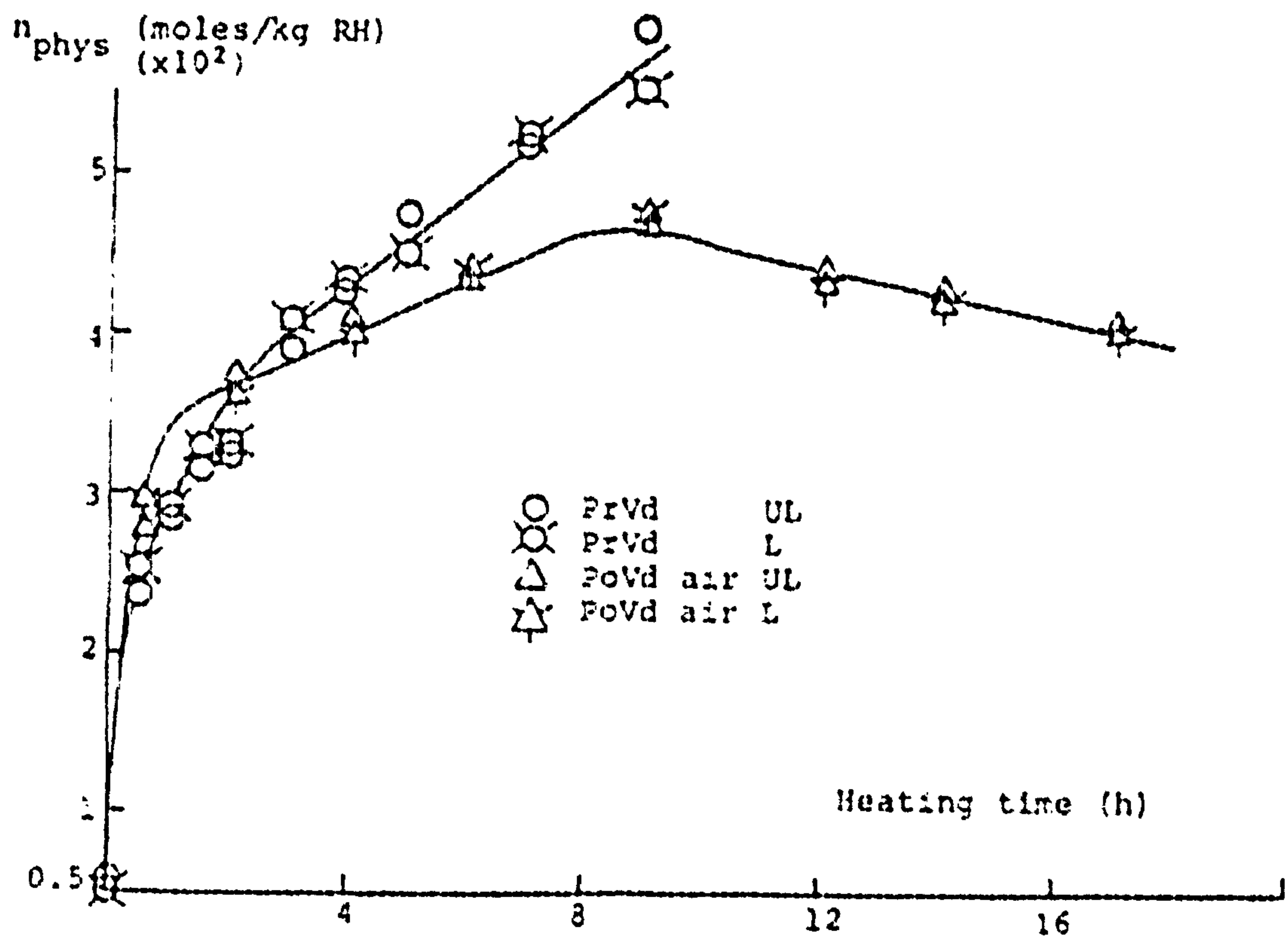
this the rate for postvulcanisation began to fall away and after 9 hours there was evidence of marked reversion. This is shown in Figure 24. Porter and Wong²⁵ suggest that one reason why the rate of prevulcanisation is believed to be faster than for postvulcanisation is that films prepared from prevulcanised latices reach maximum tensile strength at a lower degree of crosslinking than postvulcanised films and since the rates of vulcanisation are essentially the same this means that maximum tensile strength is reached after shorter vulcanisation times. However, this does not explain the difference between Loh's findings and those of Porter and Wong. In the next chapter of this thesis, in Section 4.1, the effect of varying amounts of sulphur and of temperature for postvulcanisation are discussed. Although not directly comparable, the results indicate that for a formulation with 1phr sulphur cured at 70°C there is very little increase in tensile strength until three hours after vulcanisation has begun. If the amount of sulphur in the formulation is increased to 1.5phr, tensile strength begins to increase from one and a half hours after vulcanisation has begun. The development of tensile strength is still very slow for formulations containing 1phr sulphur even at a vulcanisation temperature of 110°C; but is appreciable for formulations containing 1.5phr sulphur after only fifteen minutes. If there were a very long induction period in postvulcanisation when curative levels were low this might explain the observations made by Loh and Blackley²⁴ and in Section 4.1. Since Loh used both a lower vulcanisation temperature and lower levels of curatives than Porter and Wong the far slower rate of crosslinking is not inconsistent with the idea of an induction period for low levels of curatives, the length of which might be expected also to depend upon cure temperature.

2.5 Vulcanisate Structure and Physical Properties

The generally accepted course of accelerated sulphur vulcanisation is discussed in Section 2.2.2 as are the network maturing reactions which convert polysulphidic crosslinks to di- and monosulphidic crosslinks.

2.5.1 Dry Rubber

The relationships between physical properties and degree and type of crosslinking has



PrVd= prevulcanised

PoVd= postvulcanised

L= leached in water

UL= unleached

air = in an air atmosphere

Based on Ref. 25

Figure 24. Variation of Concentration of Physical Crosslinks for Pre- and post-vulcanization: of Latex at 70°C with ZDEC as the Accelerator

been established using dry rubber vulcanisates. The main factor affecting all physical properties is the concentration of crosslinks. The dependence of different properties upon degree of crosslinking is shown in Table 8. Tensile strength and tear strength increase initially with increasing crosslinking, pass through a maximum and begin to decrease. Stiffness (modulus) and hardness are dependent only on the degree of crosslinking but other properties are generally dependent not only upon crosslink concentration but also upon the type of crosslink present. The influence of di- and polysulphidic crosslinks upon a variety of physical properties is shown in Table 9.

The relationship between tensile strength and modulus is well established for dry rubber vulcanisates with the position of the maximum and the curve shape dependent upon the different types of crosslink present. The curves are shown in Figure 25. Polysulphidic crosslinks produce vulcanisates with higher tensile strength than other types of crosslink.

The superior strength properties of polysulphidic vulcanisates are believed to be due to the relative weakness of the polysulphide bond. Polysulphides can undergo bond interchange⁷⁰. In explaining the strength of polysulphide vulcanisates it is first necessary to make the assumption that a vulcanisate consists of network chains with a random distribution of chain lengths. When the network is deformed the stress will not be evenly distributed. The shortest chains will be the first to reach their limit of extensibility; crosslinks will break and the stress will be transferred to neighbouring chains. The process is a catastrophic one in cases where the crosslinks are mechanically strong. This is the situation where the bond-strength of the crosslink is similar to that in the polymer backbone, for instance in carbon-carbon crosslinked networks. Where the crosslinks are mechanically weak, crosslink interchange is able to occur readily. Therefore, the local stresses can be redistributed over a larger number of polymer chains and the network as a whole is able to accommodate greater stresses and will deform to a greater extent before rupturing, see Figure 26.

2.5.2 Prevulcanised Latex Films

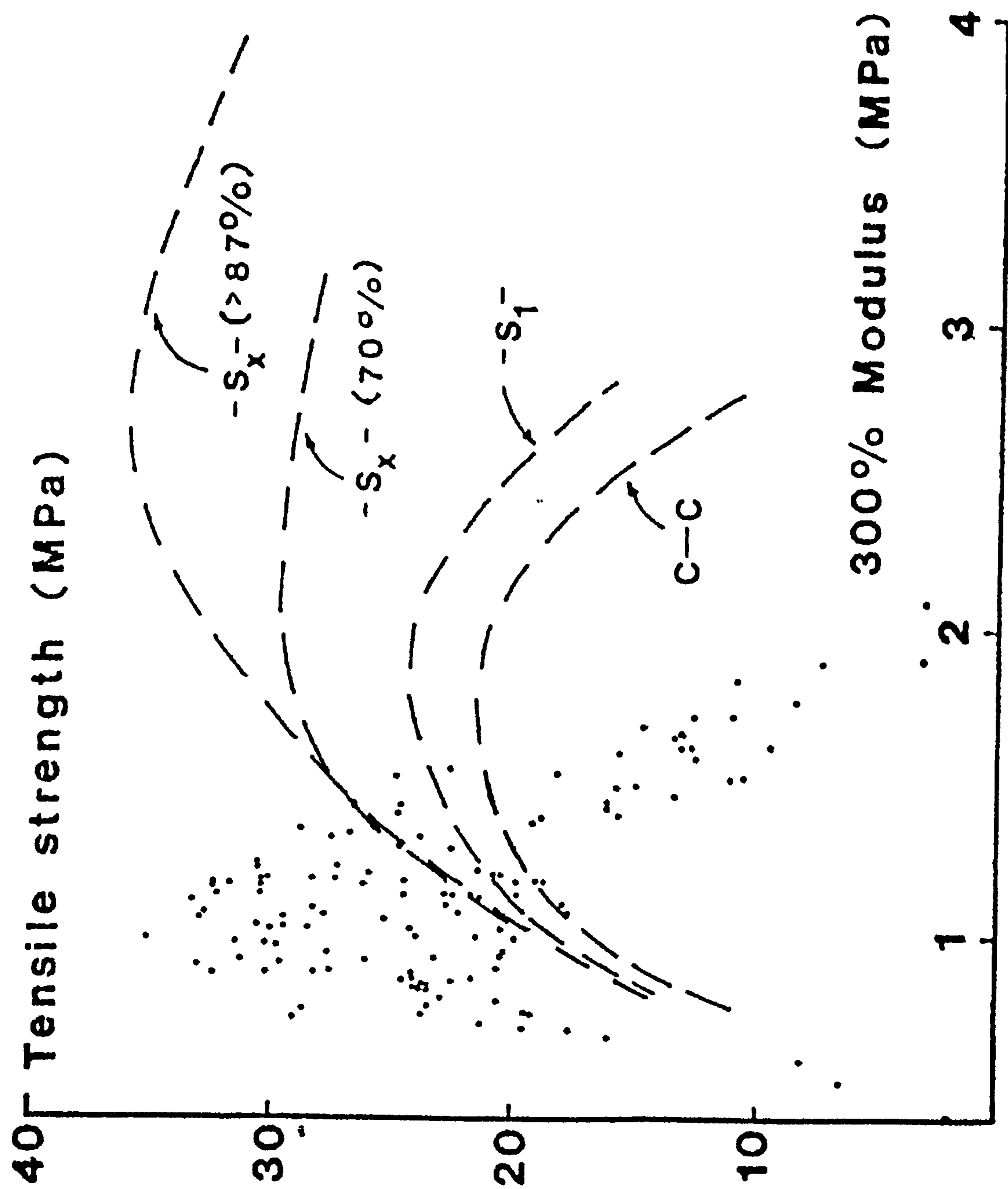
The tensile strength:modulus relationship for prevulcanised latex is different from that for dry rubber. However, the data available are limited since there are few techniques

Table 8. Influence of degree of crosslinking on physical properties of vulcanizates
Based on Ref.66

Property	Change with increase in degree of crosslinking
<u>Properties dependent only on degree of crosslinking</u>	
Stiffness (modulus)	Increase
Hardness	Increase
<u>Properties partly dependent on degree of crosslinking</u>	
Breaking elongation	Decrease
Resilience	Increase
Heat build-up	Decrease
Solvent swelling	Decrease
Creep, stress relaxation	Decrease
Set	Decrease
Abrasion resistance	Increase
Fatigue cracking	Increase
Low-temperature crystallization	Decrease in rate
Tensile strength, tear strength	Increase, then decrease

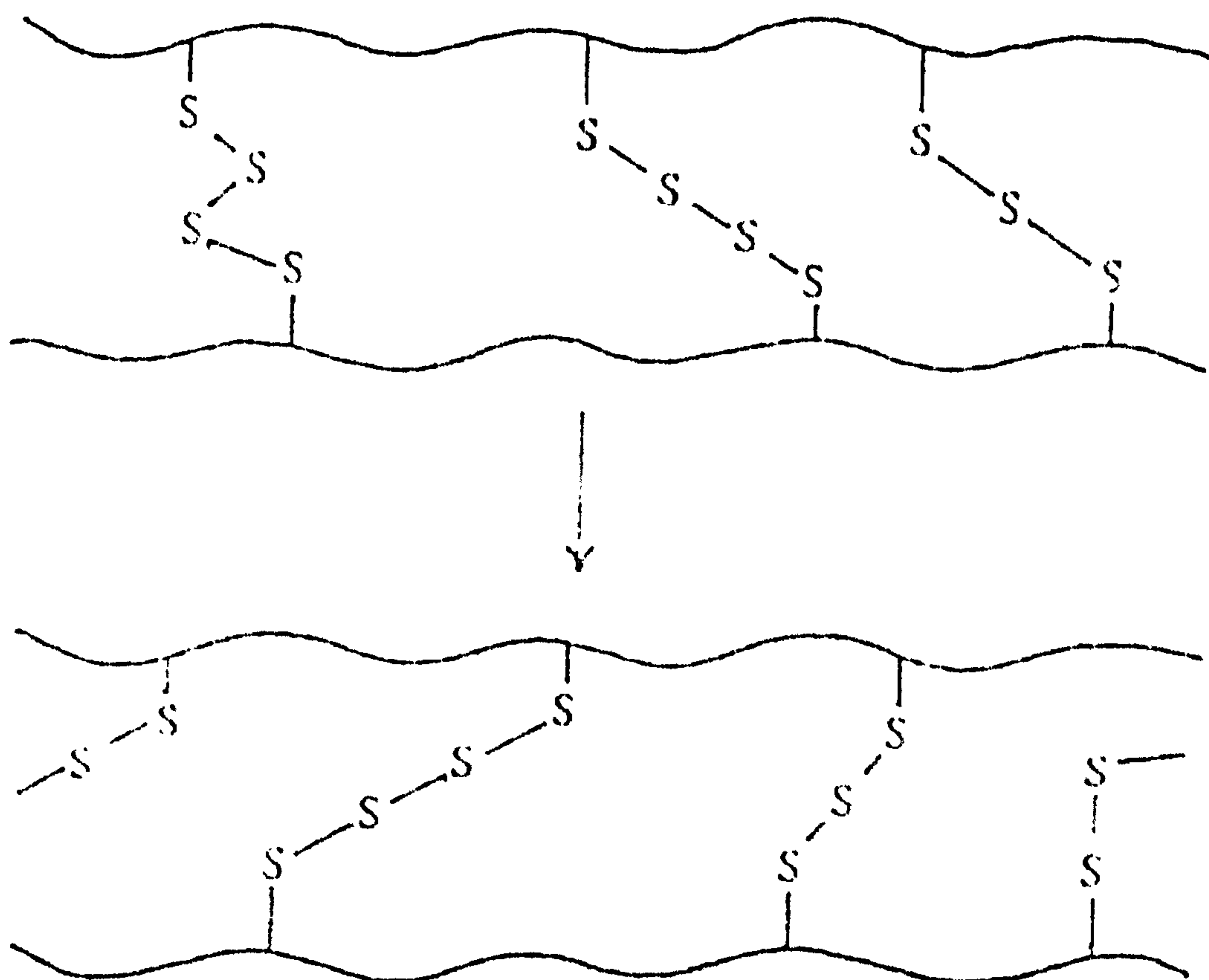
Table 9. Influence of di- and polysulphide crosslinks on properties

Property	Change with increase in proportion of di- and polysulphides
Creep, stress relaxation	Increase
Set	Increase
Incremental swelling	Increase
Tensile strength, tear strength	Increase
Resilience	Increase
Fatigue failure	Decrease
Heat resistance	Decrease
Thermal ageing resistance	Decrease



from Ref. 69

Figure 25. Dry Natural Rubber and Prevulcanised Latex Films : Dependence of Tensile Strength and Modulus on Types of Crosslink



Based on Ref. 63

Figure 26. Polysulphide Crosslink Interchange

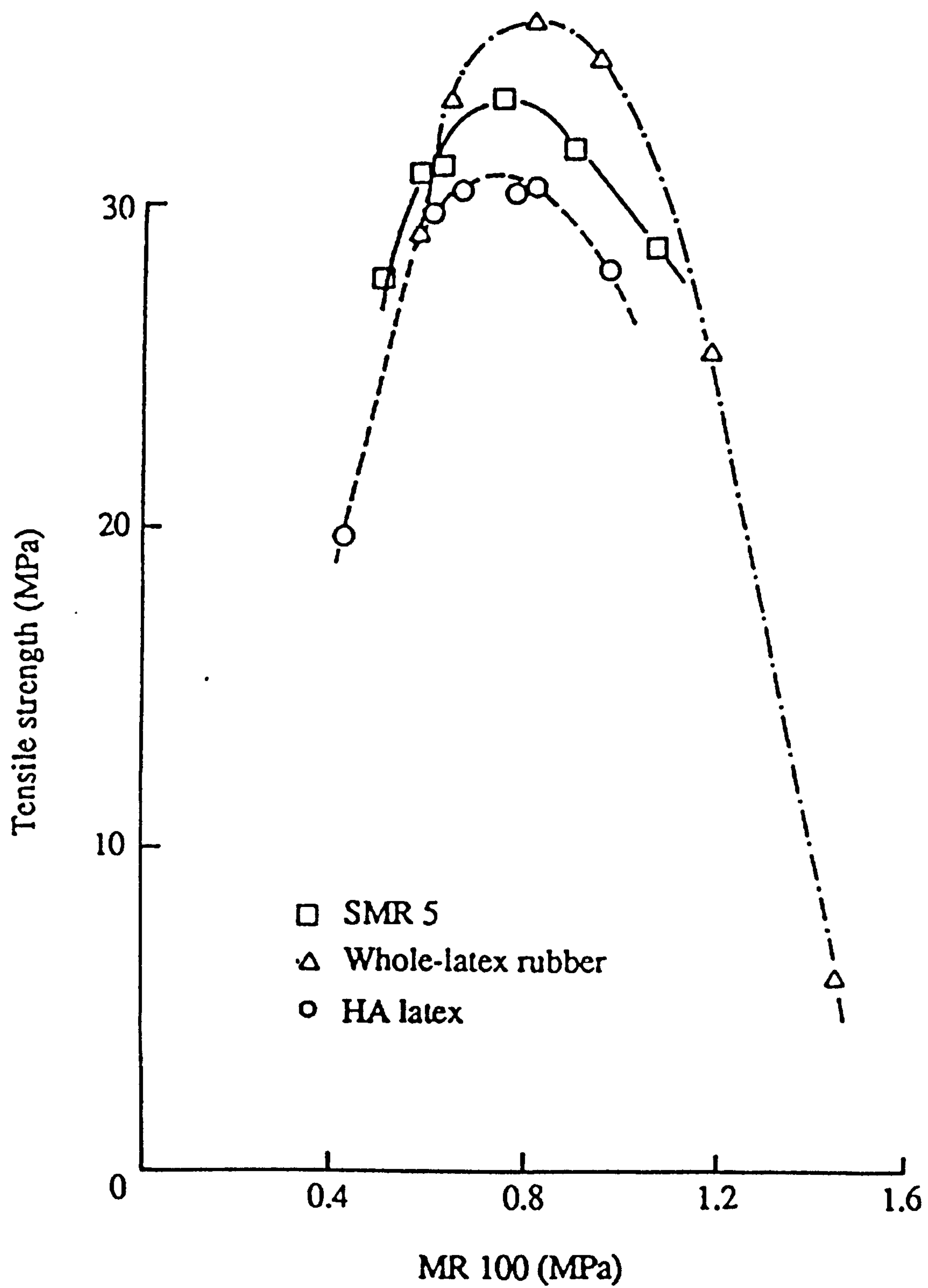
available for producing different types of crosslink during prevulcanisation. The tensile strength peak occurs at lower modulus than for dry rubber and is much sharper. This is clearly illustrated by Figure 25. Leaching prevulcanised films has the effect of increasing both tensile strength and modulus, thus altering both the size and position of the strength maximum (see also Section 1.5). Leaching is believed to remove non-rubber materials originally present in the latex (inorganic salts and surfactants) which are thought to hinder the complete coalescence of the crosslinked particles when the film is formed. Leaching is also believed to allow an increase in the number of physical entanglements between rubber molecules in neighbouring particles. Since the interfacial material has been removed it is possible for rubber molecules in neighbouring latex particles to diffuse across the boundaries. This would increase the number of physical entanglements and hence increase both tensile strength and modulus. However the degree of crosslinking, as measured by swelling in a rubber solvent, is unaffected by leaching²⁵. During swelling, leaching will also occur since films which have not been leached by water will be leached by the rubber solvent. The swelling values for vulcanisates were unaffected by whether or not they were leached²⁵. Presumably the additional entanglements produced during leaching become disentangled during subsequent swelling in a rubber solvent and hence make no contribution to the measured degree of crosslinking.

The use of modulus measurements to assess the crosslink density in prevulcanised films may not be entirely appropriate. It is a very useful guide to changes in the degree of crosslinking during vulcanisation but may be misleading if films prepared or processed under different conditions are compared.

2.5.3 Postvulcanised Latex Films

Information about the strength properties of postvulcanised latex films is quite sparse. Chong compared the results for dry rubber and postvulcanised latex films which are prepared using the same vulcanising system and cure temperature^{63,71}. The results are shown in Figure 27. They reached maximum tensile strength at approximately the same modulus. All these vulcanisates had approximately 70% polysulphidic crosslinks.

Porter and Wong²⁵ compared degrees of crosslinking for postvulcanised and



Based on Ref. 63

Figure 27. The relationship between tensile strength and 100% relaxed modulus, MR100, for dry rubber and post-vulcanised latex film

prevulcanised films, determined from swelling measurements. They found that maximum strength for postvulcanised films occurred at higher crosslink density than for prevulcanised films.

The same workers also investigated the effect of leaching postvulcanised films with water. Both modulus and tensile strength were increased by leaching but the increase was much smaller than for prevulcanised latex films. The changes in tensile strength and modulus measured after leaching during the research to be reported in later chapters are relatively small but they consist of both increases and decreases. The effect of leaching postvulcanised latex films clearly has a less significant effect upon the strength properties of the film and is less predictable than for prevulcanised films. In general, lightly crosslinked vulcanisates have increased tensile strength and modulus on leaching compared with unleached films.

Since the crosslinks are produced in postvulcanised films after the latex particles have been brought into contact the crosslinks are expected to occur not only within the boundaries of the original latex particles but also across those boundaries. The observations would accord with the explanation that leaching removes interfacial material from the original boundaries of the latex particles, allowing diffusion of rubber molecules across particle boundaries and physical entanglements to occur. Since there are already sulphur crosslinks between the original particles these have a more significant role in determining strength properties of the films than changes in the number of physical entanglements which result from leaching.

CHAPTER 3: EXPERIMENTAL METHODS

3.1 Latex Compounding

3.1.1 Latex Dispersions

The natural rubber latex used in this investigation was high ammonia latex (HA latex), 0.7% ammonia by weight. In all, three batches of latex were used; all supplied by Hecht Hayworth and Alcan. Latex was stored in sealed containers in the laboratory and therefore not exposed to extreme changes in temperature. The drum was agitated before use by rolling the drum backwards and forwards to ensure that the latex was homogeneous. Care was taken not to destabilise the latex by too vigorous agitation.

The compounding ingredients listed below were commercially produced aqueous dispersions supplied by Aquaspersions Ltd:

sulphur (S)	60% w/w
zinc diethyldithiocarbamate (ZDEC)	50% w/w (accelerator)
zinc 2-mercaptobenzthiazole (ZMBT)	50% w/w (accelerator)
zinc oxide (ZnO)	50% w/w (activator)
antioxidant 2246 (AO 2246)	40% w/w

Three batches of these dispersions were used, with the exception of ZMBT where only one batch was required. Aquaspersions Ltd also supplied a dispersion of N-cyclohexylbenzothiazole-2-sulphenamide (CBS), 33%w/w, which was prepared specifically for this study (see also Section 3.1.2).

Potassium hydroxide solution was made by dissolving the weighed pellets in deionised water and making the solution up to volume in a volumetric flask. Latex was compounded by weighing it into a 250ml or 500ml beaker and adding the required weights of the appropriate dispersions. The latex was stirred after the addition of each dispersion and again after the addition of deionised water, which was used to adjust the final solids content of the compounded latex to 52% w/w.

The formulation of compounded latex is based upon parts per hundred of rubber (phr). This relates the dry weight of the vulcanising ingredients to the dry weight of rubber in the latex. An example of the calculation is shown below:

$$\text{Weight of dispersion} = \frac{\text{phr}}{100} \times \frac{\% \text{DRC}}{100} \times \text{weight latex} \times \frac{100}{(\text{active conc. dispersion})}$$

DRC= dry rubber content (60% for HA latex)

e.g. weight of sulphur dispersion (60% solids) to give 2phr in 250g of latex

$$\text{Weight of dispersion} = \frac{2}{100} \times \frac{60}{100} \times 250 \times \frac{100}{60} = 5\text{g}$$

The solids contents of dispersions, HA latex and compounded latex were checked by accurately weighing two 1.0-1.5g samples into aluminium foil dishes and drying the contents in an oven at 100°C until they reached constant weight.

Latices were fully compounded before being allowed to "mature" (i.e. left for a period before use but kept stirred). The exceptions to this were latices containing CBS and oleate soaps where zinc oxide was omitted before "maturation" and added only just before the latices were used to cast films in order to avoid premature coagulation.

3.1.2 Preparation of CBS Dispersions

Dispersions of CBS were prepared from Santocure powder provided by the Monsanto Company. Three dispersions were made; two used CBS which had been recrystallised twice and the third used the powder without further purification.

To recrystallise CBS approximately 100g of Santocure was dissolved in 800ml heptane at 70°C. The hot solution was filtered through a fluted filter paper (Whatman no.4) and the filtrate allowed to cool overnight. The filtrate was decanted and the crystals formed in the flask were washed twice with cold heptane before they were transferred to a

Buchner funnel. There they were rewashed with several small quantities of heptane after which air was drawn through the funnel for several minutes to remove much of the heptane. The crystals were transferred to a Petri dish and the residual heptane allowed to evaporate at room temperature. The purified CBS was redissolved and recrystallised a second time following the same procedure. Its melting point and that of unpurified Santocure were measured using a Gallenkamp melting point apparatus. The twice-recrystallised CBS melted in the range 101.1-103.6°C for the material used in the first dispersion, and 103.0-107.1°C for the material in the second dispersion. The unpurified Santocure melted in the range 100-134.5°C.

CBS dispersions were produced using a Pascal model 9 ball mill. Some difficulties were encountered during the preparation of the first sample of dispersion from recrystallised CBS. The CBS crystals were ground to a powder with a pestle and mortar. 100g CBS, 4g Suparex KS (a surfactant) and 96g ammoniated water were weighed into the milling pot with the ceramic balls. The pot was sealed, placed on the rollers and the mill was run for 24h. At the end of that time a very thick powder was found to have formed which prevented the ceramic balls from tumbling freely. Therefore, the contents of the pot were diluted by the addition of a further 4g Suparex KS and 196g ammoniated water. The ball mill was run for a further 16 h. The resulting dispersion was frothy, prone to settlement and required the addition of further ammoniated water in order to remove it from the milling pot. The solids concentration of the dispersion was found to be 10.8% w/w, giving an active solids concentration of 10.0% w/w for CBS.

When a second dispersion of recrystallised CBS was prepared the total amount of surfactant, Suparex KS, was reduced and a longer milling time was adopted. 89.4g CBS, 3.6g Suparex KS and 125.8g ammoniated water were mixed and added to the milling pot. The dispersion was milled for 3 days, at intervals milling was interrupted and the dispersion checked to ensure that the ceramic balls were still free to tumble. Further ammoniated water was used to rinse out the pot when milling was completed. The percentage solids of the dispersion were found to be 24.2% w/w, giving an active solids concentration for CBS of 23.3% w/w.

A dispersion of unpurified Santocure was prepared following the procedure used for the second recrystallised CBS dispersion. 100.0g Santocure, 4.0g Suparex KS and 146.1g ammoniated water were mixed and placed in the milling pot. Further water was used to rinse out the pot after milling. The percentage solids of the Santocure dispersion was 22.1% w/w, which gave an active solids concentration of 21.3% w/w for Santocure.

3.1.3 Latex Formulations

Latex formulations used in this study were based initially upon a simple system in which a single dithiocarbamate accelerator was used: zinc diethyldithiocarbamate (ZDEC). As the study progressed it became obvious that more complex combinations and the use of other accelerators were required to provide vulcanisates with a wider range of physical properties.

3.2 Preparation and Vulcanisation of Films

Latices were compounded as described in Section 3.1. They were kept stirred, at laboratory temperature, before use, using a magnetic stirrer on a Bibby magnetic stirrer/ hotplate at a medium speed setting of 6 (it has not been possible to determine the speed of stirring). A stirring period of 16h was generally adopted in order to allow for maturation (see 1.4.3) except for those latices used in the investigation of maturation and stirring (Section 4.2). In these cases, the maturation time and whether or not stirring took place were varied. Since even when stirred, some settlement of the added dispersions occurred around the bottom edges of the beakers, a glass rod was used to redisperse the settled material immediately before the latices were used to make films.

Films were cast on level glass plates, using a Sheen 400µm casting bar, to give a dry film thickness of approximately 0.2mm. They were allowed to dry for 24h in the

Table 10 Basic Latex Formulation Containing ZDEC (Formulation A)

Composition	
	phr
KOH	0.05
ZDEC	0.5
Sulphur	2.0
ZnO	0.5
AO 2246	1.0

This formulation was used in investigations into the following-:
 Maturation and stirring (section 4.2),
 Drying regimen (section 4.4),
 Leaching (section 4.5 not table 37),
 Effect of vulcanisation time and temperature on physical properties of postvulcanised films (section 4.6),
 Addition of toluene emulsions to compounded latex (section 4.7)

Table 11 Latex Formulation Containing ZDEC and ZMBT (Formulation B)

Composition	
	phr
KOH	0.05
ZDEC	2.0
ZMBT	2.0
Sulphur	4.5
ZnO	0.5
AO 2246	1.0

This formulation was used in the investigation into leaching postvulcanised films (section 4.5, Table 37)

Table12 Formulations for Investigation into the Extraction of ZDEC

Composition					
	phr				
HA latex	100	-	100	100	-
DPNR latex	-	100	-	-	100
ZDEC	1.0	1.0	2.0	1.0	1.25
AO 2246	0	0	0	1.0	1.0
Formulation code	C(1)	C(2)	D	E	F

Table 13 Further Formulations Containing ZDEC and ZMBT

Composition					
	phr				
KOH	0.05	0.05	0.05	0.05	0.05
ZDEC	0.25	0.5	0.5	0.5	3.0
ZMBT	0.25	0.5	0.5	0.5	3.0
Sulphur	2.0	2.0	2.0	3.0	6.0
ZnO	0.5	0.5	1.5	0.5	0.5
AO 2246	1.0	1.0	1.0	1.0	1.0
Formulation code	G	H	I	J	K

Table 14 Latex Formulations Containing CBS and Thiourea

Composition										
phr										
KOH	0.05	0.05	0.05	0.05	0.05	0.1	0.1	0.05	0.05	0.1
CBS	2.4	2.4	2.4	2.4	2.4	2.4	1.2	2.4	2.4	2.4
Thiourea	-	2.1	0.35	0.7	0.7	0.35	0.35	0.7	0.7	0.7
Sulphur	1.5	1.5	4.0	4.0	4.5	4.0	4.0	4.0	4.0	4.0
ZnO	0.8	0.8	0.8	0.8	0.8	0.4	0.8	0.8	0.8	0.8
AO 2246	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ammonium oleate	1.0	1.0	1.0	1.0	1.0	-	-	-	-	-
Potassium oleate	-	-	-	-	-	0.2	0.2	1.0	-	-
Dehydol	0.2	-	-	-	0.2	-	-	-	-	-
Ammonia solution	-	-	-	-	-	-	-	-	0.5	-
Formulation code	L	M	N	O	P	Q	R	S	T	U

Table 15 Latex Formulations Containing CBS and Sodium thiosulphate

Composition				
phr				
KOH	0.1	0.1	0.1	0.1
CBS	2.4	2.4	2.4	2.4
Sodium thiosulphate	2.27	2.27	2.27	2.27
Sulphur	4.0	4.0	6.0	4.0
ZnO	0.8	0.8	0.8	0.8
AO 2246	1.0	1.0	1.0	1.0
Potassium oleate	0.2	1.0	1.0	-
Formulation code	V	W	X	Y

laboratory, except in the cases where the effect of the drying regimen was being investigated (Section 4.4).

For the investigation of the drying regimen films were cast on glass plates as described above, some plates were placed in a desiccating cabinet containing phosphorus pentoxide and others were left in a controlled environment room at 50% humidity. Both sets of films were left for 24h.

Some films were retained unheated to act as controls. The rest were vulcanised (cured) by placing them on ceramic heat-storage blocks in an air-circulating oven. Films containing ZDEC or ZDEC/ZMBT as accelerators were generally cured at 90°C, with some being cured at 100°C, 110°C and 130°C. Films containing CBS and activators as the accelerator system were cured at 100°C by the same method. The cure temperatures used in individual experiments are shown in the relevant tables and graphs.

After curing, the films and glass plates were removed from the oven and allowed to cool. At this stage portions of the films were removed for chemical analysis, if required. Then the films were dusted with talc to prevent them sticking to themselves and carefully stripped off the glass plates and stored in clean envelopes in the controlled environment room (at 23°C and 50% relative humidity).

3.3 Leaching

3.3.1 Leaching with Water

Latex films were leached in deionised water by placing the films or the films and glass plates, on which they were cast, into beakers with at least 400ml deionised water for each film. In some cases dumb-bells cut from the films (see Section 3.5.1) were leached, weighted to prevent them floating by attaching paper-clips to one of the tab ends. When leaching films at a temperature above laboratory temperature, beakers of

deionised water were placed in a thermostatically-controlled water-bath and the films were added once the desired temperature had been reached.

3.3.2 Leaching with Organic Solvents

Leaching at laboratory temperature with organic solvents was carried out using a similar procedure to that for water but the containers were sealed to prevent loss of solvent. For two of the toluene leaching experiments the air above the solvent was replaced with nitrogen in order to minimise the possibility of oxidation of the sample. Samples leached at higher temperatures were placed in a Soxhlet extraction apparatus and exposed to a solvent at a temperature close to its boiling point.

3.3.3 Drying of Leached Samples

Water-leached samples were dried by blotting them carefully with paper towels to remove any water from their surfaces. Samples leached with organic solvents were blotted dry with paper towels and then left overnight in a fume-cupboard to allow further solvent to escape. After this all samples were stored in the controlled environment room for at least 24h before they were tested.

3.4 Incorporation of Organic Solvents into Natural Rubber Latex and Latex Films

3.4.1 Films from Rubber Solutions

A solution of rubber was prepared by dissolving natural rubber latex films in toluene. Films were made from HA latex by casting and drying (Section 3.2). They were cut up into small pieces and added to toluene. The sol rubber dissolved and the gel was removed by filtering the solution through lens tissue to give a solution of approximately 2% w/v. Films were cast from the filtered solution.

3.4.2 Treatment of Cast Films with Organic Solvents

Films cast from natural rubber latex (Section 3.2) were immersed in the solvents toluene and dichloromethane (DCM). An HA latex film was immersed in toluene for 45 minutes and the toluene allowed to evaporate from the film. A film (in this case a 40mm swelling index disk) of partially compounded latex (formulation A omitting accelerator) was immersed for 16 hours in dichloromethane (containing 200 ppm ZDEC w/v). The dichloromethane was allowed to evaporate from the film, which was subsequently heated for 90 minutes at 90°C.

The procedure was repeated using films, cast on glass plates, which were immersed in DCM containing 200ppm ZDEC for 16 hours. The plates were removed from the solution and the solvent allowed to desorb for 2 hours before the films were heated for 90 minutes at 90°C.

Finally, latex films were exposed to solvent vapour. Films of compounded latex on glass plates were placed in a chromatography bath containing toluene. The films were above the level of the liquid. They were left exposed to toluene vapour for 48 hours, after which time they and similar films which had not been exposed to toluene were heated for 90 minutes at 90°C.

3.4.3 Preparation of Ammonium Oleate and Toluene Emulsions

The incorporation of toluene into HA latex without causing destabilisation was carried out by forming a fatty acid soap in situ⁷². The components were weighed out in the following ratios:-

Part A: toluene: oleic acid	50:2 or 50:1;
Part B: deionised water: 33% w/w ammonia solution (s.g. 0.88)	47.2:0.6

The components of part A were mixed and the components of part B were mixed separately. Part A was added in a slow stream, with stirring, to part B. Stirring was continued to produce a homogenous mixture.

Emulsions containing 50g toluene were stirred into 100ml and 300ml uncompounded and compounded natural rubber latices. These modified latices were used to prepared films for postvulcanisation in the way used for the unmodified latices.

The effect of ammonium oleate alone upon the properties of postvulcanised latex films was investigated by preparing ammonium oleate in situ by the previous method but omitting the toluene.

3.5 Physical Tests

3.5.1 Preparation of Test Pieces

Samples were stored in the controlled environment room (temperature $23\pm 2^{\circ}\text{C}$, relative humidity $50\pm 5\%$) for at least 24h before testing. Dumb-bells (type A2) and disks (40mm diameter) were cut from films with cutting dies and a Wallace cutting press. The dumb-bells were used in the determination of tensile strength and modulus. The disks were used for swelling index measurements. One disk was cut from each film so that at least two disks were tested for each set of experimental conditions.

3.5.2 Measurement of Tensile Strength and Modulus

Dumb-bells were wiped with paper tissues or dabbed with low-tack adhesive tape to remove talc from their surfaces before three thickness measurements were made along the central parallel portion using a type 54 Mercer gauge. The mean value for thickness was calculated and used in the calculation of tensile strength and modulus.

Tensile strength and modulus testing were carried out using an Instron 4301 Tensile Tester with optical extensometer and self-adhesive targets.

The following conditions were used throughout-:

Test conditions	{ temperature	23±2°C
	{ relative humidity	50±5%
Load cell		100N
Cross-head speed		500mm/min
Jaws		50N pneumatic grips

For measurement of modulus the self-adhesive targets were applied to the dumb-bells before they were mounted in the jaws. Five dumb-bells were used for modulus (stress) measurements and stresses were recorded for 100%,300%,500% and 700% elongation. A further five dumb-bells were used for the determination of tensile strength without the use of the optical extensometer. Separate tensile testing was necessary if insufficient cross-head travel to reach breaking point was available when the optical extensometer was used. Data were recorded and calculated by Instron Series 9 software, versions 3 and 5.

3.5.3 Measurement of Swelling Index

The determination of swelling index involved the immersion of 40mm diameter disks of rubber film in toluene. First the edges of the disks were marked with ballpoint pen ink so that they were visible when the rubber was swollen. Disks were immersed in toluene in a Petri dish and allowed to swell for 30 minutes. At the end of this time the dish was placed on top of a piece of graph paper. The swollen disks were held down flat with a microscope slide and the diameter of each disk was measured using the graph paper first in one direction and then in a direction perpendicular to the first. The swelling index was calculated from the mean of these diameters using the following formula-:

$$SI = \frac{(d_s)^2 - (d_i)^2}{(d_s)^2}$$

$d_s =$ swollen diameter

$d_i =$ initial diameter (40mm)

The disk, though swollen, retains its shape; it is not distorted. The swelling index gives a measure of the degree of crosslinking in the film, well-cured films having a swelling index below 2.5. The test provides a rapid indication of the degree of crosslinking but cannot be related directly to modulus and becomes less sensitive for highly crosslinked samples.

3.6 Chemical Analyses

The sulphur analyses were carried out at the Malaysian Rubber Producers' Research Association (MRPRA). The analyses for ZDEC and zinc were carried out at London International Group Research and Development.

3.6.1 Determination of Total Sulphur

Talc-free samples of latex film were supplied for analysis. In order to ensure that samples were homogeneous they were cold milled by passing them through a mill with unheated rollers, with exception of those samples from the investigation of stirring and maturation (section 4.2). A 30mg sample of rubber was used in each case. It was completely oxidised in an oxygen flask and the sulphur oxides were absorbed in 1ml 100 vol. hydrogen peroxide solution. The resulting solution was analysed for sulphate ions by ion chromatography with a Dionex AS4 column. The sulphate concentration was related back to the total sulphur present in the sample. The reproducibility of the method was quoted as 1% relative standard deviation (RSD).

3.6.2 Determination of Free Sulphur by High-Performance Liquid Chromatography (HPLC)

Uncombined sulphur (free sulphur) was extracted from approximately 1g of rubber by an 18h Soxhlet extraction with acetone. The acetone was removed by evaporation and the residue was redissolved in the minimum amount of chloroform. The solution was made up to 10ml with isopropyl alcohol. The free sulphur was determined by HPLC using a reverse phase octadecylsilane column, a mobile phase of 85:15

acetonitrile:water, a flow rate of 2ml/min, an oven temperature of 50°C, a sample volume of 20µl and UV detection at 260nm. The reproducibility of the method is quoted as better than 5% RSD. This method was used for the determination of free sulphur in films from the study of "maturation" time and stirring (section 4.2).

3.6.3 Determination of Free Sulphur by the Copper Spiral Method

This method is described in an International Standard ⁷³, method A was used but the apparatus described in a paper by Davey, Edwards and Higgins⁷⁴ (Figure 28) was employed.

Free sulphur was first extracted from the rubber by a Soxhlet extraction with acetone. The extraction flask also contained a copper spiral which reacted with the extracted sulphur to form a coating of copper sulphide. The copper/copper sulphide spiral was treated with a mixture of hydrochloric and acetic acids to liberate hydrogen sulphide which was passed through cadmium acetate solution. The cadmium sulphide formed was determined iodimetrically and from this the amount of free sulphur was calculated.

3.6.4 Determination of Combined Sulphur

The latex film which had been extracted with acetone, to remove the free sulphur, was used for the determination of combined sulphur. Combined sulphur is that sulphur which is chemically combined with the rubber. The extracted rubber was oxidised and analysed using the same method as that used to determine total sulphur.

3.6.5 Determination of Zinc Diethyldithiocarbamate (ZDEC)

ZDEC was determined as the copper dithiocarbamate complex. Approximately 0.5g rubber was extracted with 80ml dichloromethane in a 16h static extraction. The extract was filtered into a 100ml volumetric flask. Two aliquots of dichloromethane were used to rinse the sample and these were also added to the volumetric flask. The contents of the flask were made up to volume with dichloromethane.

25ml dichloromethane extract was transferred to a separating funnel containing approximately 15ml 20% w/v aqueous copper(II) sulphate solution. The copper dithiocarbamate complex was formed in the dichloromethane layer by shaking the contents of the separating funnel for 1 min. The layers were allowed to separate and the dichloromethane layer was run through phase separating filter paper into a test tube. The absorbance of the copper dithiocarbamate complex was determined at 435nm using a Beckman DU8 spectrophotometer or a Unicam 8700 spectrometer, the uncomplexed dichloromethane extract being used as a blank. The concentration of the complex was calculated by comparison of its absorbance with values from a calibration graph. The concentration of ZDEC in the samples was determined from this result. Further dilution of the uncomplexed dichloromethane extract was carried out if the concentration of ZDEC in the sample exceeded that of the most concentrated standard used for the calibration graph. Each analysis was carried out in duplicate or, if the sample size allowed, in triplicate. The reproducibility of this method is 3% RSD.

When the problem of extracting ZDEC from the rubber network was investigated (see Section 4.3) the method described above was modified slightly. The ratio of sample to dichloromethane was varied during the 16h static extraction and the same sample was re-extracted once and sometimes twice, in its filter paper, with further dichloromethane. The extraction was also carried out using a Soxhlet extractor instead of the static extraction. However, the treatment of the dichloromethane extract was the same in all cases.

3.6.6 Determination of Total Zinc

Wet digestion was carried out on the latex films. The rubber sample (0.2g) was placed in a beaker with approximately 2ml concentrated nitric acid and gently warmed on a hot plate. The progress of the reaction was carefully monitored and the beaker was removed from the heat source if the reaction became too vigorous. More nitric acid was added if undigested rubber was present at the end of the first digestion. Once all

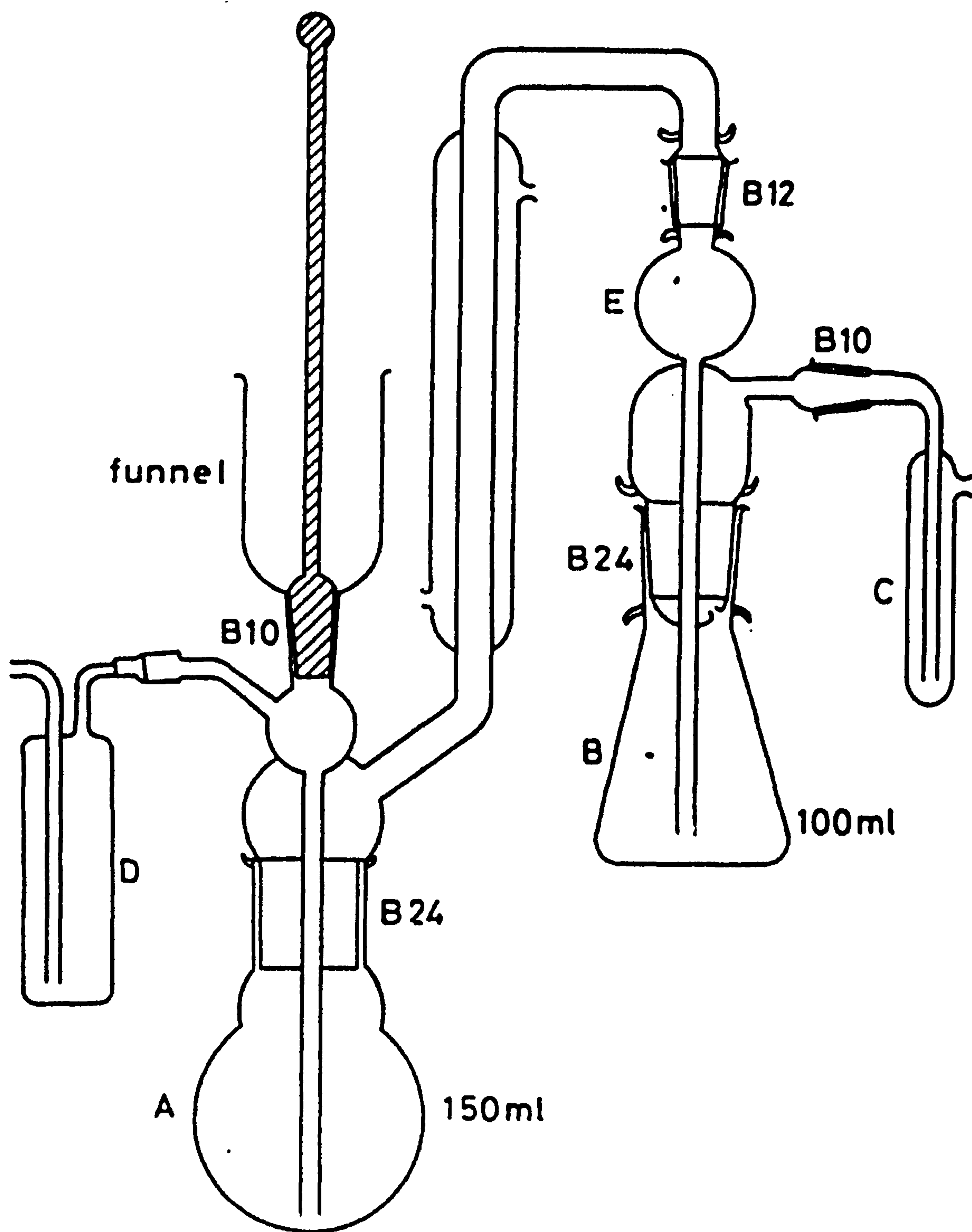


Figure 28 Apparatus for Determination of Free Sulphur by the Copper Spiral Method
Based on Ref 74

the rubber had been digested, 4-5ml 100 vol. hydrogen peroxide was added. When this digestion step was complete the solution was filtered to remove any insoluble material (e.g. talc), and the solution was made up to 100ml in a volumetric flask with deionised water. 10ml of this solution was diluted to 50ml in a volumetric flask to bring the concentration of the solution into the linear portion of the response range for atomic absorption spectroscopy. The atomic absorption of the solution was measured and the concentration of the solution was calculated by comparison with a calibration curve. The total amount of zinc present in the film was calculated from the result.

Determination of zinc in the dichloromethane extracts (see 3.6.5) is based on that of Moore and Watson⁷⁵. Dichloromethane (DCM) was removed from 50ml of the extract using a rotary evaporator. The residue was digested overnight with 40ml of a 2:1 mixture of glacial acetic acid and concentrated hydrochloric acid (s.g. 1.16). 50ml deionised water was added and the flask was heated in a beaker of boiling water for 1 hour. The resulting solution was transferred to a 250ml volumetric flask which was made up to volume with deionised water. The zinc concentration was measured by AAS (see above).

3.7 Electron Microscopy

The structures of latex films were examined by two different electron microscopic techniques. Since the equipment was not available at London International Group Research and Development samples were prepared there and taken to John Sargent, an electron microscopy consultant, for examination.

3.7.1 Preparation and Examination of Samples by Scanning Electron Microscopy (SEM)

Samples of rubber film were examined by scanning electron microscopy (SEM). A sample was mounted edge-on on a sample stud using graphite cement and frozen in a nitrogen slurry at -210°C. It was transferred to the sample preparation chamber of the Phillips 500 scanning electron microscope which was maintained at the same temperature. The rubber sample was fractured with the blunt edge of a scalpel to

produce a fractured cross-section. The fractured sample was transferred to the Hexland cryostage in the microscope's sample chamber where it was allowed to warm up to -80°C. At this temperature and at the high vacuum used in the microscope, water sublimates from the surface of the sample. The sample was observed during this time and when its underlying structure was clearly visible it was cooled to -210°C and transferred back to the sample preparation chamber for coating with gold by a diode sputter coater. Samples were given just sufficient coating to overcome electrical charge building up on them which would affect the quality of the image seen on the screen of the microscope. The coated sample was transferred to the cryostage of the microscope and viewed at a temperature of -180°C at magnifications of 5000X and 10000X with an electron gun voltage of 25kV. Different areas of the sample were examined and photographs were taken of areas felt to be typical of the cross-section.

3.7.2 Preparation of Samples for Transmission Electron Microscopy

The method was based upon that of Shiibashi⁷⁶. Two or three small pieces (5mmx5mm) were cut from each latex film. These were placed in glass vials containing 7.5ml or 10ml styrene (99%, inhibited with 10-15ppm 4-tertbutylcatechol, Aldrich). The vials were capped and the films allowed to swell in the styrene for 16h. A plasticiser, di-2-ethylhexyl phthalate, was added. The addition was made just before the initiator for polymerisation was added in the case of the 1.0% v/v plasticiser. The phthalate was added to prevent the polystyrene forming a block which was too brittle to microtome.

The polymerisation was initiated by the addition of approximately 0.5g benzoyl peroxide (97%, Aldrich). The vials were shaken to ensure that all the peroxide was mixed with the styrene and to assist its dissolution. The sealed vials were placed in a water bath at 80°C for at least 7 hours by which time the styrene had polymerised. The heater was switched off and the vials were left in the cooling water bath for a further 16 hours. The vials were removed, the glass was broken and the polystyrene blocks removed.

Rubber samples that had been embedded in the polystyrene blocks were sectioned, supported on copper grids, stained with osmium tetroxide and examined in a transmission electron microscope, micrographs being prepared of representative areas of the samples.

Sections were prepared by removing a volume (approximately 5mm x 5mm x 10mm) from each block with a hacksaw, using water as a lubricant. This volume was clamped in a parallel-jawed LKB chuck and a mesa was formed by cutting away extraneous embedding material using an LKB pyramitome. The chuck and the sample were transferred to an LKB ultramicrotome on which sections were cut using a diamond knife attached to which was a small bath. The sections were floated on 10% ethanol in water contained in the bath, thus preventing the sections from crumpling. The thickness of each section was assessed from its diffraction colour using white light and the thickness was controlled to give a gold diffraction colour before stretching. Stretching was achieved with a stream of xylene vapour from a piece of filter paper soaked in the solvent and held above the collection bath. This process removed the small amount of crumpling.

Sections were collected on copper grids, dried and floated, sections down, on a drop of osmium tetroxide solution (2.5% in water) supported on clean dental wax in a Petri dish. The osmium tetroxide reacts with double bonds in polyisoprene molecules and produces contrast between the rubber and polystyrene. After staining for 10 minutes the grids were washed well in a stream of distilled water and dried in air.

Examination of the stained sections was carried out on a Philips EM300 transmission microscope at 80kV. Micrographs were taken on Ilford EM cut film which was developed in Ilford PQ developer (5 minutes in a 10% solution), and fixed in Hypam (25% solution). The film was washed in fresh water with a trace of Ilford wetting agent and dried in a cabinet at 60°C. Prints of the enlarged micrographs were prepared on Agfa Bromvira Speed paper.

CHAPTER 4: POSTVULCANISATION: EFFECTS OF PROCESSING CHANGES

4.1 Choice of Latex Formulation and Sample Preparation

Preliminary investigations of sulphur postvulcanisation of latex films carried out in the research and development laboratories of London International Group gave a starting point for the choices of latex formulation, method of film preparation and cure temperature^{78,79,80}.

Latex formulations used initially contained a single dithiocarbamate accelerator, ZDEC. The basic formulation was as follows:

phr	
KOH (potassium hydroxide)	0.05
ZDEC	0.5
ZnO (zinc oxide)	0.5
Antioxidant 2246 (AO 2246)	1.0
Sulphur	1.0, 1.5, 2.0 or 3.0

With 1phr of sulphur the rate of cure at 70°C (vulcanisation) was found to be too slow to be convenient for the experimental time scale. Increasing the amount of sulphur to 1.5phr, 2phr and 3phr led to increased rates of vulcanisation. The same effect was seen by varying the cure temperature; 70°C, 80°C and 110°C were used. In the case of cures carried out at 110°C there were slight drops in tensile strength at the longer cure times. This is evidence of reversion in tensile strength. The maximum tensile strength attained varied very little for different concentrations of sulphur, for 1.5phr and above, or for different cure temperatures. The maximum tensile strength lay between 28MPa and 32MPa.

Initially there were difficulties in producing similar results from nominal replicate formulations and this led to an investigation into the way in which the films were cured. One of the problems in the use of air-circulating ovens for curing was that the temperature of the air fluctuated considerably when the door of the oven was opened to remove samples. In order to minimise this variation, ceramic heat-

storage blocks were placed in the oven and the plates on which the films were cast were laid on the blocks. When using ceramic blocks there was no significant difference found between samples cured on aluminium, stainless steel or glass plates. Glass is easier to clean than stainless steel and less easily scratched than aluminium. It was, therefore, the preferred material onto which films were cast.

Other steps taken to minimise variation between replicate formulations were the adjustment of the latex concentration to the same percentage solids in each formulation and the use of a longer drying time (24 h) prior to curing.

4.2 The Effects of Stirring and Maturation Time Upon the Physical Properties and Chemical Composition of Postvulcanised Latex Films

This series of experiments formed a study which was intended to identify a means of improving the reproducibility of physical properties of postvulcanised films from repeated preparations of compounded latex.

Postvulcanised latex films prepared in the same way to the same formulation, where compounded latex was used to cast films soon after compounding, showed a wide variation in physical properties. The introduction of a "maturation" period between compounding and using the latex was investigated to determine whether it would result in the production of postvulcanised films with more consistent physical properties. The literature relating to maturation has been reviewed in Section 1.4.3. This suggested that such a process would be advantageous in terms of improving consistency of the vulcanisates. Since the films were to be postvulcanised and prevulcanisation was to be eliminated as far as possible the "maturation" times employed were relatively short, a maximum of 40 hours at laboratory temperature.

4.2.1 The Effect of Stirring Compounded Latex Upon the Composition of Films

In industrial processes it is normal for compounded latices to be kept stirred during maturation and often during dipping. Stirring prevents the settlement of added dispersions during storage and use, ensuring a homogeneous latex. When latex is compounded, air may become entrapped during mixing. Slow stirring during maturation allows entrapped air bubbles to escape. Although stirring of latex is

usually carried out and the benefits are self-evident, reference to the effect upon the composition and physical properties of the resulting latex of omitting stirring from the process has not been found. For this reason the effect of stirring compounded latices was assessed during this research programme.

The formulation used in the study is shown in Table 10 (Section 3.1.3). A number of separate samples of latex were prepared to this formulation. Half the samples were stirred after compounding and half were not; for the stirring conditions and times see Section 3.2 and Table 16. One hour before the end of the maturation time, stirring was terminated to allow any entrapped air to escape from the latex. Latices matured for one hour or less were not stirred.

Films were prepared from the latices following procedures described in Section 3.2 and samples were removed from the uncured films for chemical analysis. The methods of analysis are described in Section 3.6 and the results in Table 16 and Figures 29 and 30. Some films were cured at 90°C for 30 or 90 minutes. Tensile strength, modulus (S300%) and swelling index were determined for these and the uncured films, see Sections 3.5 and Table 16.

From formulation A (Table 10, Section 3.1.3) the latices were expected to contain 0.42% w/w ZDEC and 1.95% w/w sulphur. All the results in Table 16 are below these values, indicating that at least some of the ZDEC and sulphur cannot be accounted for. The differences between the expected concentrations of ZDEC and sulphur and those determined in the films are greatest for those prepared from the unstirred latices (Figures 29 and 30). The results suggest that ZDEC and sulphur dispersions settle rapidly during the first 1-2 hours of maturation. The concentration of ZDEC in the unstirred latex matured for 2 hours, A(3), is unexpectedly high when compared with the results for other unstirred latices (Figure 29). This may be due to unintentional agitation having occurred when the latex was used to prepare films. The concentration of sulphur was also higher for this latex than might have been expected when compared with the results for other unstirred latices (Figure 30). Films prepared from the stirred latices were also deficient in ZDEC and sulphur, although the discrepancies were considerably smaller and far less dependent upon maturation time. Stirring was terminated one hour before the latices were used to

Table 16 The Effect of Stirring on Matured Compounded Latexes

Formulation Code	Maturation Time (h)	Stirred ? *	Cure Time (min)	ZDEC % w/w	Total Sulphur % w/w	n	TS (MPa)	SD (MPa)	S300% (MPa)	SD (MPa)	SI
A(1)	½	—	0	0.29	1.10	5	4.9	0.8	0.56	0.01	10.62
			34			5	7.9	4.5	0.70	0.06	5.30
			92			5	21.8	3.8	0.77	0.09	2.55
A(2)	1	—	0	0.17	0.47	5	7.4	1.1	0.55	0.02	11.25
			34			5(4)	5.0	0.7	0.55	0.03	11.25
			92			5	4.7	0.8	0.53	0.03	9.05
A(3)	2	—	0	0.34	0.66	5	3.9	0.5	0.66	0.04	11.25
			30			5	4.8	3.4	0.75	0.07	6.32
			90			5	18.0	1.6	0.91	0.04	2.68
A(4)	2	✓	0	0.36	1.30	5	2.9	0.5	0.60	0.03	7.63
			30			5	20.2	2.7	0.98	0.03	2.49
			90			5	27.3	4.6	1.08	0.06	2.15
A(5)	4	—	0	0.12	0.40	5	3.7	0.4	0.58	0.04	11.25
			30			5	2.5	0.3	0.55	0.01	11.25
			90			5	3.9	1.3	0.56	0.06	11.25
A(6)	4	✓	0	0.36	1.17	5	4.0	0.3	0.59	0.03	9.68
			30			5	23.1	2.3	0.94	0.04	2.44
			90			5	26.0	0.9	1.11	0.04	2.14
A(7)	16	—	0	0.07	0.19	5	3.7	0.4	0.61	0.02	11.25
			30			5	2.1	0.3	0.64	0.04	10.96
			90			5	3.8	0.8	0.60	0.03	10.39
A(8)	16	✓	0	0.35	1.23	5	2.7	0.5	0.77	0.06	9.97
			30			5	23.0	0.7	1.09	0.05	2.34
			90			5	29.2	1.6	1.17	0.06	2.16

continued overleaf

Table 16 (cont.)

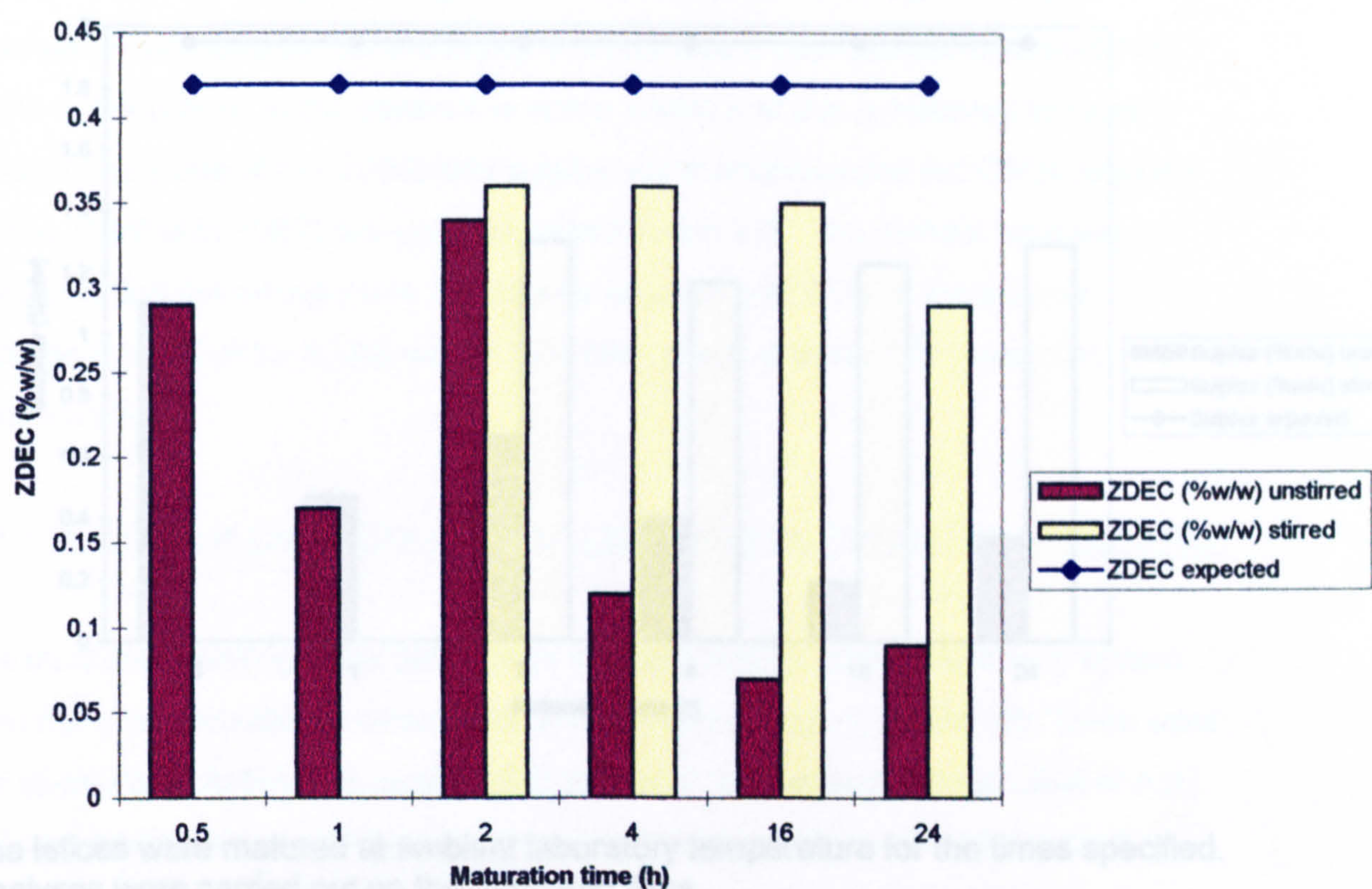
Formulation Code	Maturation Time (h)	Stirred ? *	Cure Time (min)	ZDEC % w/w	Total Sulphur % w/w	n	TS (MPa)	SD (MPa)	S300% (MPa)	SD (MPa)	SI
A(9)	24	—	0	0.09	0.34	5	5.6	0.7	0.57	0.01	11.25
			30			5	5.5	0.4	0.54	0.01	11.02
			90			5	6.6	1.3	0.54	0.03	10.70
A(10)	24	✓	0	0.29	1.29	5	9.1	1.0	0.75	0.03	8.08
			30			5	28.1	2.5	1.01	0.02	2.35
			90			5	29.7	1.7	1.10	0.03	2.21

n = Number of test pieces,
SI = Swelling index,
TS = tensile strength,
SD = standard deviation
S300% = stress at 300% elongation

* = this refers to a period of stirring between compounding the latex and one hour before it is used to cast films.

Latex was matured at ambient laboratory temperature.

Films were cured at 90°C in an air-circulating oven for the times specified.

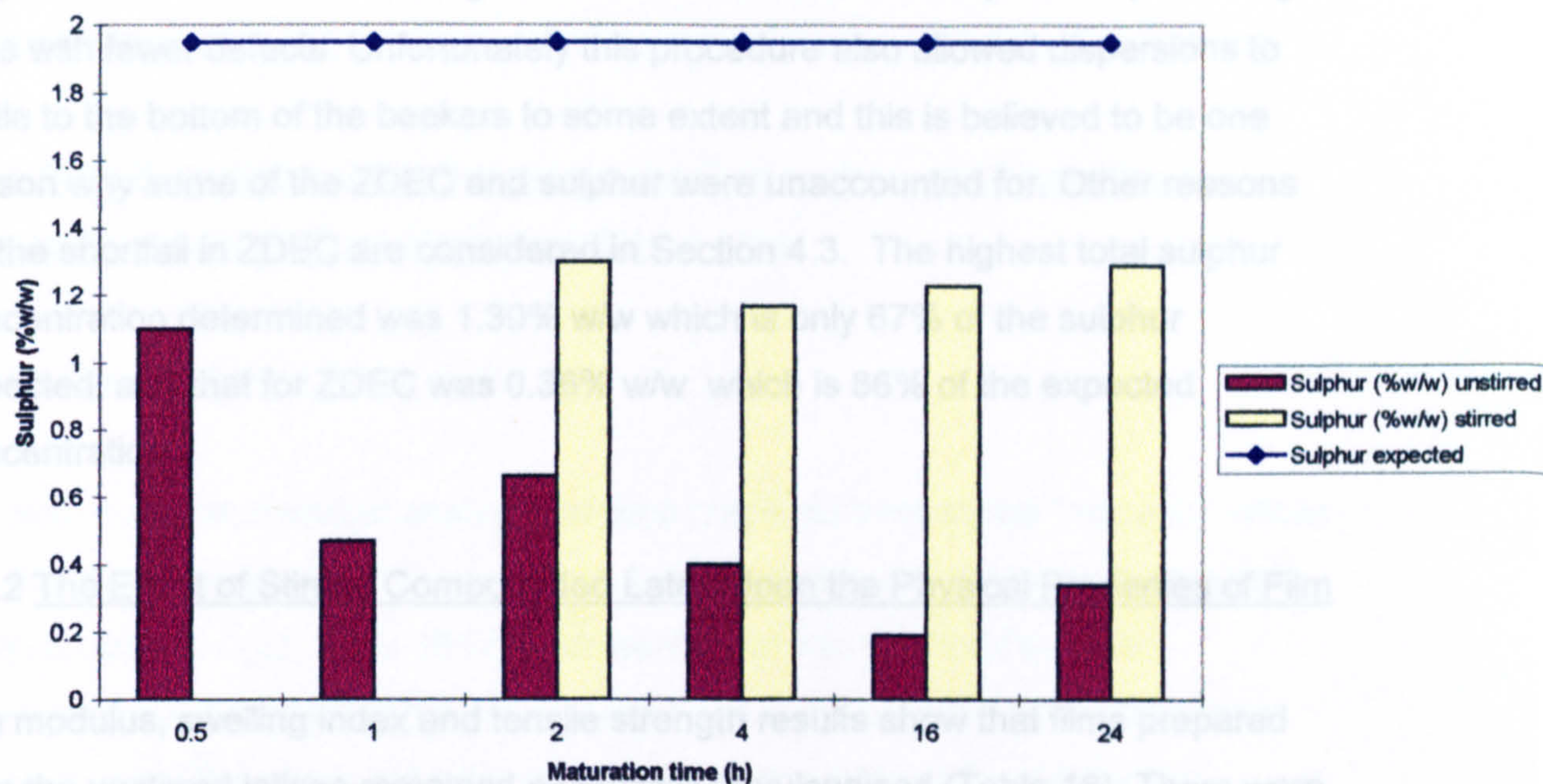


The latices were matured at ambient laboratory temperature for the times specified. Analyses were carried out on the unheated films.

Figure 30 Effect of Stirring Upon Total ZDEC in Matured Latices

The latices were matured at ambient laboratory temperature for the times specified. Analyses were carried out on the unheated films.

Figure 29 Effect of Stirring Upon Total ZDEC in Matured Latices



The latices were matured at ambient laboratory temperature for the times specified. Analyses were carried out on the unheated films.

Figure 30 Effect of Stirring Upon Total Sulphur in Matured Latices

prepare films, the intention being to allow entrained air to escape thus producing films with fewer defects. Unfortunately this procedure also allowed dispersions to settle to the bottom of the beakers to some extent and this is believed to be one reason why some of the ZDEC and sulphur were unaccounted for. Other reasons for the shortfall in ZDEC are considered in Section 4.3. The highest total sulphur concentration determined was 1.30% w/w which is only 67% of the sulphur expected, and that for ZDEC was 0.36% w/w which is 86% of the expected concentration.

4.2.2 The Effect of Stirring Compounded Latex Upon the Physical Properties of Film

The modulus, swelling index and tensile strength results show that films prepared from the unstirred latices remained essentially unvulcanised (Table 16). There were two exceptions, A(1)(0.5 h, unstirred) and A(3) (2 h, unstirred). In the case of A(1) the maturation time was only half an hour and much of the material dispersed during compounding would not yet have settled. There was sufficient sulphur and ZDEC present for vulcanisation to take place slowly. In the case of A(3) the amount of ZDEC in the film was unexpectedly high and this, together with sulphur, was sufficient to allow slow vulcanisation to take place. However, the reason for these higher levels of vulcanising ingredients cannot be explained but it seems likely that inadvertent agitation had occurred before the latex was used to prepare films.

Modulus, swelling index and tensile strength results for the stirred latices show that the films vulcanised rapidly. The strength properties were well developed by a cure time of 30 minutes. The effect of stirring was so important that no conclusions could be drawn about the effect of maturation time in this set of experiments and as a result of this investigation subsequent latices for maturation were kept stirred with a magnetic stirrer. Just before films were cast, a glass rod was used to redisperse any settled material from the bottom of the beaker because the magnetic stirrer was unable to prevent some of the additives from settling round the bottom edges of the beaker.

4.2.3 Regimen of Film Preparation

In view of the results found in the previous section the compounded latex was stirred as close as possible to the time when it was used to cast films because of

the problem of "losing" vulcanising ingredients through settlement. The risk of having air trapped in the latex was felt to be outweighed by the risk of settlement.

4.2.4 The Effect of Maturation Time Upon the Composition and Properties of Postvulcanised Latex Films Made from Stirred Latex

4.2.4.1 Composition of Films

It is clear from the chemical analyses of films prepared from stirred "matured" latices that the vulcanising ingredients are much better dispersed in the latex than in the unstirred latices (cf. Table 16 and Tables 17 and 18). The total sulphur determinations indicate that the sulphur expected to be present in the formulation can be found. The mean value for recovery from the thirteen formulations is 109.8%. However, the standard deviation is 6.9%, which is rather high. The reproducibility for the method is quoted by analysts at MRPRA as 1%, therefore the variability appears to be a feature of the compounding and not the analysis.

The total sulphur analyses gave recoveries of more than 100% hence there appears to be sulphur present which is not accounted for by sulphur in the sulphur dispersion, or ZDEC in the formulation. Another possible explanation is that the method of analysis leads to a result which has a positive bias. The third possibility is suggested by the finding that a latex film containing only added sulphur gave a higher than expected result for total sulphur.

Latex itself contains a small amount of sulphur, 0.03% w/w, and the surfactants used in the dispersions may also be sulphur-containing molecules, however, these two additional sources of sulphur are not likely to account for the extra 10% sulphur and the source of the additional sulphur has not been identified.

The free sulphur measured for the unvulcanised films was significantly lower than might be expected. This cannot be explained by vulcanisation taking place slowly at room temperature because if that were the case then a trend would be observed with changes in maturation time and that trend was not apparent. It is certainly surprising that the free sulphur determined for unvulcanised films was so low. The

Table 17 Total ZDEC and Total Zinc Results for Films from "Matured" Latex

Code	Maturation Time (h)	Calculated ZDEC % w/w	Measured dithiocarbamate expressed as ZDEC % w/w	% of Calculated Value Found	Calculated Total Zinc % w/w	Measured Total Zinc % w/w	% of Calculated Value Found
A(11)	0.5	0.44	0.39	89	0.47	0.45	96
A(12)	0.5	0.42	0.34	81	0.45	0.41	91
A(13)	1	0.43	0.36	84	0.47	0.42	89
A(14)	1	0.43	0.47	110	0.45	0.40	89
A(15)	2	0.43	0.35	82	0.46	0.42	91
A(16)	2	0.43	0.35	82	0.45	0.41	91
A(17)	4	0.43	0.40	93	0.45	0.40	89
A(18)	4	0.43	0.34	79	0.44	0.39	89
A(19)	16	0.42	0.39	94	0.43	0.38	88
A(20)	16	0.43	0.37	86	0.45	0.41	91
A(21)	24	0.42	0.38	90	0.44	0.39	89
A(22)	24	0.43	0.34	79	0.45	0.42	93
A(23)	40	0.43	0.37	86	0.46	0.41	89

mean = 87.3%
sd = 8.4%
RSD = 9.6%

mean = 90.4%
sd = 2.2%
RSD = 2.4%

Latex was matured at ambient laboratory temperature. Analyses were carried out on unheated films.

Table 18 Sulphur Results for Films from "Matured" Latex

Code	Maturation Time (h)	Cure Time (min)	Calculated Total Sulphur % w/w	Measured Total Sulphur % w/w	% of Calculated Value Found	Calculated Free Sulphur % w/w	Measured Free Sulphur % w/w	% of Calculated Value Found	Calculated Combined Sulphur	
									as %	as % w/w
A(11)	0.5	0 35 96	1.96	2.28	116	1.81	1.63 1.14 0.33	90	30 78	0.49 1.30
A(12)	0.5	0 30 90	1.94	2.01	104	1.79	1.73 1.09 0.49	97	37 72	0.64 1.24
A(13)	1	0 30 90	1.95	2.00	103	1.80	1.54 1.07 0.34	86	31 78	0.47 1.20
A(14)	1	0 30 92	1.96	2.24	114	1.81	1.63 1.25 0.54	90	23 67	0.38 1.09
A(15)	2	0 30 90	1.95	1.94	99	1.80	1.64 1.07 0.40	91	35 76	0.57 1.24
A(16)	2	0 39 90	1.95	2.38	122	1.80	1.65 1.08 0.54	92	35 67	0.57 1.11

continued overleaf

Table 18 Sulphur Results for Films from "Matured" Latex (cont.)

Code	Maturation Time (h)	Cure Time (min)	Calculated Total Sulphur % w/w	Measured Total Sulphur % w/w	% of Calculated Value Found	Calculated Free Sulphur % w/w	Measured Free Sulphur % w/w	% of Calculated Value Found	Calculated Combined Sulphur	
									as %	as % w/w
A(17)	4	0 30 90	1.98	2.16	109	1.83	1.60 0.99 0.44	87	38 73	0.61 1.16
A(18)	4	0 30 90	1.98	2.27	115	1.82	1.70 1.14 0.52	93	33 69	0.56 1.18
A(19)	16	0 37 90	1.94	2.22	114	1.79	1.65 0.94 0.44	92	43 73	0.71 1.21
A(20)	16	0 37 90	1.98	2.20	111	1.82	1.62 0.92 0.42	89	40 69	0.64 1.12
A(21)	24	0 37 90	1.93	2.16	112	1.78	1.62 0.92 0.42	91	43 74	0.70 1.20
A(22)	24	0 37 90	1.97	2.15	109	1.82	1.61 0.96 0.44	88	40 73	0.83 1.17
A(23)	40	0 30 90	1.95	1.93	99	1.80	1.48 0.65 0.61	82	56 59	0.83 0.87

mean = 109.8%
s.d. = 6.9%
R.S.D. = 6.3%

mean = 89.8%
s.d. = 3.7%
R.S.D. = 4.1%

analysis for free sulphur depends upon sulphur being extracted from the rubber network by acetone and since the results for total sulphur indicate that all the sulphur is present in the film it seems likely that the sulphur rapidly forms an entity which is unextractable by acetone. The results also indicate that a considerable excess of sulphur was present in the film and even after 90 min cure 0.33 - 0.60% w/w sulphur remained uncombined (Table 18).

The ZDEC present in the unvulcanised films was also measured, as dithiocarbamate, and the results were considerably lower than might be expected and the variation between results was higher (Table 17). The dithiocarbamate determined is expressed as ZDEC in Table 17. Approximately 13% of the added ZDEC could not be found. The possibility that ZDEC had become combined in a slow, room temperature vulcanisation could not be accepted in this case either since no trend with increasing maturation time was apparent

Films from latex to which only a sulphur dispersion had been added were analysed to discover whether all the sulphur could be extracted when no other vulcanising ingredients were present. The total sulphur calculated in the formulation was 1.87% w/w and that measured was 2.10% w/w. This was an over-estimate of 7.5% (cf. 9.8% for compounded latices, Table 18). The free sulphur determined on a lightly cold-milled sample of the same film was 1.73% w/w. Cold milling homogenises the materials present in the uncured rubber. The combined sulphur on the unmilled sample was 0.06% w/w. The free sulphur represented 92.5% of the expected value of sulphur (cf. 89.8% for compounded latices, Table 18), or 86.0% of the measured total sulphur. Since there was no accelerator present in the latex nor was it heated, the free sulphur present was expected to be the same as the total sulphur present. The free sulphur measured was lower than expected. The combined sulphur was slightly higher than expected but not inconsistent with the errors expected for determination of such low levels of sulphur. These observations also support the suggestion that a proportion of the sulphur forms an entity not readily extractable with acetone. There was also a discrepancy between the sum of the free and combined sulphur and the total sulphur. The pattern observed for fully compounded latex was also observed for latex to which only the sulphur had been added.

The films were also analysed for zinc, present as zinc oxide and ZDEC, with zinc oxide being the major zinc-containing compound (Table 17). The deficit of 10% is probably mainly due to settlement by some of the zinc oxide, which is the densest of the added dispersions (5.6 g cm^{-3}).

The consistent deficit in the dithiocarbamate (expressed as ZDEC) and the total zinc in the films suggested that there was a common cause (see Table 17, mean ZDEC and mean zinc), with some settlement of the dispersions being a likely explanation. However, this was found subsequently not to be the case, when the fate of the ZDEC was further investigated. The extraction of ZDEC from latex films has been examined in greater depth and is discussed in Section 4.3.

4.2.4.2 Physical Properties of Films

The tensile strength, modulus (S300%) and swelling index were measured for latex films derived from latices which had been matured for different lengths of time before use (Table 19 and Figures 31 and 32). The experiments were carried out to ascertain whether the length of maturation of latices affected the physical properties of the derived films. A visual examination of the data did not reveal any obvious relationship between modulus (stress) and maturation time or tensile strength and maturation time (Table 19 and Figures 31 and 32, on each side of the mean there are points showing the 95% confidence interval).

It is possible to assess the effect of varying one of the conditions in an experiment by applying a statistical method called analysis of variance (ANOVA) to the results. Analysis of variance allows the variation in results due to changes in controlled factors (e.g. changes in experimental conditions) to be compared with the random variations found in the results: interactions between controlled factors may also be found. Using this method it is possible to find out if small differences are of statistical significance. A two-way ANOVA was carried out for both the modulus (stress) and tensile strength data. The two controlled factors examined were maturation time of the latex and cure time for the films. The latex was compounded separately for each individual experiment. Each formulation code in Table 19 represents a separate latex preparation. The same two latex preparations were not used for each

Table 19 Physical Properties of Films Made from Stirred "Matured" Latex

Formulation Code	Maturation Time (h)	Cure Time (min)	n	TS (MPa)	sd (MPa)	S300% (MPa)	sd (MPa)	SI
A(11)	0.5	0	5	7.3	0.7	0.63	0.01	10.73
		35	5	23.8	3.8	0.99	0.02	2.28
		96	5	27.9	2.5	1.12	0.03	2.11
A(12)	0.5	0	5	8.4	0.5	0.61	0.01	10.17
		30	5	26.1	2.2	1.00	0.03	2.37
		90	5	31.0	1.5	1.17	0.04	2.11
A(13)	1	0	5	7.0	0.8	0.65	0.02	9.43
		30	5	26.3	2.4	1.05	0.03	2.26
		90	5	29.7	1.2	1.21	0.02	2.07
A(14)	1	0	5	8.8	1.7	0.56	0.01	8.87
		30	5	23.1	2.5	0.87	0.04	2.38
		92	5	32.1	1.9	1.03	0.05	2.15
A(15)	2	0	5	7.7	1.1	0.65	0.01	9.78
		30	5	26.8	2.0	1.03	0.02	2.23
		90	5	26.5	3.5	1.15	0.03	2.04
A(16)	2	0	5	7.4	1.1	0.61	0.02	9.86
		39	5	24.2	1.6	0.94	0.04	2.37
		90	5	31.6	1.4	1.09	0.06	2.11
A(17)	4	0	5	6.2	0.2	0.64	0.05	6.98
		30	5	30.0	2.2	1.04	0.03	2.17
		90	5	28.2	1.7	1.19	0.03	2.08
A(18)	4	0	5	6.8	0.9	0.61	0.02	10.23
		30	5	23.8	2.7	0.96	0.03	2.34
		90	5	29.6	2.0	1.08	0.07	2.11
A(19)	16	0	5	11.3	1.0	0.60	0.02	9.34
		37	5	29.4	2.9	1.02	0.01	2.21
		90	5	34.0	1.8	1.15	0.04	2.10

continued overleaf

Table 19 Physical Properties of Films Made from Stirred "Matured" Latex(cont.)

Formulation Code	Maturation Time (h)	Cure Time (min)	n	TS (MPa)	sd (MPa)	S300% (MPa)	sd (MPa)	SI
A(20)	16	0	5	6.7	1.4	0.63	0.02	8.93
		37	5	32.3	1.5	1.10	0.02	2.23
		90	5	31.2	3.1	1.21	0.02	2.10
A(21)	24	0	5	7.8	1.5	0.66	0.07	3.29
		37	5	32.7	1.6	1.02	0.02	2.21
		90	5	33.2	1.8	1.15	0.03	2.11
A(22)	24	0	5	6.6	0.8	0.67	0.01	9.61
		37	5	30.6	2.3	1.10	0.03	2.25
		90	5	31.2	0.8	1.16	0.03	2.09
A(23)	40	0	5	8.8	0.9	0.71	0.02	2.99
		30	5	29.2	1.3	1.05	0.02	2.16
		90	5	29.3	2.4	1.12	0.07	2.14

Latices matured at laboratory temperature

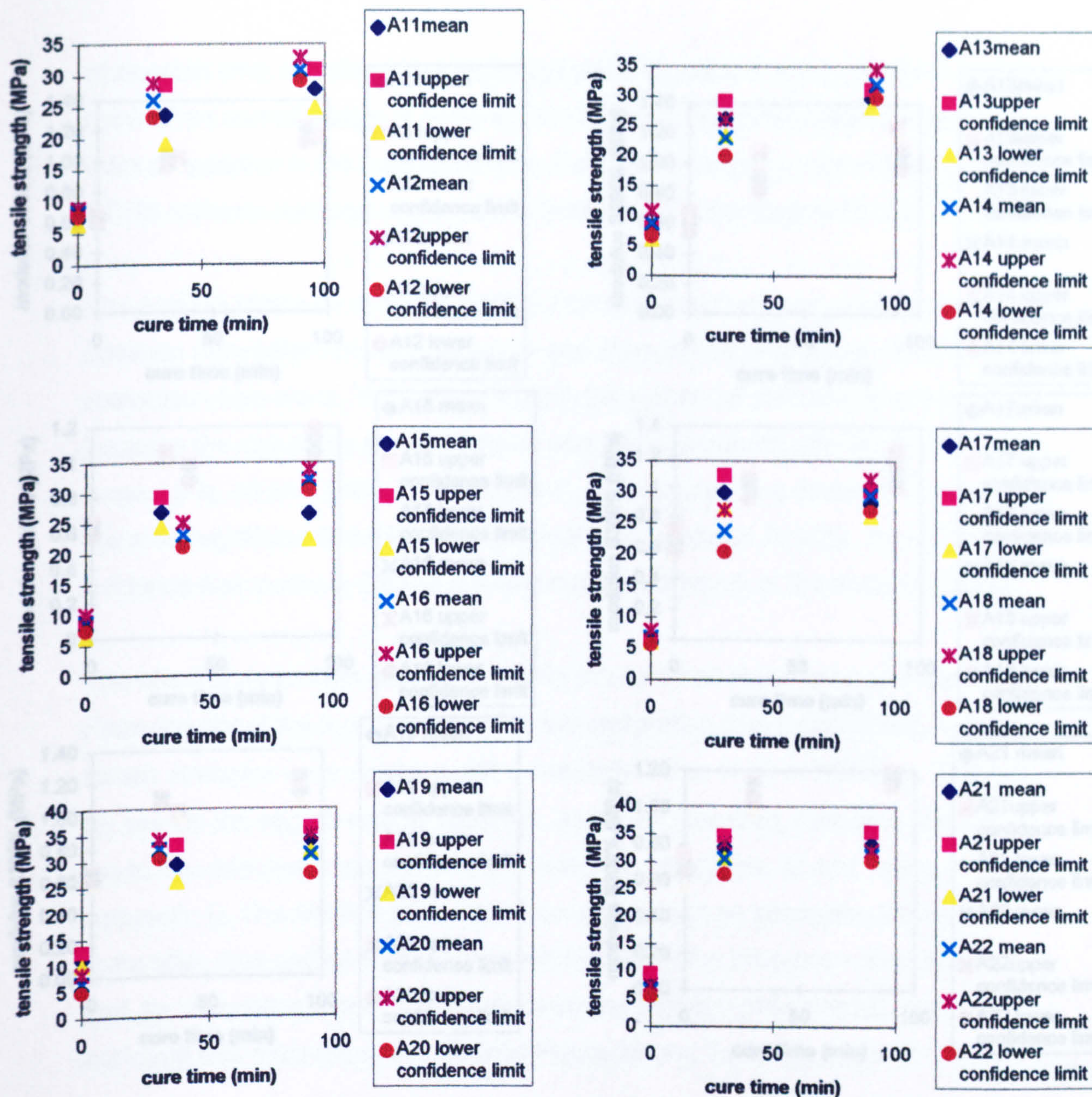
Films cured at 90°C

n = Number of samples

SI = Swelling index

TS = Tensile strength

S300%= Modulus at 300% elongation



All latices matured at laboratory temperature and kept stirred until films cast. Maturation times were varied:

A(11) and A(12) = 0.5 h

A(13) and A(14) = 1 h

A(15) and A(16) = 2 h

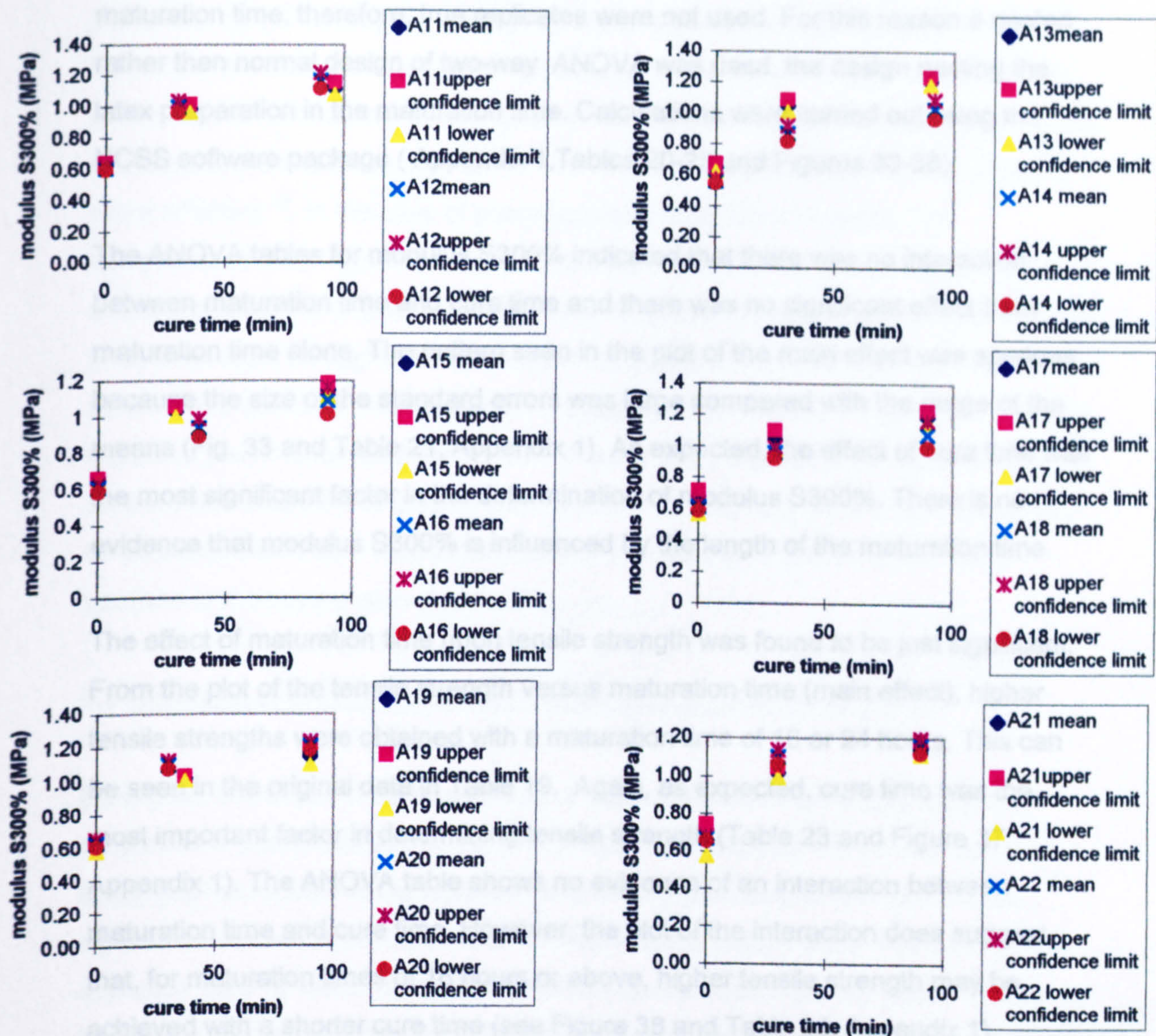
A(17) and A(18) = 4 h

A(19) and A(20) = 16 h

A(21) and A(22) = 24 h

Films were cured at 90°C

Figure 31 Tensile Strength of Films Prepared from Matured Latices



All latices matured at laboratory
Films were cured at 90°C.

Maturation times were varied:

A(11) and A(12) = 0.5 h

A(13) and A(14) = 1 h

A(15) and A(16) = 2 h

A(17) and A(18) = 4 h

A(19) and A(20) = 16 h

A(21) and A(22) = 24 h

Figure 32 Modulus S300% of Films Prepared from Matured Latices

temperature and kept stirred until films cast.

maturation time, therefore, true replicates were not used. For this reason a nested rather than normal design of two-way ANOVA was used, the design nesting the latex preparation in the maturation time. Calculations were carried out using the NCSS software package (Appendix 1, Tables 20-23 and Figures 33-38).

The ANOVA tables for modulus S300% indicated that there was no interaction between maturation time and cure time and there was no significant effect from maturation time alone. The pattern seen in the plot of the main effect was spurious because the size of the standard errors was large compared with the range of the means (Fig. 33 and Table 21, Appendix 1). As expected, the effect of cure time was the most significant factor in the determination of modulus S300%. There is no evidence that modulus S300% is influenced by the length of the maturation time.

The effect of maturation time upon tensile strength was found to be just significant. From the plot of the tensile strength versus maturation time (main effect), higher tensile strengths were obtained with a maturation time of 16 or 24 hours. This can be seen in the original data in Table 19. Again, as expected, cure time was the most important factor in determining tensile strength (Table 23 and Figure 37, Appendix 1). The ANOVA table shows no evidence of an interaction between maturation time and cure time. However, the plot of the interaction does suggest that, for maturation times of 16 hours or above, higher tensile strength may be achieved with a shorter cure time (see Figure 38 and Table 23, Appendix 1).

The physical properties of vulcanised films prepared from stirred latices did not appear to alter markedly with the use of different maturation times. The modulus S300%, which is believed to be dependent upon crosslink density, was unaffected by maturation time. The tensile strength of films did appear to have some dependence on the maturation of the latex at maturation times of 16 hours and 24 hours. At these longer maturation times high tensile strengths were attained at shorter cure times and slightly higher tensile strengths appeared to be attained overall.

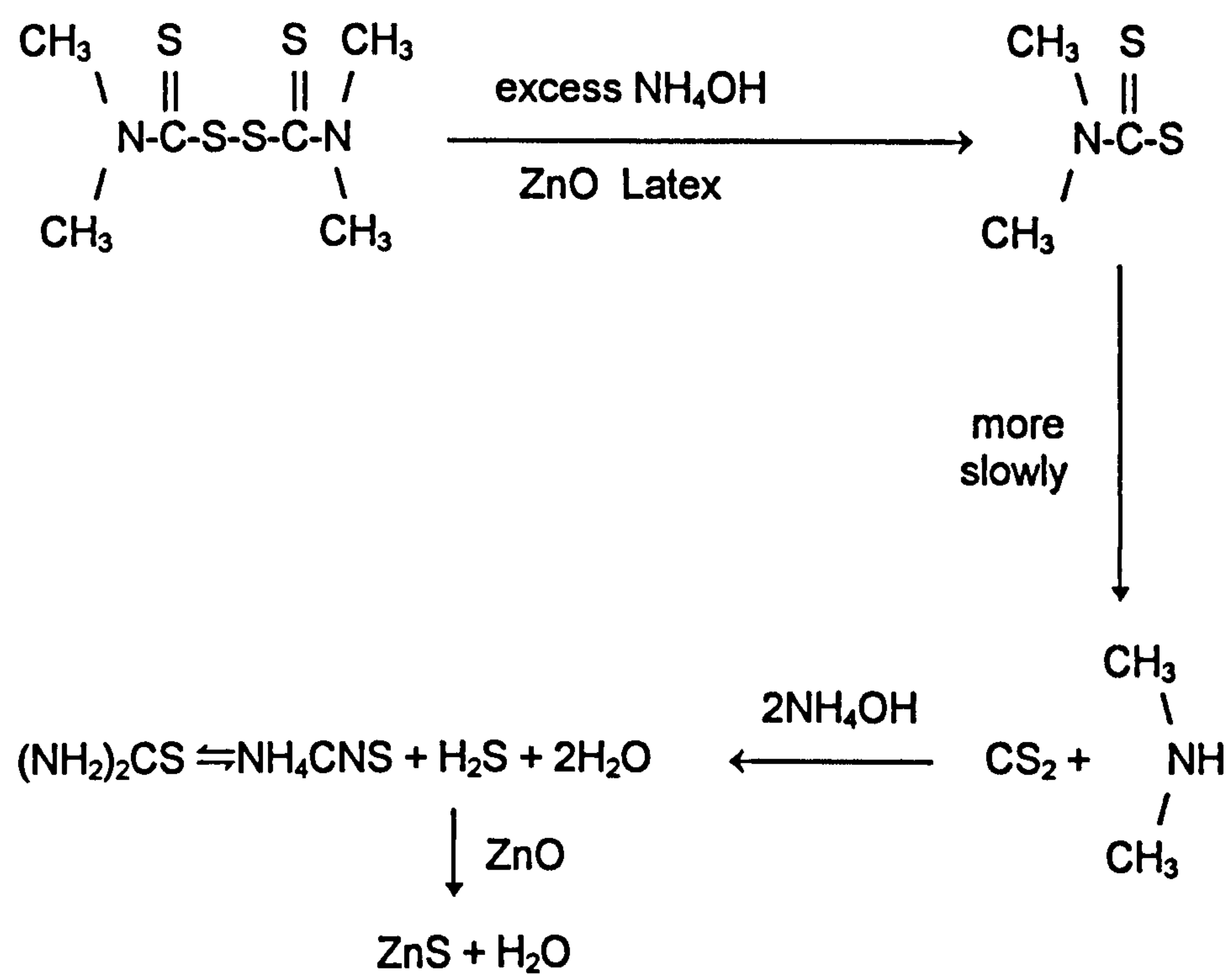
Maturation of prevulcanised latices is known to be important in affecting the physical properties of the derived films (Section 1.4.3). In prevulcanised latices, because the sulphur crosslinks occur between rubber molecules within latex

particles, the vulcanising ingredients must have transferred themselves in some form from the solid particles of the dispersions to the latex particles. Maturation of compounded latices allows this migration of vulcanising ingredients to occur before prevulcanisation takes place. Hence, the formation of crosslinks within the latex is more effective¹². In the case of postvulcanised latex films, maturing the compounded latex appears to have little effect upon the modulus or tensile strength of the derived films. In postvulcanised latex films the sulphur crosslinks are believed to be distributed throughout the film, not only between rubber molecules within latex particles but also between molecules in adjacent latex particles. Therefore, it seems likely that the homogenous distribution of vulcanising ingredients throughout the film before vulcanisation is of greater importance in determining the physical properties of postvulcanised films than the transfer of vulcanising ingredients into latex particles in the case of prevulcanisation.

4.3 Extraction of Zinc Diethyldithiocarbamate (ZDEC) from Latex Films

During the investigation into the effects of maturation time and stirring upon the properties of postvulcanised latex films (Section 4.2.1-4.2.2), the concentration of the accelerator ZDEC in the uncured films was measured and was found to be significantly less than expected from the formulation used (Tables 16 and 17). This apparent "loss" of ZDEC from latex films had earlier been noted by Merrill²³, who had found that the concentration of non-rubbers in the latex affected the size of the "loss". He encountered a "loss" of 17-32% for HA latex (3% non-rubbers) and 6-8% for centrifuged substage special latex (0.71% non-rubbers). Independently, Loadman observed a decrease with time in the concentration of zinc dimethyldithiocarbamate (ZDMC) in latex. He and other workers at MRPRA were investigating the fate of TMTD after addition, with zinc oxide, to field latex⁸¹. Over a short period of time the TMTD reacted with the zinc oxide to form ZDMC in the latex. The ZDMC formed began to decompose during the time that the latex was stored. A number of decomposition products were identified; zinc sulphide (as a major product), dimethylamine, ammonium thiocyanate and thiourea. The proposed route for decomposition of TMTD/ZDMC is shown in Scheme 6. Therefore, it seems reasonable to suggest that ZDEC, or at least a portion of that added, also undergoes decomposition in the latex.

Scheme 6 The Proposed Major Routes for the Decomposition of TMTD in Latex



Based on Ref. 81

Clearly, quantitative estimation of ZDEC or ZDMC in a latex film depends upon quantitative extraction of the zinc dithiocarbamate from the film. The results of experiments to investigate the efficiency of the extraction method will be discussed in this section.

Simplified latex formulations (C(1),D and E) which contained only HA latex and known weights of ZDEC dispersion were used (Table 12, Section 3.1.3). Since no sulphur was added, the possible disappearance of ZDEC during vulcanisation was avoided. The ZDEC incorporated in the film was, therefore, the only source of both zinc and diethyldithiocarbamate, i.e. no zinc oxide or other zinc-containing accelerator was used. It is possible to account for the added ZDEC in terms of both the zinc and diethyldithiocarbamate groups by estimating them with separate analytical procedures. Zinc analyses were carried out on unextracted rubber films, dichloromethane-extracted rubber films and dichloromethane extracts (Section 3.6.6). The results of the extractions of latex films are shown in Tables 24-27.

Measurement of the diethyldithiocarbamate present in dichloromethane extracts showed that the static extraction is inefficient (Table 24): only 50-70% of the added ZDEC was present in the first extract and even three extractions were evidently not sufficient to remove all the ZDEC present. Dynamic (Soxhlet) extraction is more efficient and is complete in one sequence (Table 25), although the total quantities extracted are generally lower than those from multiple static extractions. The results for multiple static extractions are consistent (74-78%) and are the highest values obtained when HA latex was used to prepare the films. However, if all the results for experiments with HA latex are included (except those from single static extractions), this range broadens to 52-78%.

These results indicate that some 22-48% (average 32%) of the ZDEC added has been converted into other zinc-containing material which is insoluble in dichloromethane. This conclusion is supported by the amounts of non-extractable zinc found in the extracted films (24-53%; average 35%). It may be concluded that about one-third of the ZDEC added is decomposed or otherwise insolubilised by material present in the HA latex.

Table 24 Static Extraction with Dichloromethane of Latex Films

Sample code	Sample weight and solvent volume	Zinc expected (%w/w)	Zinc in unextracted film (%w/w)	Zinc in extracted film (%w/w)	Zinc unextractable from film (%)	Zinc in unextracted film expressed as ZDEC (% w/w)	Diethyldithiocarbamate in extracts expressed as ZDEC (%w/w)				ZDEC extracted from film (%)	Total ZDEC accounted for (%)
							1	2	3	Total		
D	1g in 80ml DCM	0.366	0.375 (0.008)	0.172 (0.002)	46	2.077	1.241 [60%]			1.241	60	104
D	1g in 80ml DCM	0.366	0.375 (0.008)	0.092 (0.005)	25	2.077	1.152 [55%]	0.329 [16%]	0.101 [5%]	1.582	76	101
D	0.5g in 80ml DCM	0.366	0.375 (0.008)	0.089 (0.008)	24	2.077	1.410 [68%]	0.217 [10%]		1.627	78	102
C(1)	1g in 80ml DCM	0.186	0.198 (0.006)	0.082 (0.000)	41	1.097	0.594 [54%]			0.594	54	95
C(1)	1g in 80ml DCM	0.186	0.198 (0.006)	0.074 (0.002)	37	1.097	0.574 [52%]	0.173 [16%]	0.068 [6%]	0.815	74	111
C(1)	0.5g in 80ml DCM	0.186	0.198 (0.006)	0.078 (0.002)	39	1.097	0.736 [67%]	0.089 [8%]		0.821	75	114
C(2)	1g in 80ml DCM	0.185	0.185 (0.000)	0.036 (0.003)	19	1.021	0.592 [58%]	0.188 [18%]		0.780	76	95

Films C(1) and D were prepared from HA latex, Film C(2) was prepared from DPNR latex, () = standard deviation, [] = % of material present in the unextracted film

Values are based on the weights of unextracted films

Table 25 Soxhlet Extraction with Dichloromethane of Latex Films

Sample code	Sample weight and solvent volume	Zinc expected (%w/w)	Zinc in unextracted film (%w/w)	Zinc in extracted film (%w/w)	Zinc unextractable from film (%)	Zinc in unextracted film expressed as ZDEC (% w/w)	Diethyldithiocarbamate in extracts expressed as ZDEC (%w/w) Number of extractions			Zinc in extracts (%w/w)	ZDEC extracted from film (%)	Total ZDEC accounted for (%)
							1	2	Total			
D	1g in 80ml DCM	0.366	0.375 (0.008)	0.101 (0.007)	27	2.077 (0.043)	1.339 (0.010)		1.339	0.229 (0.008) [61%]	64	91 [88]*
D	0.5g in 40ml DCM	0.366	0.375 (0.008)	0.119 (0.007)	32	2.077 (0.043)	1.484 (0.021)	0.003 (0.001)	1.486		72	104
C(1)	1g in 80ml DCM	0.186	0.198 (0.006)	0.084 (0.003)	42	1.097 (0.031)	0.573 (0.054)		0.573	0.096 (0.003) [48%]	52	94 [90]*
C(1)	0.5g in 40ml DCM	0.186	0.198 (0.006)	0.104 (0.001)	53	1.097 (0.031)	0.569 (0.004)	0.010 (0.008)	0.579		53	106
C(2)	1g in 80ml DCM	0.185	0.185 (0.000)	0.024 (0.001)	13	1.021 (0.000)	0.876 (0.003)		0.876		86	99

Values are based on the weights of unextracted films. () = standard deviations, [] = % of material in the unextracted film, []* = ZDEC based on determination of zinc in extracts.

Table 26 Comparison of Different Methods for Extracting ZDEC from Latex Films which also contained Antioxidant 2246

Sample code	Zinc expected (%w/w)	Zinc in unextracted film (%w/w)	Zinc in unextracted film expressed as ZDEC (% w/w)	Diethyldithiocarbamate in extracts expressed as ZDEC (%w/w)					Zinc in extract from Soxhlet extraction under nitrogen (%w/w)
				Static Extraction			Soxhlet extraction under		
				1	2	total	Air	Nitrogen	
E	0.184	0.191 (0.000)	1.055 (0.000) 104%	0.581 (0.004) 57%	0.207 (0.007) 20%	0.788 77%	0.707 (0.027) 70%	0.743 (0.025) 73%	0.13 69%
F	0.227	0.231 (0.000)	1.277 (0.000) 102%	0.746 (0.011) 59%	0.336 (0.009) 27%	1.082 86%	1.013 (0.061) 81%	1.098 (0.015) 88%	0.19 85%

Values are based on the weights of unextracted films.

()= standard deviations.

%=% of material present in the unextracted films

Table 27 Extraction of ZDEC from Latex Films which also contained Antioxidant 2246 and have been Stored for 62 days

Sample code	Zinc in unextracted film (%w/w)	Zinc in unextracted film expressed as ZDEC (% w/w)	Zinc in extracted film (% w/w)	Total sulphur in extracted film (% w/w)	Sulphide sulphur (%w/w)	Sulphide sulphur expressed as zinc sulphide (% w/w)	Diethyldithiocarbamate in extracts expressed as ZDEC (% w/w)
E	0.191	1.055	0.079 (41%)	0.08	0.02	0.06	0.503 (48%)
F	0.231	1.277	0.016 (7%)	0.07	0.03	0.09	1.176 (92%)

Values are based on the weights of unextracted films.

In two experiments, the zinc concentrations in the extracts were measured, in addition to the diethyldithiocarbamate concentrations (Table 25). The former were in good agreement with the latter (61% cf. 64%; 48% cf. 52%), indicating that the extracted material is ZDEC and that zinc is extracted only if it is present as ZDEC.

In both Tables 24 and 25 the final column quotes totals of ZDEC accounted for, by adding the percentage found to be extracted to the percentage of unextractable zinc. The totals vary between 94% and 114% (average, 103%). This large spread of values may be due to deviation from the stated concentration of the commercially supplied ZDEC dispersion, or lack of homogeneity in the dispersion when used, or loss of water from the dispersion by evaporation.

As has been noted at the beginning of this section, the disappearance of ZDEC from HA latex films has been linked by Merrill to the non-rubbers present in the latex. This was further investigated here using a sample, C(2), made from deproteinised (DPNR) latex instead of HA latex. The low protein concentration in this latex was demonstrated by carrying out nitrogen analysis (found: 0.01 wt.% N). on a total-solids film prepared from the uncompounded latex.

It is clear from the entry for sample C(2) in Table 25, that loss of ZDEC from a DPNR latex film is much less than from a HA latex film. In this case, 86% of the added ZDEC was extracted from the film and the zinc remaining in the film was equivalent to 13% of the added ZDEC. (Even after two static extractions (Table 24), 76% of the added ZDEC is recovered). It is concluded that in DPNR latex, about one-eighth of the added ZDEC is converted into some insoluble form, confirming that latex proteins are involved in much, but not all, of the insolubilisation of ZDEC.

ZDEC behaves as an antioxidant, so to establish that ZDEC was not being oxidised during the extraction procedure, latices were prepared containing ZDEC and antioxidant 2246 (formulations E and F, Tables 26 and 27). Static extraction was carried out using 1%w/v antioxidant 2246 dissolved in dichloromethane. Soxhlet extractions were carried out in air and under nitrogen (Table 26). The extractions yielded 70-77% dithiocarbamate for the HA latex film (E) and 81-88% for the DPNR latex film (F). The amounts of dithiocarbamate extracted when these special precautions were taken to avoid the possibility of oxidation were very similar to those extracted in the experiments of Tables 24 and 25. The amounts of zinc present in the

DCM extracts from Soxhlet extraction under nitrogen were 69% and 85% compared with 73% and 88% for dithiocarbamate in the same extracts. This lends further support to the suggestion that the unextracted ZDEC is not available for extraction either because of decomposition or because it has been insolubilised. From the results in Table 26 it can be concluded that the low dithiocarbamate values in Table 25 are not due to decomposition during extraction or during storage of the extract. Further support for this view is given by the reasonable agreement between the percentages of zinc and of dithiocarbamate in the extracts (Tables 24 and 26).

Extraction and analysis of films described in Table 26, which had been stored at room temperature in the dark for 62 days after preparation, provided further information about the process of ZDEC loss. Comparison of Table 27 with Table 26 shows that, whereas the percentage of dithiocarbamate extracted from DPNR films had been maintained (or has even increased slightly), the percentage extracted from HA latex films has dropped from 70-77% to 48%. In view of the presence of Antioxidant 2246 and the similar treatment of the two types of film, it is thought to be highly unlikely that this difference can be due to any loss of ZDEC during the storage period. We must therefore conclude that the reaction which occurs between ZDEC and the non-rubbers (almost certainly protein) in HA latex is slow and may continue over the course of several months.

As we have seen in the results of Table 27, about half of the ZDEC expected to be present in the film of sample E has been converted into some other form. Sulphur analyses were therefore carried out on the extracted, stored films in the expectation that light might be shed on the nature of this other form. Loadman et al ⁸¹ found that zinc sulphide was the major product of the decomposition of ZDMC in latex. The results of sulphide sulphur analyses shown in Table 27 are not conclusive. If the unextracted zinc in the films were all present as zinc sulphide we could expect sulphide sulphur values of 0.04% w/w and 0.01% w/w for films E and F respectively (cf. 0.02% w/w and 0.03% w/w in Table 27) But with the small samples available for analysis the errors were quoted as $\pm 0.03\%$ w/w. Therefore it is not possible from these results to decide whether the unextracted zinc is present in the film as zinc sulphide. If the unextracted zinc were present as an insolubilised form of ZDEC the total sulphur present would be 0.15% w/w and 0.03% w/w for films E and F respectively. The total sulphur determined for film E is 0.08% w/w which is approximately half the value calculated using the zinc results, whereas that for film F is 0.07% w/w which is about twice the calculated value.

Although the result for film F is slightly disconcerting it can be argued that when determining such low levels of zinc and sulphur the errors may be large and that the difference between 0.03%w/w and 0.07% w/w is not in fact significant. However, in the case of film E the difference between the calculated value of 0.15% w/w and the measured value of 0.08%w/w for total sulphur is sufficiently great to be significant. It lends further support to the view that the unextractable ZDEC no longer exists as ZDEC in the rubber. The sulphur which has disappeared may have done so in the form of a volatile compound, such as carbon disulphide (Scheme 6), or as a species which is soluble in DCM (since no sulphur analyses were carried out on the extracts).

The results of analyses for ZDEC in natural rubber latex films are in general agreement with the findings of other workers ^{12,23}. There is a proportion of the added ZDEC which cannot be extracted from the rubber matrix using successive static extractions. Nor can it be removed by the more efficient method of Soxhlet extraction. The fraction of added ZDEC which can be extracted from the rubber is dependent upon the amount of non-rubbers present in the latex. The lower the non-rubber content of the latex, the greater the fraction of added ZDEC which can be extracted. The amount of ZDEC which can be extracted from HA latex films decreases with increasing storage time. In the case of DPNR latex films, where the amount of non-rubbers in the latex is extremely low, storage time hardly affected the amount of ZDEC extractable. This indicates that the reaction between ZDEC and non-rubbers continues in dry films over a period of many months. Loadman describes the decomposition of ZDMC in latex⁸¹ The reaction is slow, taking place over a period of several weeks. In the proposed reaction scheme (Scheme 6), ammonium hydroxide (present in the ammoniated latex) reacts with dimethylamine and carbon disulphide (formed by decomposition of TMTD) to form ammonium thiocyanate and hydrogen sulphide which further reacts with zinc oxide to form zinc sulphide.

From the results of the present investigation, slow decomposition of ZDEC in latex films, continuing for many weeks, also appears to take place. However, although ammonium hydroxide is present in latex, once the film has dried most of it will have been lost as ammonia by evaporation. Therefore, the route for the decomposition of ZDEC in dry latex films is unlikely to be exactly the same as that proposed for ZDMC in latex. The evidence from the dry films indicates that it is non-rubbers that are involved in the decomposition. Although the results of sulphur analyses are not absolutely conclusive as to whether zinc sulphide is formed in the latex films, they do provide

evidence that the ZDEC unextracted from the film has decomposed and that volatile or solvent-soluble sulphur compounds have been removed from the rubber.

The lower recoveries of ZDEC in the Soxhlet extracts compared to those for static extractions may also be explained in terms of the decomposition of ZDEC in the films. Soxhlet extractions were carried out on films C(1), C(2) and D after all the static extraction experiments (see Tables 24 and 25). By this time the films were approximately seven weeks old and significant decomposition would have taken place. This factor was not anticipated when the experiments were carried out.

The results suggest that upon storage any unreacted ZDEC in a rubber product produced from HA latex will undergo a slow decomposition. Therefore, residual accelerator levels in finished products are best determined the same length of time after production if comparison is to be made between results. Another fact to be borne in mind when storing compounded latex is that a decomposition reaction will also have been taking place in the latex from the time that the accelerator was added.

4.4 Drying Regimen for Latex Films

While it is recognised in the rubber industry that the physical properties of a rubber vulcanisate are to some extent sensitive to the humidity conditions under which they are measured, there appears to be very little information in the literature on the extent of the effect of moisture. This is true even for products made directly from latex, which seem to be particularly sensitive to humidity.

No data relating specifically to postvulcanised latex films have been found but Low⁸² subjected films prepared from prevulcanised latex to different drying conditions before measuring their physical properties. He found that films with high moisture contents had lower tensile strengths and moduli. Thus, the highest strengths and moduli were shown by films which had been desiccated and then tested immediately. On standing in moist air, the properties of these films decreased progressively with time and their content of volatile matter increased. Oven drying had a similar initial effect to desiccation but there were indications of other changes occurring, which could be attributed to increases in crosslinking (postvulcanisation). [In all the work reported here, drying was conducted at room temperature in order to avoid this effect as far as possible].

Low also found that aqueous leaching of prevulcanised films prior to drying resulted in lower equilibrium moisture contents and higher physical strengths. He attributed this to the removal of hydrophilic non-rubber materials during leaching. He did not comment on the nature of these materials but Chong and Porter⁶⁰ found evidence that the protein present in latex behaves as a reinforcing filler in dry postvulcanised latex films. When the films were swollen with water, the reinforcing effect was much reduced. Low's observations are therefore explicable if they are due to protein which is removed or partially removed by leaching, now a known fact. Literature relating to the effect of leaching films has been discussed in Section 2.5.2 and further work concerning the leaching of postvulcanised latex films will be found in Section 4.5.

Experiments were carried out here to compare the effect upon the physical properties of resultant postvulcanised latex films of gelation and equilibration of films in different conditions of humidity. All films were cast at laboratory temperature and allowed to gel and equilibrate at 25°C. It is believed that the hydrated non-rubbers form a layer around the surface of latex particles which hinders their fusion and reduces the possibility of secondary valence interactions^{10,46}. Therefore, if the moisture in a latex film is reduced by drying it over a desiccant (e.g. phosphorus pentoxide), the fusion of latex particles might be expected to be greater and to lead to increases in modulus and tensile strength when the films are postvulcanised.

Latex was prepared to formulation A (Table 10, Section 3.1) and films cast (Sections 3.1 and 3.2). Subsequent treatment of the films is described in Section 3.2. Physical tests were carried out on the samples (Sections 3.5.1-3.5.2). The experiments were repeated with a second latex preparation. The results are shown in Table 28.

Comparisons were made between films subjected to different drying conditions and also between films from the two latex preparations subjected to the same drying conditions, in order to obtain an indication of the degree of variation between latex preparations. A Student t-test⁸³ was applied to pairs of data sets (Tables 29-32). In Tables 31 and 32, the results of drying two different preparations of the same latex formulation were compared (A(24) and A(25)) for each of the conditions of humidity. In Tables 29 and 30 the differences in tensile strength and modulus have been compared. For latex preparation A(24), one set of samples out of four showed a significant difference in tensile strength. For latex preparation A(25), three sets out of

Table 28 Use of Different Drying Regimens for Latex Films - Physical Properties

Formulation Code	Drying Conditions	Cure time (min)	n	Tensile Strength (MPa)	s.d.	Modulus S300% (MPa)	s.d.
A(24)	Controlled environment	30	5	21.8	1.7	1.01	0.09
	Phosphorus pentoxide	30	5	15.2	4.5	0.97	0.07
	Controlled environment	60	5	26.9	1.9	1.08	0.03
	Phosphorus pentoxide	60	5	25.8	1.8	1.20	0.04
	Controlled environment	90	5	30.4	1.8	1.22	0.03
	Phosphorus pentoxide	90	5	27.2	3.5	1.26	0.06
	Controlled environment	120	5	28.9	2.2	1.25	0.04
	Phosphorus pentoxide	120	5	29.6	0.4	1.40	0.01
A(25)	Controlled environment	30	5	16.3	1.9	1.07	0.07
	Phosphorus pentoxide	30	5	21.3	2.5	1.09	0.04
	Controlled environment	60	5	23.7	1.6	1.16	0.05
	Phosphorus pentoxide	60	5	26.5	0.9	1.11	0.01
	Controlled environment	90	5	24.1	2.3	1.27	0.04
	Phosphorus pentoxide	90	5	26.5	1.5	1.29	0.03
	Controlled environment	120	5	25.5	0.8	1.19	0.06
	Phosphorus pentoxide	120	5	27.5	1.0	1.28	0.03

All films cured at 90°C

four showed significant differences. When moduli were compared two sets out of four for each latex preparation showed significant differences. There was no clear indication that drying a film before vulcanisation leads to any significant increase in either modulus or tensile strength.

When both sets of films were equilibrated in the controlled environment room there were significant differences in tensile strength for all four sets of data. When they were equilibrated over phosphorus pentoxide there were significant differences in two out of the four data sets (Table 31). When modulus data were compared (Table 32), they showed significant differences in one set out of four for films equilibrated in the controlled environment room, and for three sets out of four for films dried over phosphorus pentoxide. Once again the results give no clear indication that drying latices over phosphorus pentoxide reduces variability in physical properties.

The variability seen between replicate latex preparations appears to be as great as any differences in physical properties observed when different drying conditions were used. In the case of postvulcanised films, additional drying of the film using phosphorus pentoxide appeared to make little contribution to an increase in its modulus or tensile strength.

4.5 Leaching of Postvulcanised Films

Leaching prevulcanised latex films has a significant effect upon their tensile strength and modulus, both being increased. This has been described in Section 2.5.2. The limited information available relating to the leaching of postvulcanised latex films indicated that although increases in tensile strength and modulus were observed on leaching they were smaller than for the equivalent prevulcanised films²⁵. Therefore, a series of experiments were carried out leaching postvulcanised latex films with water and with organic solvents at various temperatures in order to obtain more data from which to assess the effect of leaching upon their physical properties.

Table 29 Comparison of Effect of Drying Regimen on Tensile Strength for Latex Compounds A(24) and A(25)

Cure time (min)	A(24)		A(25)	
	t		t	
30	3.07	✓	3.56	✓
60	0.94	x	3.41	✓
90	1.82	x	1.95	x
120	0.7	x	3.67	✓

✓ = difference significant at 5% level
x = no significant differences at 5% level
t_{tab} = 2.31 (for 8 degrees of freedom)^{ay}

Table 30 Comparison of Effect of Drying Regimen on Modulus S300% for Latex Compounds A(24) and A(25)

Cure time (min)	A(24)		A(25)	
	t		t	
30	0.77	x	0.81	x
60	5.88	✓	2.38	✓
90	1.11	x	0.86	x
120	7.26	✓	3.23	✓

Table 31 Comparison of Nominal Replicate Latex Compounds A(24) and A(25) in Under Different Conditions - Tensile Strength

Cure time (min)	Controlled Environment		Phosphorus Pentoxide	
	t		t	
30	4.82	✓	2.65	✓
60	2.88	✓	0.78	x
90	4.82	✓	0.41	x
120	3.25	✓	4.15	✓

Table 32 Comparison of Nominal Replicate Latex Compounds A(24) and A(25) Dried Under Different Conditions - Modulus S300%

Cure time (min)	Controlled Environment		Phosphorus Pentoxide	
	t		t	
30	1.09	x	3.26	✓
60	3.26	✓	5.57	✓
90	1.95	x	1.04	x
120	1.92	x	83.6	✓

4.5.1 Leaching with Water After Postvulcanisation

Postvulcanised latex films, or dumb-bells cut from those films, leached in deionised water for periods of 24 and 44 hours at laboratory temperature generally showed relatively small changes in tensile strength and modulus (Table 33). When the individual sets of data were examined in detail a less clear-cut picture emerged. F and Student t-tests were applied to the data⁸³. In the twenty-eight sets of samples examined there were statistically significant increases in tensile strength on leaching for seven sets, a statistically significant decrease for one set and twenty sets showing changes which were not statistically significant. Twelve sets of samples showed statistically significant increases in modulus (S300%) on leaching, one set had a statistically significant decrease in modulus and fourteen sets had changes in modulus which were not statistically significant.

It has therefore been concluded that the effect of leaching postvulcanised latex films with deionised water at laboratory temperature had no consistent effect upon their physical properties. Some increases in tensile strength and modulus resulted but the variation between the samples was often greater than the size of the changes seen on leaching.

Leaching of postvulcanised latex films with deionised water was also carried out at elevated temperatures (Table 34). Leaching at 75°C lead to significant increases in modulus for samples leached for 30 and 60 min .For the shorter leach times of 10 and 20 min there were increases in modulus but these were not statistically significant. There were significant increases in tensile strength for all leach times up to 60 minutes. At the higher leach temperature of 88°C there were significant changes in modulus for all leach times but the increases in tensile strength were too small to be significant. These findings are in line with those of Porter and Wong²⁵. Use of a long leach time (11½ hours) and a high temperature (97°C) gave a significant increase in modulus, compared to the unleached sample. There was also a small decrease in tensile strength but this was not statistically significant.

Leaching at elevated temperatures may lead to further vulcanisation, which would explain the increases in modulus and tensile strength. However, swelling index data for

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Table 33 The Effect of Leaching Postvulcanised Latex Films with Deionised Water at Room Temperature(cont.)

Formulation Code	Cure time (min)	Cure temp (°C)	Leach time (hours)	Leach temp (°C)	(MPa)					% change		Difference Significant	
					n	TS	s.d.	S300%	s.d.	TS	S300%	TS	S300%
A(32)	15	110	0	-	5	26.3	1.3	1.08	0.06	-	-	-	-
A(32)	15	110	24	≈20	4	29.4	1.5	1.16	0.03	+11.8	+7.4	✓(3.33)	✓(2.41)
A(32)	30	110	0	-	5	27.9	2.7	1.22	0.03	-	-	-	-
A(32)	30	110	24	≈20	5	30.5	2.4	1.33	0.05	+9.3	+9.0	x(1.61)	✓(4.22)
A(32)	3	130	0	-	5	7.9	3.5	0.77	0.10	-	-	-	-
A(32)	3	130	24	≈20	4	9.1	2.1	0.81	0.06	+15.2	+5.2	x(0.60)	x(0.70)
A(32)	5	130	0	-	5	23.2	1.7	1.10	0.04	-	-	-	-
A(32)	5	130	24	≈20	4	24.7	1.2	1.16	0.05	+6.4	+5.4	x(1.48)	x(2.01)
A(32)	10	130	0	-	5	26.9	2.8	1.23	0.05	-	-	-	-
A(32)	10	130	24	≈20	5	29.9	1.3	1.33	0.02	+11.1	+8.1	x(2.17)	✓(4.15)
A(32)	12	130	0	-	5	26.4	2.2	1.22	0.03	-	-	-	-
A(32)	12	130	24	≈20	3	32.5	0.5	1.33	0.04	+23.1	+9.0	✓(4.59)	✓(4.47)
A(32)	15	130	0	-	5	24.6	4.3	1.27	0.07	-	-	-	-
A(32)	15	130	24	≈20	4	30.6	2.8	1.37	0.03	+24.4	+7.9	✓(2.40)	✓(2.64)
A(33)	60	90	0	-	5	25.8	2.9	1.13	0.02	-	-	-	-
A(33)	60	90	44	≈20	4	22.3	2.0	1.12	0.04	-13.6	-0.9	0(3.45)	x(0.32)
A(33)	120	90	0	-	5	27.1	1.0	1.24	0.05	-	-	-	-
A(33)	120	90	44	≈20	5	25.1	1.7	1.18	0.03	-7.4	-4.8	x(2.27)	✓(2.30)

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Table 33 The Effect of Leaching Postvulcanised Latex Films with Deionised Water at Room Temperature(cont.)

Formulation Code	Cure time (min)	Cure temp (°C)	Leach time (hours)	Leach temp (°C)	(MPa)					% change		Difference Significant	
					n	TS	s.d.	S300%	s.d.	TS	S300%	TS	S300%
A(33)	150	90	0	-	5	26.5	1.4	1.28	0.02	-	-	-	-
A(33)	150	90	44	≈20	5	26.8	1.3	1.21	0.02	+0.3	-0.7	x(0.35)	✓(5.53)
A(33)	180	90	0	-	5	24.4	1.7	1.26	0.07	-	-	-	-
A(33)	180	90	44	≈20	5	25.6	1.6	1.25	0.04	+4.9	-0.8	x(1.15)	x(0.28)
A(33)	30	110	0	-	5	26.3	1.9	1.17	0.04	-	-	-	-
A(33)	30	110	44	≈20	4	23.3	2.0	1.16	0.03	-3.0	-0.01	x(2.30)	x(0.41)
A(33)	60	110	0	-	5	24.3	2.2	1.25	0.05	-	-	-	-
A(33)	60	110	44	≈20	4	23.7	1.8	1.23	0.05	-2.5	-1.6	x(0.44)	x(0.60)
A(33)	90	110	0	-	5	23.7	1.2	1.24	0.02	-	-	-	-
A(33)	90	110	44	≈20	5	25.3	2.5	1.18	0.05	+6.8	-4.8	x(1.29)	✓(2.49)
A(33)	120	110	0	-	5	20.2	2.7	1.19	0.02	-	-	-	-
A(33)	120	110	44	≈20	5	21.1	0.5	1.17	0.02	+4.5	-1.7	x(0.73)	x(1.58)
A(33)	20	130	0	-	5	21.0	2.3	1.20	0.03	-	-	-	-
A(33)	20	130	44	≈20	4	22.2	1.0	1.19	0.02	+5.7	-5.9	x(0.96)	x(0.57)
A(33)	30	130	0	-	5	16.3	0.6	1.12	0.08	-	-	-	-
A(33)	30	130	44	≈20	4	21.2	2.9	1.06	0.00	+30.1	-5.4	✓(3.32)	-
A(33)	60	130	0	-	5	11.7	1.1	0.92	0.06	-	-	-	-
A(33)	60	130	44	≈20	4	12.7	2.2	0.87	0.01	+8.5	-5.4	x(0.89)	x(1.83)

() = Student's t value

Table 34 The Effect of Leaching Postvulcanised Latex Films at Elevated Temperatures

Formulation Code	Cure time (min)	Cure temp (°C)	Leach time (min)	Leach temp (°C)	(MPa)						% change in property		Difference Significant (at 5%)		Swelling index
					n	TS	s.d.	S300%	s.d.	TS	TS	S300%	TS	S300%	
A(27)	60	90	0	-	5	29.0	2.8	1.03	0.10	-	-	-	-	-	2.14
A(27)	60	90	10	75	5	32.9	0.9	1.14	0.08	+13.4	✓(2.97)	+10.7	✓(2.97)	x(1.92)	2.14
A(27)	60	90	20	75	5	32.4	1.4	1.13	0.03	+11.7	✓(2.43)	+9.7	✓(2.43)	x(2.14)	2.14
A(27)	60	90	30	75	5	33.1	2.6	1.18	0.07	+14.1	✓(2.40)	+14.6	✓(2.40)	✓(2.75)	2.10
A(27)	60	90	60	75	5	34.6	2.8	1.27	0.11	+19.3	✓(3.16)	+23.3	✓(3.16)	✓(3.61)	2.06
A(26)	60	90	0	-	5	27.1	0.6	1.13	0.05	-	-	-	-	-	2.07
A(26)	60	90	30	88	5	27.8	1.2	1.38	0.06	+2.6	x(1.17)	+22.1	x(1.17)	✓(7.16)	2.04
A(26)	60	90	60	88	5	26.1	2.3	1.29	0.10	-3.7	x(0.94)	+14.2	x(0.94)	✓(3.20)	1.97
A(26)	60	90	90	88	5	27.3	1.1	1.46	0.05	+0.7	x(0.36)	+29.2	x(0.36)	✓(10.44)	1.95
A(26)	60	90	120	88	5	28.2	2.4	1.43	0.07	+4.1	x(0.99)	+26.5	x(0.99)	✓(7.80)	1.97
A(28)	90	90	0	-	5	27.5	2.0	1.21	0.04	-	-	-	-	-	-
A(28)	90	90	690	97	5	25.2	2.6	1.36	0.07	-8.4	x(1.57)	+12.4	x(1.57)	✓(4.16)	-

the samples indicate that there is little change in the degree of crosslinking. Therefore, it seems more likely that the changes in physical properties are the result of leaching and not further vulcanisation. In the case of films leached at 97°C for 11.5 h, it is quite probable that further vulcanisation has occurred; the increase in modulus accompanied by the decrease in tensile strength indicates that the results fall beyond the tensile strength maximum on the tensile strength:modulus curves (see Figure 25, Section 2.5.1).

4.5.2 Leaching with Organic Solvents After Postvulcanisation

Postvulcanised latex films were leached with a variety of organic solvents, (Table 35). Isopropyl alcohol (propan-2-ol, IPA), methanol (MeOH) and acetone do not swell the rubber network appreciably, whereas, toluene causes substantial swelling. Leaching with acetone at room temperature (about 20°C) and at approximately 56°C (using a Soxhlet extractor) for 6¼ hours led to no significant changes in tensile strength or modulus. This contrasts with Merrill's findings for prevulcanised latex films where leaching in acetone at 25°C for 16 hours led to substantial increases in tensile strength^{23,24}. Films were also leached with methanol for 6¼ hours at room temperature (about 20°C) and at approximately 65°C (using a Soxhlet extractor). The changes in tensile strength were not statistically significant but changes in modulus were. There were no changes in swelling index, suggesting that there were no appreciable changes in the degree of crosslinking. A room-temperature leach (at about 20°C) with isopropyl alcohol for 6¼ hours led to a statistically significant increase in tensile strength but not modulus. When a 24 hour room-temperature leach was employed there was a significant decrease in tensile strength and a significant increase in modulus. When leaching was carried out at approximately 97°C (using a Soxhlet extractor) for a 6¼ hour leach there were significant increases in both tensile strength and modulus; employing a 12 hour leach gave a decrease in tensile strength which was not significant and an increase in modulus which was significant statistically. The available swelling index data show only small increases which do not indicate any appreciable loss of crosslinking. Alcohols do not cause substantial swelling of rubber but are expected to remove some of the

Table 35 The Effect of Leaching Postvulcanised Latex Films with Organic Solvents

Formulation Code	Cure time (min)	Cure temp (°C)	Leach liquid	Leach time (h)	Leach temp (°C)	(MPa)					% change in property		Difference Significant (at 5%)		Swelling index
						n	TS	s.d.	S300%	s.d.	TS	S300%	TS	S300%	
A(26)	90	90	None	0	-	5	28.6	2.7	1.08	0.05	-	-	-	-	2.06
A(26)	90	90	IPA	12	≈97	5	26.7	1.0	1.41	0.15	-6.6	+30.6	x(1.48)	✓(4.67)	2.24
A(26)	90	90	IPA	24	≈20	5	23.4	1.1	1.24	0.09	-18.2	+14.8	✓(3.99)	✓(3.47)	2.20
A(26)	90	90	MeOH	6.25	≈65	5	29.3	2.4	1.49	0.14	+2.4	+38.0	x(0.18)	✓(6.17)	2.06
A(26)	90	90	MeOH	6.25	≈20	5	29.5	1.9	1.37	0.04	+3.1	+26.9	x(0.61)	✓(10.13)	2.06
A(27)	90	90	None	0	-	5	30.1	1.5	1.05	0.09	-	-	-	-	2.13
A(27)	90	90	Acetone	6.25	≈20	5	30.7	2.9	1.04	0.05	+2.0	-1.0	x(0.41)	x(0.22)	-
A(27)	90	90	Acetone	6.25	≈56	5	31.9	2.4	1.16	0.08	+6.0	+10.5	x(1.42)	x(2.04)	-
A(27)	90	90	IPA	6.25	≈20	5	32.8	1.7	1.14	0.06	+9.0	+8.6	✓(2.66)	x(1.86)	-
A(27)	90	90	IPA	6.25	≈97	5	34.5	1.8	1.21	0.10	+14.6	+15.2	✓(4.20)	✓(2.66)	-
A(31)	90	90	None	0	-	5	31.9	1.5	1.14	0.05	-	-	-	-	2.07
A(31)	90	90	Toluene	65	≈20	5	23.5	3.9	1.22	0.04	-26.3	+7.0	✓(4.50)	✓(2.79)	2.15
A(34)	30	90	None	0	-	5	31.0	0.9	1.06	0.04	-	-	-	-	2.30
A(34)	30	90	Toluene	65	≈20	5	24.0	1.9	0.98	0.02	-22.6	-7.5	✓(4.63)	✓(4.00)	2.40
A(34)	90	90	None	0	-	5	31.5	2.8	1.18	0.03	-	-	-	-	2.10
A(34)	90	90	Toluene	65	≈20	5	24.1	2.0	1.15	0.04	-23.5	-2.5	✓(4.81)	x(1.34)	2.30

unreacted vulcanizing ingredients like sulphur and accelerators by dissolution and diffusion out of the rubber network and into the solution. Again the results are contradictory and do not point to any clear conclusion about the effect of leaching postvulcanised films with solvents which do not cause significant swelling of the rubber.

When toluene was used to leach films at room temperature for 65 hours there were substantial decreases in tensile strength on all three samples. The changes in modulus were less informative. One sample had a statistically significant increase in modulus, a second a statistically significant decrease in modulus and a third a decrease in modulus which was not statistically significant. The swelling index data show small increases on leaching but do not indicate any appreciable change in the degree of crosslinking. Toluene is a good swelling solvent for rubber and is also expected to remove unreacted vulcanising ingredients. These results contrast with those of Porter for prevulcanised latex films⁸⁴. For prevulcanised latex films there were substantial increases in both modulus and tensile strength after leaching in toluene.

Leaching with non-swelling solvents did not have a large effect upon tensile strength. The changes in tensile strength were generally small and similar in magnitude to the inherent variation between test pieces taken from the same sample sheet. Leaching with toluene caused substantial decreases in tensile strength. In the case of modulus measurements for all solvents, although the results were mixed, the effect of leaching was to leave modulus either essentially unchanged or slightly increased.

Leaching of prevulcanised latex films is believed to increase tensile strength and modulus by removing non-rubber materials from the latex particle interfaces, allowing the entanglement of mobile segments of rubber molecules across the particle boundaries²⁴. These physical entanglements appear to make a significant contribution to modulus and tensile strength of prevulcanised latex films.

In the case of postvulcanised films, crosslinks are believed to be formed not only within the latex particle boundaries but also between them. Whilst leaching is expected to remove soluble non-rubbers and, in the case of organic solvents, unreacted vulcanising ingredients, any further entanglements formed, while leading to some small increases in modulus, do not generally contribute to significant increases in tensile strength. They make only a small contribution to the overall strength which appears to be largely

dependent upon the number of sulphur crosslinks.

In the case of leaching with toluene there is a large degree of swelling involved which means that the unconstrained segments of the rubber molecules are able to physically distance themselves from each other and many of the physical entanglements can become disentangled. The decrease in tensile strength may be attributed to the loss of a large number of physical entanglements which are not reformed to the same extent when the film is deswollen after leaching. This is in direct contrast to the situation with prevulcanised latex films where the increase in tensile strength and modulus were attributed to increases in physical entanglements across particle boundaries during swelling which were retained when the toluene evaporated from the film.

4.5.3 Leaching Films with Water before Postvulcanisation

The postvulcanised latex films used in the previous leaching experiments had a structure in which the latex particles had been brought into contact and coalesced. The non-volatile non-rubbers present in the latex were present in the film. On heating, sulphur crosslinks were believed to be formed within and between latex particles thereby restricting the mobility of rubber molecules in the particles. Leaching removed water-soluble or solvent-soluble materials from between the particles. If the crosslinking between particles makes the rubber network fairly rigid and restricts the mobility of rubber molecules, the interdiffusion of molecules between latex particles is restricted and there is no enhancement of tensile strength or modulus on leaching. In prevulcanised latex films the removal of soluble non-rubbers from between the latex particles is believed to allow contact and interdiffusion between rubber molecules in neighbouring latex particles²⁴.

Leaching of films prepared from compounded latex before they were postvulcanised was carried out in order to remove non-rubbers from between the particles and to allow the uncrosslinked, mobile segments of rubber molecules to interdiffuse across the particle boundaries and hence improve film integrity. After leaching and drying, the films were heated to introduce sulphur crosslinks. The accelerator system used was a combination of ZDEC and ZMBT, which were not expected to be removed from the film by leaching. ZDEC is only very slightly soluble in water and ZMBT is insoluble.

Leaching before curing resulted in three sets of samples with increased tensile strength, three sets with decreased tensile strength and eight sets where the changes in tensile

strength were not statistically significant (Table 36). From these results it was concluded that the interdiffusion of rubber molecules upon leaching did not make an appreciable contribution to the tensile strength of postvulcanised latex films. Modulus did appear to have been affected by leaching before postvulcanisation (see also Figure 39). For two sets of samples modulus was increased; in both cases these were uncured films where no sulphur crosslinking had taken place. In eight cases there were decreases in modulus and in four the changes were not statistically significant. The reason for the decreases in modulus may be attributable to the removal of non-rubbers from the film which enhance the rate of vulcanisation (Figures 40 and 41). It is known that non-rubbers present in HA latex increase the rate of prevulcanisation^{24,67}. Therefore, it is conceivable that leaching a latex film before postvulcanisation may remove some of the same non-rubbers which enhance the rate of prevulcanisation and results in a decreased rate of postvulcanisation.

4.6 The Effect of Vulcanisation Time and Temperature Upon the Physical Properties of Postvulcanised Latex Films

Postvulcanised latex films which contained ZDEC as the only accelerator were found to reach a maximum tensile strength of approximately 32MPa and a maximum modulus (S300%) of approximately 1.4MPa. Changing the formulations to vary the accelerator:sulphur ratio made little difference^{79,80}. The fact that a maximum tensile strength was attained came as no surprise since this is observed with dry rubber and prevulcanised latex films (Sections 2.5.1 and 2.5.2 and Figure 25). What was very surprising was that it has not been possible to prepare vulcanisates with higher modulus which would allow the relationship between tensile strength and modulus to be determined for such films. This will be discussed again in Section 5.1.

A postvulcanised latex film is produced by forming an unvulcanised film throughout which are distributed the vulcanising ingredients. Natural rubber has a very low glass transition temperature ($T_g \approx -72^\circ\text{C}$). Therefore, latex particles are very soft and are believed to coalesce quite readily to form homogeneous coherent films (see Section 1.6).

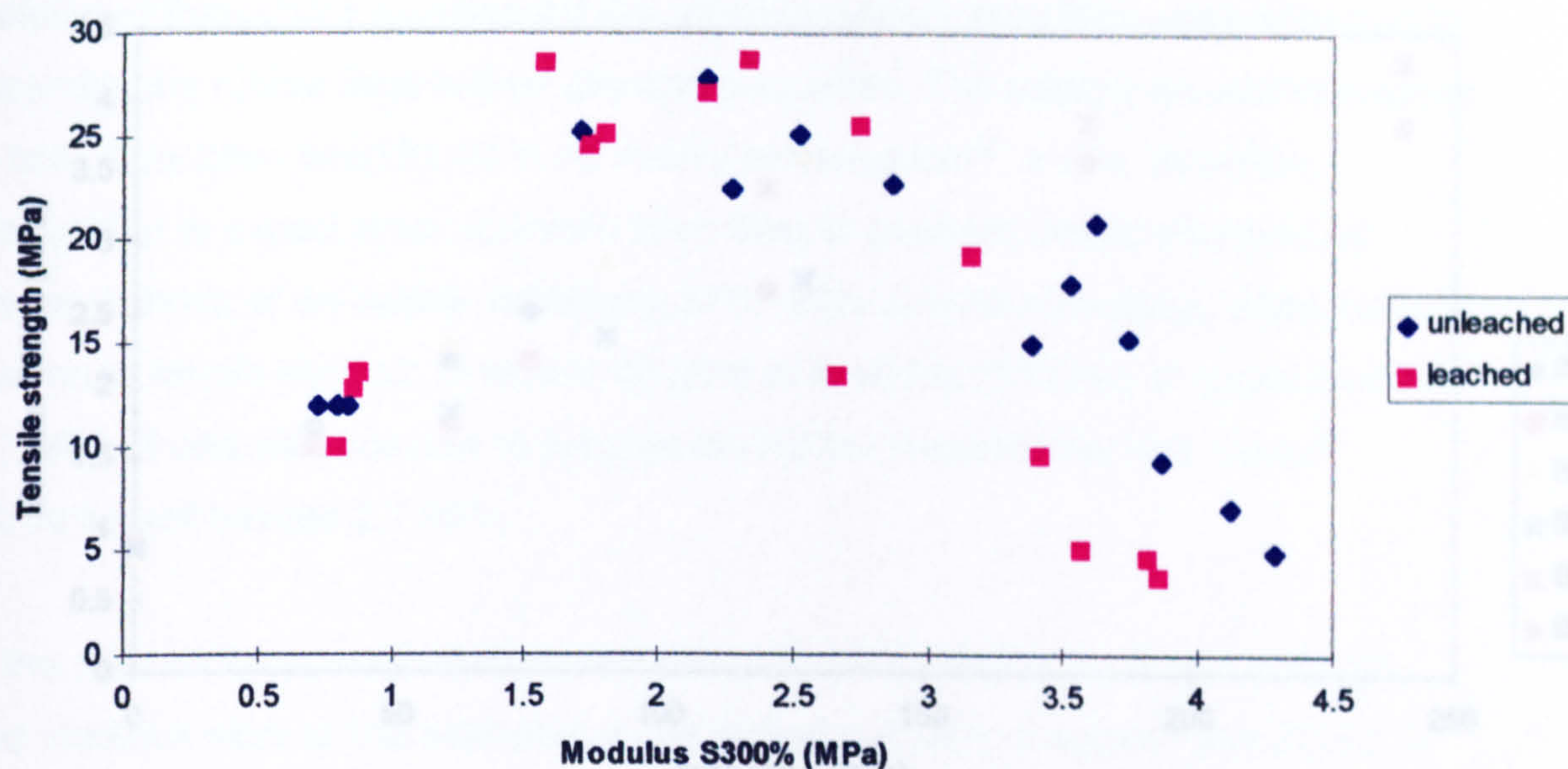
The crosslinks, which would increase modulus and decrease film formation, are only produced in a postvulcanised latex film after the film has been laid down and, therefore, after the particles have coalesced. Since crosslinks are thought to be homogeneously

Table 36 The Effect of Leaching Films Before Postvulcanisation

Formulation Code	Cure time (min)	Cure temp (°C)	Leach time (day & hours)	Leach temp (°C)	(MPa)								% change		Difference Significant	
					n	TS	s.d.	n	S300%	s.d.	TS	S300%				
B(1)	0	90	-	-	5	12.0	1.0	5	0.84	0.03	-	-	-	-	-	-
B(1)	0	90	2d 8h	»20	5	13.5	2.3	5	0.88	0.02	+12.5	+4.8	x(1.34)	ū(2.48)	-	-
B(1)	34	90	-	-	5	25.2	1.3	5	1.71	0.08	-	-	-	-	-	-
B(1)	34	90	2d 8h	»20	5	28.5	2.2	5	1.58	0.08	+13.1	-7.6	ū(2.89)	ū(2.57)	-	-
B(1)	60	90	-	-	1	27.7	0.0	5	2.18	0.23	-	-	-	-	-	-
B(1)	60	90	2d 8h	»20	3	24.6	4.3	3	1.74	0.14	-11.2	-20.2	N/A	ū(2.85)	-	-
B(1)	75	90	-	-	3	25.1	3.6	3	2.52	0.06	-	-	-	-	-	-
B(1)	75	90	2d 8h	»20	4	27.1	2.3	4	2.18	0.20	+8.0	-13.5	x(0.91)	ū(2.79)	-	-
B(2)	0	90	-	-	5	11.9	0.7	5	0.80	0.03	-	-	-	-	-	-
B(2)	0	90	3d	»20	3	12.7	1.0	5	0.86	0.02	+6.7	+7.5	x1.35)	ū(3.72)	-	-
B(2)	60	90	-	-	3	22.5	0.5	3	2.28	0.09	-	-	-	-	-	-
B(2)	60	90	3d	»20	5	25.1	2.5	4	1.80	0.12	+11.6	-21.1	x(1.73)	ū(5.77)	-	-
B(2)	90	90	-	-	3	22.7	2.5	3	2.87	0.20	-	-	-	-	-	-
B(2)	90	90	3d	»20	5	28.7	1.9	5	2.34	0.42	+6.3	-18.5	ū(5.01)	x2.01)	-	-
B(2)	127	90	-	-	5	20.9	2.8	5	3.62	0.15	-	-	-	-	-	-
B(2)	127	90	3d	»20	5	25.5	2.9	5	2.75	0.21	+22.0	-24.0	ū(2.55)	ū(7.54)	-	-
B(3)	120	90	-	-	5	15.0	8.0	5	3.38	0.47	-	-	-	-	-	-
B(3)	120	90	3d	»20	3	13.4	1.9	3	2.67	0.37	-10.7	-21.0	x(0.33)	ū(3.71)	-	-

Table 36 The Effect of Leaching Films Before Postvulcanisation(cont.)

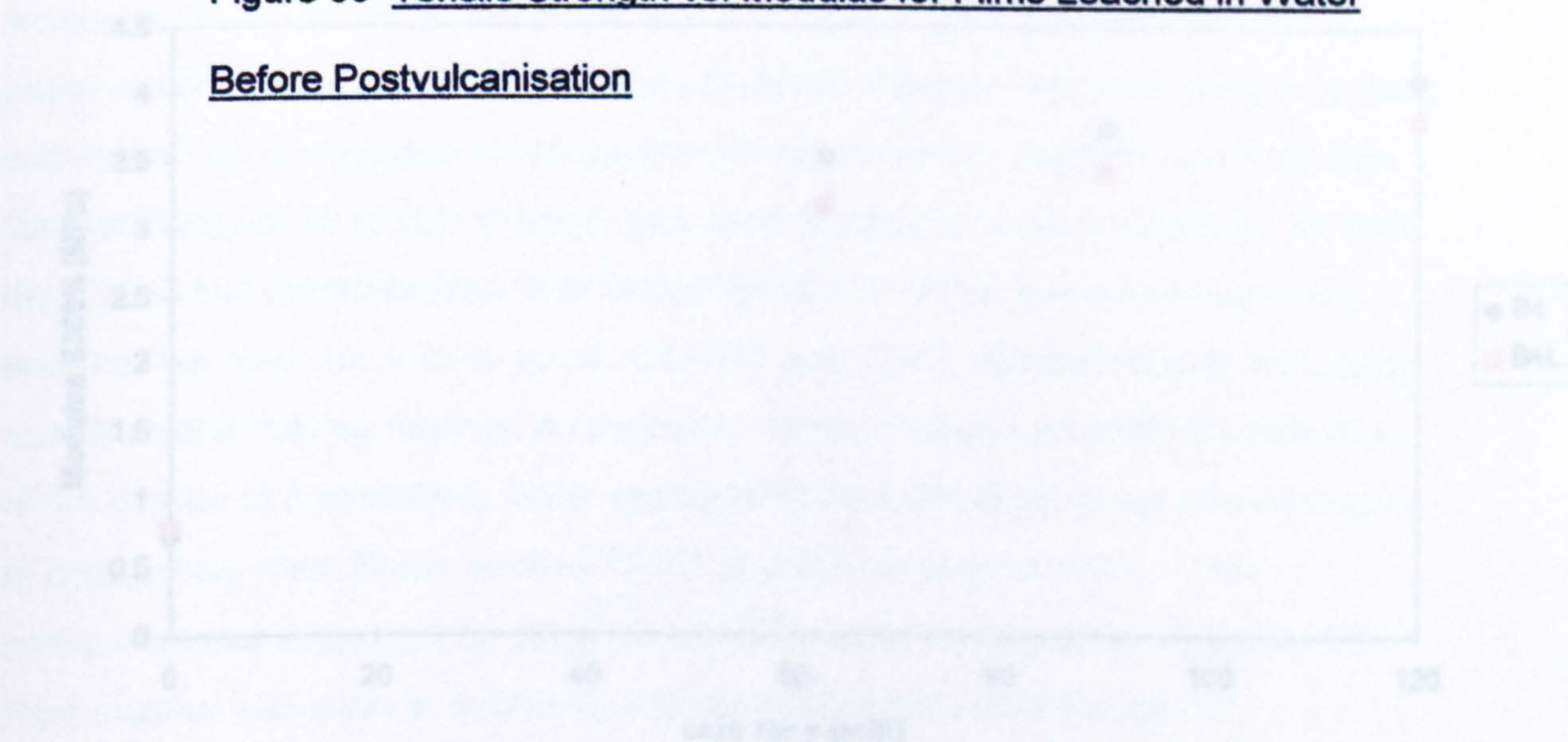
Fomulation Code	Cure time (min)	Cure temp (°C)	Leach time (day & hours)	Leach temp (°C)	(MPa)								% change		Difference Significant	
					n	TS	s.d.	n	S300%	s.d.	TS	S300%				
B(1)	0	90	-	-	5	9.3	3.6	5	3.86	0.20	-	-	-	-	-	-
B(3)	180	90	3d	»20	5	5.0	0.8	5	3.57	0.30	-46.2	-7.5	ū(2.61)	x(1.80)		
B(3)	240	90	-	-	5	4.9	0.5	5	4.28	0.60	-	-	-	-	-	-
B(4)	240	90	3d	»20	5	3.7	0.6	1	3.85	0.00	-24.5	-10.0	x(3.44)	N/A		
B(4)	0	100	-	-	4	12.0	1.6	4	0.73	0.01	-	-	-	-	-	-
B(4)	0	100	3d	»20	5	9.9	1.1	5	0.80	0.02	-17.5	+9.6	ū(2.74)	ū(6.33)		
B(4)	63	100	-	-	5	17.9	2.2	5	3.53	0.16	-	-	-	-	-	-
B(4)	63	100	3d	»20	4	19.3	1.9	4	3.16	0.22	+7.8	-10.5	x(1.00)	ū(2.93)		
B(4)	90	100	-	-	5	15.3	6.0	5	3.74	0.32	-	-	-	-	-	-
B(4)	90	100	3d	»20	5	9.5	6.9	5	3.41	0.35	-37.9	-8.8	x(1.42)	x(1.56)		
B(4)	120	100	-	-	3	7.1	0.9	3	4.12	0.10	-	-	-	-	-	-
B(4)	120	100	3d	»20	5	4.6	0.4	5	3.81	0.39	-35.2	-7.5	ū(5.58)	x(1.31)		



The key shows the formulation code, L refers to leached samples

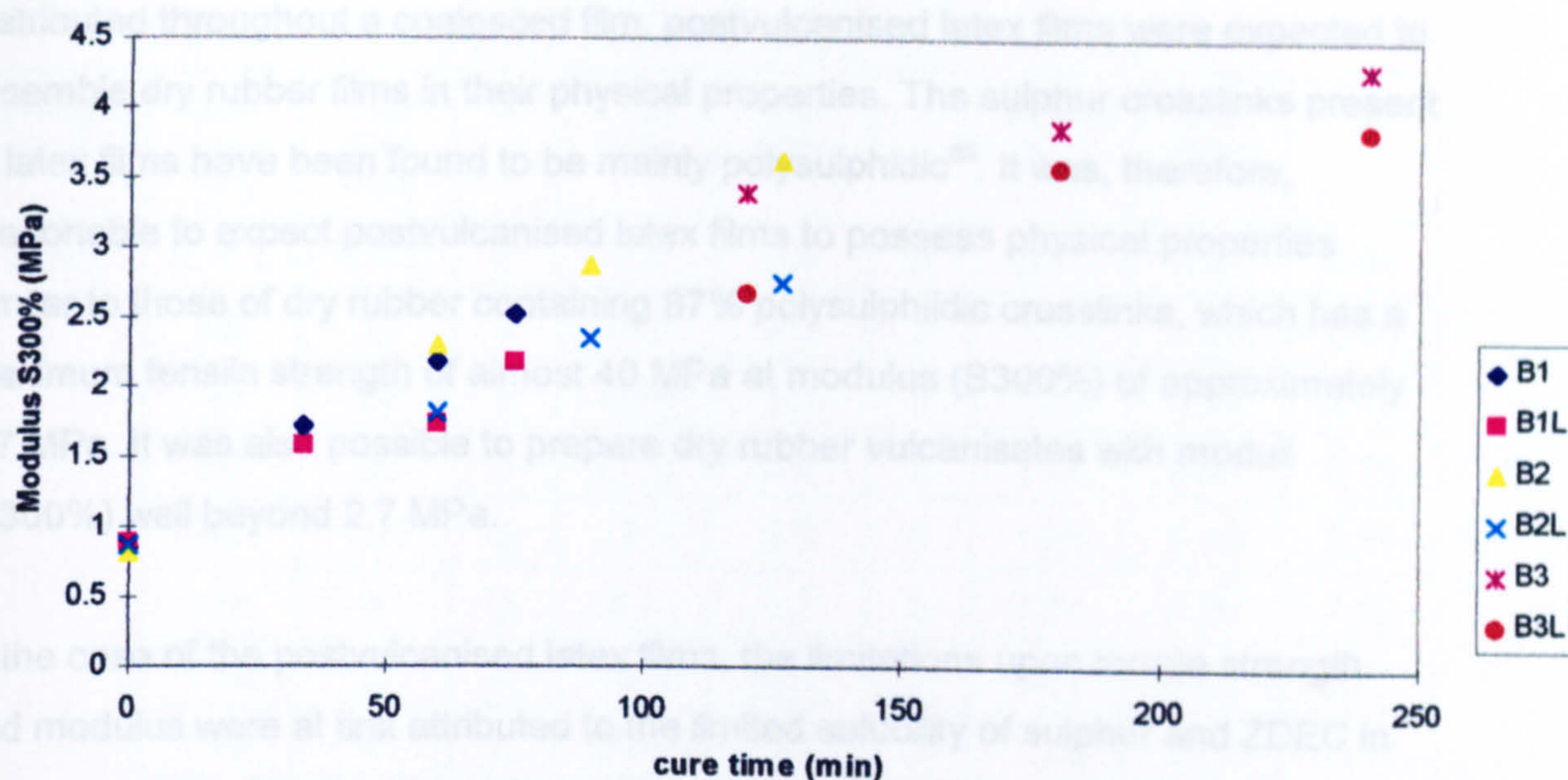
Figure 40 Films prepared to formulation B, leached in deionised water at laboratory temperature and cured at 90°C and 100°C

Figure 39 Tensile Strength vs. Modulus for Films Leached in Water Before Postvulcanisation



The key shows the formulation code, L refers to leached samples

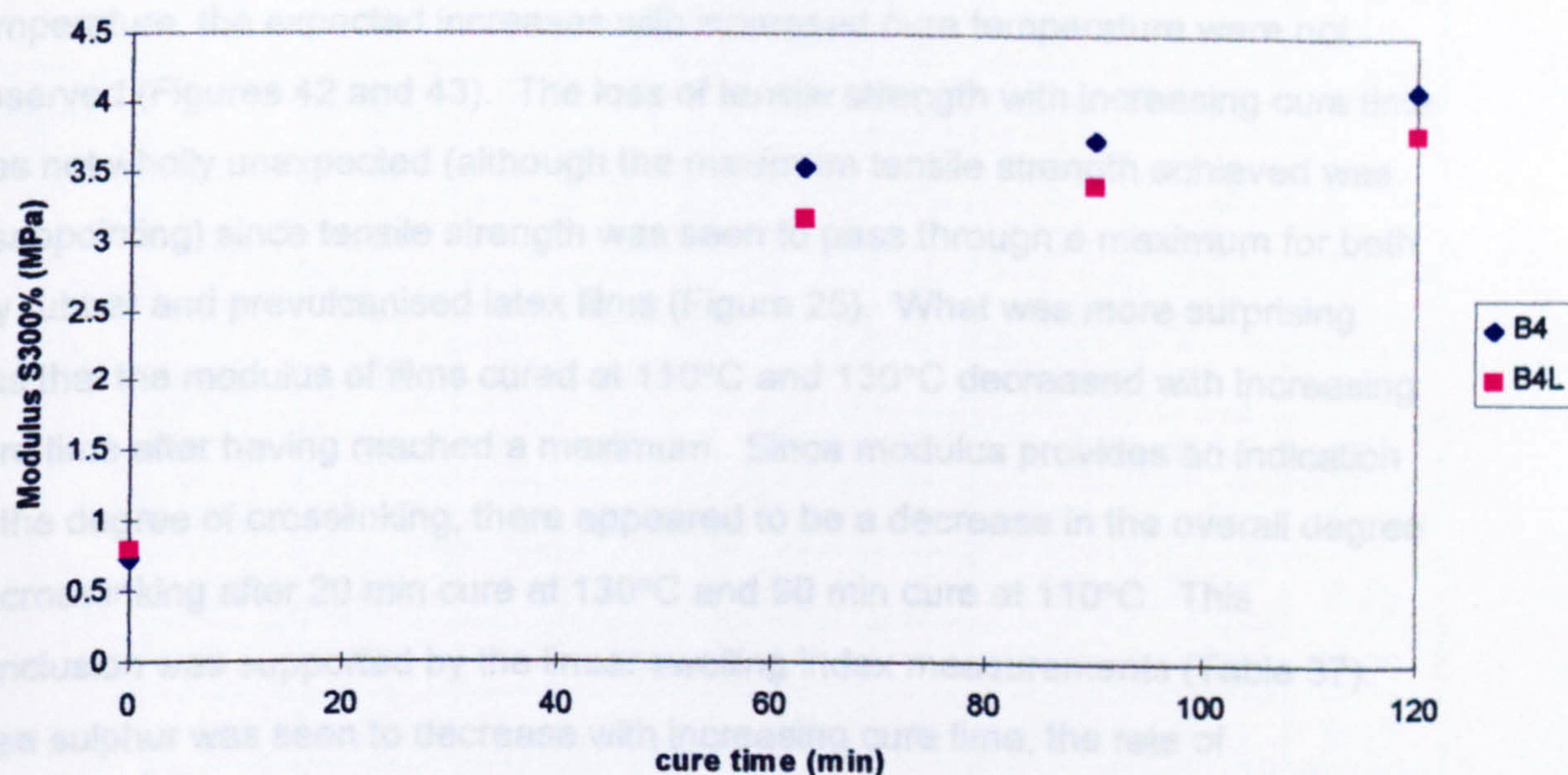
Figure 41 Modulus S300% Versus Cure Time for Leached & Unleached Films Cured at 100°C



The key shows the formulation code , L refers to leached samples

Figure 40 Modulus S300% Versus Cure Time for Leached & Unleached Films

Cured at 90°C



The key shows the formulation code , L refers to leached samples

Figure 41 Modulus S300% Versus Cure Time for Leached & Unleached Films
Cured at 100°C

distributed throughout a coalesced film, postvulcanised latex films were expected to resemble dry rubber films in their physical properties. The sulphur crosslinks present in latex films have been found to be mainly polysulphidic⁶⁸. It was, therefore, reasonable to expect postvulcanised latex films to possess physical properties similar to those of dry rubber containing 87% polysulphidic crosslinks, which has a maximum tensile strength of almost 40 MPa at modulus (S300%) of approximately 2.7 MPa. It was also possible to prepare dry rubber vulcanisates with moduli (S300%) well beyond 2.7 MPa.

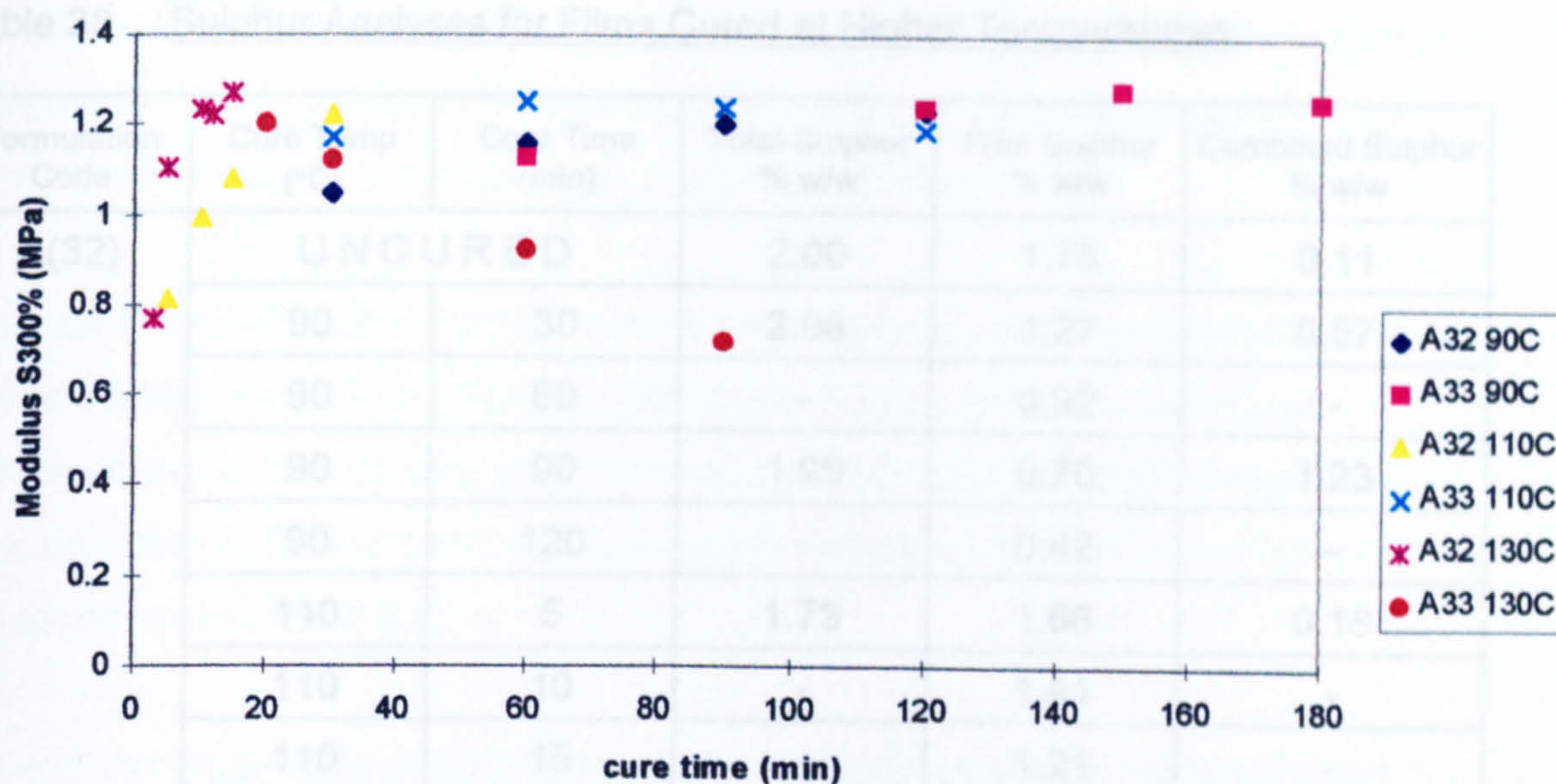
In the case of the postvulcanised latex films, the limitations upon tensile strength and modulus were at first attributed to the limited solubility of sulphur and ZDEC in rubber at 90°C. The solubility of both these substances increases at higher temperatures and for this reason films were vulcanised at the higher temperatures of 110°C and 130°C (Table 37).

When modulus and tensile strength were plotted against cure time for each temperature, the expected increases with increased cure temperature were not observed (Figures 42 and 43). The loss of tensile strength with increasing cure time was not wholly unexpected (although the maximum tensile strength achieved was disappointing) since tensile strength was seen to pass through a maximum for both dry rubber and prevulcanised latex films (Figure 25). What was more surprising was that the modulus of films cured at 110°C and 130°C decreased with increasing cure time after having reached a maximum. Since modulus provides an indication of the degree of crosslinking, there appeared to be a decrease in the overall degree of crosslinking after 20 min cure at 130°C and 90 min cure at 110°C. This conclusion was supported by the linear swelling index measurements (Table 37). Free sulphur was seen to decrease with increasing cure time, the rate of disappearance increasing with increasing cure temperature (Table 38). The decrease in free sulphur was accompanied by an increase in combined sulphur. The results for modulus and swelling index taken together with those for free and combined sulphur suggested that although sulphur was being combined in the network beyond the time when the modulus had reached its maximum value it was not forming crosslinks which were effective in enhancing physical properties. In fact the observed modulus reversion and increases in swelling index indicate that

Table 37 Physical Properties of Films Cured at Higher Temperatures

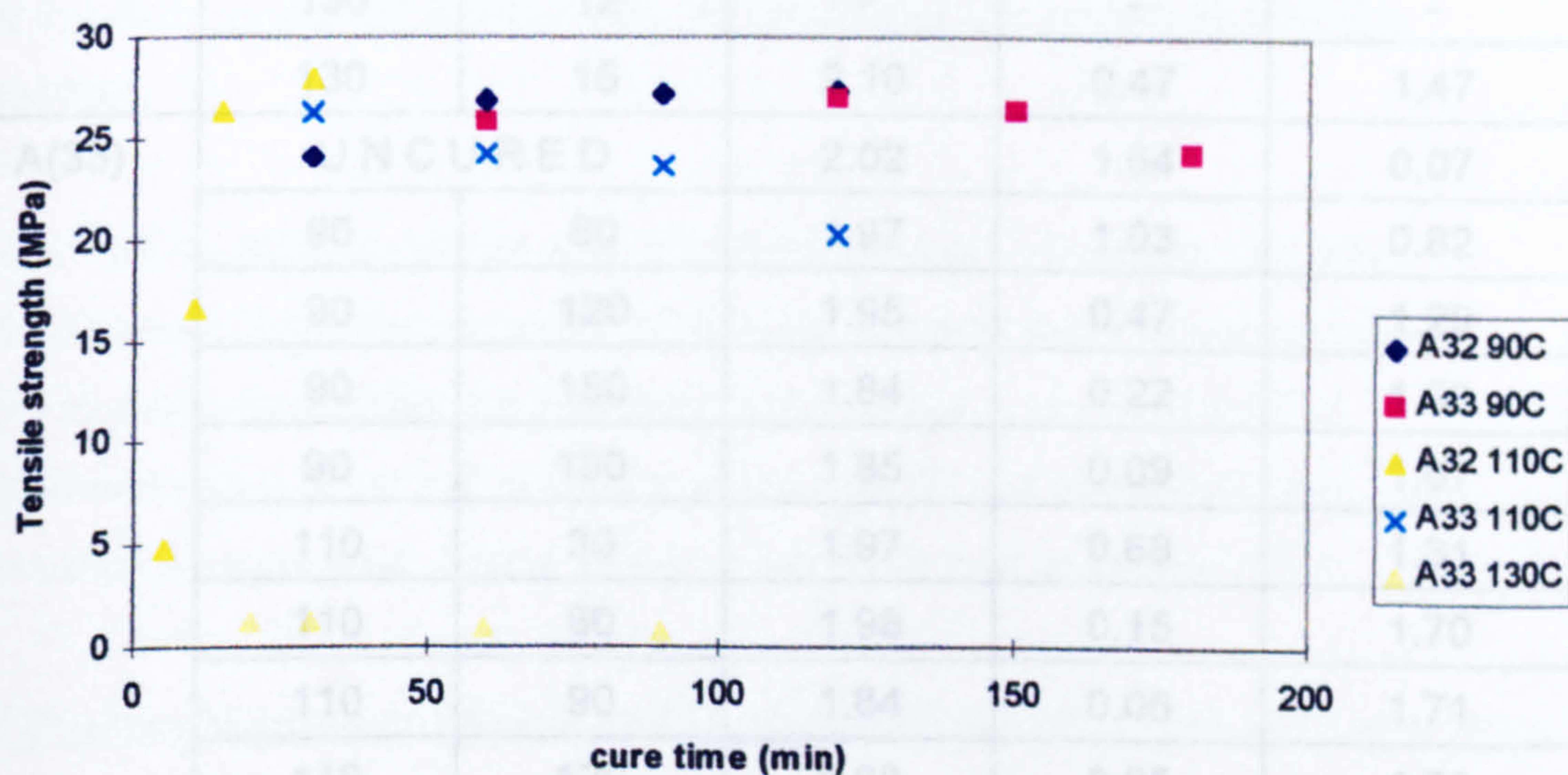
Formulation Code	Cure Temp (°C)	Cure Time (min)	n	TS (MPa)	s.d. (MPa)	n	S300% (MPa)	s.d. (MPa)	SI
A(32)	UNCURED		5	2.3	0.9	5	0.64	0.02	8.04
	90	30	5	24.1	2.3	5	1.05	0.02	2.45
	90	60	5	26.9	1.6	5	1.16	0.02	2.19
	90	90	5	27.2	3.1	5	1.20	0.03	2.13
	90	120	5	27.3	3.7	5	1.23	0.10	2.11
	110	5	5	4.7	0.7	5	0.81	0.04	7.22
	110	10	5	16.5	5.3	5	0.99	0.05	2.71
	110	15	5	26.3	1.3	5	1.08	0.06	2.29
	110	30	5	27.9	2.7	5	1.22	0.03	2.13
	130	3	5	7.9	3.5	5	0.77	0.10	3.59
	130	5	5	23.2	1.7	5	1.10	0.04	2.35
	130	10	5	26.9	2.8	5	1.23	0.05	2.11
	130	12	5	26.4	2.2	5	1.22	0.03	2.14
	130	15	5	24.6	4.3	5	1.27	0.07	2.09
A(33)	UNCURED		5	2.8	1.2	5	0.64	0.03	-
	90	60	5	25.8	2.9	5	1.13	0.02	2.39
	90	120	5	27.1	1.0	5	1.24	0.05	2.21
	90	150	5	26.5	1.4	5	1.28	0.02	2.14
	90	180	5	24.4	1.7	5	1.26	0.07	2.14
	110	30	5	26.3	1.9	5	1.17	0.04	2.20
	110	60	5	24.3	2.2	5	1.25	0.05	2.17
	110	90	5	23.7	1.2	5	1.24	0.02	2.25
	110	120	5	20.2	2.7	5	1.19	0.02	2.29
	130	20	5	21.0	2.3	5	1.20	0.03	2.17
	130	30	5	16.3	0.6	5	1.12	0.08	2.36
	130	60	5	11.7	1.1	5	0.92	0.06	2.67
	130	90	5	9.4	3.6	4	0.72	0.06	8.03

TS = Tensile strength
s.d. = Standard deviation
S300% = Modulus 300%
SI = Swelling index
n = Number of samples



The key shows the formulation code and the cure temperature

Figure 42 Modulus Versus Cure Time for Postvulcanisation at Higher Temperatures



The key shows the formulation code and the cure temperature

Figure 43 Tensile Strength Versus Cure Time for Postvulcanisation at Higher Temperatures

N.D. = none detected

Table 38 Sulphur Analyses for Films Cured at Higher Temperatures

Formulation Code	Cure Temp (°C)	Cure Time (min)	Total Sulphur % w/w	Free Sulphur % w/w	Combined Sulphur % w/w
A(32)	UNCURED		2.00	1.75	0.11
	90	30	2.06	1.27	0.57
	90	60	-	0.92	-
	90	90	1.99	0.70	1.23
	90	120	-	0.42	-
	110	5	1.79	1.66	0.18
	110	10	-	1.41	-
	110	15	-	1.21	-
	110	30	1.94	0.49	1.33
	130	3	-	1.57	-
	130	5	2.21	1.18	0.59
	130	10	-	0.71	-
	130	12	-	-	-
	130	15	2.10	0.47	1.47
A(33)	UNCURED		2.02	1.64	0.07
	90	60	1.97	1.03	0.82
	90	120	1.95	0.47	1.29
	90	150	1.84	0.22	1.50
	90	180	1.85	0.09	1.67
	110	30	1.97	0.68	1.31
	110	60	1.98	0.15	1.70
	110	90	1.84	0.06	1.71
	110	120	1.83	0.05	1.75
	130	20	1.86	0.31	1.39
	130	30	1.91	0.05	1.75
	130	60	1.83	0.01	1.76
	130	90	1.86	N.D.	1.85

N.D. = none detected

crosslinks formed at shorter cure times were decomposing and instead of sulphur in the crosslinks being recycled into new crosslinks it was combining in the network to form other groups (for example cyclic sulphides, Section 2.2.2).

The rate of crosslink decomposition does become more significant than the rate of desulphuration as cure temperature increases above 100°C, but the higher temperatures employed here were still modest when compared with those used to cure dry rubber. The competing reactions are described with particular reference to dry rubber in Section 2.2.2.

For a cure temperature of 90°C the modulus reached an almost constant value and changed very little between cure times of 120 minutes and 180 minutes (Figure 42). At a cure time of 120 minutes there was still over 0.4% w/w free sulphur present in the film. This fell with longer cure times to 0.1% w/w free sulphur and the combined sulphur increased but there was no significant increase in the modulus, indicating that the extra combined sulphur was not producing any physically effective crosslinks.

There was no obvious reason why this limitation upon modulus existed for postvulcanised latex films in which ZDEC was used as the only accelerator. In order to discover whether the restriction upon modulus was a feature of postvulcanisation of latex or a feature of using ZDEC as the accelerator, other formulations were used. These systems are discussed in section 5.1.1.

4.7 The Incorporation of Toluene and Dichloromethane into Latex and Latex Films

Latex films have a particulate structure rather than the homogeneous structure which might have been expected, bearing in mind the low glass-transition temperature and low modulus of natural rubber (see Section 1.5). A transmission electron micrograph showing the structure of a latex film is to be found in Roberts⁶².

Cryogenic scanning electron microscopy (cryo-SEM), where samples were freeze-fractured and maintained at very low temperatures when examined (see Section 3.7.1), was used in the present research programme. The micrographs showed the

structure of films to be distinctly particulate whether they were prepared from uncompounded or prevulcanised latex or were postvulcanised (see Figures 44-46). Although the particles were partly coalesced they were by no means sufficiently fused to form a homogeneous film and it was not possible to differentiate between films prepared from latices which had undergone different vulcanisation treatments or indeed none at all. It is most likely that the proteins and soaps naturally present on the surface of latex particles are responsible for preventing their complete coalescence when films are formed. The literature on changes in film structure and the fate of emulsifiers has been discussed earlier (see Sections 1.6.3 and 1.6.4). Voyutskii^{45,46} described the gradual changes in the structure of natural rubber latex films which took place over an extended period (eight months) resulting in the film becoming more homogeneous. It would have been impracticable in this current programme of research to try to maintain a film, which was later to be postvulcanised, in an unvulcanised state for several months in order for gradual particle coalescence to occur.

From Figure 25 (Section 2.5.1) it can be seen that it is possible to obtain dry rubber vulcanisates with tensile strengths of around 40 MPa. It had been hoped that similar or even higher tensile strengths would be obtained by postvulcanising latex films. The rubber in latex has not undergone mastication. Therefore, it has a higher molecular weight than that in dry rubber so, there are fewer free chain ends and the crosslinks introduced by vulcanisation are expected to be more effective⁶². Since tensile strengths of prevulcanised latex films (where the crosslinks are confined to individual latex particles) may be in excess of 35 MPa (see Figure 25), it was reasonable to expect that this would be exceeded for postvulcanised latex films where the crosslinks were expected to be uniformly distributed. The relationship between tensile strength and modulus for postvulcanised films is discussed in Section 5.1 (see also Section 4.6).

The difference in film structure between dry rubber and latex films is seen in this research programme as the probable reason why postvulcanised latex films did not reach tensile strengths greater than those for prevulcanised latex films. Therefore, various methods for producing a well coalesced film were investigated. They were based upon the use of solvents which would swell the rubber particles, increasing

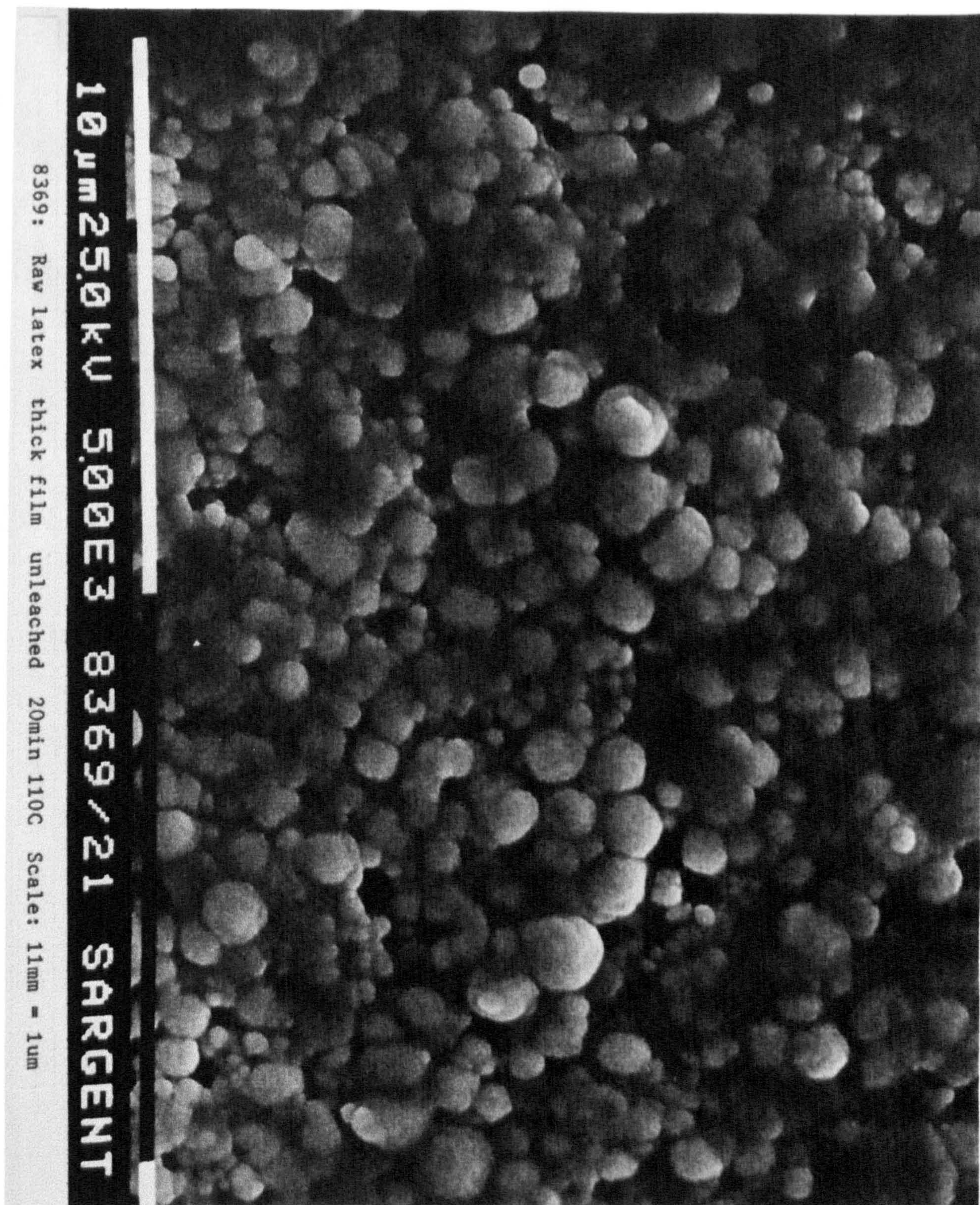


Figure 44 SEM of Uncompounded Latex Film (freeze-fractured cross-section)

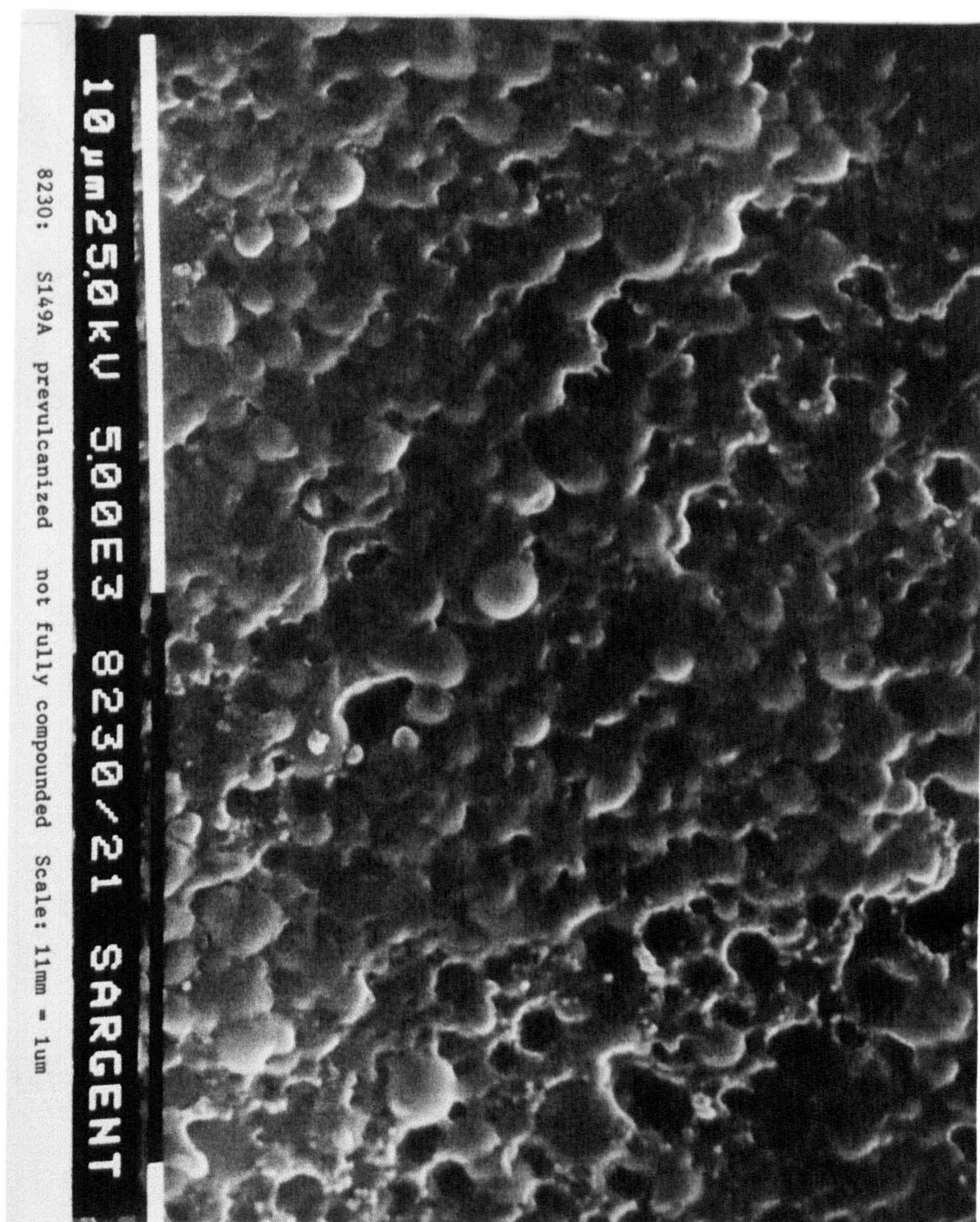


Figure 45 SEM of a Pre-vulcanised Latex Film (freeze-fractured cross section)

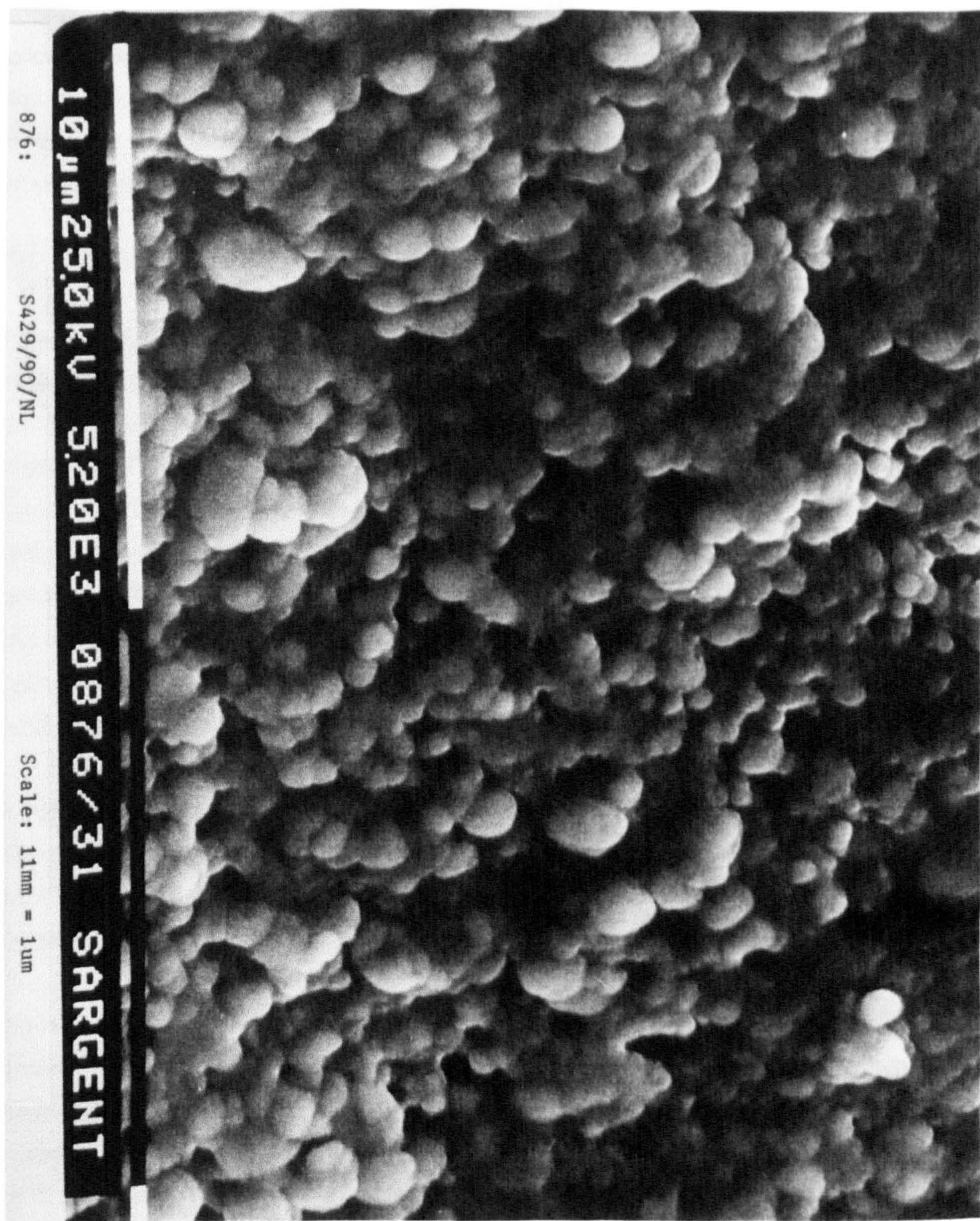


Figure 46 SEM of a Postvulcanised Latex Film

their surface area and reducing the concentration of surfactants on their surfaces, allowing greater rubber to rubber contact between particles. Swelling also increases the mobility of the rubber molecules, allowing them to intermingle more readily across particle boundaries. The solvents were removed, by evaporation, before the physical properties of the derived films were measured.

4.7.1 Films from Rubber Solutions

Films cast from polymers in solution are homogeneous. Therefore, a solution of rubber was prepared by dissolving natural rubber latex films in solvent (Section 3.4.1). Films cast from the filtered solution were indeed found to be moderately coalesced (Figure 47). Attempts were made to incorporate vulcanising ingredients (sulphur and ZDEC) in the solution and to produce films for vulcanisation. However, the vulcanising ingredients had low solubility in toluene and crystallised out of solution as the film was drying so this method was not pursued further. In addition, the insolubility of the higher molecular weight rubber (gel) meant that the rubber solution consisted of lower molecular weight rubber which would be expected to vulcanise less effectively than whole latex rubber.

4.7.2 Treatment of Cast Films with Solvents

The improvement of particle integration of latex particles was undertaken using films cast from natural rubber latex immersed in the solvents toluene and dichloromethane (DCM) (Section 3.4.2).

An improvement in particle integration is seen in Figure 48 (cf. Figure 44), which shows a freeze-fractured cross-section of an HA latex film which has been immersed in toluene. Figure 49 shows a film of partially compounded latex (formulation A omitting accelerator) which has been immersed in dichloromethane (containing 200 ppm ZDEC w/v). This micrograph also shows improved particle coalescence.

The accelerator ZDEC is very soluble in chlorinated solvents (which are also good swelling agents for natural rubber), so by swelling a partially compounded latex film (one containing no ZDEC) with a solution of ZDEC dissolved in dichloromethane it was possible to ensure that no prevulcanisation could have taken place in the latex before the film was cast and also to swell the latex particles in the film to increase

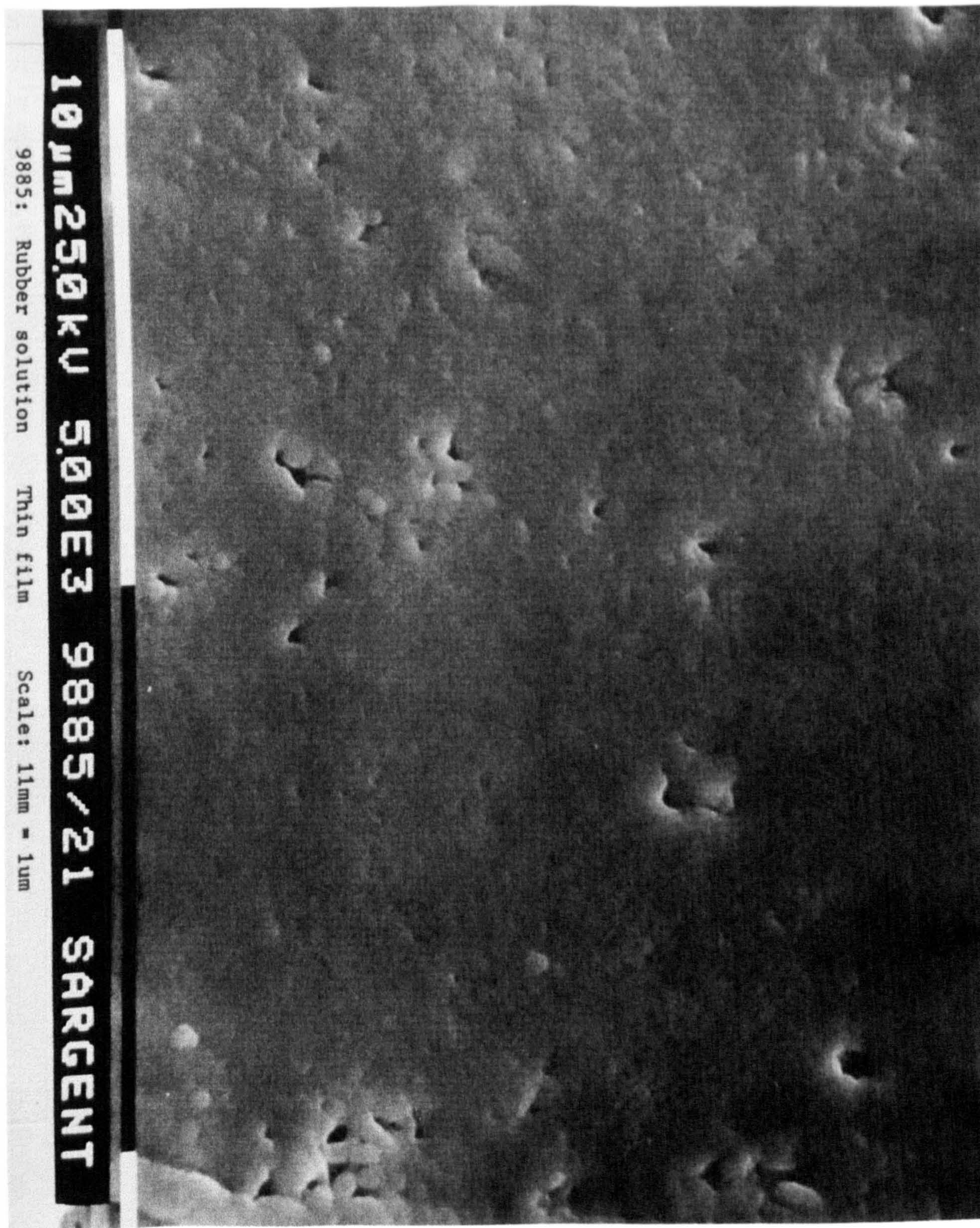


Figure 47 SEM of a Film Cast From a Solution of Natural Rubber Dissolved in Toluene (freeze-fractured cross-section)

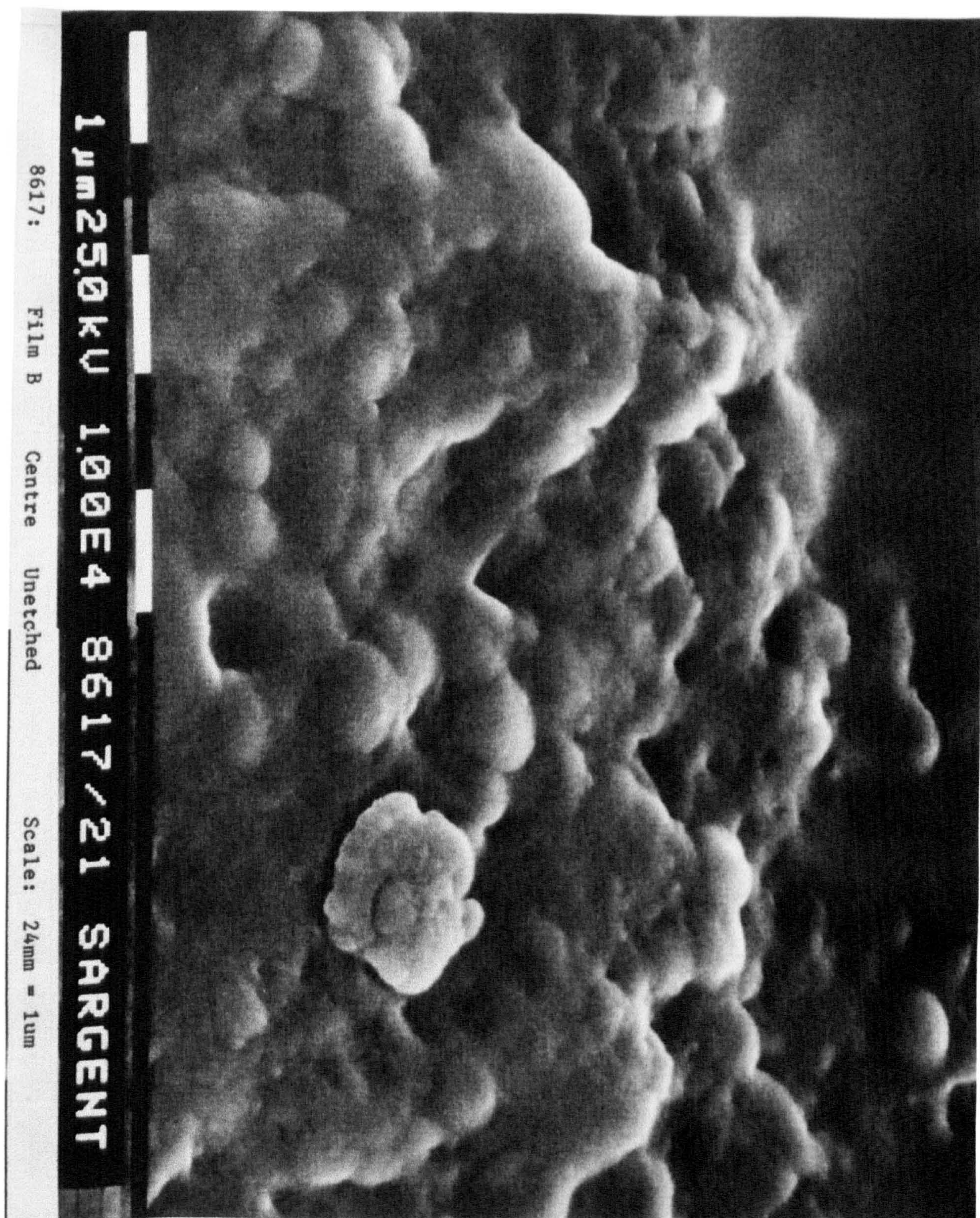


Figure 48 SEM of an film of Uncompounded Latex which has been immersed in toluene for 45 min then allowed to dry

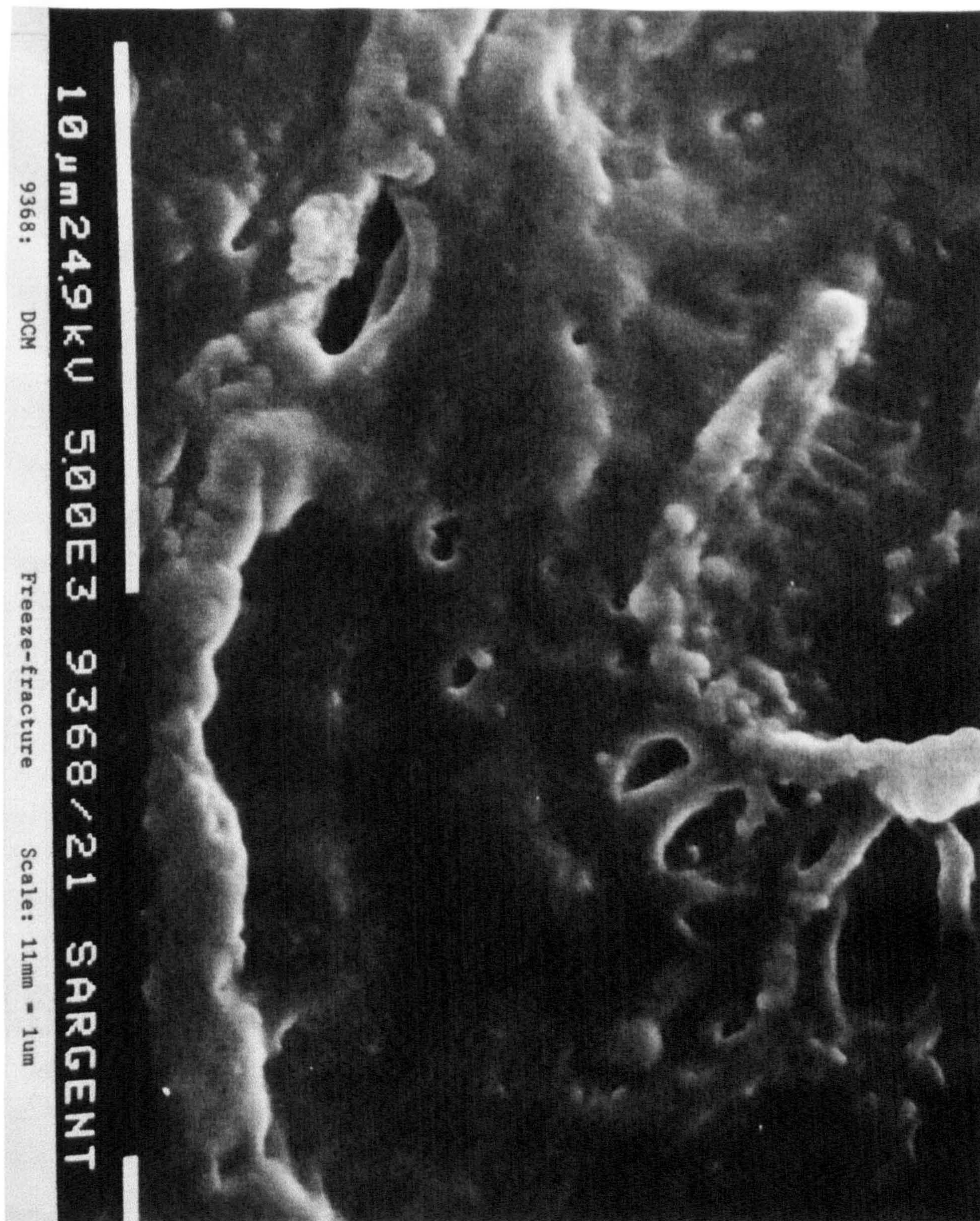


Figure 49 SEM of a Partially Compounded Latex Film (ZDEC omitted), immersed for 16h in a solution of ZDEC dissolved in dicloromethane (DCM), DCM was allowed to evaporate from the film before the film was heated for 90 min at 90°C (freeze-fractured cross-section)

the opportunity for particle integration. After heating, swelling index measurements were made on the film and compared with those for a film of the same latex which had not been swollen or heated. The swollen and heated film had a swelling index of 2.08, showing it to be well crosslinked, whilst the swelling index of the unswollen and unheated film was 6.6, which indicated an uncrosslinked film.

The procedure was repeated using films, cast on glass plates, which were immersed in DCM containing 200ppm ZDEC (Section 3.4.2). The plates were removed from the solution and the solvent allowed to desorb before the films were heated. The resulting films had a reticulated surface which subsequently led to difficulties in obtaining accurate thickness measurements for use in calculation of physical properties (eg tensile strength and modulus). Measurements of swelling index (SI) were made and showed the films to be well cross-linked, SI= 2.6. Tensile strength and modulus (S300%) were determined but must be regarded as approximate, bearing in mind the difficulties in obtaining an accurate value for sample thickness. Tensile strength of 6.5 MPa (s.d=0.7 MPa) and modulus (S300%) of 0.83MPa (s.d.=0.05MPa) were found. The tensile strength of this film is very poor when one considers that modulus and swelling index measurements both show the film to be well crosslinked. The results indicate that in spite of swelling with dichloromethane leading to better particle integration, there is no improvement in tensile strength; in fact there is a large reduction in tensile strength.

In an attempt to eliminate the unevenness from the surface of the swollen films, a film was taken off its glass backing plate and placed in dichloromethane (containing ZDEC). Unfortunately the swollen film was so fragile that it could not be removed from the solvent without breaking up or sticking to itself. The practical difficulties led to no further work on this system.

Finally, latex films were exposed to solvent vapour in order to ascertain whether this would lead to improved particle coalescence and improvements in their physical properties (Section 3.4.2). They were left exposed to toluene vapour; after which time they and similar films which had not been exposed to toluene were heated. The physical properties of the films were found to be:

	Tensile strength (MPa)	Modulus S300% (MPa)
Exposed to toluene vapour	24.5 (3.7)	0.96 (0.04)
Not exposed to toluene vapour	31.9 (1.6)	1.00 (0.05)

The figures in brackets are the standard deviations. The number of test pieces, n, was five.

A Student t-test on the data shows the difference in tensile strength to be highly significant, even at the 1% level, but the differences in modulus are insignificant. Since modulus is an indication of crosslink density the results show that exposure to toluene has not affected the crosslink formation in the film but has drastically affected the tensile strength. Latex films owe some of their tensile strength to the electrostatic forces between the molecules on the surface of adjacent latex particles. It is likely that these have been disrupted by the toluene-induced swelling of films and have not fully reformed when the toluene has evaporated from the film.

It was somewhat suprising that the improvements in film integration brought about by the use of solvents did not result in increase in tensile strength. However, treatment of films with solvent led to problems with film quality and handling. For this reason methods of adding solvent to the latex were sought.

4.7.3 Addition of Toluene to Natural Rubber Latex

Although it was possible to incorporate some toluene by direct addition, with stirring, to diluted latex there were signs that it had separated from the latex and some destabilisation had occurred (coagulum had formed around the stirrer). Films cast from the toluene-containing latices were rather patchy. Where toluene was added 25%v/v to the diluted latices (giving ratios 1:1.3 and 1:0.9 toluene to rubber by volume) a considerable quantity of coagulum formed around the stirrer and the modified latices would not completely wet the glass plates onto which they were spread to form films . The problem of "wetting" is probably due to the decrease in surface cover of latex particles by surfactant, because of increasing surface area as the latex particles absorb toluene and swell. Lower surfactant concentration on the latex particle surfaces leads to the surface tension of the latex being higher and less

able to wet glass.

The practical problems of producing a stable latex which would wet the substrate on which it was cast and form coherent films led to an alternative approach to the problem. Liquids which are not miscible with latex may be added to it in the form of emulsions. Toluene was added to latex by first forming an emulsion using the surfactant ammonium oleate ⁷². The compositions of the emulsions are shown in Section 3.4.3.

Emulsions containing 50g toluene with either 1g or 2g oleic acid added were prepared (Section 3.4.3 and Table 39). The emulsion prepared using 2g oleic acid was stable over several days whereas that prepared using 1g oleic acid separated within 2 hours. Both emulsions when freshly prepared were readily incorporated into HA latex and compounded HA latex (see Table 10, formulation A, Sections 3.1.3 and 3.4.3) and the latices remained uncoagulated for at least 11 days. However, the ratio of emulsion to latex did have an effect upon the appearance of the films. Films prepared from approximately 1 part emulsion to 1 part latex (by volume) had a dimpled appearance while drying. The latex had a toluene to rubber ratio of 1:1.1 by volume (see Table 39). Once dry the films had a "marbled" appearance and felt sticky. No further work was carried out on these films. When approximately 1 part emulsion to 3 parts latex were mixed (producing a latex with a toluene to rubber ratio of 1:3.2, Table 40) the derived films were similar in appearance and feel to unmodified latex films.

The addition of toluene emulsions to uncompounded latex resulted in small changes to the tensile strength and modulus of the derived films (Table 40). More information was obtained from emulsions mixed with compounded latices (Tables 10 (Section 3.1.3) and 39). Films prepared from these latices were postvulcanised at 90°C using an air-circulating oven. When the toluene emulsion was added 1 part to 3 parts of compounded latex (formulation A) the films prepared from that latex could be postvulcanised to produce vulcanisates with a reasonable degree of crosslinking (Table 41). However, for films made from latex into which the emulsion had been freshly mixed there was a delay in the onset of cure. With the modified latex after 30 minutes heating the film was still largely uncrosslinked , judging from

Table39 Latices Modified By the Addition of Toluene Emulsions

Formulation	Volume latex (ml)	Mass rubber (g)	Volume rubber (ml)	Mass toluene (g)	Volume toluene (ml)	Toluene: rubber ratio	Mass oleic acid added (g)	ammonium oleate (phr)
HA latex	100	57.0	62.0	50.0	57.5	1:1.1	1.0	1.9
HA latex	300	161.0	186.0	50.0	57.5	1:3.2	1.0	0.7
HA latex	100	57.0	62.0	50.0	57.5	1:1.1	2.0	3.7
HA latex	300	161.0	186.0	50.0	57.5	1:3.2	2.0	1.3
A(34,35)	300	144.8	157.4	50.0	57.5	1:2.7	1.0	0.7
A(25,34,35)	300	144.8	157.4	50.0	57.5	1:2.7	2.0	1.5

Table 40 Physical Properties of Uncompounded Latex Films with Toluene Emulsions

Description	Tensile Strength (MPa)		Modulus (MPa) S300%	
	x	SD	x	SD
Uncompounded HA latex dried at ambient	6.9	0.8	0.59	0.03
Latex + Toluene Emulsion (2g oleic acid) 1:1	1.0	0.5	0.60	0.07
Latex + Toluene Emulsion (2g oleic acid), 3:1	5.1	0.6	0.74	0.04
Latex + Toluene Emulsion (1g oleic acid), 3:1	2.1	0.3	0.60	0.07

Table 41 Physical Properties of Vulcanisates from Compounded Latex Films with Toluene Emulsion (2g oleic acid)

Description		Tensile Strength (MPa)		Modulus (MPa) S300%		SI
Formulation	Cure Time (mins)	x	SD	x	SD	
A(25) No emulsion	30	21.3	2.5	1.09	0.04	2.23
	60	26.5	0.9	1.11	0.01	2.17
	90	26.5	1.5	1.29	0.03	2.09
	120	27.6	1.0	1.28	.03	2.09
A(25)+ Toluene Emulsion (2g oleic acid) 3:1, Cured Fresh	30	3.6	0.4	0.95	0.07	6.22
	60	13.0	5.5	0.75	0.08	3.10
	90	26.7	2.0	1.07	0.06	2.18
	120	26.4	2.9	1.18	0.04	2.03
A(25)+ Toluene Emulsion (2g oleic acid) 3:1, 11 days old	90	31.1	1.6	0.98	0.09	2.35
	120	32.1	1.7	1.00	0.04	2.35
A(25) + Toluene Emulsion (2g oleic acid) 3:1, 22 days old	90	31.7	2.9	1.09	0.05	2.30
	120	33.4	1.4	1.12	0.07	2.30

the swelling index measurements and the low tensile strength (evidence from the modulus is contradictory, seeming somewhat higher than expected). After 60 minutes heating the process of vulcanisation was under way; support for this comes from swelling index and tensile strength measurements. Again the modulus measurement is contradictory in this case being lower than expected. By the time the films had been heated for 90 and 120 minutes the swelling indices of films were similar, as were their tensile strengths. Moduli for the toluene emulsion-containing films remained lower than for those without the emulsion.

Some of the mixed latex and emulsion was allowed to "mature" in the laboratory for 11 and 22 days in order to allow the toluene time to diffuse into the latex particles and the ammonium oleate to redistribute itself on the surfaces of the swollen particles. After the maturation period, films were prepared and heated for 90 and 120 minutes (see Table 41). The films had slightly higher swelling indices than those from unmaturred latex, indicating a lower crosslink density, but similar modulus and higher tensile strength. It is probable that prevulcanisation occurred in the latex during its maturation. This was considered in subsequent experiments.

Cure delay appears to have arisen because of the presence of oleic acid or ammonium oleate in the latex. Reference to the literature showed that ammonium oleate has been recognised as responsible for cure delays in other latex systems⁷¹. To test this, an emulsion containing only 1g oleic acid was added to approximately three times its volume of compounded latex. Films were prepared from the freshly prepared latex and from the latex after 6 and 11 days' maturation. After 18 days' maturation the latex had coagulated. Comparison of crosslinking during postvulcanisation of this latex with a latex where 2g of oleic acid were used in the preparation of the emulsion is made in Tables 42 and 43.

A delay in the onset of cure was seen for films prepared from both the freshly mixed latices (Tables 42 and 43). The length of the delay appeared to be related to the amount of oleic acid used to make the emulsion. When 1g oleic acid was used to prepare the emulsion the cure delay had largely disappeared by a cure time of 60 minutes. When 2g oleic acid was used the cure delay lasted beyond 90 minutes. "Maturing" the latex for 6 days eliminated the cure delay for films prepared from

Table 42 Physical Properties of Cured Films of Latex and Toluene Emulsion with a Reduced Level of Ammonium Oleate

Description		Tensile Strength (MPa)		Modulus (MPa) S300%		SI
Formulation	Cure Time (mins)	x	SD	x	SD	
A(34) + Toluene Emulsion (1g oleic acid) 3:1, Cured Fresh	35	4.1	1.1	0.68	0.06	2.40
	60	24.8	2.7	0.98	0.05	2.08
	90	28.0	1.1	1.10	0.08	2.08
	120	25.6	1.8	1.19	0.04	2.09
A(34) + Toluene Emulsion (1g oleic acid) 3:1, 6 days old	33	30.1	1.9	1.01	0.03	2.08
	60	31.4	2.2	1.11	0.05	2.06
	90	29.4	2.3	1.10	0.10	2.11
	120	30.4	2.8	1.15	0.04	2.13
A(34) + Toluene Emulsion (1g oleic acid), 3:1, 11 days old	60	32.5	2.5	1.18	0.02	2.06
	90	31.3	1.9	1.26	0.05	2.11

Table 43 Physical Properties of Latex Films and Toluene Emulsions

Description		Tensile Strength (MPa)		Modulus (MPa) S300%		SI
Formulation	Cure Time (mins)	x	SD	x	SD	
A(34) + Toluene Emulsion (2g oleic acid) 3:1, Cured Fresh	32	5.4	0.7	0.55	0.04	7.61
	60	6.2	0.7	0.55	0.06	3.23
	90	18.4	2.4	0.74	0.07	2.53
	120	24.4	2.8	0.88	0.03	2.36
A(34) + Toluene Emulsion (2g oleic acid) 3:1, 6 days old	30	19.9	1.3	0.72	0.04	2.78
	60	25.7	3.1	0.79	0.05	2.45
	90	29.4	2.9	0.81	0.04	2.42
	120	28.8	2.1	0.81	0.03	2.42
A(34) + Toluene Emulsion (2g oleic acid), 3:1, 11 days old	60	28.8	2.7	0.86	0.04	2.54
	90	29.4	0.8	0.82	0.07	2.46
A(34) + Toluene Emulsion (2g oleic acid), 3:1, 18 days old	90	29.5	0.7	0.86	0.06	2.52
	120	28.8	1.1	0.90	0.03	2.48

Table 44 Latex and Toluene Emulsion Matured for 13 Days Before Final Compounding

Cure time	90 mins	
Cure Temp	90°C	
Tensile Strength	32.6MPa	(n = 5, s.d. = 1.8)
Modulus S300%	1.14MPa	(n = 5, s.d. = 0.01)
SI	2.23	

latex containing the lower level of oleic acid and considerably reduced it for films prepared from latex containing the emulsion prepared with 2g oleic acid. From these results it is clear that the amount of oleic acid used to prepare the emulsion, and, therefore, the amount of ammonium oleate present in the emulsion (formed from oleic acid reacting with an excess of ammonia solution), affects the initial rate of cure in the films cast from the freshly mixed latices. When the mixed latices were "matured" for 6-18 days before film preparation, swelling index measurements indicated that some room temperature prevulcanisation had taken place (Table 45). Evidently the cure delay during postvulcanisation has been eliminated to some degree by the prevulcanisation in the latex prior to film formation.

The contribution to the delay in the onset of cure by ammonium oleate was investigated. Ammonium oleate was prepared by mixing oleic acid with deionised water and ammonia solution in the same proportions used to prepare the toluene emulsions (see Section 3.4.3 and Table 39). The ammonium oleate solution was added to compounded latex (formulation A) to give mixtures containing 0.7 phr, 1.5phr and 4.4phr ammonium oleate. Films were prepared from the freshly mixed latices and from the same latices after 6 and 12 days maturation.

During the 6 day maturation time, latices containing 0.7phr and 1.5phr ammonium oleate formed gels and films could not be cast. The formulation containing 4.4phr ammonium oleate was uncoagulated even after 12 days, by which time the latex to which no ammonium oleate had been added had also formed a gel.

The coagulation of two of the latices on maturation meant that less information about the effects of maturation was available than had been hoped. However, some conclusions can be drawn from the results for the uncoagulated formulation (4.4phr ammonium oleate). The cure delay observed during the postvulcanisation of films prepared from freshly mixed latices containing toluene emulsions was also observed when only ammonium oleate was added (Table 46). The length of the delay appears to depend upon the concentration of ammonium oleate in the formulation. When 4.4phr ammonium oleate was present in the latex the derived films only reached a substantial extent of cure between 90 and 120 minutes of heating. The large standard deviations for the tensile strength for 60-120 minute

Table 45 Swelling Index Measurements on Unvulcanised Latex and Toluene Emulsions after Maturation

Maturation Time (days)	A(34) + Toluene Emulsion 3:1	
	1g oleic acid	2g oleic acid
6	4.33	3.84
11	3.48	3.49
18	Coagulated, no films could be prepared	2.83

Table 46 The Effect of Ammonium Oleate upon the Postvulcanisation of Latex Films

Formulation	Ammonium oleate (phr)	Maturation time (days)	Cure time (min)	n	Tensile Strength	s.d.	n	S300%	s.d.	SI
A(35)	0	0	30	5	23.2	5.6	5	0.86	0.02	2.43
			60	5	26.4	2.7	5	1.00	0.01	2.17
			90	5	28.1	3.0	5	1.07	0.03	2.08
			120	5	24.6	3.6	5	1.10	0.03	2.07
A(35)b	0.7	0	30	5	11.7	5.3	5	0.72	0.11	4.02
			60	5	22.1	5.7	5	0.95	0.02	2.30
			90	5	24.9	2.1	5	1.03	0.02	2.16
			120	5	23.8	3.2	5	1.04	0.01	2.12
A(35)a	1.5	0	30	5	4.4	0.7	5	0.57	0.05	7.56
			60	5	24.7	1.9	5	0.89	0.03	2.35
			90	5	27.0	3.3	5	1.01	0.02	2.15
			120	5	27.5	1.2	5	1.01	0.03	2.16
A(35)c	4.4	0	30	5	2.4	0.3	5	0.43	0.01	7.48
			60	5	7.6	6.8	5	0.58	0.13	7.30
			90	5	6.5	6.7	5	0.70	0.10	2.32
			120	5	21.2	7.0	5	0.90	0.08	2.47

continued overleaf

Table 46 (cont.) The Effect of Ammonium Oleate upon the Postvulcanisation of Latex Films

Formulation	Ammonium oleate (phr)	Maturation time (days)	Cure time (min)	n	Tensile Strength	s.d.	n	S300%	s.d.	SI
A(35)	0	6	0	5	10.8	1.8	5	0.65	0.01	6.46
			30	5	29.7	3.0	5	1.03	0.02	2.18
			60	5	29.9	1.9	5	1.09	0.03	2.08
			90	5	28.7	2.7	5	1.18	0.01	2.08
			120	5	28.0	0.9	5	1.25	0.02	2.06
A(35)c	4.4	6	0	5	5.1	1.1	5	0.64	0.03	7.34
			30	5	21.5	1.8	5	0.87	0.03	2.75
			60	5	27.8	1.9	5	0.98	0.02	2.28
			90	5	26.6	2.7	5	1.03	0.04	2.20
			120	5	26.1	3.0	5	1.05	0.03	2.12
A(35)c	4.4	12	0	5	9.9	0.6	5	0.61	0.05	4.37
			30	5	24.1	2.5	5	0.88	0.03	2.41
			60	5	27.5	1.6	5	1.02	0.06	2.14
			90	5	29.1	1.8	5	1.09	0.09	2.13
			120	5	27.5	2.4	5	1.14	0.03	2.13

cures and for the modulus at 60 and 90 minute cures suggest that there is inhomogeneity in the films and that some areas have begun to crosslink before others. This might also explain why the swelling index results for 90 minute cure are at odds with the tensile strength and modulus values. Where 0.7phr ammonium oleate was present in the latex, crosslinking had begun by a cure time of 30 minutes and was largely complete by 60 minutes. Where 1.5phr ammonium oleate was present, after 30 minutes heating there was little evidence of crosslinking in the film but by a cure time of 60 minutes crosslinking had almost finished.

It is the ammonium oleate rather than the presence of toluene which determines the length of the cure delay. As maturation time increased the observed cure delay decreased (see Table 46). After 6 days maturation of the latex, crosslinking in the derived films was observed after 30 minutes heating and was largely complete by 60 minutes. After 12 days maturation of the latex similar results were obtained. However, the unheated latex showed an increased degree of crosslinking (due to room temperature prevulcanisation).

The observation of a cure delay has been noted by other workers. Chong⁷¹ used ammonium oleate as a stabiliser for deproteinised NR latex. On postvulcanisation the latex films showed a long cure delay. Loo⁸⁵ also observed a cure delay which was dependent upon the concentration of fatty acid soap present in formulations of dry rubber. In addition, the rate of cure was found to be dependent upon the soap concentration.

It is interesting to note that latices to which toluene emulsions had been added remained stable for much longer than the latices containing only added ammonium oleate solutions (between 18 and 22 days). As described in Section 1.4.2, fatty acid anions (like oleate) form insoluble soaps with zinc ions (from zinc oxide in the formulation) and the loss of surface charge on the latex particles reduces the colloidal stability of the latex, resulting in coagulation. This explains why two of the latices containing added ammonium oleate coagulated more rapidly (after 6 days) than the latex to which no soap had been added (after 12 days). In the case of latex containing 4.4phr ammonium oleate, it is believed that the volume of ammonium oleate solution mixed with the compounded latex caused sufficient dilution for

destabilisation not to occur. For the latices to which toluene emulsions were added the surface area of latex particles was expected to increase due to absorption of toluene leading to a decrease in concentration of the surfactant on the particle surfaces. This would lead to destabilisation of the latex. However, the ammonium oleate which was present as part of the toluene emulsion may itself be absorbed at the surface of the latex particles. In this way the surface cover by surfactant would be maintained and the latices stabilised, as was observed.

The incorporation of toluene into latex was originally undertaken to determine whether there would be an improvement in the physical properties of films by improving particle integration. The extent of particle integration will be discussed in the following section, Section 5.3, where scanning electron micrographs will be considered. The cure delay caused by the presence of ammonium oleate was an unwelcome complication. The use of a maturation period to eliminate it in compounded latex introduced room-temperature prevulcanisation, so that truly postvulcanised latex films were not obtained.

HA latex and a toluene emulsion (made with 1g oleic acid) were mixed in the ratio 3:1 by volume and matured for 13 days before the other compounding ingredients were added (see Table 10 and Section 3.4.3). Films were cast and heated for 90 minutes at 90°C to produce films which were postvulcanised and in which prevulcanisation had been minimised. The physical properties of the films were very similar to those obtained from latices where the compounded latex and emulsion had been matured and in which prevulcanisation had taken place (Tables 42, 44 and 45).

Allowing time for toluene to be absorbed by the latex particles and eliminating prevulcanisation in the latex did not produce postvulcanised latex films with tensile strength higher than that for films in which there was both prevulcanisation in the latex phase and postvulcanisation in the dry film. Nor were the tensile strengths of films made from the toluene-containing latices significantly higher than those made from latex to which no toluene had been added.

CHAPTER 5: POSTVULCANISATION: PHYSICAL PROPERTIES OF CAST FILMS

5.1 The Relationship Between Tensile Strength and Modulus

The relationships between tensile strength and modulus for both dry rubber vulcanisates and films prepared from prevulcanised latex have been investigated by other workers and their findings were discussed in sections 2.5.1 and 2.5.2 and shown in Figure 25. There are a number of curves for dry rubber vulcanisates. Different crosslink types and the concentrations of these crosslinks appear to determine the curve shapes and the size and positions of their tensile strength maxima (Figure 25, Section 2.5.1). The curves appear to originate from a similar point but deviate depending upon the composition of their crosslinks. The curve for carbon-carbon crosslinked films has the lowest tensile strength maximum, and beyond it the tensile strength falls away sharply as modulus increases. Carbon-carbon crosslinks are physically stronger than sulphur crosslinks and do not readily allow stresses to be accommodated by the vulcanisates before the structures rupture (see Section 2.5.1). The curve shape for monosulphidic crosslinks is similar to that for carbon-carbon crosslinks but the tensile strength maximum is higher and is displaced to higher modulus reflecting that the slightly weaker crosslinks are better able to accommodate stresses in the vulcanisate. For polysulphidic vulcanisates, not only are the tensile strength maxima higher but the curve shapes have changed. Beyond the tensile strength maxima the curves fall away only gradually with increasing modulus. The curve shapes can be explained in terms of the ability of the relatively weak polysulphidic bonds to undergo bond interchange and accommodate stresses applied to the vulcanisate (Section 2.5.1 and Figure 26). All dry rubber curves are distinctly different from the curve found for prevulcanised latex films.

For films prepared from prevulcanised latex there appears to be a single curve; this is probably due to the presence of predominantly polysulphidic crosslinks in the films. The curve is sharper and has a tensile strength maximum at lower modulus than for any of the dry rubber vulcanisates (Figure 25). The curve shape is believed to be determined by both the concentration of crosslinks and the interactions, especially molecular entanglements, between neighbouring vestigial latex particles in the films. As the concentration of crosslinks increases (as shown by increasing modulus) there is an increase in tensile strength up to a maximum, around 35 MPa. In prevulcanised latex the crosslinks are formed between rubber molecules within the latex particles. The ability of latices to form well-integrated films is dependent upon the ability of molecules within vestigial latex particles to move and form entanglements with molecules in neighbouring vestigial particles. "Soft", lightly-crosslinked particles merge with each other more readily than "hard", highly-crosslinked particles. Therefore, there is a point for prevulcanised latex films where the difficulty in forming well

integrated films begins to affect film strength to a larger extent than the introduction of more crosslinks within the latex particles and the overall tensile strength decreases.

The difficulties experienced in preparing postvulcanised latex films which cover the range of modulus necessary to identify the tensile strength:modulus relationship have already been adequately described in Section 4.6. Data produced for postvulcanised films prepared using a number of different accelerator systems are plotted in Figure 50 together with the curves for prevulcanised latex films and two curves for polysulphidic dry rubber vulcanisates. The use of a single dithiocarbamate accelerator, ZDEC, produced films with tensile strengths of 30-35MPa but with a very limited range of modulus.⁷⁸⁻⁸⁰ The use of this accelerator alone would not have allowed the relationship between tensile strength and modulus to be determined for postvulcanised latex films. The data for films containing ZDEC, although showing considerable scatter, are within or close to the rising curve for prevulcanised latex films. This is believed to be partly because of the mainly polysulphidic crosslinks present, as determined by Calver⁶⁸, although other factors which will be discussed later are also involved.

5.1.1 The ZDEC/ZMBT System

When ZDEC and ZMBT are used in combination (1:1 by weight) there is a synergistic effect upon the degree of crosslinking observed, as described in the literature⁸⁶. Using this combination it was found possible to prepare a range of vulcanisates covering a modulus range right up to $S_{300\%}=4.28\text{MPa}$ by varying the amounts of sulphur and accelerator in the formulations and varying the cure time. The formulations used are shown in Table 13 (Section 3.1.3) and the physical properties in Table 47 and Table 36 (Section 4.5.3). The results showed the limitation on the modulus to be a feature of the accelerator system used rather than a feature of postvulcanisation of latex films. However, the anticipated increases in tensile strength were not obtained. The greatest tensile strength obtained was 29.1MPa at a modulus of $S_{300\%}=1.92\text{MPa}$ (Figure 50).

The shape of the tensile: modulus curve for postvulcanised latex films containing ZDEC and ZMBT in combination is quite different from that for films containing ZDEC as the only accelerator. The curve shape is more like that seen for dry rubber, following the same rising curve. It reaches a tensile strength maximum close to that found for 70% polysulphidic dry rubber, its maximum being lower than for the 87% polysulphidic dry rubber.

POSTVULCANISED LATEX MODULUS VS TENSILE STRENGTH

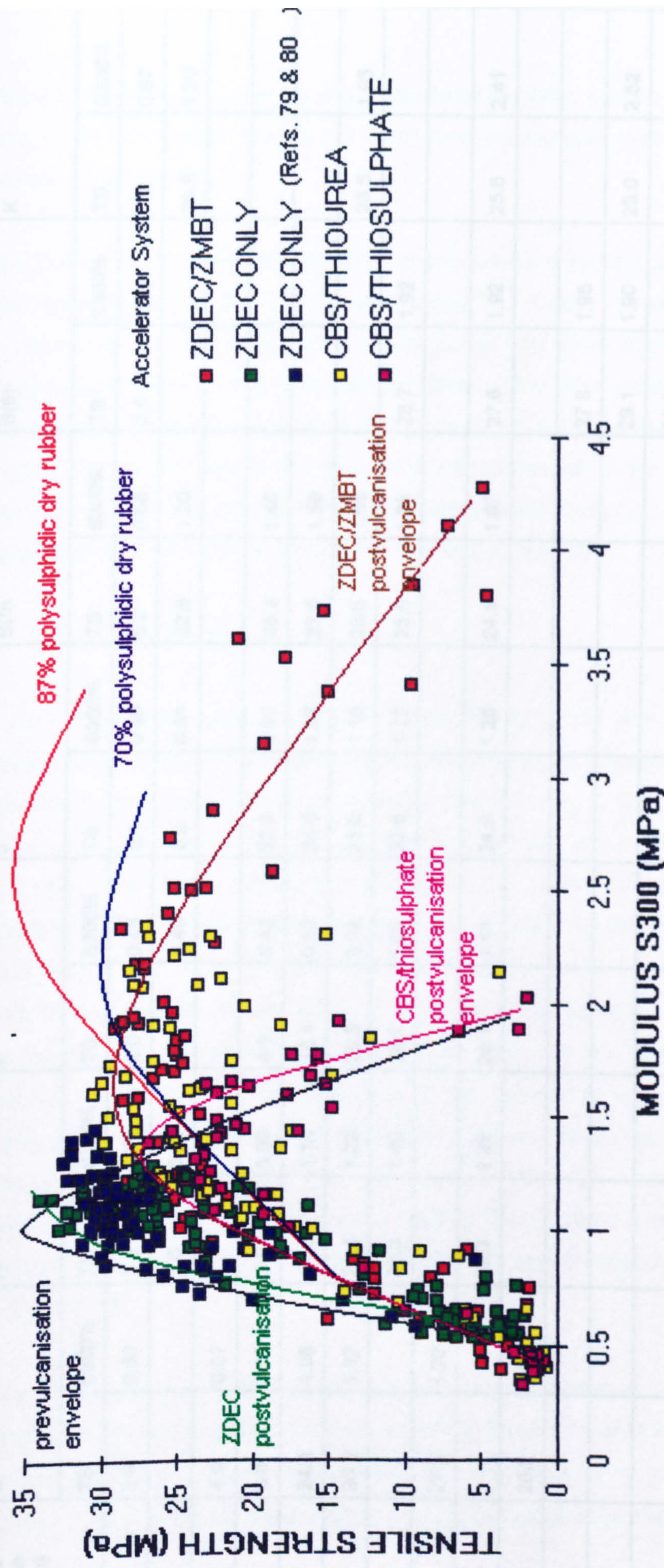


Figure 50 Tensile Strength: Modulus Data for Postvulcanised Latex Films

Table 47 Physical Properties of Postvulcanised Latex Films Containing ZDEC/ZMBT

Cure Time (min)	G			H			I			J			B(5)			B(6)			K		
	TS	S300%		TS	S300%		TS	S300%		TS	S300%		TS	S300%		TS	S300%		TS	S300%	
0	5.9	0.60		1.8	0.76		2.0	0.45		5.1	0.49		5.2	0.66		2.5	0.56		7.4	0.57	
15				2.0	0.68		3.7	0.40		3.2	0.51		22.6	1.20					25.9	1.20	
23	4.0	0.57																			
30	9.0	0.63		5.9	0.93		4.9	0.43		22.6	0.96		26.3	1.40							
45	24.4	1.06		21.6	1.15		15.1	0.62		24.0	1.07		27.5	1.59							
60	26.5	1.12		24.4	1.23		23.8	0.94		25.6	1.10		26.6	1.68					28.5	1.93	
90				23.3	1.40		24.7	1.02		23.5	1.23		25.0	1.85		28.7	1.92				
94	27.0	1.22																			
120				23.3	1.29		25.1	1.14		24.9	1.26		24.5	1.87		27.6	1.92		25.6	2.41	
125	28.2	1.23																			
150																27.8	1.95				
180																29.1	1.90		23.0	2.52	
210																25.9	2.02				
240																			18.7	2.59	
300																			18.7	2.60	

Formulations shown in Tables 11 and 13, Section 3.1.3
Cure temperature 90°C
Values of tensile strength (TS) and modulus (S300%) are given in MPa

The down-turn on the curve for this postvulcanised latex system is more rapid than for the dry rubber curves but much less pronounced than that seen for prevulcanised latex films.

The ZDEC/ZMBT accelerator system not only shows a synergistic effect but is also more active than the ZDEC system alone^{86,87}. It was, therefore, important to check that no room temperature vulcanisation had taken place in either the compounded latex or the unvulcanised films. This was done by including unvulcanised films as samples at the same time as vulcanised films were tested. The results appear in Figure 50 at the bottom left of the curve. There was no evidence that room temperature vulcanisation had occurred during the period between compounding the latex and testing the films.

5.1.2 The CBS System

A third accelerator system (CBS) was investigated which was known to be inactive at room temperature and was slow to bring about vulcanisation even at elevated temperatures unless an activator was present. CBS is used in dry rubber vulcanisation but has not usually been used with latex. Philpott carried out work with latex, using a number of dry rubber accelerators and activators^{88,89}. He found that a range of sulphur-bearing accelerators which were almost inactive at temperatures below 100°C, due to the comparatively high thermal stability of their sulphur bonds, could be converted into effective accelerators at temperatures of 100°C and below by the presence of S-reactive nucleophiles. In the presence of the activators, vulcanisation was rapid, taking less than 2 hours and in some cases as little as half an hour for a well-crosslinked vulcanisate to be formed. On the basis of this, postvulcanisation was carried out using CBS as the accelerator and thiourea or sodium thiosulphate as the activator. (Tables 14 and 15 (Section 3.1.3), and Tables 48-52).

CBS is known as a "delayed action" accelerator. It is one of a class of accelerators where the functional sulphur atom is covalently bonded to another sulphur, or a carbon or nitrogen atom. These accelerators are ineffective at or below 100°C, whereas accelerators in which the sulphur atom carries an ionic charge are relatively active at

Table 48 Physical Properties of Postvulcanised Latex Films Containing CBS/Thiourea

Cure Time (min)	L			M			O(1)			P			Q(1)			Q(2)			R			S		
	TS	S300%	TS	TS	S300%	TS	TS	S300%	TS	S300%	TS	S300%	TS	S300%	TS	TS	S300%	TS	TS	S300%	TS	S300%	TS	S300%
0	1.01	0.46	0.65	0.41	0.42	1.9	0.52	2.6	0.45	2.4	0.36	1.2	0.45	0.36	1.2	0.45	0.36	1.2	0.45	0.36	0.9	0.48	0.48	0.48
15			1.47	0.56		6.5	0.90																	
16																			1.5	0.45				
30			10.3	0.84		18.4	1.16											5.4	0.61					
60			9.0	0.92																				
90																						22.1	1.08	1.08
120	0.33	0.29	13.2	0.92		17.5	1.44											13.9	0.74					1.26
127																								
180																			21.4	1.36				
240	0.30	0.27																20.4	1.11					
245																								
360	0.27	0.25																20.3	0.92	20.5	2.00			
405																		17.1	1.02					
435																								
480																								
510																								
525																								
960																			23.6	2.09				

Continued overleaf

Table 48 Physical Properties of Postvulcanised Latex Films Containing CBS/Thiourea) (cont.)

Cure Time (min)	L			M			O(1)			P			Q(1)			Q(2)			R			S		
	TS	S300%		TS	S300%		TS	S300%		TS	S300%		TS	S300%		TS	S300%		TS	S300%		TS	S300%	
963													-		0.98									
1020										18.1		1.91												
1320																								
1420																			3.8		2.15			
1440							26.9		2.31	15.2		2.32										12.2		1.86
1443																	0.88							
1447													16.0		1.01									
1683													-		1.03									

Formulations shown in Table 14, Section 3.1.3
Cure temperature 100°C
Values of tensile strength (TS) and modulus (S300%) are given in MPa

**Table 49 Physical Properties of Postvulcanised Latex Films Containing CBS and Thiourea
- Effect of Ammonium Oleate**

Cure Time (h)	T						O(2)					
	n	S300%	sd (MPa)	n	TS (MPa)	sd	n	S300%	sd (MPa)	n	TS (MPa)	sd
0	5	0.63	0.03	3	5.5	0.9	5	0.54 (1.18)	0.05 (0.02)	5	3.8 (22.9)	1.1 (3.1)
1.5	5	1.25	0.02	5	25.7	1.1	4	1.20	0.02	4	25.3	1.7
3.0	5	1.36	0.04	5	24.7	1.7	4	1.40	0.02	4	25.1	3.7
6.0	5	1.56	0.04	5	5.4	2.8	4	1.63	0.03	4	23.5	4.1
16.0	4	1.75	0.21	4	21.4	3.0	5	2.12	0.09	5	22.0	2.8
24.0	3	2.22	0.01	3	25.1	1.7	3	2.31	0.03	3	22.8	2.5

() = Uncured samples containing crystals

n = Number of samples

S300% = Mean modulus at 300% elongation (MPa)

TS = Mean tensile strength (MPa)

Cure temperature = 100°C

Latex O(2) included added ammonium oleate and Latex T did not.

Table 50 Further Physical Properties of Postvulcanised Latex Films Containing CBS and Thiourea

Cure Time (h)	U(1)						U(2)					
	n	S300%	sd (MPa)	n	TS (MPa)	sd	n	S300%	sd (MPa)	n	TS (MPa)	sd
0	5	0.42	0.01	5	1.1	0.2	5	0.37	0.01	5	1.4	0.3
1	5	1.16	0.03	5	23.3	1.7						
2	5	1.27	0.03	5	26.2	2.6						
4	5	1.53	0.06	5	24.9	2.3						
6	5	1.64	0.05	5	23.4	5.6	5	1.49	0.02	5	27.7	2.8
16							5	1.57	0.04	1	21.3	-
24							5	1.69	0.04	1	14.7	-

n = Number of samples

S300% = Mean modulus at 300% elongation (MPa)

TS = Mean tensile strength (MPa)

Cure temperature = 100°C

Table 51 Physical Properties of Postvulcanised Latex Films Containing CBS and Thiosulphate

Cure Time (min)	V(1)		V(2)		W(1)		W(2)		X	
	TS	S300%	TS	S300%	TS	S300%	TS	S300%	TS	S300%
0	1.7	0.43	1.6	0.45	1.8	0.48	1.2	0.40	1.7	0.43
15	2.8	0.48								
30	0.9	0.44			1.2	0.47			1.6	0.42
60	12.6	0.84			1.7	0.46	10.0	0.66	5.9	0.65
90			23.2	1.34						
93							17.6	1.02		
120			23.8	1.32	19.3	1.08	22.1	1.19		
121	22.1	1.43								
126									19.3	1.16
150							23.6	1.22		
185							23.5	1.23		
240	14.8	1.55			2.3	1.42				
249			23.1	1.65						
252									20.5	1.45
364									21.1	1.47
429			21.3	1.66						
480	15.7	1.76			22.3	1.49			22.3	1.61
960					17.7	1.60	17.0	1.44	15.2	1.65
973	2.6	1.89								
976			16.2	1.69						
1440	1.9	2.03			17.4	1.78	26.2	1.64	6.5	1.88

Formulations shown in Table15, Section 3.1.3

S300% = Mean modulus at 300% elongation (MPa)

TS = Mean tensile strength (MPa)

Cure temperature 100°C

Table 52 Physical Properties of Postvulcanised Latex Films Containing CBS and Thiosulphate without added Potassium Oleate

Cure Time (min)	Y(1)						Y(2)					
	n	S300% (MPa)	sd (MPa)	n	TS (MPa)	sd (MPa)	n	S300% (MPa)	sd (MPa)	n	TS (MPa)	sd (MPa)
0	5	0.39	0.01	5	1.5	0.2	5	0.34	0.01	5	2.2	0.5
60	5	1.10	0.06	5	22.5	1.5						
120	4	1.27	0.01	5	22.8	2.55						
240	4	1.44	0.01	4	25.3	2.0						
360	5	1.71	0.08	-	-	-	5	1.40	0.07	3	26.9	2.0
960							5	1.78	0.06	4	15.8	8.8
1440							5	1.93	0.23	1	14.3	-

Formulations shown in Table 15, Section 3.1.3

S300% = Mean modulus at 300% elongation

TS = Mean tensile strength

n = Number of samples

sd = standard deviation

Cure temperature 100°C

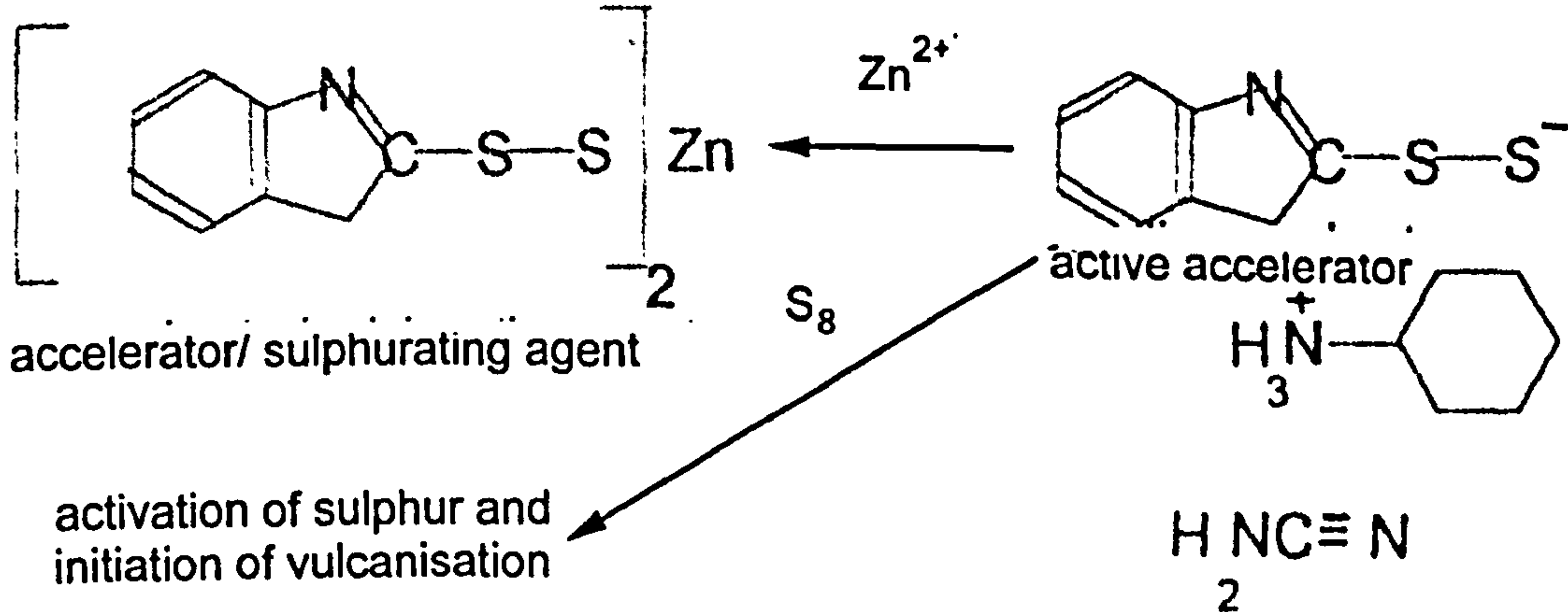
100°C^{88,89}. Philpott suggested that if the sulphur atom in the blocked thiol group was uncovered by cleavage of the S-S, S-C or S-N bond a reactive entity would be produced which was capable of setting off a series of rapid reactions leading to vulcanisation. This scission may be achieved by vulcanisation at the high temperatures used to vulcanise dry rubber (140-180°C) or by reducing the activation energy of bond scission by the addition of nucleophiles, for example thiourea or thiosulphate ions. The suggested scheme for the formation of an "active accelerator" from the CBS is shown in Scheme 5. This reaction of CBS with thiourea is based on that proposed for the reaction of tetramethylthiuram disulphide (TMTD) with thiourea⁹⁰.

The rate of postvulcanisation at 100°C of films containing CBS and an activator is much slower than for ZDEC/ZMBT or ZDEC-containing films at 90°C. In the case of films in which thiosulphate ions were used as the activator a "cure delay" of between 30 and 60 min. was observed (Table 51). This was not observed when thiourea was used as activator (Table 48). The initiation of vulcanisation is expected to be dependent upon the formation of the active accelerator at a concentration sufficient for reaction with the sulphur to form the "active sulphurating agent". Whilst the thiosulphate ion is a strong nucleophile towards carbon, it is only weakly thiophilic (S-nucleophile)⁹¹. Its lower thiophilicity compared with thiourea leads to a slower reaction with CBS than is seen for thiourea (Scheme 5), leading to slower formation of the "active" accelerator.

The tensile strength versus modulus curves for postvulcanised films containing CBS with thiourea and thiosulphate ions as the activator are shown in Figure 50. They differ in shape from each other and show a high degree of scatter. The scatter may be partly explained by the difficulties encountered in handling the compounded latex. The presence of ammonium oleate in the latex formulation initiated rapid thickening and coagulation as soon as zinc oxide was added. This only occurred when oleate soaps were present (being less severe when the oleate was added as potassium oleate) and when CBS was present. When ZDEC was substituted for CBS in the formulation the latex did not thicken. In order to prepare films from unstable latex they had to be cast immediately after the final addition of zinc oxide with no opportunity for filtering to remove coagulum or time to allow trapped bubbles to escape. However, if a curve were drawn through the points with the highest tensile strength for a given modulus for CBS/thiourea the curve shape would be similar to that for ZDEC/ZMBT although slightly displaced, reaching its maximum at slightly higher tensile strength and slightly

Scheme 5

Proposed Scheme for the Activation of CBS by Thiourea



lower modulus. The shape of the curve beyond modulus S300% of 2.3MPa for the CBS/thiourea system is unknown.

The most unexpected observation was the curve shape for postvulcanised latex films with CBS as the accelerator and thiosulphate ions as the activator. Whilst the rising part of the tensile strength/modulus curve is similar to that for CBS/thiourea the curve reached a maximum at lower tensile strength, about 26MPa, and lower modulus, S300%, about 1.4MPa. However, the most striking difference was in the falling part of the curve. Beyond a modulus (S300%) of 1.4MPa the tensile strength fell away rapidly. The curve shape had a greater similarity to that seen for prevulcanised latex films (although the maximum tensile strength was lower and it was displaced to a higher modulus) than to that for dry rubber vulcanisates or postvulcanised latex films with other accelerator systems(see Figure 25, Section 2.5.1). However, prevulcanisation of the latex can be ruled out because unheated films (cure time =0 min) showed no signs of vulcanisation (they had low moduli and low tensile strengths). The difference in curve shape between postvulcanised latex films in which the same accelerator was used and only the activator varied was a great surprise since they are expected to form crosslinks in exactly the same manner, although the rate may have been expected to vary due to the difference in nucleophilicity of thiourea and thiosulphate ions.

5.2 Discussions of Curve Shapes for Postvulcanised Latex Films

Postvulcanised latex films appear to have tensile strength/modulus curves which, in terms of shape and position of the maximum, lie somewhere between those for polysulphidic dry rubber vulcanisates and prevulcanised latex films.

In dry rubber, crosslinks are thought to be randomly distributed throughout the vulcanisate. The tensile strength/modulus curve is broad and tensile strength falls away only very gradually (see Figure 25, Section 2.5.1). Tensile strength increases with increases in crosslink density (shown by the corresponding increasing modulus). Eventually the concentration of crosslinks is so high that, when the vulcanisate is subjected to stress, the polysulphidic crosslinks cannot as readily undergo crosslink interchange to minimise the stress (as described in 2.5.1) and the tensile strength begins to decrease with increasing modulus.

In contrast to this, the shape of the tensile strength/modulus curve for prevulcanised latex

films is believed to be determined initially by the concentration of crosslinks within the latex particles²⁴. At low crosslink density, and therefore low modulus, particle coalescence is believed to be good but this is believed to have only a small effect upon tensile strength. At the tensile strength maximum, the combination of crosslinks within the latex particles, the entanglements and the attractive forces due to particle-particle coalescence reached its optimum value. Beyond the maximum tensile strength it is particle-particle coalescence which is believed to become more important in the determination of tensile strength. As the crosslink density and modulus further increase rubber molecules within the latex particles are believed to become less mobile and particles less able to coalesce. As particle integration becomes poorer the tensile strength falls, failure occurring between particles rather than within them. However, there is evidence that natural rubber latex films are less well integrated than was previously thought see Section 5.3).

The tensile strength/modulus data in Figure 50 show that postvulcanised latex films with moduli above 1.4 MPa can be obtained when ZMBT (in combination with ZDEC) or CBS and an activator are used as accelerators but not with ZDEC alone. CBS is a delayed action accelerator which forms the active accelerator ZMBT by interaction with an activator and zinc oxide. Since ZMBT is present as an accelerator in both systems where high modulus vulcanisates were prepared it seems likely that it is the mode of reaction of ZMBT rather than the reaction of ZDEC which results in the development of the higher modulus vulcanisates.

The data for the ZMBT/ZDEC and the CBS/ thiourea accelerator systems are believed to be typical of postvulcanised films, the large amount of scatter for the CBS/ thiourea data being due to imperfections in the films (see 5.1). The broad curve seen for the ZDEC/ZMBT accelerator system indicates that the crosslinks are more uniformly distributed throughout postvulcanised films but they are not completely homogeneous and the downturn suggests that the films retain some of their particulate nature. The rising parts of the curves indicate that, like the curves for prevulcanised latex and dry rubber, tensile strength is initially determined by increasing crosslink density and the contribution to tensile strength by particle integration is less important than the overall concentration of crosslinks whether they occur within latex particles, between latex particles or uniformly between rubber molecules where the vulcanisate has no particulate structure. The observation that the curve for ZMBT/ZDEC and CBS/thiosulphate-containing postvulcanised films falls away more rapidly than for dry rubber beyond the tensile strength maximum indicated that these films retain their inherent particulate nature where crosslinks are concentrated within latex particles rather than being homogeneously distributed throughout the film.

Postvulcanisation appears to give rise to physical properties which are intermediate between those for prevulcanised latex films and dry rubber vulcanisates.

The sharp curve seen for films with the CBS/thiosulphate accelerator system is anomalous and suggests that the crosslink distribution is more like those in prevulcanised latex films, perhaps concentrated within the latex particles, where at high crosslink densities the inability of highly crosslinked particles to integrate leads to a fall in tensile strength.

It is not possible to locate the crosslinks in order to differentiate between crosslinks within latex particles and crosslinks between latex particles. Therefore, it is only possible to speculate about the relative distribution of these crosslinks.

ZDEC gives a rapid rate of vulcanisation but in postvulcanisation appears to reach a point where sulphur cannot be combined further in physically effective crosslinks. It was initially believed that the limitation upon the development of higher crosslink density and hence higher modulus was the result of limited solubility of ZDEC in the rubber at the vulcanisation temperature of 90°C. However, when films were vulcanised at 110°C and 130°C there was no further increase in modulus (see Section 4.6). The explanation that the unusual behaviour of the ZDEC system, is due to poor solubility in rubber is even less likely since neither ZMBT nor CBS are particularly soluble in rubber⁹².

The production of physically effective sulphur crosslinks throughout vulcanisation, when ZMBT is also present, suggests that as the polysulphide crosslinks formed initially using ZDEC as an accelerator decompose or desulphurate, the sulphur is recycled into useful crosslinks by the ZMBT. It is, therefore, suggested that the synergistic effect is seen because ZDEC is capable of rapidly producing a polysulphidic vulcanisate with long sulphur crosslinks but is not able to recycle the sulphur from these unstable crosslinks into further shorter crosslinks. ZMBT is not used as a primary accelerator since it gives a rate of vulcanisation too slow for industrial processes. ZMBT alone forms sulphur crosslinks only slowly but is believed, from the data obtained here, to be far more efficient at converting long polysulphidic crosslinks into shorter sulphur crosslinks. This suggestion is purely speculative since no determinations have been made of the number of sulphur atoms present in crosslinks of vulcanisates during this work.

5.3 The Use of Electron Microscopy to Examine Film Structure

5.3.1 Cryo-scanning Electron Microscopy

As discussed in Section 4.7, films of unvulcanised and postvulcanised latex were expected to be largely homogeneous. However, when unvulcanised, prevulcanised and postvulcanised latex films were examined by cryo-SEM (Section 3.7.1). this was found not to be the case. Micrographs of the freeze-fractured cross-sections showed particulate structures which look similar (see Figures 44, 45 and 46 in Section 4.8).

Film integration was also believed to be improved by increasing film processing temperatures and the length of heating^{26,29}. A series of micrographs of latex films (preparation A(33)) vulcanised at 130°C are shown in Figures 51-55. They show the unvulcanised film (Figure 51) and films vulcanised for between 20 and 90 minutes. The unvulcanised film clearly has a particulate structure but, as the films were heated for longer the particles became less distinct. In films heated for 20 and 30 minutes, most of the particles had fused to form large indistinct groups (Figures 52 and 53). However, some vestiges of the particles remain in the rather uneven surfaces of the cross-sections. By the time the films had been heated for 60 minutes it is very difficult to detect many latex particles and the surface of the cross-section is much smoother (Figure 54). There are a number of very small particles (of about 0.2-0.4µm in diameter) visible in this and earlier micrographs. Indeed, particles of similar size are seen in Figure 44 (Section 4.8) which is a latex film containing no vulcanising ingredients ; it is, therefore, believed that these are small natural rubber latex particles. However, the reason why these particles persist in the heated films whilst larger ones coalesce is not clear (see also Sections 1.5.1 and 1.5.2). Once the film had been heated for 90 minutes (Figure 55) it was not possible to detect particles in the cross-section. Heating natural rubber latex films at 130 °C does appear to improve their integration.

The physical properties and sulphur analyses for the films are recorded in Tables 37 and 38 and Figures 42 and 43 in Section 4.6. It can be seen from Table 38 that, for a previous preparation (A(32)), heating the film for up to 15 minutes led to increases in modulus and tensile strength. For films of latex A(33), on heating for longer than 20 minutes at 130°C, both the modulus and tensile strength of the films decreased and the swelling index increased. The modulus and swelling index results indicate a decrease in the degree of crosslinking in the film (reversion), sulphur crosslinks were decomposing faster than they were being formed. From the results in Section 4.7 and themicrographs, it can be concluded that films which have good

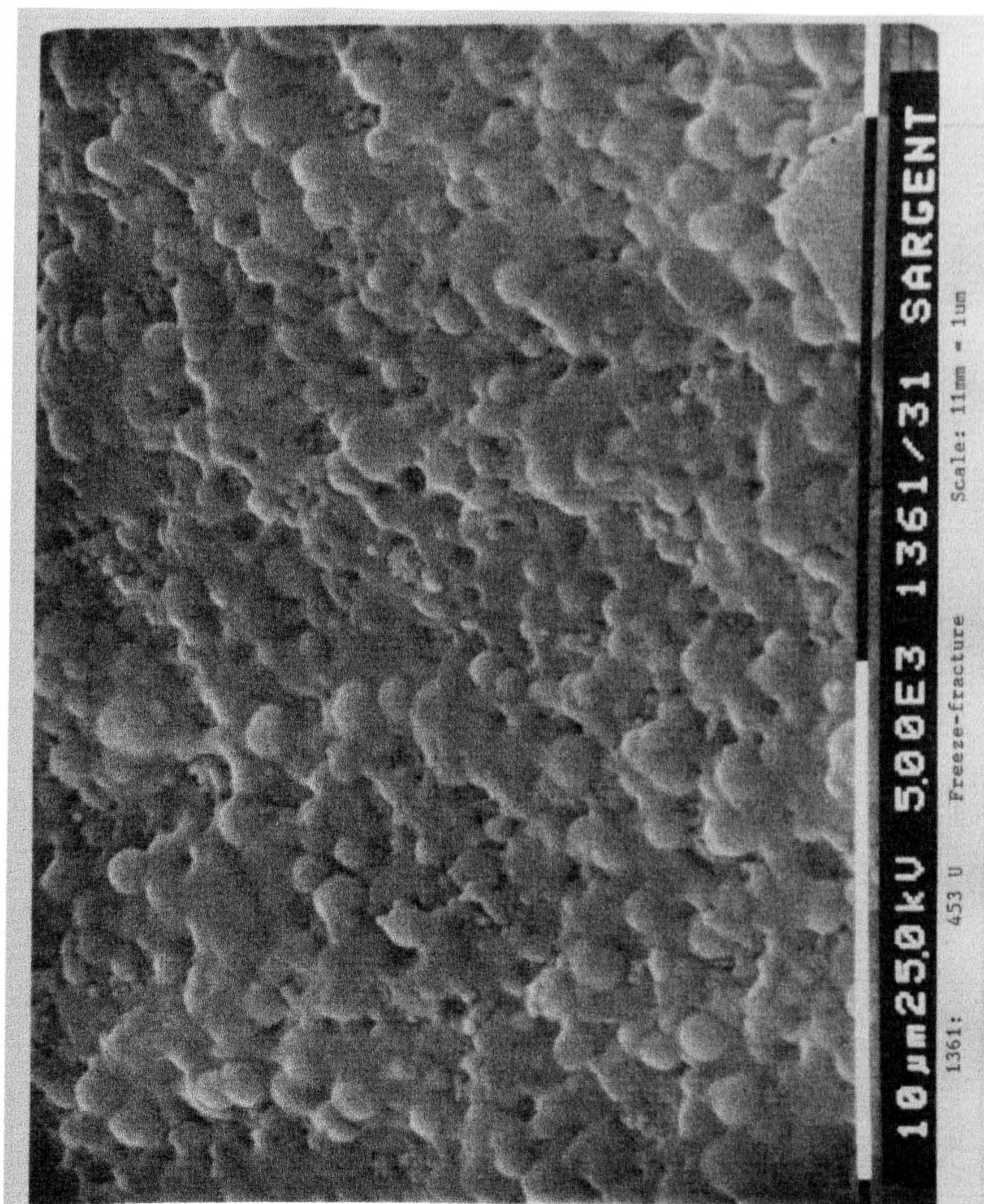


Figure 51 Unvulcanised Film of Compounded Latex A(33) (containing ZDEC as the accelerator)

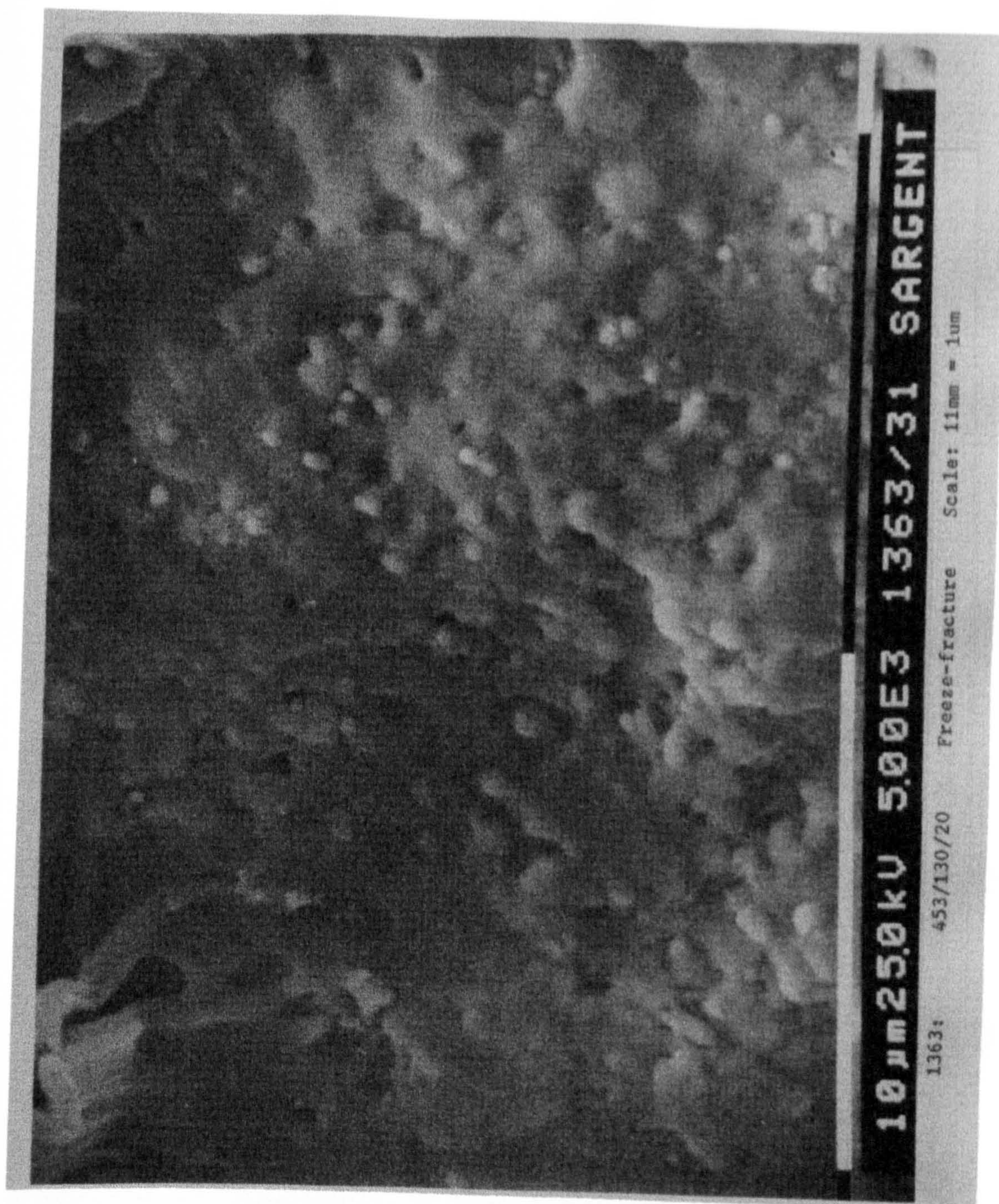


Figure 52 Latex Film A(33) Postvulcanised for 20 min. at 130°C

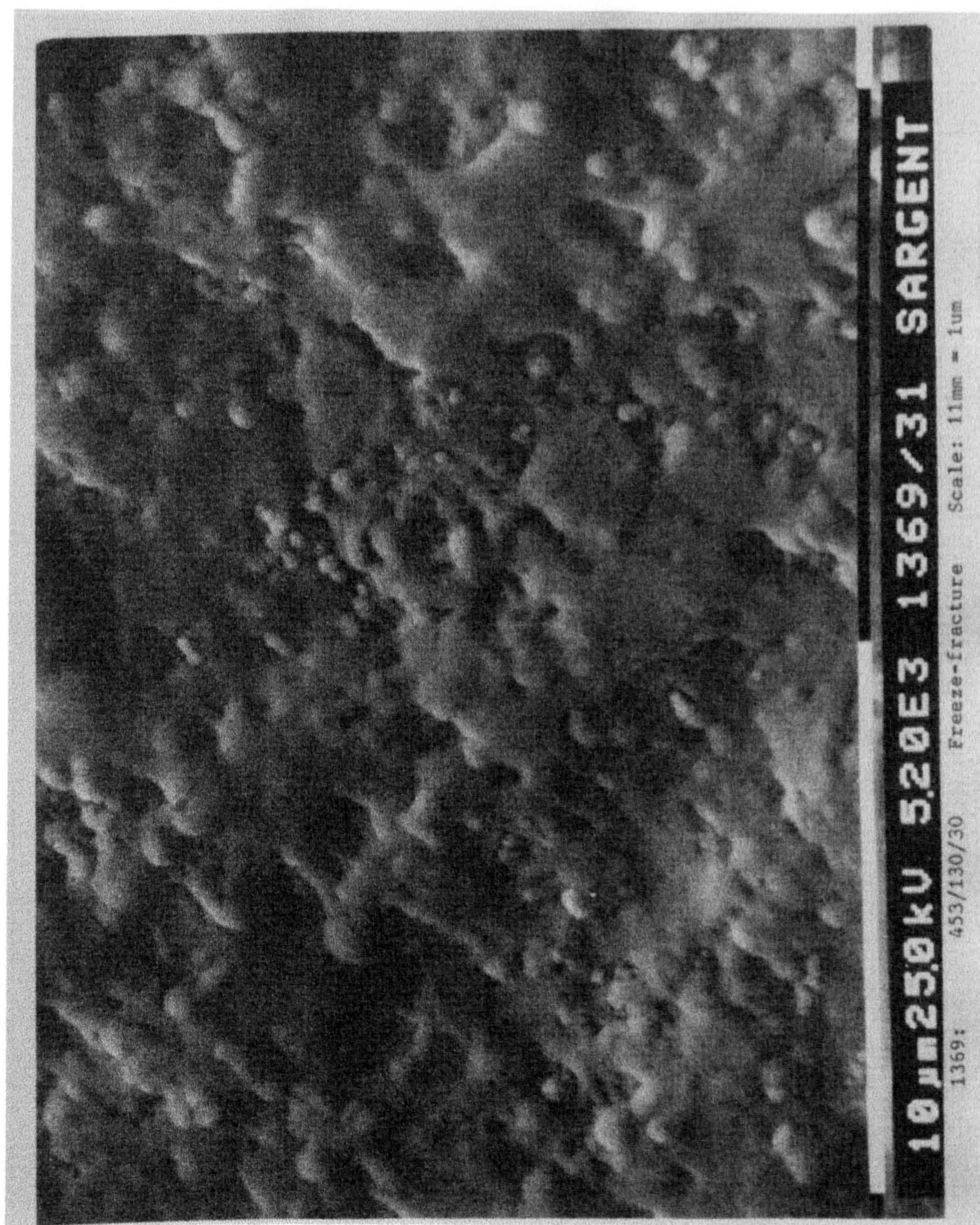


Figure 53 Latex Film A(33) Postvulcanised for 30 min. at 130°C

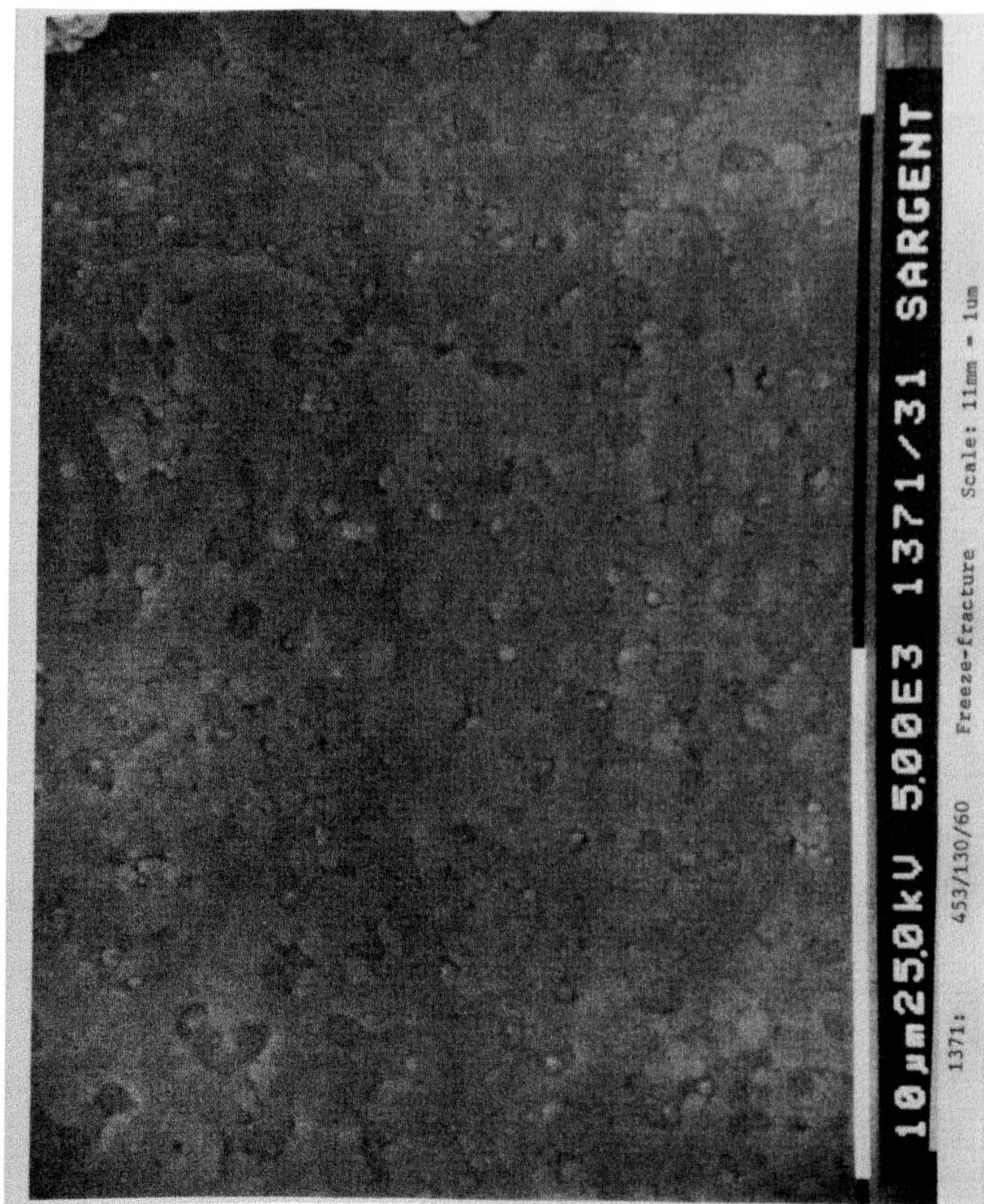


Figure 54 Latex film A(33) Postvulcanised for 60 min. at 130°C

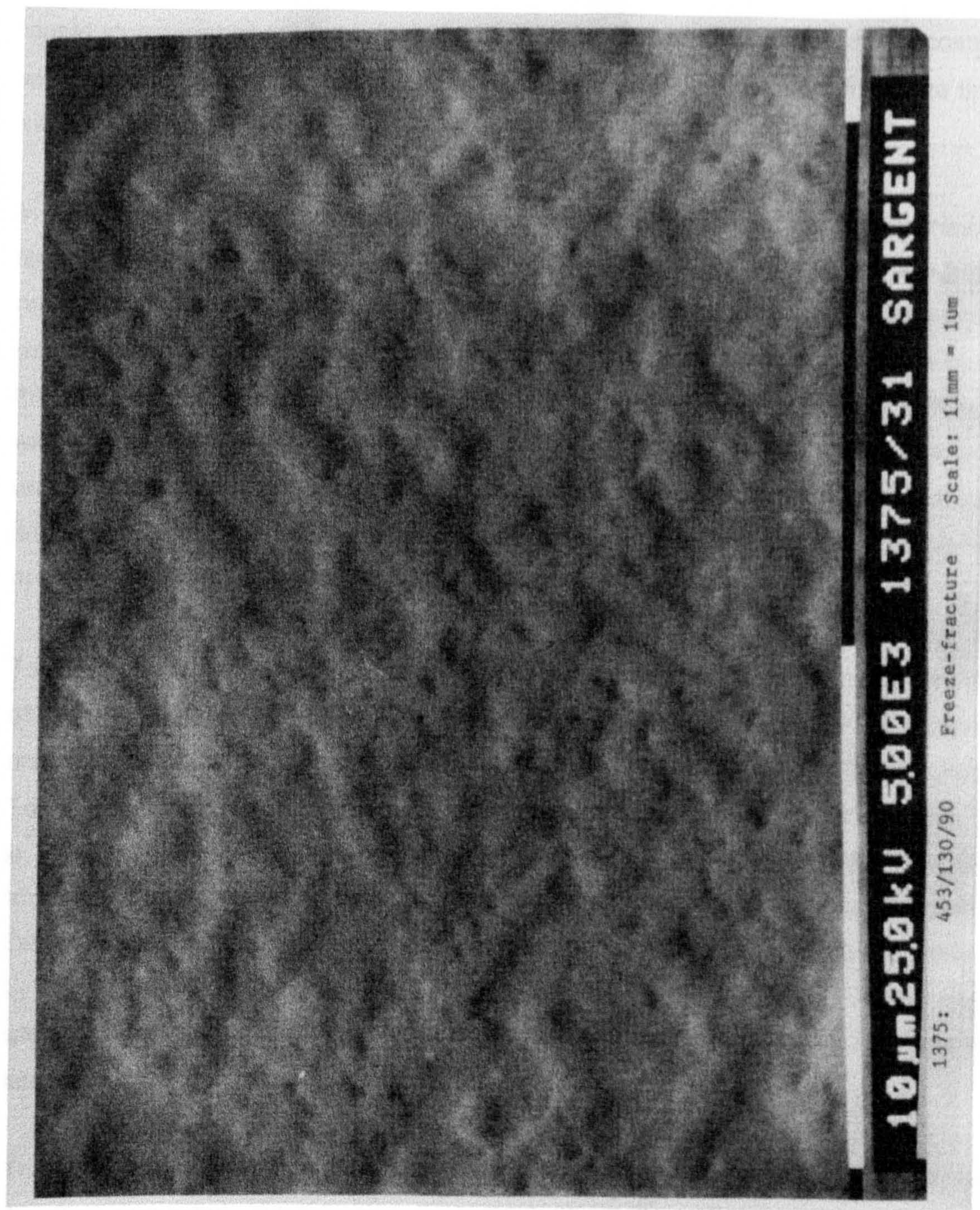


Figure 55 Latex film A(33) Postvulcanised for 90 min. at 130 °C

tensile strength need not be well-integrated and that at 130°C crosslinks are decomposing, with corresponding decreases in modulus and tensile strength, whilst at the same time film integration is improving.

In Section 4.5 the effect of leaching upon the physical properties of postvulcanised latex films is described. Leaching films with water was expected to improve film integration by removing water-soluble non-rubbers from the surfaces of latex particles and allowing better rubber- rubber contact. However, when a leached film was examined by SEM (Figure 56), the structure still appeared largely particulate and no obvious improvement in integration was observed (cf. Figure 46, an unleached film, in Section 4.7). Films were also leached with organic solvents. Which were also expected to improve film integration by dissolving, and removing, some of the unreacted compounding ingredients and swelling the rubber-network, leading to increasing mobility of the rubber molecules.

Toluene is a very good swelling solvent for rubber, and its absorption increases the mobility of rubber molecules; this was expected to increase particle integration by allowing the unconstrained chain-ends to move across particle boundaries to form entanglements. Toluene is also a good solvent for dithiocarbamate accelerators and sulphur and is, therefore, capable of removing unreacted compounding ingredients for the films, leading to a more homogeneous material. Toluene left in the films after they were removed from the leach liquid was allowed to evaporate for several days before the films were examined by SEM. When the micrograph for a film leached with toluene (Figure 57), was compared with one for an unleached film (Figure 58) there was no apparent improvement in film integration.

The solvents acetone and alcohols cause only a small amount of swelling in rubber but will dissolve unreacted sulphur and antioxidant 2246. They were also used to leach postvulcanised latex films. When the micrograph for an unleached film (Figure 58) was compared with those for films after leached with hot acetone (Figure 59) and with hot IPA (Figure 60) there was little visible effect upon film integration for these postvulcanised films.

Leaching postvulcanised latex films with water or organic solvents made no apparent difference to the physical structure of the films. The structure being largely fixed by the crosslinks in the film. Therefore, swelling solvents were used to treat natural rubber latex and

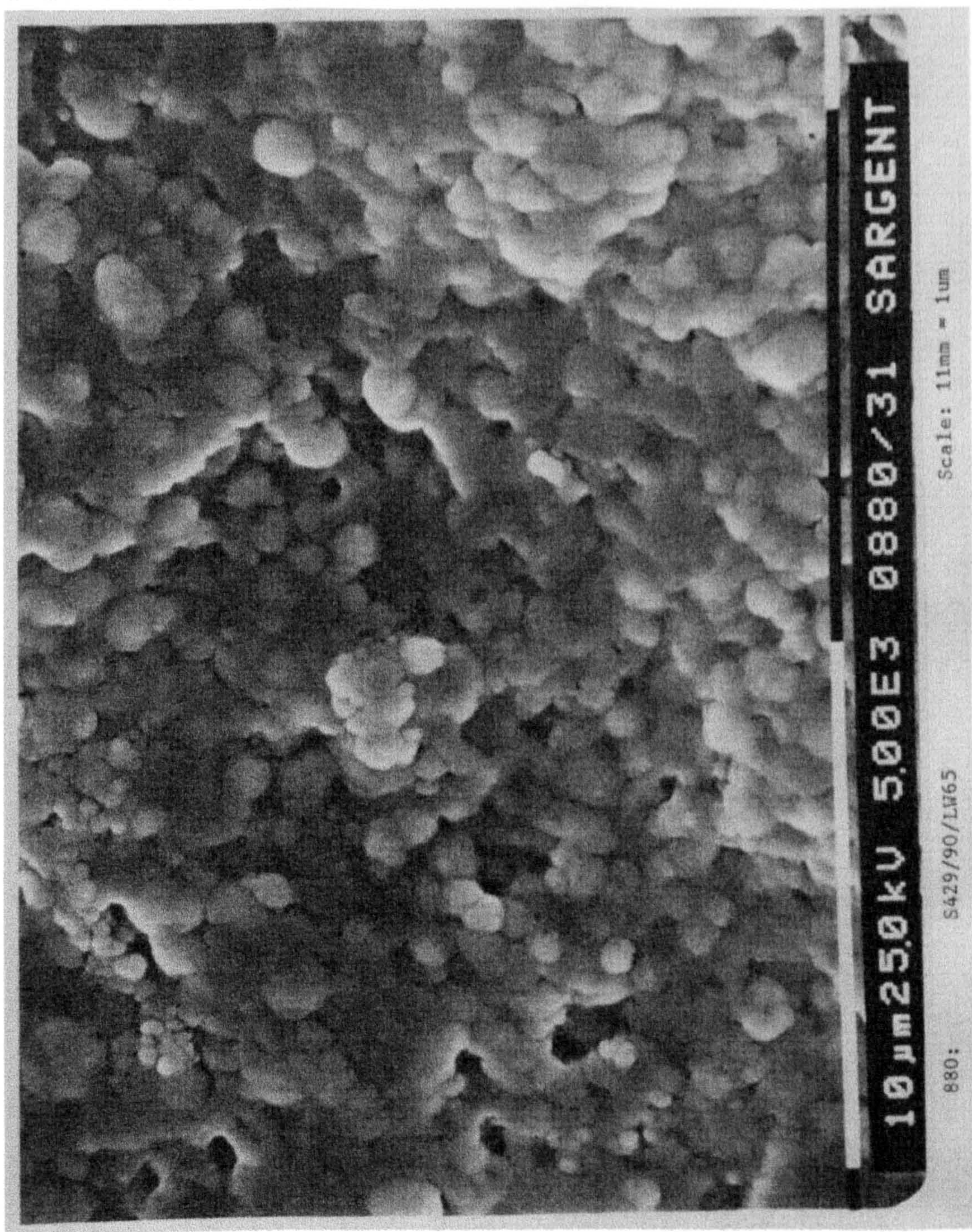


Figure 56 Latex Film Postvulcanised for 90 min. at 90 °C Followed by an Aqueous Leach for 65 h. at Room Temperature

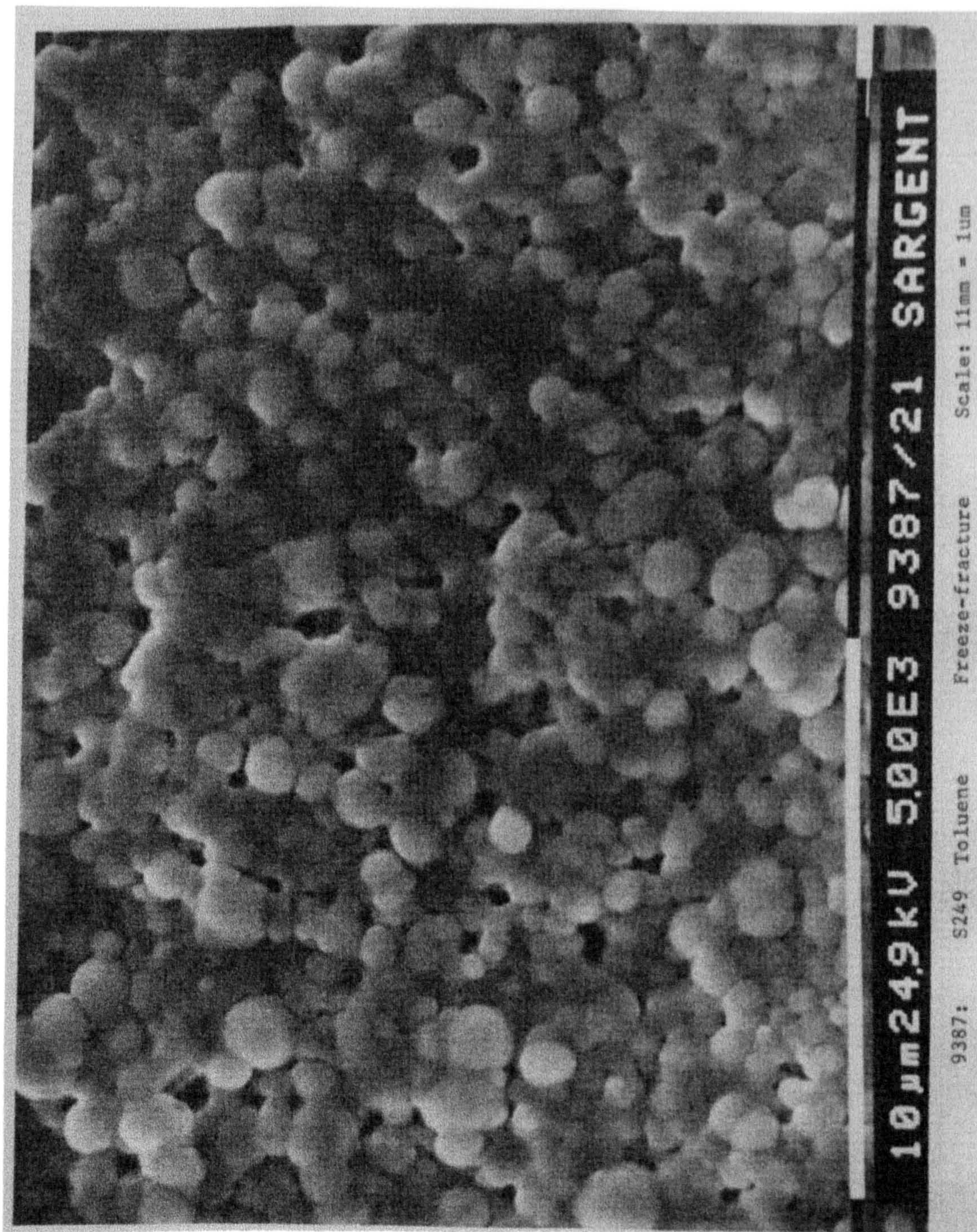


Figure 57 Water-Leached Postvulcanised Latex Film Further Leached with Toluene

Film postvulcanised for 90 min at 90°C. Leached with deionised water for 24h at room temperature and allowed to dry. Further leached with toluene for 45 min.

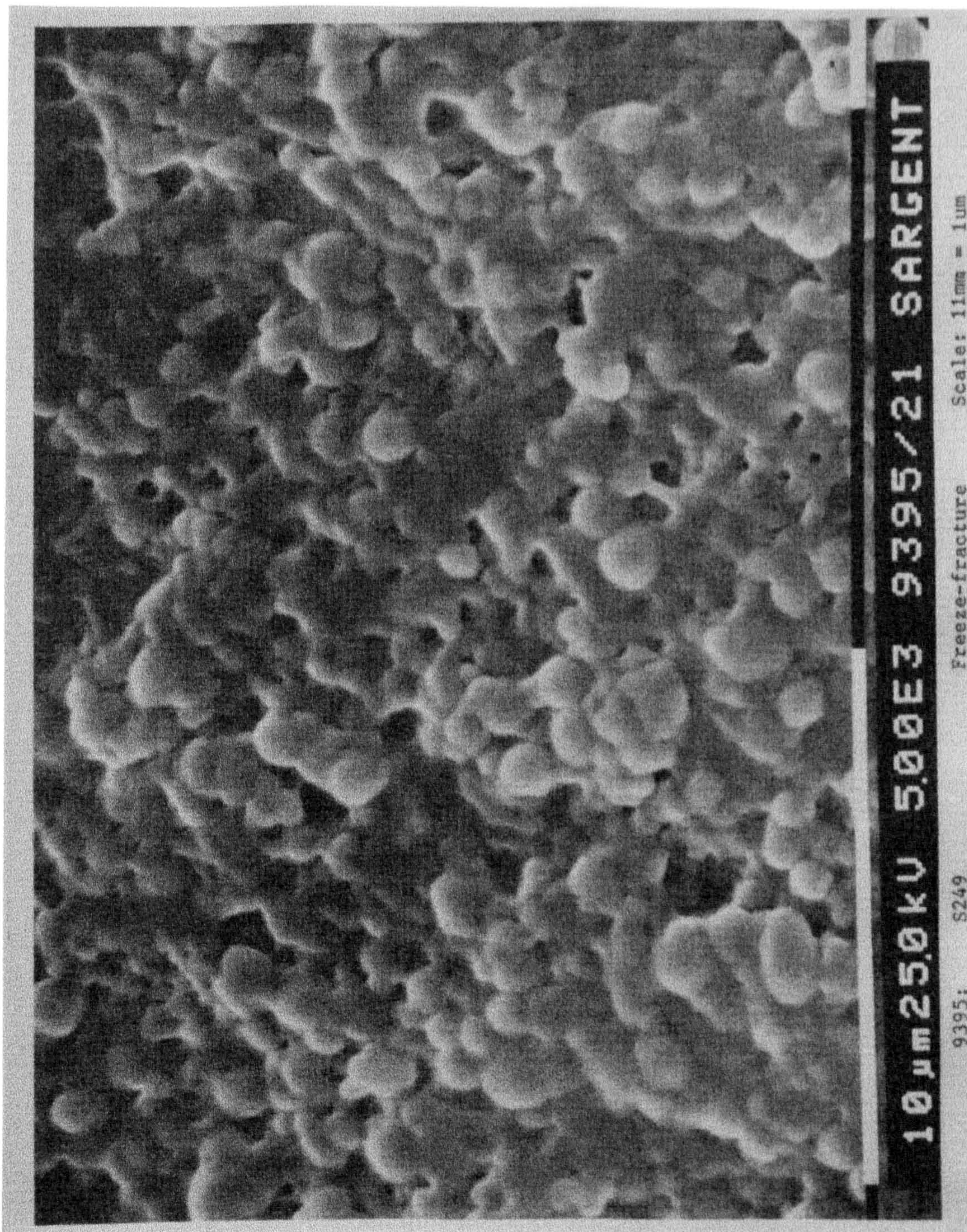


Figure 58 Water-Leached Postvulcanised Latex Film No Further Leaching
Film postvulcanised for 90 min at 90°C. Leached with deionised water for 24h at room temperature and allowed to dry.

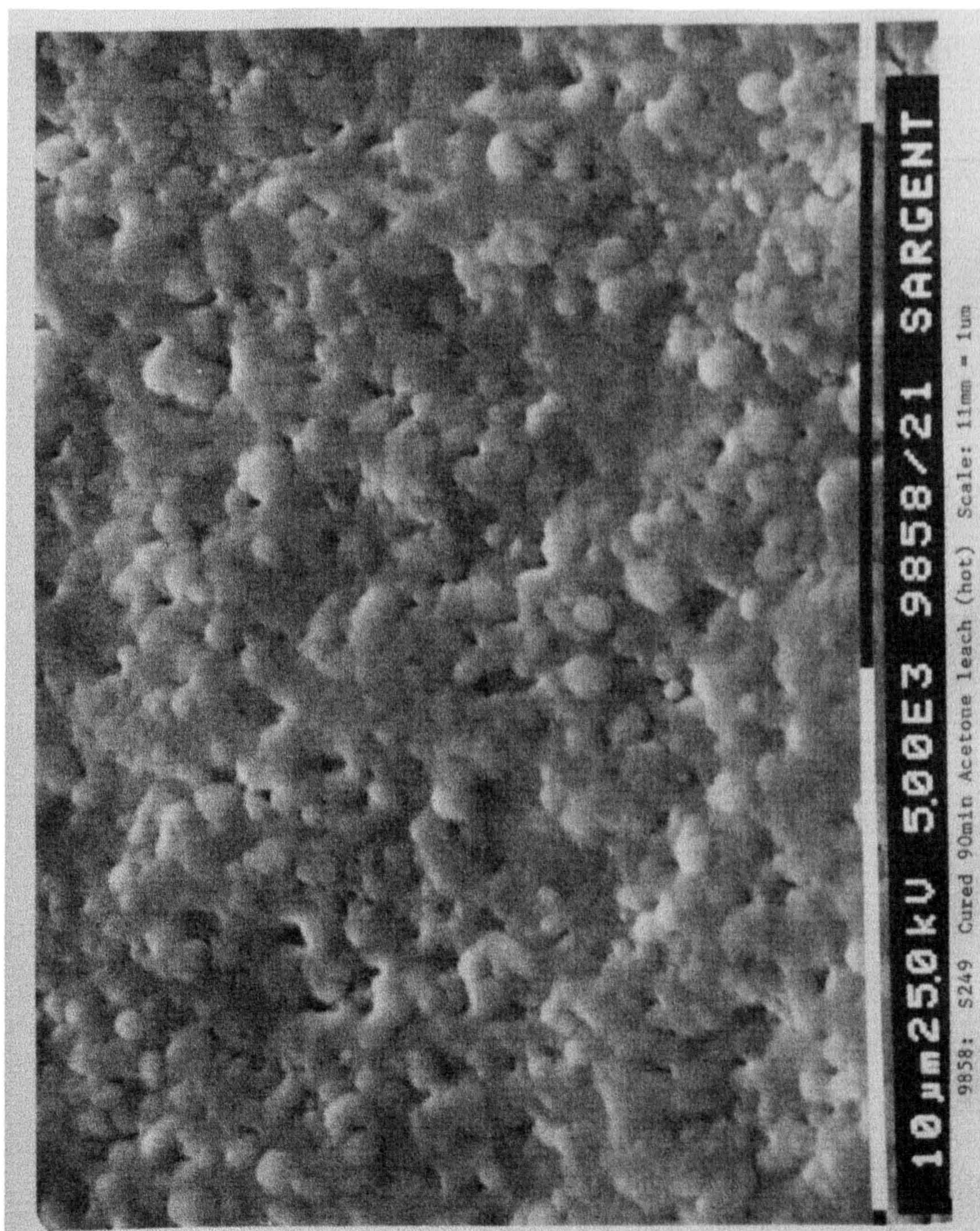


Figure 59 Water-Leached Postvulcanised Latex Film Further Leached with Hot Acetone

Film postvulcanised for 90 min at 90°C. Leached with deionised water for 24h at room temperature and allowed to dry. Leached with acetone in a Soxhlet extractor for 6.25 h

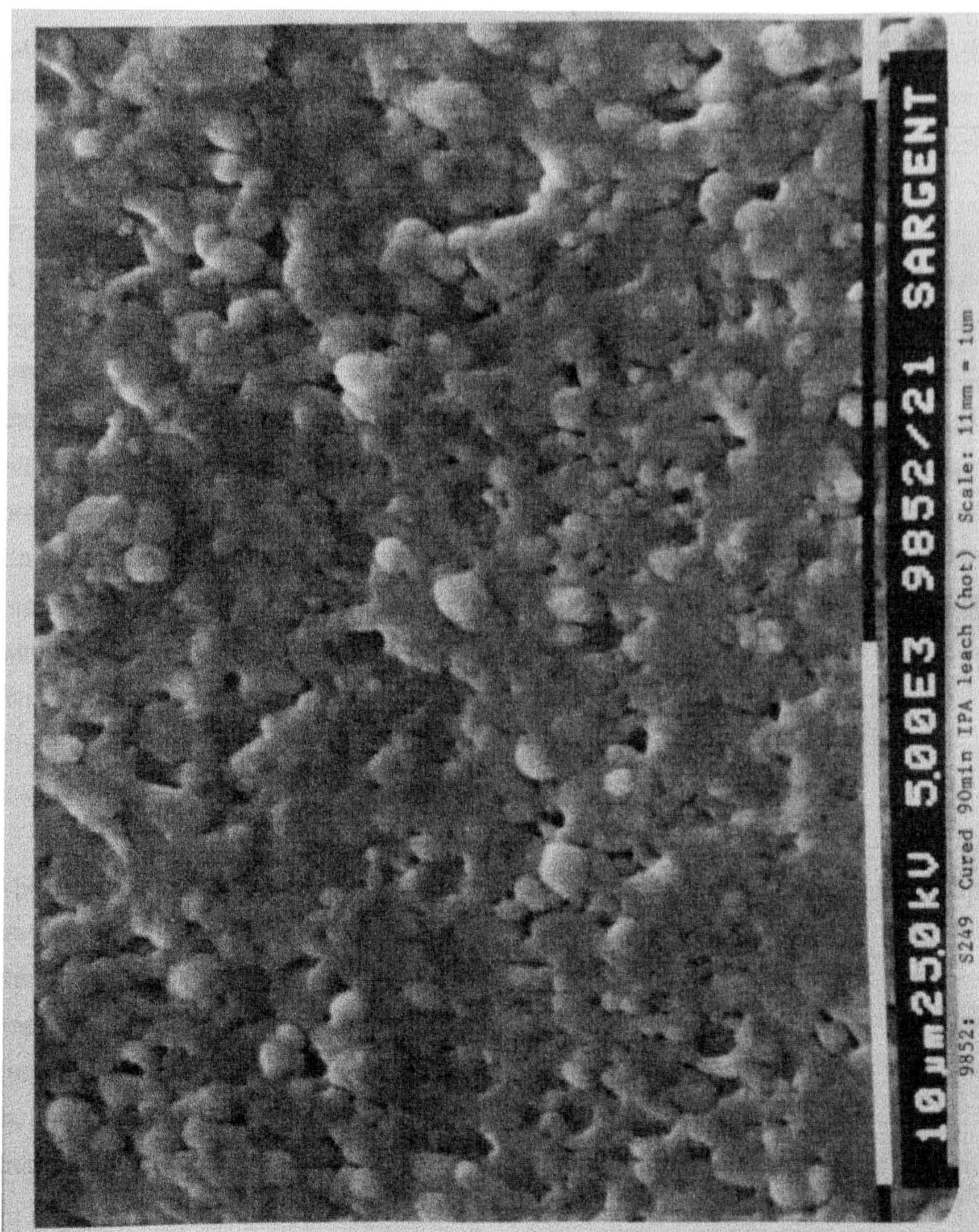


Figure 60 Water-Leached Postvulcanised Latex Film ,Further Leached with Hot Propan-2-ol (Isopropyl alcohol (IPA)

Film postvulcanised for 90 min at 90°C. Leached with deionised water for 24h at room temperature and allowed to dry. Leached with IPA in a Soxhlet extractor for 6.25 h

latex films before sulphur crosslinks were introduced into the films. In Section 4.7.2 the treatment with swelling solvents of unvulcanised cast films is described (see Figures 48 and 49). These films did show improvements in particle integration.

Toluene was also added to natural rubber latex in the form of an emulsion (see Section 4.7.3). The addition of the emulsions produced films with improved particle integration. Figure 61 shows the cross-section of a postvulcanised film prepared from natural rubber latex and a toluene emulsion which were mixed and allowed to mature for 13 days before the compounding ingredients were added and the film was cast, dried and vulcanised. Although integration is not complete, there are large areas where the particles have fused to become indistinguishable (cf. Figure 44 and Figure 48). Figure 62 shows a postvulcanised film prepared from a compounded latex mixed with a toluene emulsion and allowed to mature for 22 days before the film was cast and vulcanised. It is a very well-integrated film with only a few vestigial particles visible. In this case, in addition to postvulcanisation in the film, prevulcanisation occurred in the latex during the maturation period (see Section 4.7.3). The long periods during which the natural rubber latex particles were in contact with the toluene led to much better integrated films.

The presence of toluene in the uncrosslinked films or in latex appears to improve the degree of particle integration in the derived films (toluene was allowed to evaporate from the treated film for several days before they were examined by SEM). However, the improvements in particle integration do not produce significant increases in tensile strength (see Sections 4.7.2 and 4.7.3). In the case of unvulcanised latex films, the tensile strength is in any case very low but in the cases of postvulcanised latex films, the differences between films made with and those without the emulsions in the latex were not significant.

In summary, cryo- SEM can be used to examine film integration but will only distinguish gross changes in the structures of the films. It is not capable of distinguishing between unvulcanised, prevulcanised and postvulcanised latex films. The micrographs indicate that latex films largely retain their particulate structure and fracture along existing particle boundaries, since particles seen in the films or "holes" are seen where particles have been pulled out.

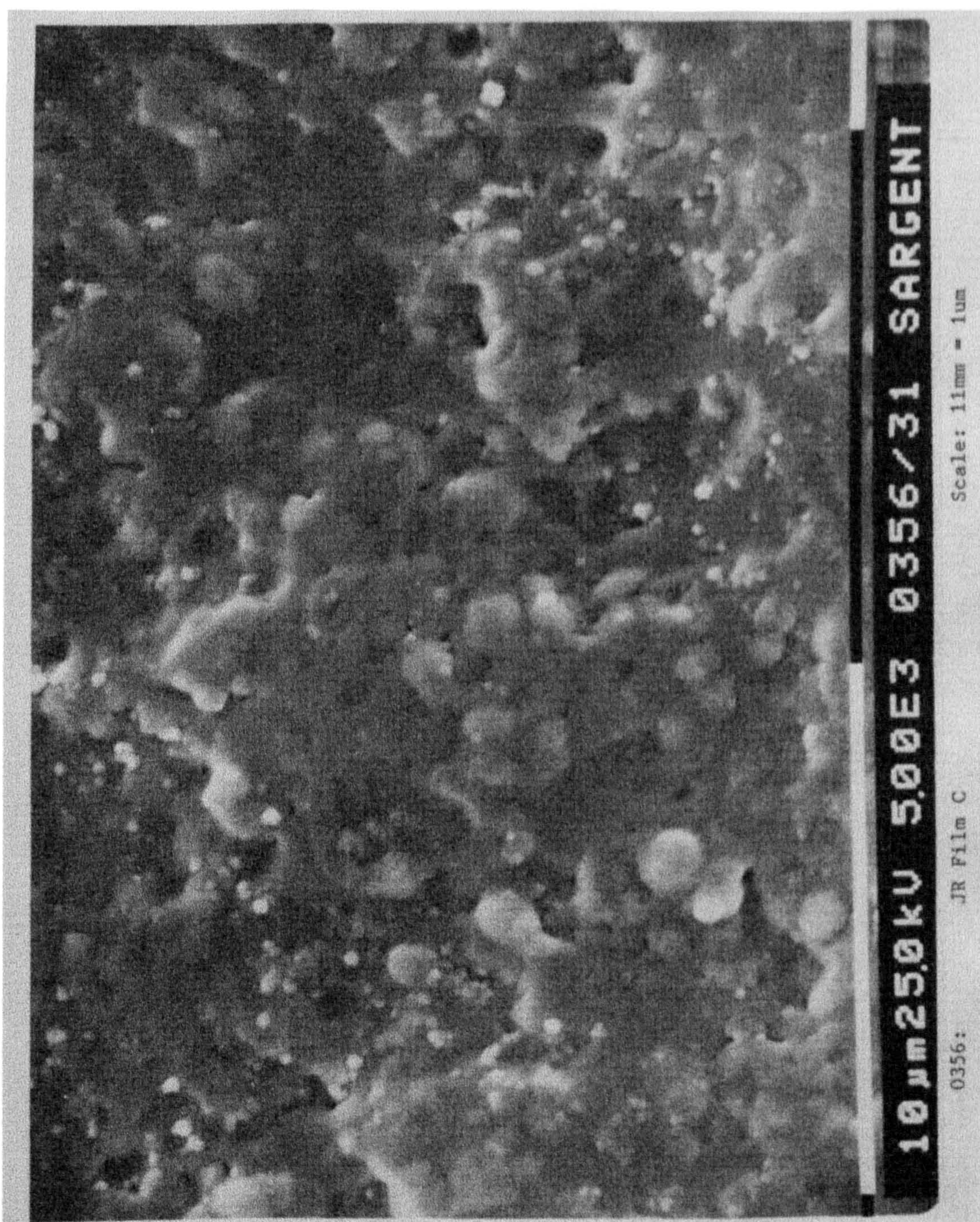


Figure 61 Postvulcanised Latex Film Prepared from HA Latex Matured with a Toluene-containing Emulsion before Compounding

HA latex and an emulsion containing toluene were mixed and allowed to mature at room temperature for 13 days before compounding ingredients were added (see Formulation A, Table 10 , Section 3.1.2). The film was cast, dried and cured for 90 min. at 90°C.

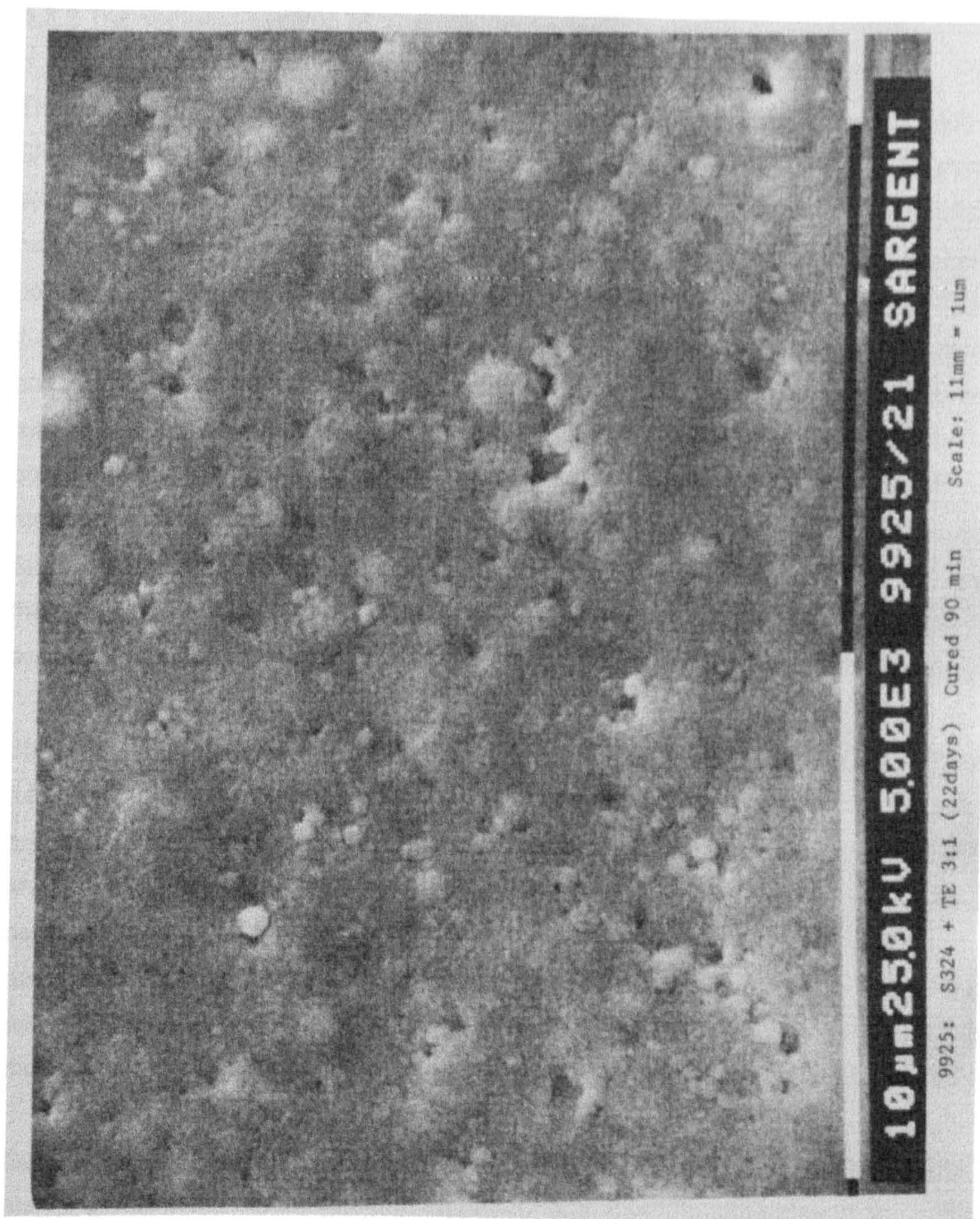


Figure 62 Postvulcanised Latex Film Prepared from Compounded HA Latex Matured with a Toluene-containing Emulsion

Compounded HA latex (A(25) and an emulsion containing toluene were mixed and matured for 22 days at room temperature before films were prepared and cured for 90 min. at 90°C.

5.3.2 Transmission Electron Microscopy

The method of preparing samples is described in Section 3.7.2 and is based upon that of Shiibashi⁷⁶. It has also been used by Cook et al to examine crosslink distribution in vulcanised blends of rubber^{93,94}. The rubber was swollen to equilibrium with a polymerisable monomer, styrene, producing an expanded rubber network. Then the styrene was polymerised, fixing the rubber network in an expanded state. As the polystyrene polymerised it and the rubber formed separate phases. Ultra-thin sections were cut from the composite and they were stained with osmium tetroxide. Osmium tetroxide stains and further fixes the rubber but has no effect upon the polystyrene. This provides the contrast between the polymers which allows observations to be made by TEM. The micrographs show dark mesh-like areas of rubber contrasted against pale grey or white areas of polystyrene. Shiibashi attributed the dark strands to individual network chains but Cook et al suggested that they represent bundles of network chains which form on phase separation as a ternary system of rubber, polystyrene and styrene develops during the polymerisation process⁹⁴.

Shiibashi used this embedding technique to examine gel and sol fractions from natural rubber and polyisoprene. He found areas of the gel where the rubber network was densely packed and parts where it was sparse. In the sol he found a dispersion of small particles (a few hundred angstroms in diameter). The same technique was also used to look at the network structure of crosslinked polyisoprenes of different crosslink densities. The micrographs showed mesh-like networks, the more highly crosslinked rubbers having a smaller "mesh" size. Shiibashi was able to correlate the square root of the mean area of the network "mesh" with the average molecular mass between crosslinking points (M_c).

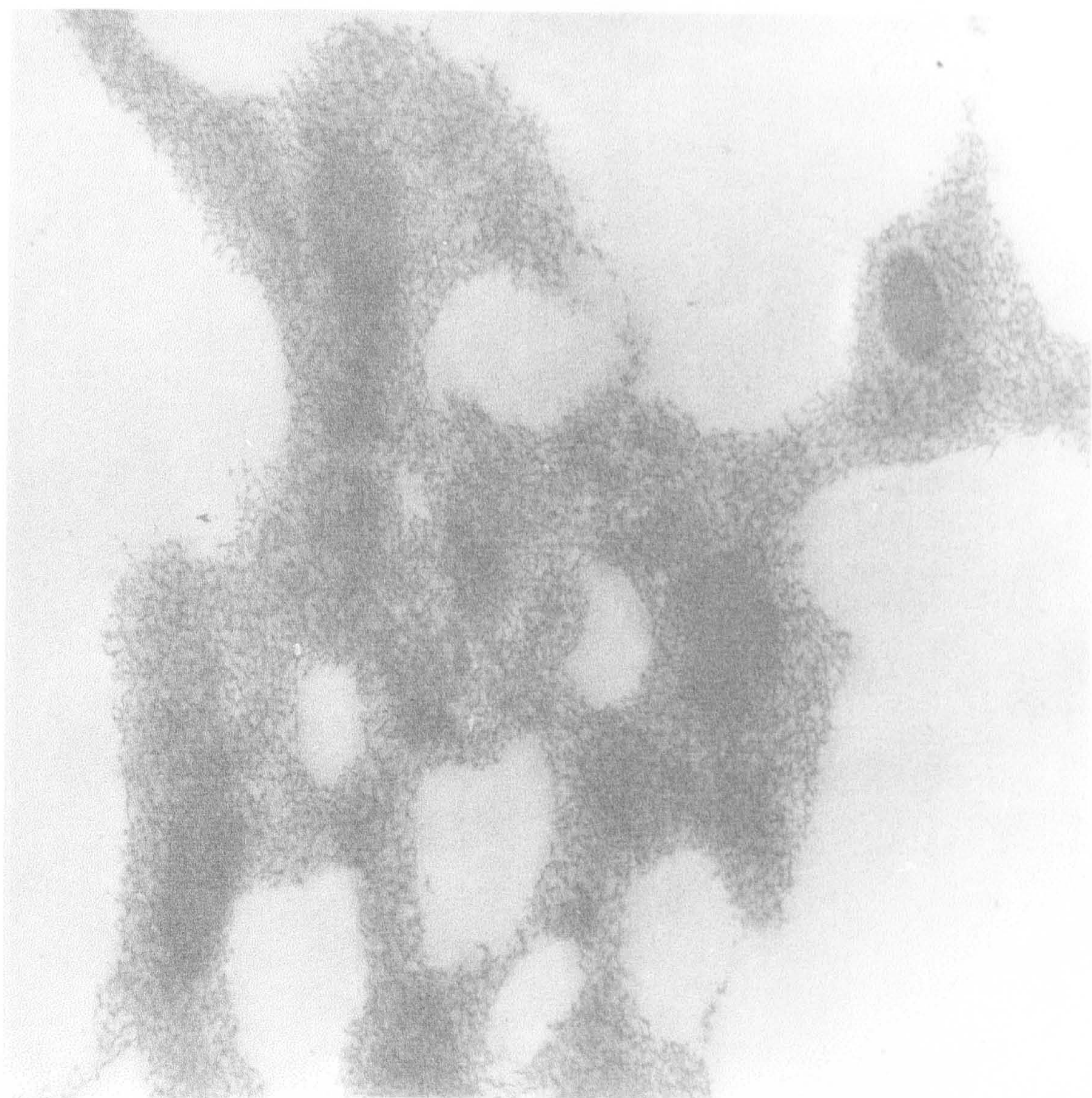
Cook et al also used the same method to examine crosslink distribution in vulcanised blends of rubber^{93,94}. While expressing reservations about the derivation of the relationship between "mesh" (cell) size and M_c , they also found that there was a clear correlation between them. Applying the technique to vulcanised blends they were able to identify the separate component rubbers, and to estimate their crosslink densities.

It is clear that the mesh structure is characteristic of the crosslink density of the rubber and is useful in providing a method for examining film integration. Therefore, Shiibashi's method of preparing and examining samples was applied to a number of natural rubber latex films which had been vulcanised by different methods and which had been subjected to a range of cure conditions. A number of interesting observations about film structure were made.

A micrograph of an HA latex film (to which no compounding ingredients had been added) is shown in Figure 63. The coherent rubber phase is punctuated by domains of polystyrene which have apparently phase-separated from the swollen gel as polymerisation occurred. There are no signs of discrete latex particles. There are areas where the rubber network is denser and these are probably volumes of gel, which are known to be present in natural rubber latex⁹⁵. Similar features were observed by Shiibashi⁷⁶. A sample of the same film which had been heated for 60 minutes at 130°C is shown in Figure 64. Since it contains no compounding ingredients sulphur crosslinks cannot form. However, exposure to the higher temperature might be expected to lead to increased mobility of the rubber molecules across particle boundaries. The film has fragmented but does not show discrete latex particles. The areas which are thought to be gel are seen again. The film may well once have been reasonably homogeneous but without the presence of crosslinks will have been extensively swollen by the styrene. Since the swollen gel would be very weak it could easily fragment in the styrene.

A micrograph of a purely prevulcanised film is shown in Figure 65, an irradiation prevulcanised latex film. Carbon-carbon crosslinks have been formed between rubber molecules in the latex particles and there is no possibility of postvulcanisation occurring in the film. The micrograph shows a structure made up of discrete particles. Separation of the individual particles in the film was brought about by swelling it with styrene before polymerisation. Some strands can be seen between neighbouring latex particles but these are relatively few. A micrograph of a sulphur-prevulcanised latex film (Figure 66) shows similar features to those of the irradiation-prevulcanised latex film. The elliptical shapes of the latex particles in the micrographs are thought to be the result of compression arising during the cutting of thin sections from the polymerised block. Figure 67 is a micrograph of the previous sulphur-prevulcanised latex film which had been heated for 60 minutes at 100°C. The latex film contained some unreacted vulcanising ingredients. Therefore, postvulcanisation also occurred in the film on heating. This section has suffered badly from compression and the particles have been distorted. However, comparison with Figure 66 shows that the latex particles have separated far less on swelling with styrene and there appear to be more strands of rubber chains between the particles.

This TEM technique allows a distinction to be made between unvulcanised and prevulcanised latex films and also discriminates between a purely prevulcanised film and one which has been heated to bring about postvulcanisation.



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Scale: 43mm = 1μm

Figure 63 Uncompounded HA Latex Film

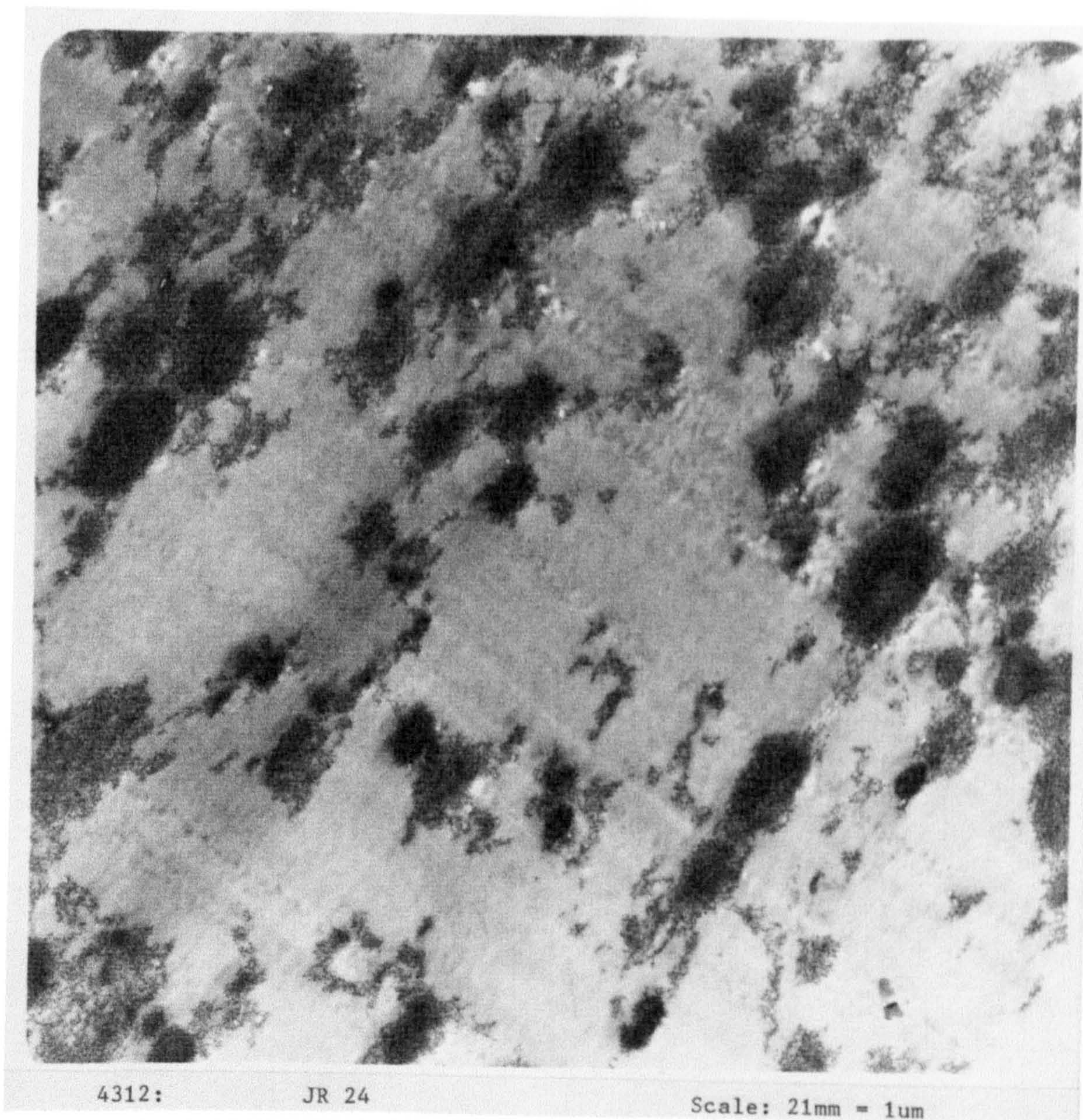


Figure 64 Uncompound HA Latex Film Heated for 60 min. at 130°C

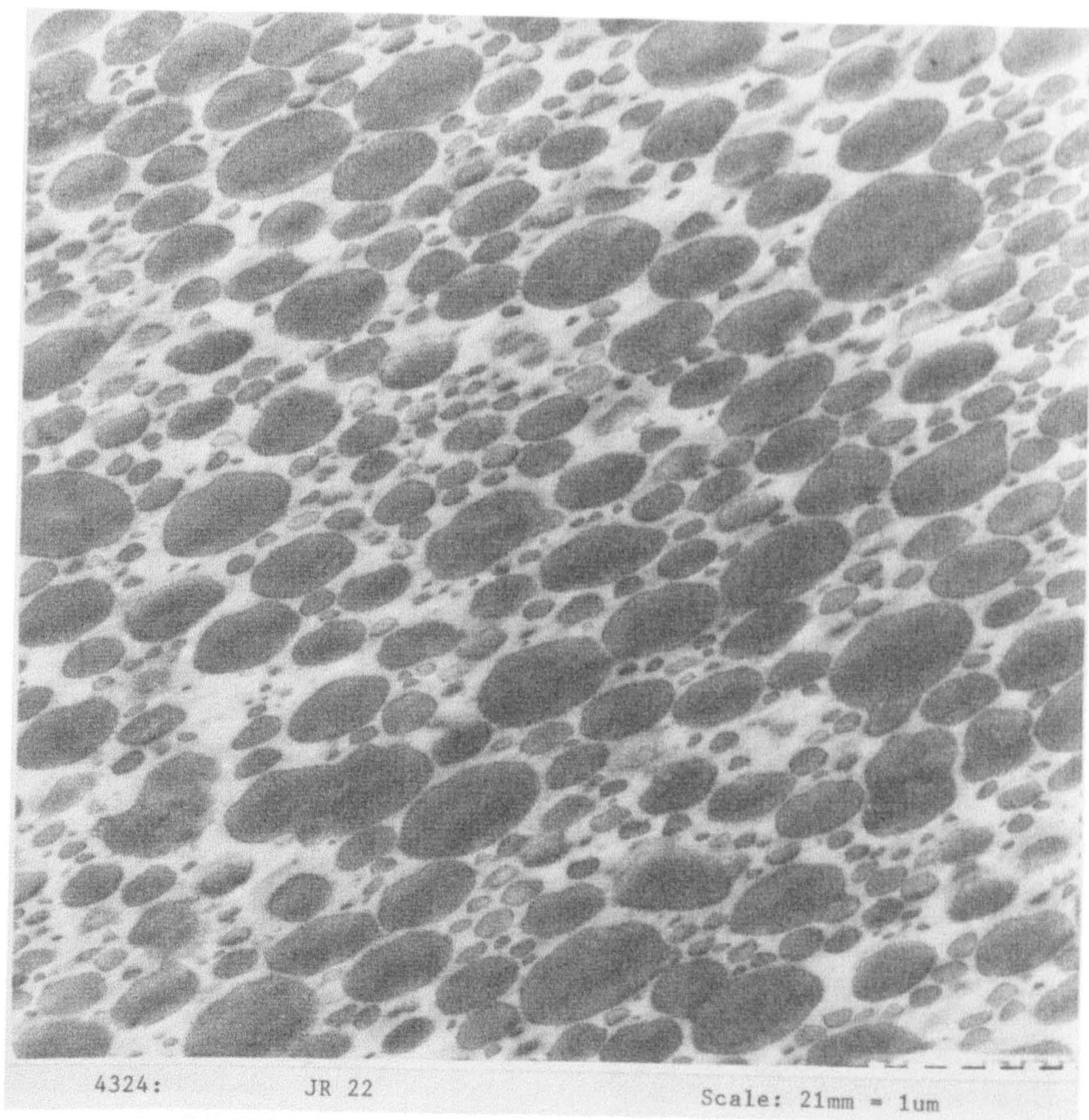


Figure 65 Irradiation Prevulcanised Latex Film

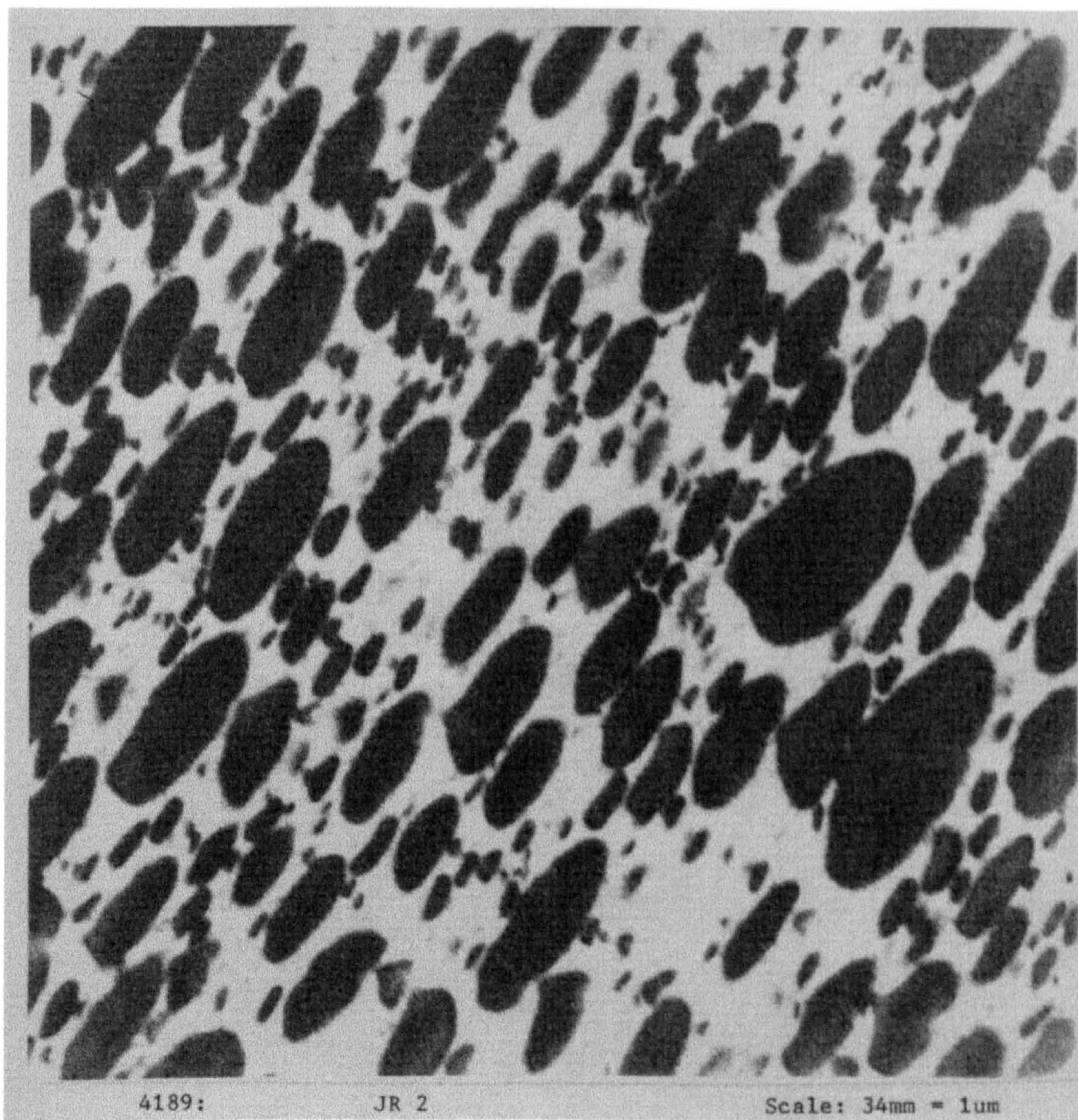


Figure 66 Prevulcanised HA Latex Film

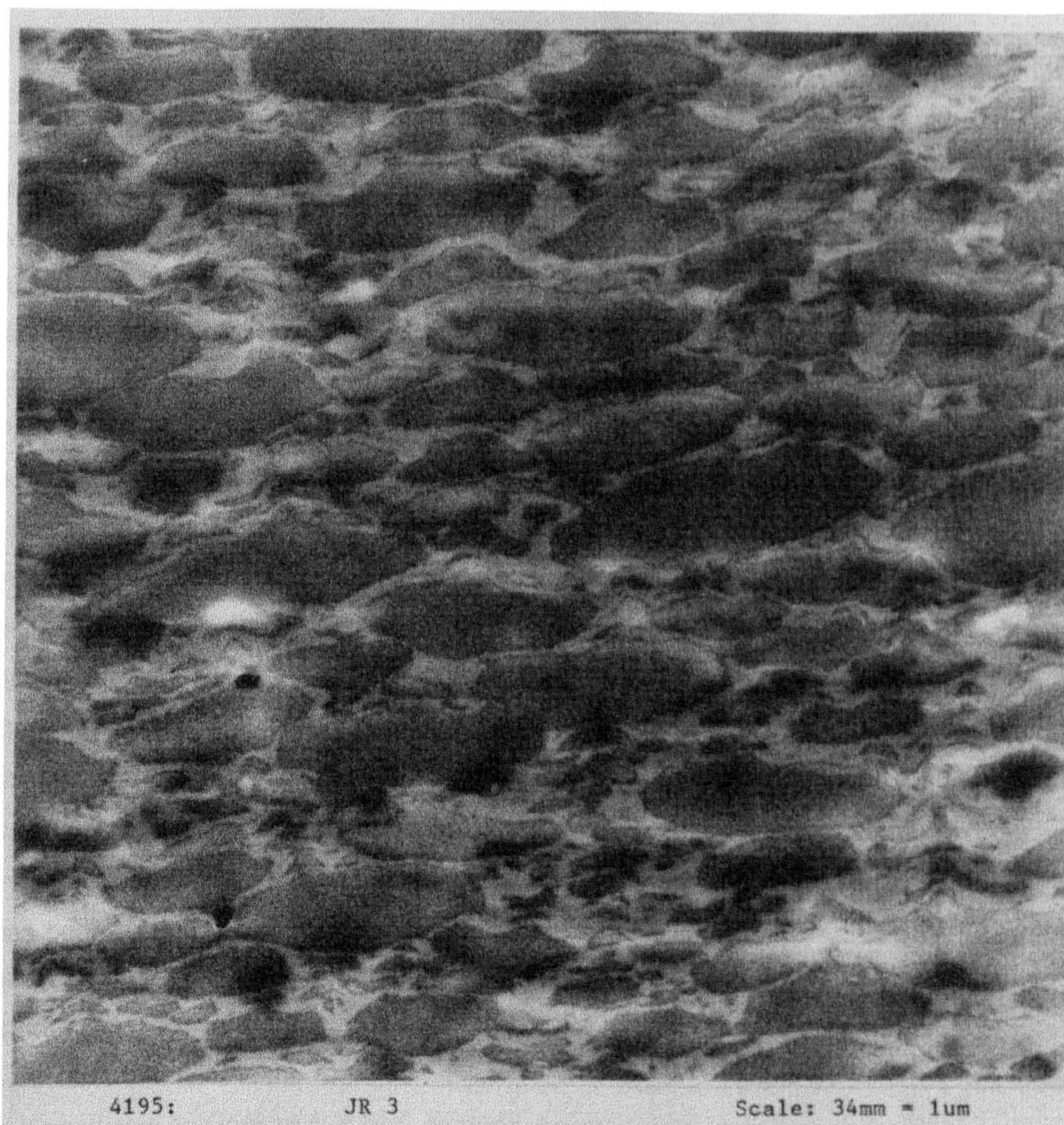


Figure 67 Prevulcanised HA Latex Film Further Postvulcanised for 60 min at 100°C

The next series of micrographs shows how useful this TEM technique is in showing changes in film structure for postvulcanised latex films. A micrograph of an unheated compounded HA latex film (preparation A(33)) is shown in Figure 68. The rubber is largely dispersed in the polystyrene but there are some vestiges of particulate structure. The film was not expected to contain sulphur crosslinks and was, therefore, expected to be similar to an uncompounded HA latex film (cf. Figure 63). There are similarities in that the film has largely disintegrated, however, the signs of particulate structure suggest that even after a short time at room temperature some crosslinking may have occurred in the latex particles. Figure 69 shows a film postvulcanised for 3 minutes at 130°C (preparation A(32)). The film is particulate but the particles are quite close indicating that the rubber has absorbed less styrene prior to polymerisation. Now there are many rubber strands visible between individual latex particles, indicating rubber anchored in different particles. Figure 70 shows the film after 5 minutes heating at 130°C. It is clearly particulate but the separation between particles is less and there are more rubber strands between them. Figure 71) shows the film after heating for 10 minutes at 130°C. It is still made up of particles but some have merged and the separation of the others has decreased. Figure 72 shows a film after 15 minutes postvulcanisation at 130°C. Many of the particle boundaries have disappeared and there is hardly any separation between the remaining particles. In Figure 73, where the film has been heated for 20 minutes at 130°C, it is not possible to identify individual particles although there are a few pockets of polystyrene between particles scattered though the film. In Figure 74 the film had been heated for 30 minutes at 130°C. There is no evidence of particulate structure in the film. The larger areas of polystyrene seen in this film are similar to those noted by Cook et al in their samples and attributed to defects in the film⁹³.

This series of micrographs clearly showed improvements in film integration upon prolonged heating at 130°C. The physical properties of the films are recorded in Table 37 and Figures 42 and 43 (Section 4.6). Similar effects were seen when lower vulcanisation temperatures were used but the process was slower. Figures 75 and 76 show films heated at 110°C for 30 and 120 minutes respectively. Both films have a particulate structure but this is less marked in the film which had been heated longer. Figures 77 and 78 show the same effect for films heated at 90°C for 60 and 180 minutes respectively.

The micrographs suggest the following scheme for film integration in postvulcanised latex films. Initially crosslinking is concentrated within the latex particles: hence the initial particulate structure. As vulcanisation proceeds crosslinks are also formed between adjacent latex particles forming a more rigid structure: hence the increase in concentration of rubber strands between particles and their decrease in separation of the particles upon swelling with styrene. After prolonged heating some of the crosslinks begin to break down. When this occurs faster than the rate of crosslink formation it results in an overall loss of crosslinks in the film. At the same time, film integration increases with prolonged heating but it is a slower process than the loss of crosslinks. Therefore, a point is never reached where the film is fully integrated and none of the crosslinks formed have decomposed.

Further results show that leaching the film with water does not appear to have significantly improved film integration (see also Section 4.5.1). Figure 79 shows a film which has been postvulcanised at 90°C for 90 minutes then leached in water for 24 hours. The film is particulate, though the particles are close together and have many rubber strands between them. The structure of the film is similar to many of the micrographs of postvulcanised latex films discussed earlier.

To summarise, the extent of separation of rubber particles in the polystyrene matrix gives a qualitative indication of the degree of crosslinking between particles. Postvulcanised latex films in the early stages of postvulcanisation appear to be very similar to prevulcanised latex. Crosslinking appears to occur largely within the latex particles (which is where the rubber is concentrated) in the early stages of vulcanisation. At later stages, the micrographs indicate rubber chains bridging two or more latex particles (the chains being anchored in each latex particle).

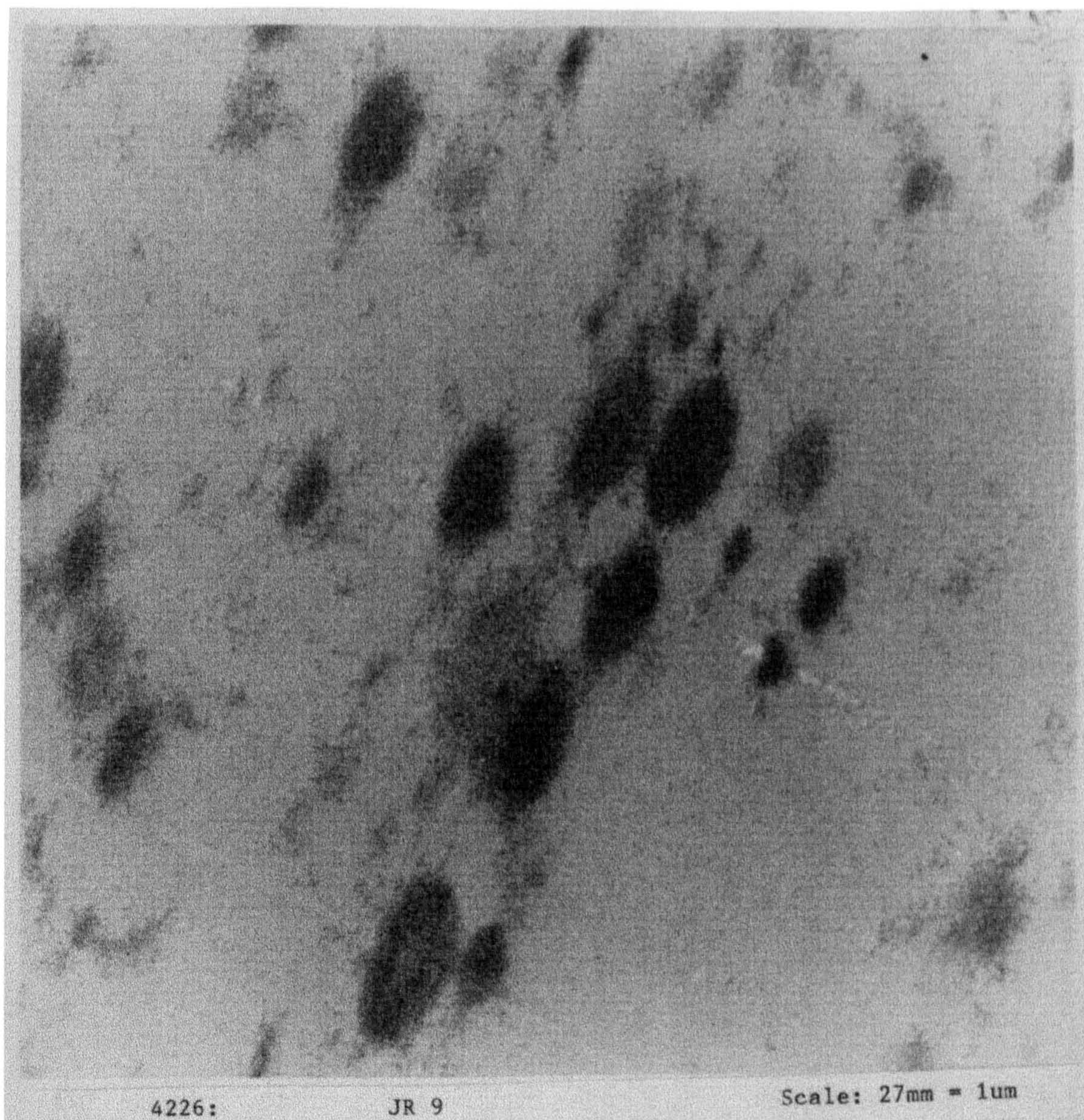


Figure 68 Compounded Latex Film Unheated (preparation A(33))

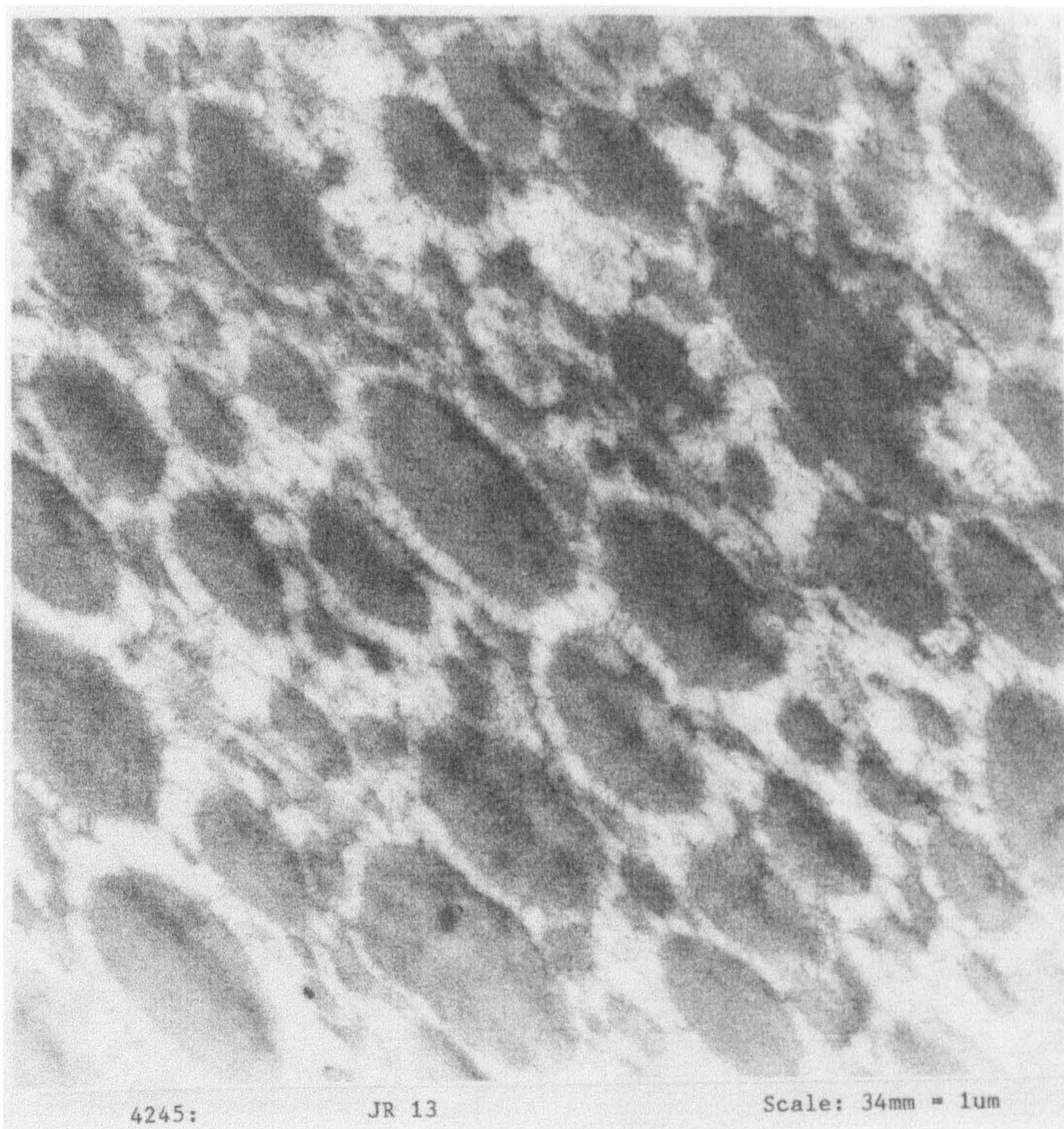


Figure 69 Compounded Latex Film Heated for 3 min at 130°C (preparation A(33))



Figure 70 Compounded Latex Film Heated for 5 min at 130°C (preparation A(32))

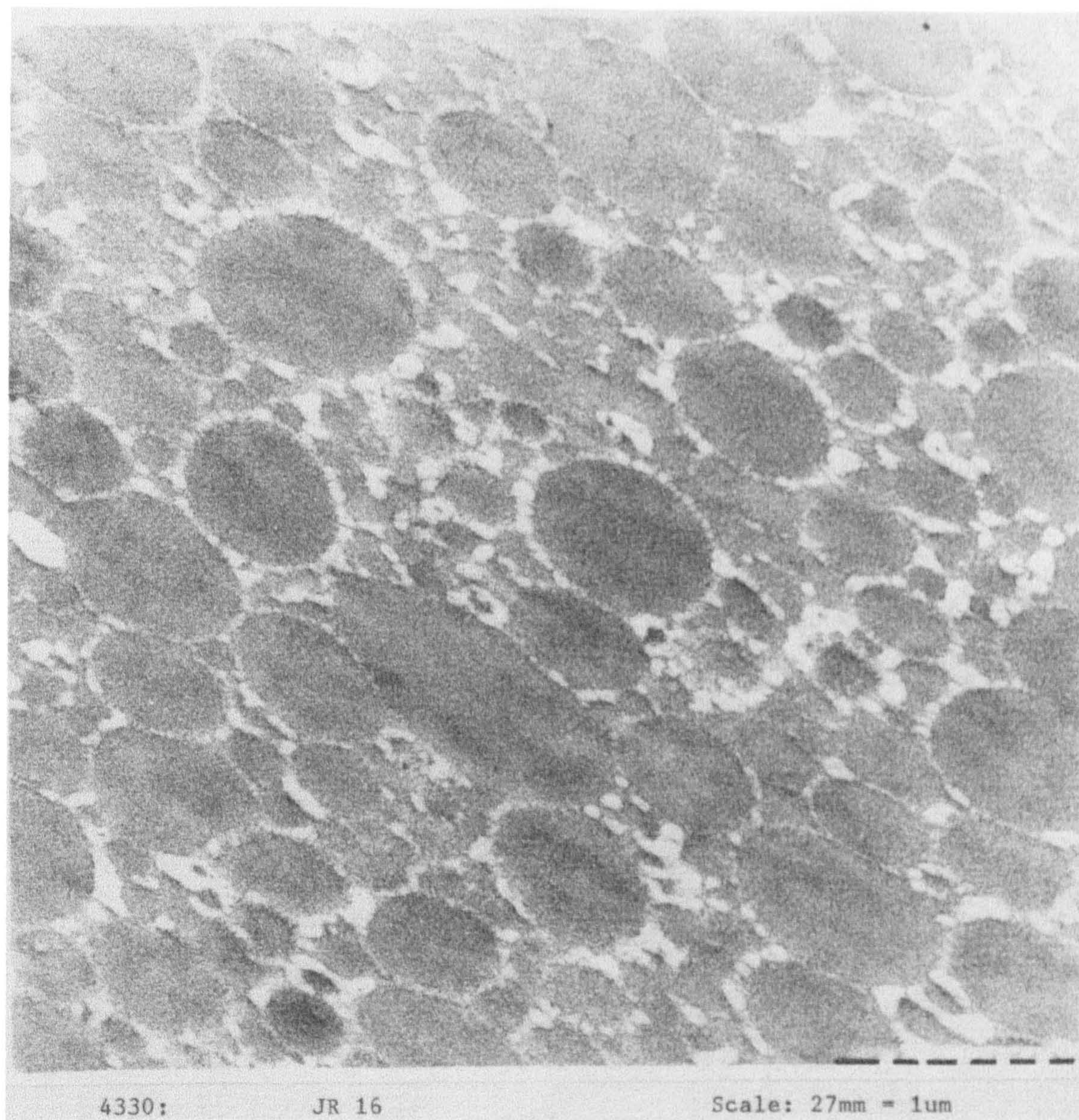


Figure 71 Compounded Latex Film Heated for 10 min at 130°C (preparation A(32))

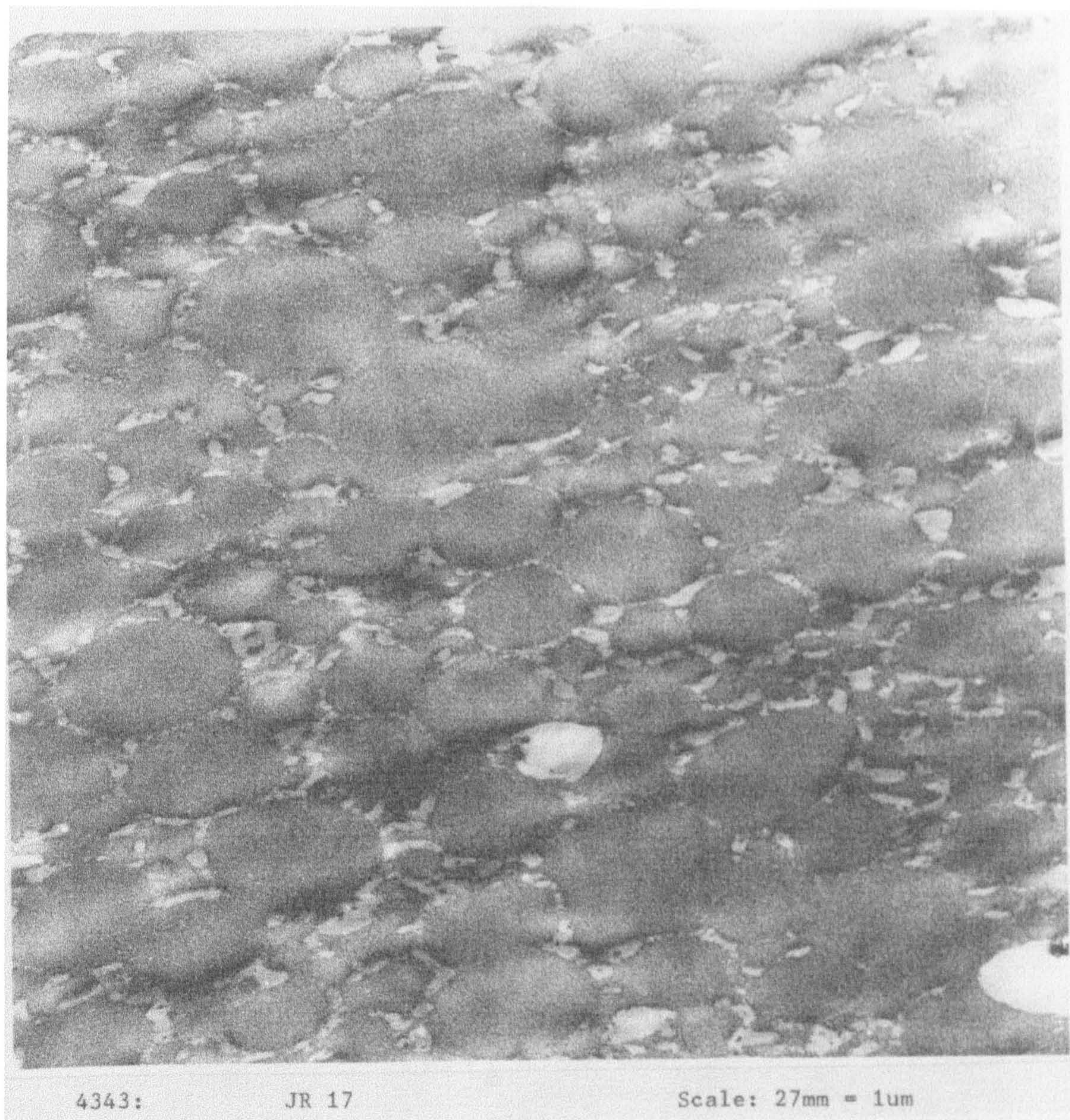


Figure 72 Compounded Latex Film Heated for 15 min at 130°C (preparation A(32))



Figure 73 Compounded Latex Film Heated for 20 min at 130°C (preparation A(33))



Figure 74 Compounded Latex Film Heated for 30 min at 130°C (preparation A(33))

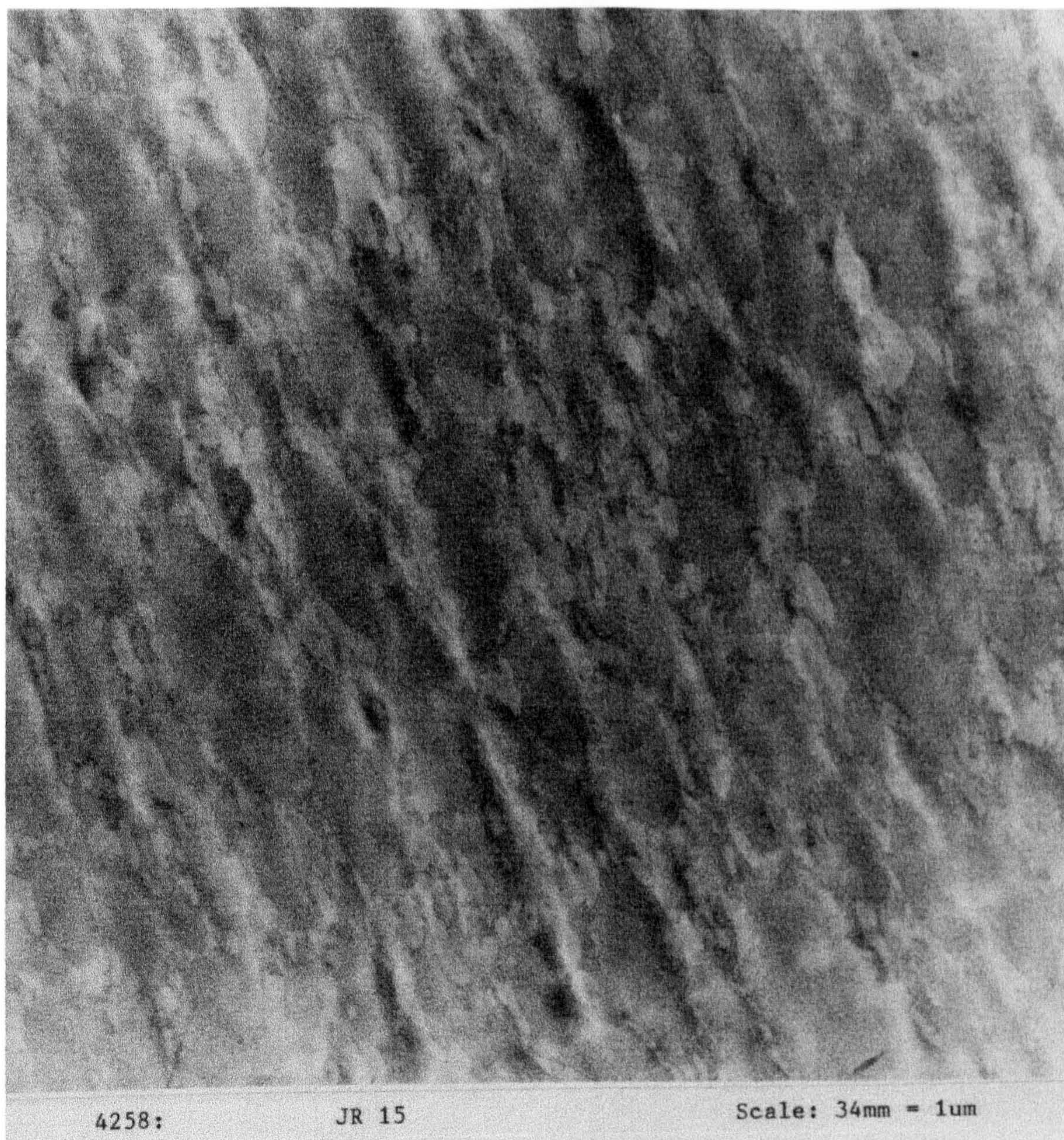


Figure 75 Compounded Latex Film Heated for 30 min at 110°C (preparation A(32))

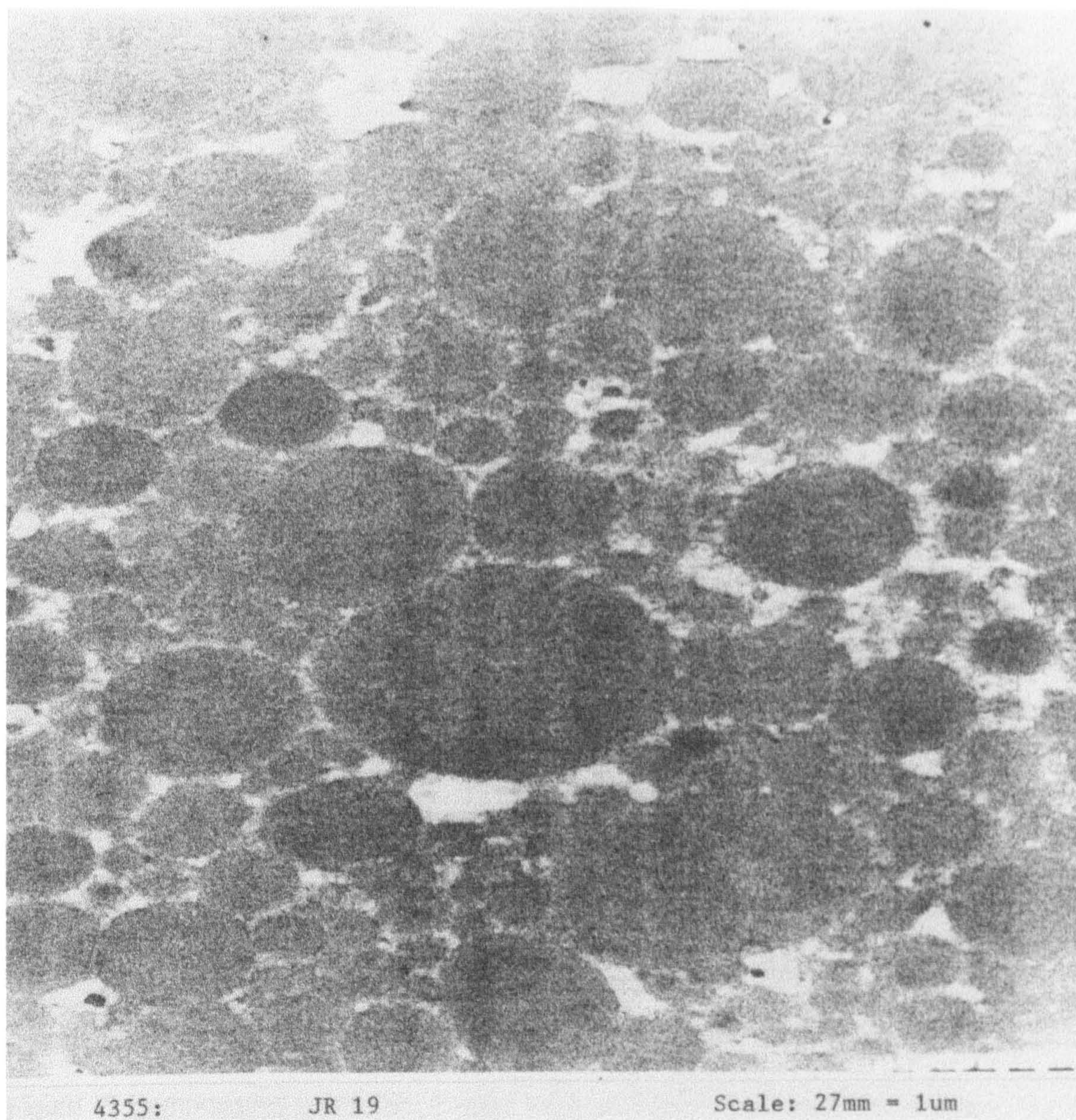


Figure 76 Compounded Latex Film Heated for 120 min at 110°C (preparation A(33))

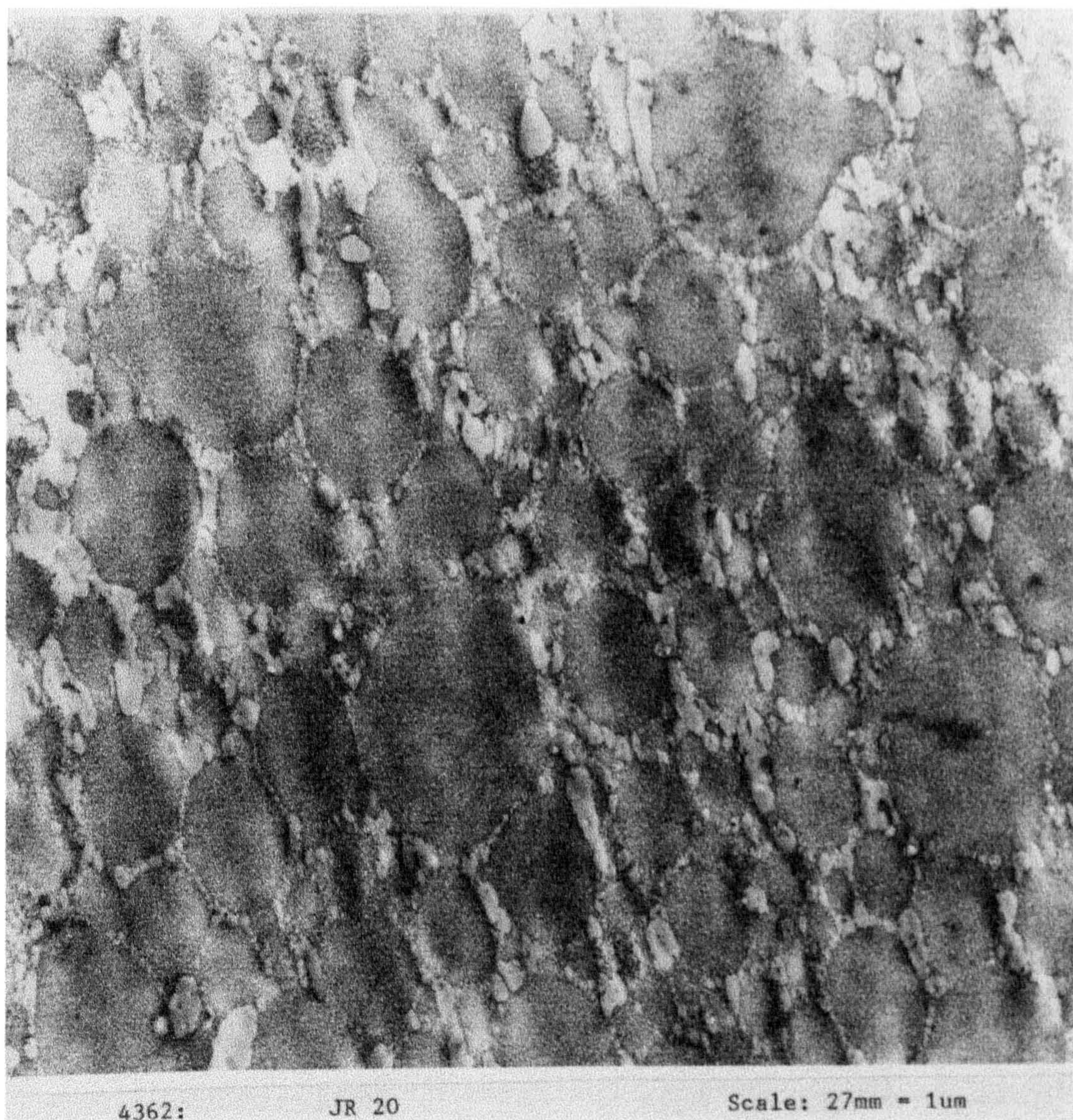


Figure 77 Compounded Latex Film Heated for 60 min at 90°C (preparation A(33))

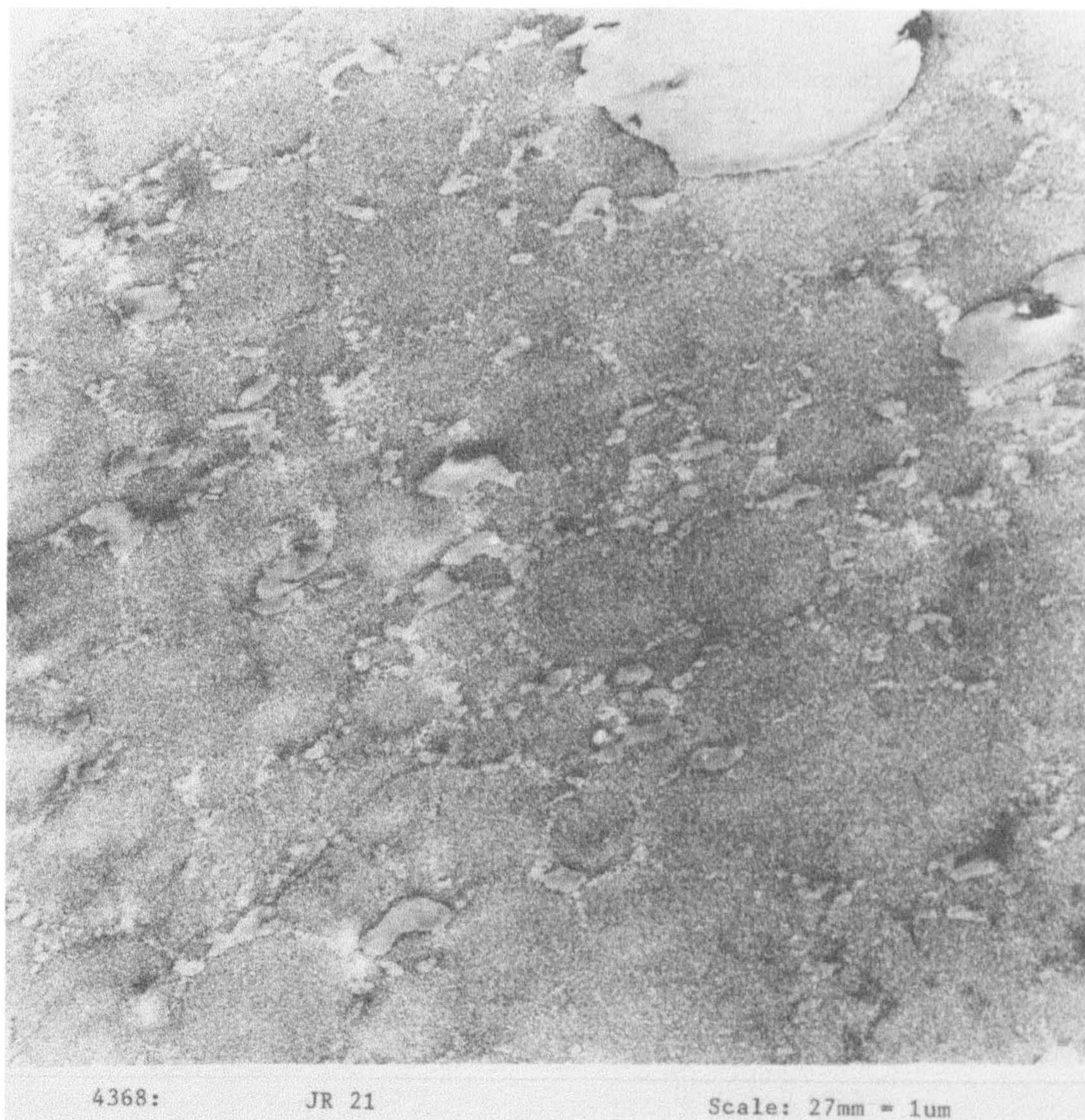


Figure 78 Compounded Latex Film Heated for 180 min at 90°C (preparation A(33))



Figure 79 Compounded Latex Film Heated for 90 min at 90°C followed by Aqueous Leach
24 h at Room Temperature (preparation A(31))

CHAPTER 6 : CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1 Introduction and Summary

In this study it has been possible to establish the tensile strength /modulus relationship for postvulcanised latex films using a number of accelerator systems and to compare it with those for prevulcanised latex films and dry rubber.

Processes which were known to affect the properties of prevulcanised latex films were examined using for their effect on postvulcanised latex films. These included stirring and maturation of the latex, conditions for drying films and leaching films with water and with solvents. Most of these processes had no significant effect upon the properties of postvulcanised latex films, the notable exception being stirring.

Two electron microscopy techniques were employed to examine the structure of latex films. Only gross differences in film structure could be distinguished using cryo-SEM. TEM on samples which had been swollen and embedded in polystyrene permitted discrimination between films which were prepared by prevulcanisation and those prepared by postvulcanisation. It was also capable of discriminating between films which had been vulcanised for different lengths of time. Both techniques highlighted the finding that postvulcanised latex films are not homogeneous and remain particulate after long heating/vulcanising times.

6.2 Stirring and Maturation

When latex films are cast, all the compounding ingredients (both dissolved and suspended) and the non-volatile components in the serum are incorporated in the dry film. This is not the case for coagulant-dipped films; here latex serum is expelled from the wet gel by syneresis and undissolved, suspended compounding ingredients are largely left behind in the latex.

The importance of having properly stirred latex prior to casting films has been demonstrated. Stirring is essential to produce a homogeneous latex for the preparation of postvulcanised latex films. The settlement of compounding ingredients from the unstirred latices produced films with considerably lower modulus and tensile strength. Stirring led to films with more consistent chemical compositions and physical properties. The average

relative standard deviations for the tensile strength of films prepared from unstirred latices was 19.5% compared with 10.1% for stirred latices (for maturation times of 2-24h); those for modulus were 5.3% and 4.4% respectively.

Maturation of compounded latices had little discernible effect upon the final physical properties of the films. There was no significant effect upon modulus and only a very small increase in tensile strength after longer maturation times (16h and 24 h). Provided that the compounding ingredients were present and homogeneously distributed in the film, upon postvulcanisation, the physical properties of the resulting films were much the same irrespective of the maturation time of the latex. Whilst in prevulcanisation, the dissolution of sulphur and accelerator in the serum and transfer to latex particles is an important preliminary to vulcanisation this does not appear to be the case in postvulcanisation. In postvulcanisation, the sulphur and accelerator in contact with the rubber, formerly present as latex particles, are able to dissolve, diffuse through the film and vulcanise it on heating.

6.3 Extraction of ZDEC from NR Latex Films

The determination of ZDEC in natural rubber latex films shows that there is a discrepancy between the amount of ZDEC added and the amount which can be extracted and analysed. This study has indicated that the unextractable material no longer exists as ZDEC in the rubber matrix. The discrepancy is thought to arise as the result of a chemical reaction between a portion of the ZDEC with other materials in the latex film and not as the result of inefficient extraction. However, the inefficiency of a single static extraction has been highlighted. The amount of ZDEC which “disappears” from the film is related to the concentration of non-rubbers in the latex. With deproteinised natural rubber latex (DPNR latex) films the “loss” was smaller than for HA latex films, though still significant. Another interesting finding was that the decomposition of ZDEC in the HA latex film continued in the dry film for many weeks but that this did not appear to happen for DPNR latex films. This decomposition is analogous to the reaction observed by Loadman et al⁸¹ for ZDMC in latex but is believed to involve the nitrogenous non-rubbers rather than ammonium hydroxide (as postulated by Loadman), which would have evaporated when the films dried.

6.4 Drying Regimen

Latex particles have a surface covering of hydrophilic non-rubbers. In prevulcanised latex films the strength is derived not only from the sulphur crosslinks within the vestigial latex

particles but also, very importantly, from the interactions at the surfaces of the vestigial particles. Particle integration involving entanglements in adjacent latex particles is believed to be hindered by the presence of the non-rubbers. A thicker hydrated layer, in films which are incompletely dried, will further hinder the formation of such entanglements.

In the case of postvulcanised latex films, they are not significantly affected by the conditions of humidity under which they are dried before heating. It is somewhat surprising that the humidity of their surroundings during drying has no significant effect upon film strength, since reducing the thickness of the hydrated surfactant layer and bringing the particles closer might be expected to increase the number of entanglements and also to facilitate the formation of sulphur crosslinks in adjacent vestigial latex particles. However, entanglements and crosslinks appear to have formed to a similar extent for both sets of drying conditions. This contrasts with the behaviour of prevulcanised latex films which are sensitive to humidity during the drying and testing of films ⁸²(see also Section 4.4).

6.5 Leaching

Like drying conditions, leaching of prevulcanised latex films significantly affects their physical properties, increasing both modulus and tensile strength. Leaching removes many of the non-rubbers from the surfaces of latex particles, allowing better contact between rubber molecules and increased physical entanglements.

The maximum tensile strength of postvulcanised latex films is similar to that of leached prevulcanised latex films but occurs at a higher modulus, indicating that more crosslinks are present in the postvulcanised films (see Figure 50). Entanglements and surface interactions make a significant contribution to the strength of prevulcanised latex films, making them more susceptible to changes in film preparation and processing. The strength of crosslinks between vestigial latex particles in postvulcanised latex films is sufficient to compensate for any loss of strength due to change in the extent of entanglements or the surface interactions of the vestigial latex particles. This renders postvulcanised latex films largely insensitive to changes in film preparation and treatment (provided that the composition of the latex remains uniform, see Section 6.2).

When postvulcanised latex films were leached in toluene there were significant decreases in tensile strength. Toluene swells the network enormously and many physical entanglements may disentangle during swelling. However, why the tensile strength of

postvulcanised films should be so severely decreased whilst that of prevulcanised films is increased⁸⁴ after the removal of solvent is unclear. If the entanglements did not reform after deswelling that would also be expected to be the case for prevulcanised films.

6.6 The Effect of Vulcanisation Time and Temperature Upon the Physical Properties of Postvulcanised Latex Films Using ZDEC as the Accelerator

When films are postvulcanised for longer times or at higher temperatures, instead of observing increases in modulus, reversion is observed after the films have reached a maximum modulus. Free sulphur decreases throughout the vulcanisation period. When tensile strength reaches a maximum there is still a considerable proportion of free sulphur in the films. The free sulphur continues to decrease with increasing vulcanisation times, even after the maximum modulus has been reached, which means that sulphur must be combining with the rubber without forming physically effective crosslinks.

This is similar to what is observed for unaccelerated sulphur vulcanisation, where sulphur is combined in the network but does not contribute to forming physically effective crosslinks. Instead it produces modifications to the polymer chain and vicinal crosslinks which act like a single crosslink (see Section 2.2.1). It has been shown in Section 4.3 that ZDEC, added to latex during compounding, decomposes in the films and it might, therefore, be reasonable to suppose that this "loss" of ZDEC led to the vulcanisation being unaccelerated. However, this does not seem a likely explanation since the initial rate of crosslink formation is rapid, unlike unaccelerated sulphur vulcanisation (see Section 4.6, Figure 40 and Table 38).

According to earlier work by Calver, the sulphur crosslinks in postvulcanised latex films which had ZDEC as the accelerator contain predominantly polysulphidic crosslinks (over 90%)⁶⁸. These results suggest that there is an upper limit to the concentration of polysulphidic crosslinks formed, and extended heating at 90°C results in no further crosslinking. When the vulcanisation temperature is increased to 110°C and 130°C the concentration of crosslinks reaches a maximum, after which decomposition occurs and ZDEC is unable to recycle the sulphur into shorter crosslinks. It would seem that the accelerator ZDEC although excellent at producing polysulphidic crosslinks is poor at converting them to shorter crosslinks and recycling the sulphur to form more crosslinks (see also Section 6.8).

TEM micrographs indicate that upon extended heating the films become less particulate and eventually become homogeneous. It appears that crosslinking occurs at a more rapid rate than the formation of homogeneous films. The particulate films which have a high crosslink density have far higher tensile strengths than the homogeneous ones with low crosslink density.

These results lead one to believe that postvulcanised films consist largely of crosslinked particles with comparatively few crosslinks between them. However, the crosslinks between particles result in postvulcanised latex films being largely unaffected by processing changes like leaching.

6.7 Addition of Solvents to Latex and Latex Films

Although it was possible to treat latex and unvulcanised latex films with good swelling solvents (ie toluene and dichloromethane) and produce well-integrated films, there was no corresponding increase in their physical strength and in many cases tensile strength was lower than for untreated films. In addition, there were problems in handling the swollen materials which made them difficult to vulcanise. Introduction of toluene into latex as an emulsion with ammonium oleate solved the handling problems but introduced the complication of a delay in the onset of cure, the length of which was related to the concentration of fatty acid soap in the film.

The results again support the view that for postvulcanised latex films, good film integration does not significantly increase tensile strength, which is determined largely by the sulphur crosslinks within and between latex particles rather than by the entanglements at their surfaces.

6.8 The Relationship Between Tensile Strength and Modulus for Postvulcanised Latex Films

The relationship between tensile strength and modulus for postvulcanised NR latex films is different from that seen for prevulcanised films (see Figure 50). The curves obtained appear to depend upon the accelerator system used. This is similar to dry rubber where different accelerator systems give rise to different crosslink types.

For postvulcanised latex films in which ZDEC was the only accelerator, the tensile strength and modulus increased in tandem reaching a maximum for tensile strength in the region of 35 MPa at modulus S300% of 1.20-1.25 MPa. (see Figure 50). It was not possible to obtain films with modulus beyond 1.5 MPa for this accelerator system. Increases in vulcanisation temperature only resulted in the decomposition of crosslinks.

The use of a dual accelerator system, ZDEC/ZMBT, produced vulcanisates with a wide range of moduli. The tensile strength/modulus curve followed that of the ZDEC curve at low modulus to about 1.0 MPa. Beyond this modulus the curve began to flatten with the maximum at a modulus of about 2.0 MPa and maximum tensile strength in the region of 28 MPa. Tensile strength began to fall more rapidly at moduli above 2.5 MPa (see Figure 50). The curve shape is similar to that seen in Figure 25 for dry rubber films with 70% polysulphidic crosslinks. The tensile strength maximum is similar but the down-turn is more pronounced. In films where ZDEC was the only accelerator used the crosslinks were found to be predominantly polysulphidic (greater than 90%)⁶⁸. If in the ZDEC/ZMBT system polysulphidic crosslinks were formed initially via the ZDEC and afterwards converted to shorter polysulphidic, disulphidic and monosulphidic crosslinks, this would explain why the maximum tensile strength was lower and why the curve shape was similar to that for 70% polysulphidic dry rubber. Since postvulcanised latex films retain much of their particulate structure it is to be expected that at higher modulus they will behave more like prevulcanised latex films than dry rubber and tensile strength will fall more rapidly beyond the maximum than for dry rubber. In the model envisaged for a postvulcanised latex film, the crosslinks are concentrated between rubber molecules within the latex particles plus some crosslinks between molecules in neighbouring latex particles and some entanglements.

Postvulcanised latex films which contained CBS and thiourea as the accelerator system had a tensile strength/modulus curve which fell in the same envelope as that for ZDEC/ZMBT but with much greater scatter, probably as a result of the difficulty in producing films free from defects (see 5.1.2). In the case of films which contained the CBS and sodium thiosulphate accelerator system, the curve shape was rather different (see Figure 50). It followed the initial rising curve but maximum tensile strength was attained at about 26 MPa and modulus 1.6 MPa, beyond which tensile strength fell sharply after the fashion of prevulcanised latex films. It would be surprising if the crosslink types were different in such similar accelerator systems. However, perhaps the differences in thiophilicity of the activators would lead to a lower concentration of crosslinks being formed

in the CBS/thiosulphate accelerated films. The crosslinks may also be concentrated within the latex particles rather than between them, leading to a vulcanisate which resembles prevulcanised latex films more closely.

6.9 Suggestions for Further Work

It would be instructive to determine the types of crosslink found in postvulcanised latex films with ZDEC/ZBMT and CBS/activator accelerator systems. It might also be useful to use TEM to examine film integration for the system and compare the results with those which were obtained for films which used ZDEC as an accelerator.

If cast latex films had been left to form under conditions of higher humidity it is possible that greater differences in properties of the postvulcanised films would have been observed when compared with films allowed to dry over phosphorus pentoxide. This may be worth investigation in order to confirm or refute the belief that the tensile strength of postvulcanised latex films is unchanged by changes in humidity during film preparation.

Since (rather surprisingly) the rate of film integration in natural rubber latex films appears to be much slower than the rate of vulcanisation of the films, when ZDEC is used as an accelerator, it has been difficult to assess the contribution of film integration to tensile strength. It would be interesting to prepare films for postvulcanisation which could be heated for long periods to bring about particle integration before they were vulcanised. This might be achieved either by using an accelerator with a long induction period or by heating the film at a low temperature (90°C or below) for several hours before vulcanising it at a temperature at which a delayed-action accelerator became active (e.g. CBS at 100°C or above). The films could be examined by TEM after the Shiibashi method.

It would be very instructive if the location of crosslinks in sulphur-crosslinked natural rubber latex films could be examined. It may be possible to combine the styrene embedding technique of Shiibashi for latex films with some type of fluorescence technique which would allow the sulphur crosslinks to be visualised. This could then be used to examine and compare prevulcanised and postvulcanised latex films and even dry rubber films.

REFERENCES

- 1 Gazeley K.F., Gorton A.D.T. and Pendle T.D., 1988, "Latex Concentrates: properties and composition", "Natural Rubber Science and Technology" (Roberts A.D. ed.), Chapter 3 Oxford: Oxford University Press
- 2 Calvert K.O., 1982, "Natural Rubber Latices", "Polymer Latices and their Applications" (Calvert K.O. ed.) Chapter 2, London: Applied Science Publishers Ltd.
- 3 Blackley D.C., 1966, "High Polymer Latices", Chapter 4, London: Maclaren & Sons Ltd.
- 4 Archer B.L., Barnard D., Cockbain E.G., Dickenson P.B. and McMullen A.I., 1963 "Structure, Composition and Biochemistry of Hevea Latex", "The Chemistry and Physics of Rubber-Like Substances" (Bateman L., ed.), Chapter 3, London: Maclaren and Sons Ltd.
- 5 Gazeley K.F., Gorton A.D.T. and Pendle T.D., 1988, "Technological processing of natural rubber latex", "Natural Rubber Science and Technology", (Roberts A.D. ed.), Chapter 4, Oxford: Oxford University Press
- 6 Gorton A.D.T. and Pendle T.D., 1981, NR Technol, 12(2), 21
- 7 Calvert K.O., 1982, "Introduction", "Polymer Latices and their Applications" (Calvert K.O. ed.), Chapter 1, London: Applied Science Publishers.
- 8 McRoberts T.S., Proc. Third Rubber Tech. Conf., 1954, Paper 48.
- 9 Gorton A.D.T., Proc. International Polymer Latex Conf., London 1978, paper 11.
- 10 Blackley D.C., 1966, "High Polymer Latices", Chapter 1, London: Maclaren and Sons Ltd.
- 11 Van Gils G.E., 1977, Rubber Chem. Tech, 50, 141.

- 12 Porter M., Rosemaze R. and Sapi'ai Abdul R., 1991, J. Nat. Rubb. Res 7(2), 85.
- 13 Loh A.C.P., 1982, "Further Investigations of the Pre-vulcanization of Natural Rubber Latex", PhD Thesis, CNA A.
- 14 Bratby D.M., 1982, "Latex Dipping", "Polymer Latices and their Applications" (Calvert K.O. ed.) Chapter 9, London: Applied Science Publishers.
- 15 Mausser R.F. (ed.) 1987, Vanderbilt Latex Handbook, 3rd Edn., Connecticut, USA, 109.
- 16 Wong N.P. and Loo C.T., Proc. Int. Rubb. Conf., 1985 Kuala Lumpur, 2, 487
- 17 Loo C.T. and Wong, N.P. Proc. Int. Conf. Dev Plastics and Rubber Prod. Indust., 1987, Kuala Lumpur, 265.
- 18 Gorton A.D.T., 1967, J.R.R.I. Malaya, 20, 27.
- 19 Gorton A.D.T. and Iyer G.C., 1973, J.R.R.I. Malaya, 23(4), 263.
- 20 Subramanian A., 1992, Proc. Int. Latex Conf: Sensitivity to Latex in Medical Devices, Baltimore, FDA, Abstract 51.
- 21 Gazeley K.F., 1985, NR Tech 16(3), 61.
- 22 Gorton A.D.T., 1979, NR Tech, 10(1), 9.
- 23 Merrill R.W.T., 1980, M.Phil. Thesis, CNA A.
- 24 Blackley D.C., Proc. Int. Rubber Tech. Conf., Penang, 1988, 3.
- 25 Porter M. and Wong W.S., Polymer Latex III, 1989, London, Paper 25.
- 26 Eckersley S.T. and Rudin A., J. Coatings Tech., 1990, 62 (780), 89.

- 27 Nicholson J.W., JOCCA, 1989, 72(12), 475.
- 28 Kendall K. and Padget J.C., Int. J. Adhesion & Adhesives, July 1982, 149.
- 29 Vanderhoff J.W., Br. Polym J., 1970, 2, 161.
- 30 Vanderhoff J.W., Tarkowski H.L., Jenkins M.C. and Bradford E.B., J. Macromol. Chem. 1966, 1, 361.
- 31 Dillon R.E., Matheson L.A. and Bradford E.B., J. Colloid Sci, 1951, 6, 108.
- 32 Frenkel J., J. Phys USSR 1945, 9, 385.
- 33 Brown G.L., J. Polym. Sci. 1956, 22, 423.
- 34 Mason G., Br. Polym. J., 1973, 5, 101.
- 35 Sheetz D.P., J. Appl. Polym. Sci. 1965, 9, 3759.
- 36 Vanderhoff J.W., Bradford E.B. and Carrington W.K., J. Polym. Sci. 1973, Symposium No. 41, 155.
- 37 Gazeley K.F. and Swinyard P.E., NR Technology, 1987, 18(4), 81.
- 38 Johnson K.L., Kendall K. and Roberts A.D., Proc. R. Soc. Lond. 1971, A324, 301.
- 39 El-Aasser M.S. and Robertson A.A., J. Colloid Interface Sci. 1971, 36(1), 86.
- 40 Hwa J.C.H., J. Polym. Sci. Part A, 1964, 2, 783
- 41 Cansell F., Henry F. and Pichto C., J. Appl. Polym. Sci, 1990, 41, 547.

- 42 Cansell F, Grabielle-Madelmont C. and Ollivon M., J. Colloid and Interface Sci., 1991, 144(1), 1.
- 43 Brodnyan J.G. and Konen T., J. Appl. Polym. Sci. 1964, 8, 687.
- 44 Jensen D.P. and Morgan L.W., J. Appl. Polym. Sci. 1991, 42, 2845.
- 45 Voyutskii S.S., J. Polym. Sci., 1958, 32(125), 528.
- 46 Voyutskii S.S. and Ustinova Z.M., J. Adhesion, 1977, 9, 39.
- 47 Bradford E.B. and Vanderhoff J.W., J. Macromol. Chem., 1966, 1, 335
- 48 El-Aasser M.S. and Robertson A.A., J. Paint Tech., 1975, 47(611), 50.
- 49 Hahn K., Ley G., Schuller H. and Oberthür R., Colloid Polym. Sci., 1986, 264, 1092.
- 50 Hahn K., Ley G., Schuller H. and Oberthür R., Colloid Polym. Sci., 1988, 266, 631.
- 51 Linné M.A., Klein A., Miller G.A., Sperling L.A. and Wignall G.D., J. Macromol. Sci. Phys., 1988, B27(2&3), 217.
- 52 Zhao C.L., Wang Y., Hruska Z. and Winnik M.A., Macromolecules, 1990, 23, 4082.
- 53 Chainey M., Wilkinson M.C. and Hearn J., J. Polym. Sci. Polymer Chem. Ed., 1985, 23, 2947.
- 54 Distler D. and Kanig G., Colloid Polym. Sci., 197, 256, 1052.
- 55 Kanig G. and Neff H., Colloid Polym. Sci., 1975, 253, 29.
- 56 Zhao C.L., Holl Y., Pith T. and Lambla M., Br. Polym. J., 1989, 21, 155.
- 57 Urban M.W. and Evanson K.W., Polym. Comm., 1990, 31 (July), 279.

- 58 Roulstone B.J., Wilkinson M.C. and Hearn, J. Polymer International, 1992, 27,43.
- 59 Khodzhaeva I.D., Ustinova Z.M., Tarasova Z.N., Voyutskii S.S., Sedakova L.I. and Griskova I.A., Colloid J., 1976, 38(2), 374.
- 60 Chong K.L. and Porter M., Int. Polym. Latex Conf. London, 1978, Preprint 16.
- 61 Bateman L., Moore C.G., Porter M. and Saville B., 1963, "Chemistry of Vulcanization", "The Chemistry and Physics of Rubber-like Substances" (Bateman L., ed.) Chapter 15, London: Maclaren and Sons Ltd.
- 62 Chapman A.V. and Porter M., 1988, "Sulphur Vulcanization Chemistry" Natural Rubber Science and Technology (Roberts A.D. ed.), Chap. 12, Oxford: Oxford University Press.
- 63 Porter M., Proc. Int. Rubber Tech. Conf., Penang, 1988, 26.
- 64 Chapman A.V., "Phosphorous Sulphur and Silicon", 1991, 59, 271.
- 65 Milligan B., Rubber Chem. Technol., 1966, 39, 1115.
- 66 Morrison N.J. and Porter M., Rubber Chem. Tech., 1984, 57(1), 63
- 67 Gorton A.D.T., Blackley D.C. and Hafsah b.M.G., 1989, Proc. Polymer Latex III, Paper 24.
- 68 Calver L., 1991, Project Report GRSC Part II, Anglia Polytechnic.
- 69 Porter M., Lecture to International Rubber Science Hall of Fame Symposium in Honor of Herman Mark, University of Akron, Akron, Ohio, 12 Nov. 1993
- 70 Bateman L., Cunneen J.I., Moore C.G., Mullins L. and Thomas A.G., 1963, "Vulcanizate Structure and Physical and Ageing Properties", "The Chemistry

- and Physics of Rubber-like Substances", (Bateman L. ed.), Chapter 19, London: Maclaren and Sons Ltd.
- 71 Chong K.L., 1977, "The Chemistry of Sulphur Vulcanization of Natural Rubber Latex", PhD Thesis, CNAA.
- 72 Natural Rubber Technical Information Sheets, Latex Series L37, Malaysian Rubber Producers Research Association (MRPRA), 1980
- 73 International Standard ISO 7269: 1987 (E)
- 74 Davey J.E., Edwards A.D. and Higgins G.M.C., Plastics and Rubber: Materials and Applications, November 1978, 145
- 75 Moore C.G. and Watson A.A., J. Appl. Polym. Sci., 1964, 8, 581
- 76 Shiibashi T., International Polymer Science and Technology, 1987, 14, (12), T33
- 77 Blackley D.C., 1966, High Polymer Latices, Chapter 8, London, Maclaren and Sons Ltd.
- 78 Regester J., 1990, Report 119, London International Group, R&D.
- 79 Calver L.J., 1991, Report 215, London International Group, R&D.
- 80 Calver L.J., Report 341, London International Group, R&D.
- 81 Loadman M.J.R. and Tidd B.K., 1988, "Chemical Analysis" Natural Rubber Science and Technology (Roberts A.D. ed.), Chapter 22, Oxford: Oxford University Press
- 82 Low E.H., Proc. RRIM Planters' Conf., 1977, 1978, 307
- 83 Miller J.C. and Miller J.N., 1984, Statistics for Analytical Chemistry, Chapter 3 and Appendix 2, Chichester: Ellis Horwood Ltd.

- 84 Porter M., Private communication(Paper subsequently given at IRC 96)
- 85 Loo, C.T. Rubber Research Institute of Malaysia- Internal Report, 1976
- 86 Gorton A.D.T., NR Technology, 1975 6(3), 52.
- 87 Blackley D.C., 1966, High Polymer Latices, Chapter 2, London, Maclaren and Sons Ltd.
- 88 Philpott M.W., Proc. Fourth Rubber Technol. Conf., 1962, 470.
- 89 Philpot M.W., J. Rubb. Res. Inst. Malaysia, 1969, 22(5), 441.
- 90 Moore C.G., Saville B. and Watson A.A., 1960, J. App. Polym. Sci., 3(9), 373.
- 91 Davies R.E., 1968, Inorganic Sulphur Chemistry (Nickless G., ed.), 97, Elsevier
- 92 Crowther B.G., Lewis P.M. and Metherell C., 1988 "Compounding" Natural Rubber Science and Technology (Roberts A.D. ed.), Chapter 6, Oxford: Oxford University Press
- 93 Cook S., Cudby P.E.F., and Tinker A.J., Paper No. 3 Presented at a Meeting of the Rubber Division, ACS, Nashville, Tennessee, November 1992
- 94 Tinker A.J., Rubber Chem. Tech., 1995, 68(3),461
- 95 Allen P.W. and Bristow G.M. J. Appl. Polym. Sci., 1963,7, 603

APPENDIX 1 ANALYSIS OF VARIANCE FOR PHYSICAL PROPERTIES OF MATURED LATICES

Terms Used in the Analysis of Variance Report and Summaries for Means and Standard Errors

A refers to the maturation time

- 1 = 30 min
- 2 = 1 h
- 3 = 2 h
- 4 = 4 h
- 5 = 16 h
- 6 = 24 h

B refers to the formulation number

- 1 = A(11)
- 2 = A(12)
- 3 = A(13)
- 4 = A(14)
- 5 = A(15)
- 6 = A(16)
- 7 = A(17)
- 8 = A(18)
- 9 = A(19)
- 10 = A(20)
- 11 = A(21)
- 12 = A(22)

C refers to the cure time

- 1 = 0 min
- 2 = 30-39 min
- 3 = 90-96 min

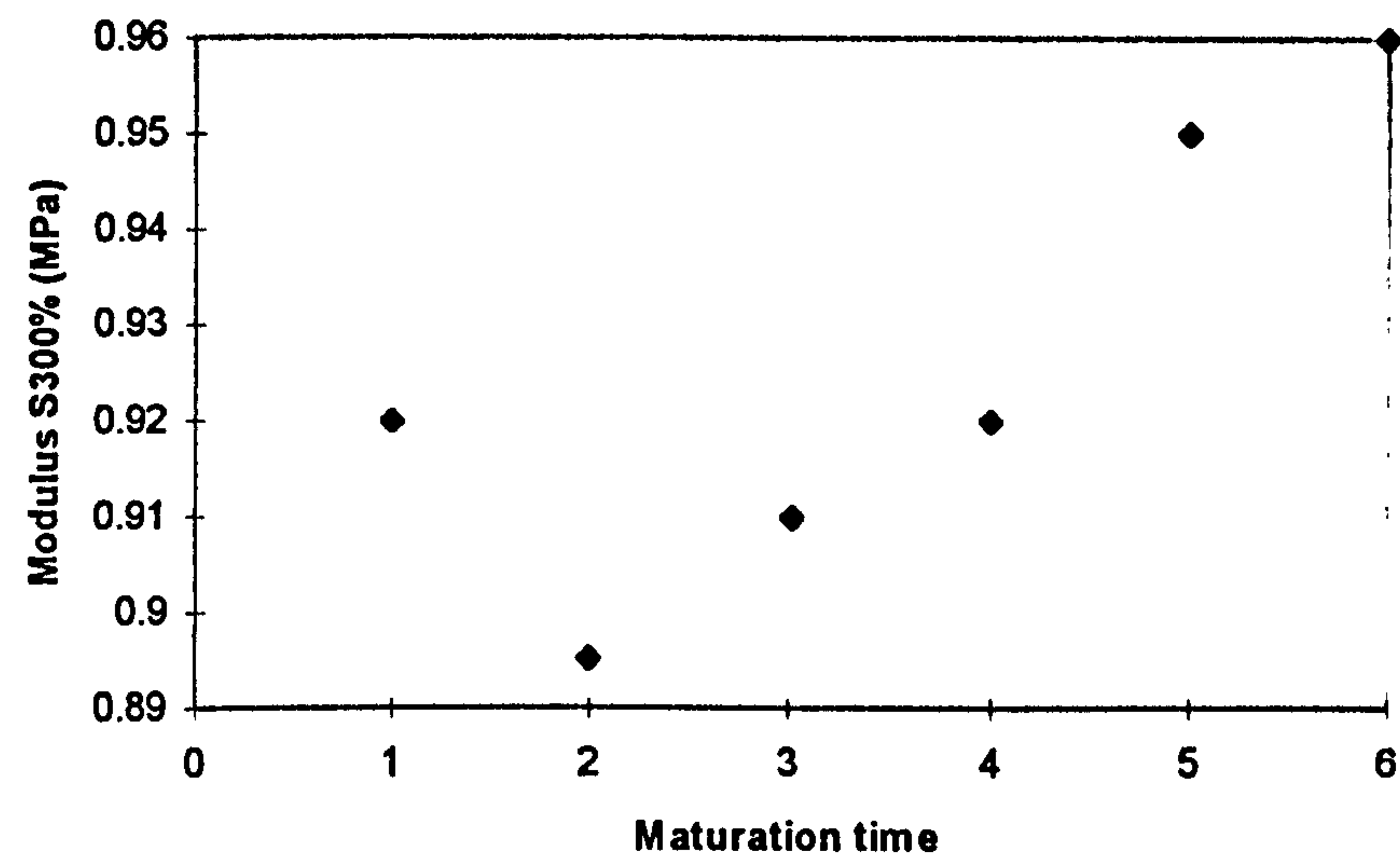
Table 20 ANOVA Table for Response Variable: Modulus S300%

Variable Source	DF	Sum-Squares	Mean-Squares	F-Ratio	Prob>F	Error Term
[MAT] A	5	1.83E-02	3.66E-03	0.40	0.8315	B (A)
[FORM] B (A)	6	5.46E-02	9.10E-03			S (ABC)
[CURE] C	2	1.72	.86	1220.55	0.0000	BC (A)
AC	10	8.13E-03	8.13E-04	1.15	0.4023	BC (A)
BC (A)	12	8.47E-03	7.06E-04			S (ABC)
S (ABC)	0	0	0			
TOTAL (Adj)	35	1.811				

Table 21Advanced ANOVA (Means & Standard Errors for Modulus S300%)

Term	Count	Mean	Std. Error
ALL	36	0.926	
A: MAT			
1	6	.92	3.893E-02
2	6	.895	3.893E-02
3	6	.91	3.893E-02
4	6	.92	3.893E-02
5	6	.95	3.893E-02
6	6	.96	3.893E-02
C: CURE			
1	12	.63	7.667E-03
2	12	1.01	7.667E-03
3	12	1.14	7.667E-03
AC: MAT, CURE			
1.1	2	.62	.0187824
1.2	2	1.00	.0187824
1.3	2	1.15	.0187824
2.1	2	.61	.0187824
2.2	2	.96	.0187824
2.3	2	1.12	.019
3.1	2	.63	.019
3.2	2	.99	.019
3.3	2	1.12	.019
4.1	2	.63	.019
4.2	2	1	.019
4.3	2	1.14	.019
5.1	2	.61	.019
5.2	2	1.06	.019
5.2	2	1.18	.019
6.1	2	.66	.019
6.2	2	1.06	.019
6.3	2	1.16	.019

Figure 33 Plot of Maturation Time (A) Main Effect for Modulus S300%



- 1 = 30 minute maturation time
- 2 = 1 hour maturation time
- 3 = 2 hour maturation time
- 4 = 4 hour maturation time
- 5 = 16 hour maturation time
- 6 = 24 hour maturation time

Figure34 Plot of Cure Time (C) Main Effect for Modulus S300%

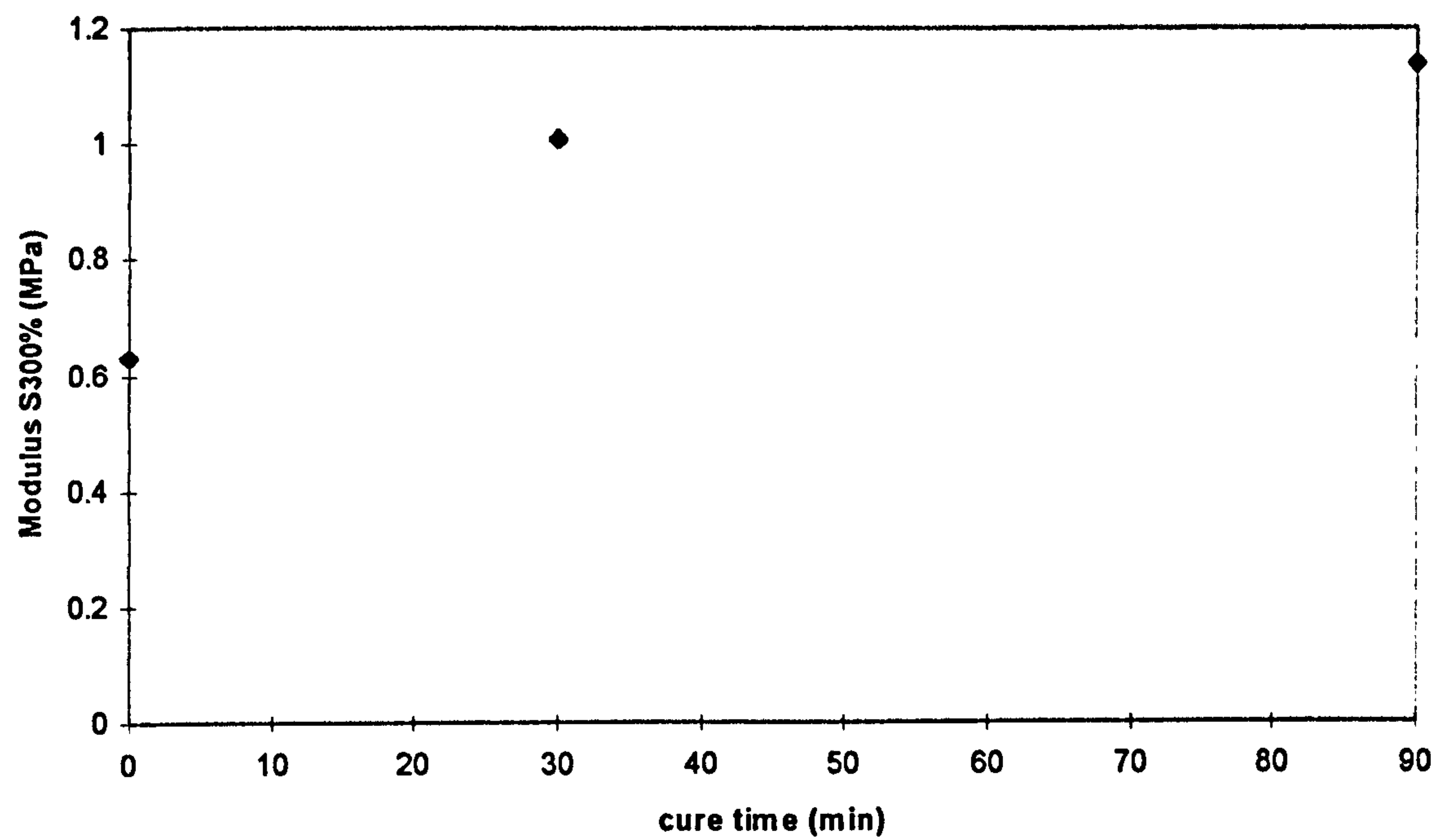
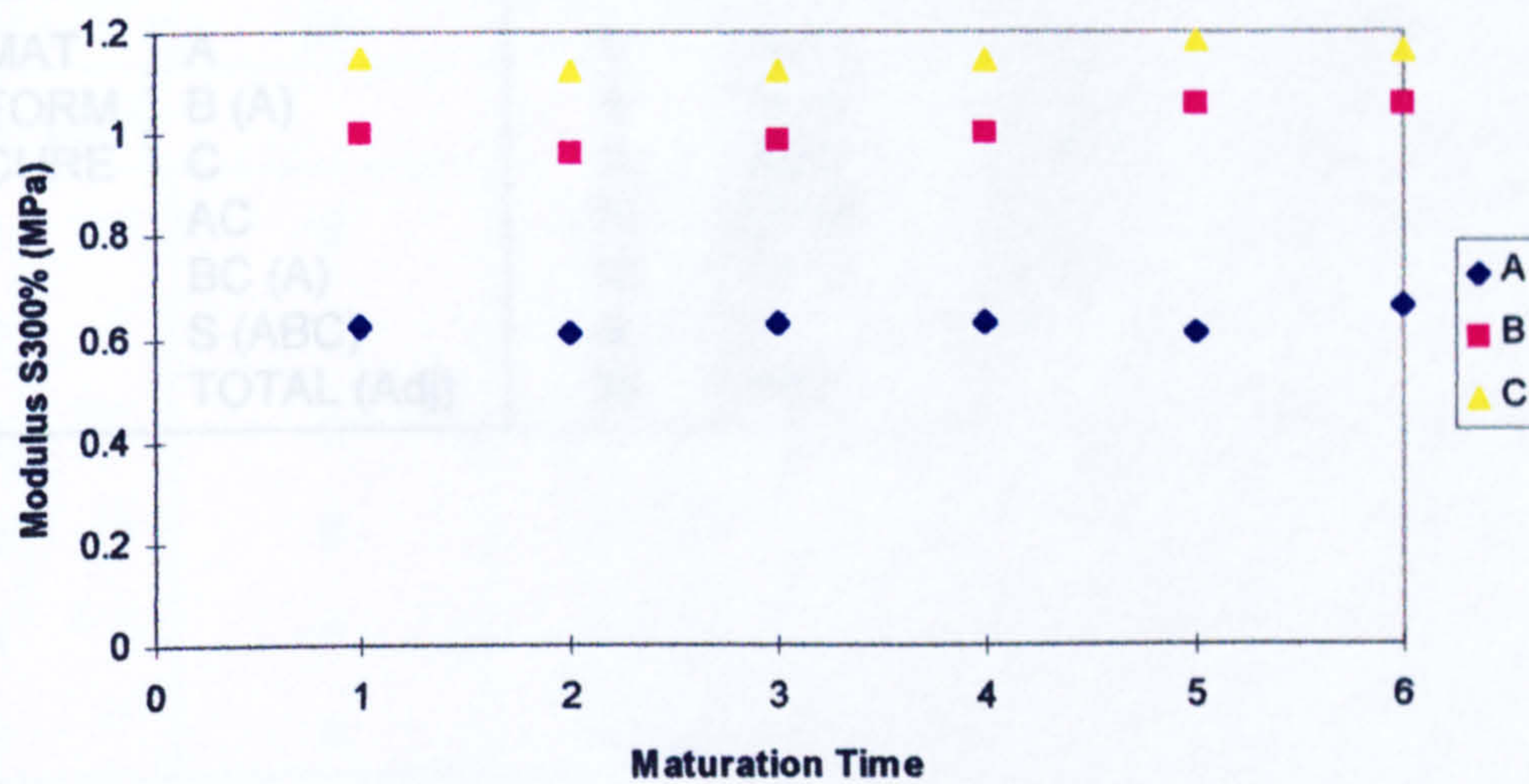


Figure 35 Plot of Interaction between Maturation Time and Cure Time (AC) for Modulus S300%



A = No Cure
B = 30 minute cure
C = 90 minute cure

1 = 30 minute maturation time
2 = 1 hour maturation time
3 = 2 hour maturation time
4 = 4 hour maturation time
5 = 16 hour maturation time
6 = 24 hour maturation time

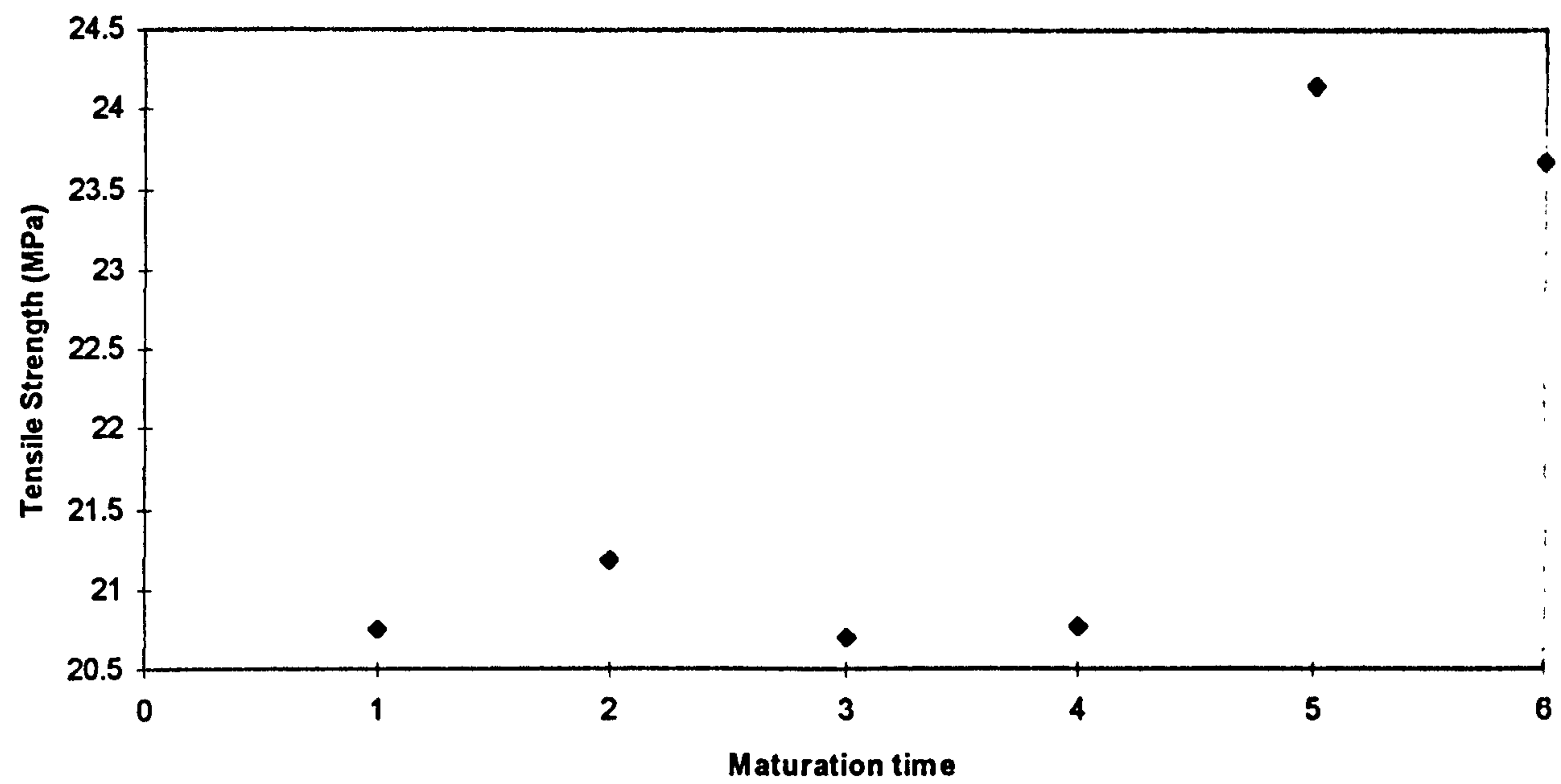
Table 22 ANOVA Table for Response Variable: Tensile Strength

Variable Source	DF	Sum-Squares	Mean-Squares	F-Ratio	Prob>F	Error Term
[MAT] A	5	76.93	15.39	4.86	0.0401	B (A)
[FORM] B (A)	6	19.01	3.169			S (ABC)
[CURE] C	2	3688	1844	374.42	0.0000	BC (A)
AC	10	50.66	5.07	1.03	0.4745	BC (A)
BC (A)	12	59.10	4.93			S (ABC)
S (ABC)	0	9	0			
TOTAL (Adj)	35	3894				

Table 23 Advanced ANOVA (Means & Standard Errors for Tensile Strength

Term	Count	Mean	Std. Error
ALL	36	21.869	
A: MAT			
1	6	20.75	.727
2	6	21.17	.727
3	6	20.7	.727
4	6	20.77	.727
5	6	24.15	.727
6	6	23.68	.727
C: CURE			
1	12	7.67	.641
2	12	27.43	.641
3	12	30.52	.641
AC: MAT, CURE			
1.1	2	7.85	1.57
1.2	2	24.95	1.57
1.3	2	29.45	1.57
2.1	2	7.90	1.57
2.2	2	24.7	1.57
A: MAT, CURE			
2.3	2	30.9	1.57
3.1	2	7.55	1.57
3.2	2	25.5	1.57
3.3	2	29.05	1.57
4.1	2	6.5	1.57
4.2	2	26.9	1.57
4.3	2	28.9	1.57
5.1	2	9	1.57
5.2	2	30.85	1.57
5.3	2	32.6	1.57
6.1	2	7.20	1.57
6.2	2	31.65	1.57
6.3	2	32.20	1.57

Figure 36 Plot of Maturation Time (A- Main Effect) for Tensile Strength



- 1 = 30 minute maturation time
- 2 = 1 hour maturation time
- 3 = 2 hour maturation time
- 4 = 4 hour maturation time
- 5 = 16 hour maturation time
- 6 = 24 hour maturation time

Figure 37 Plot of Cure Time (C- Main Effect) for Tensile Strength

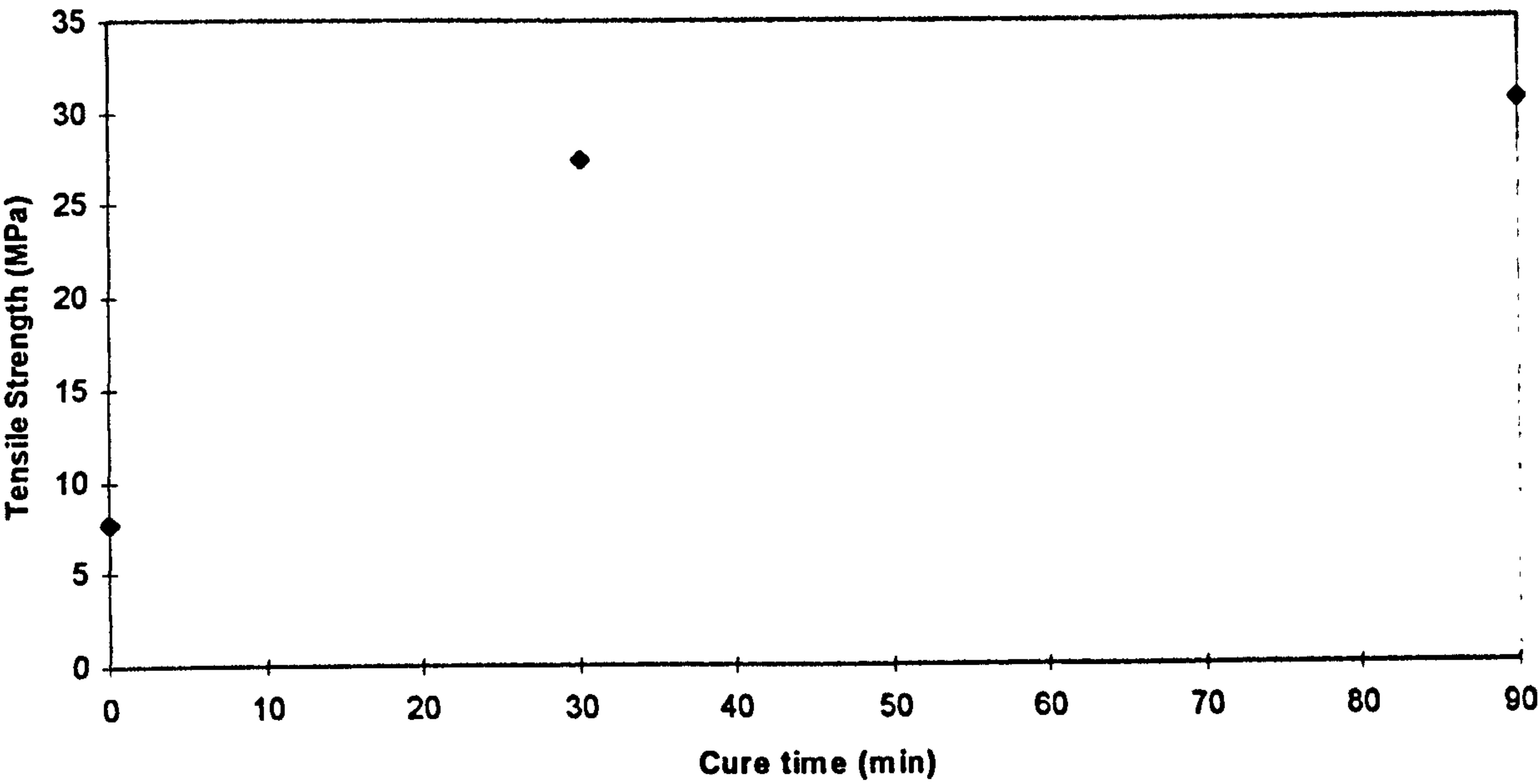
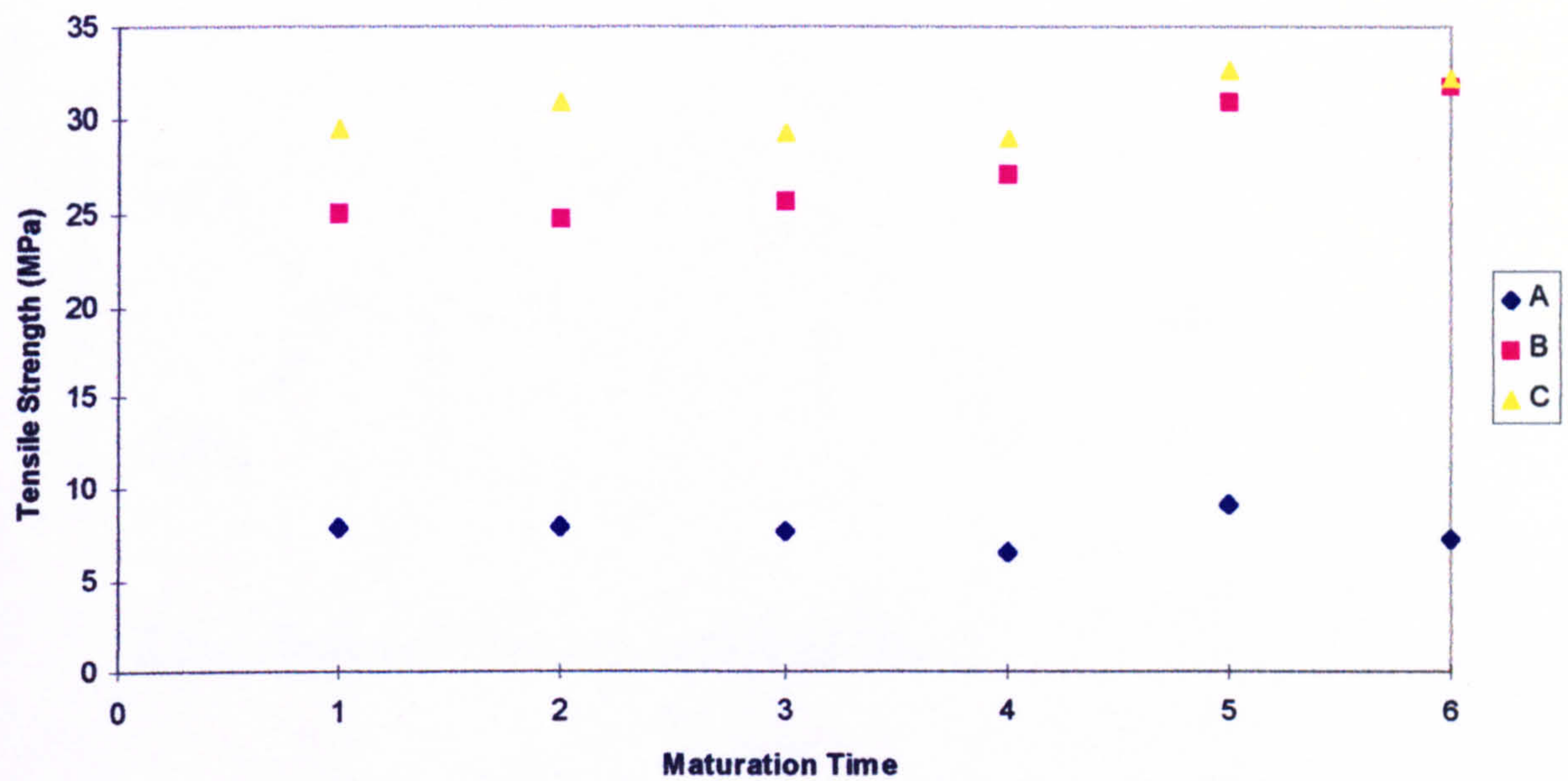


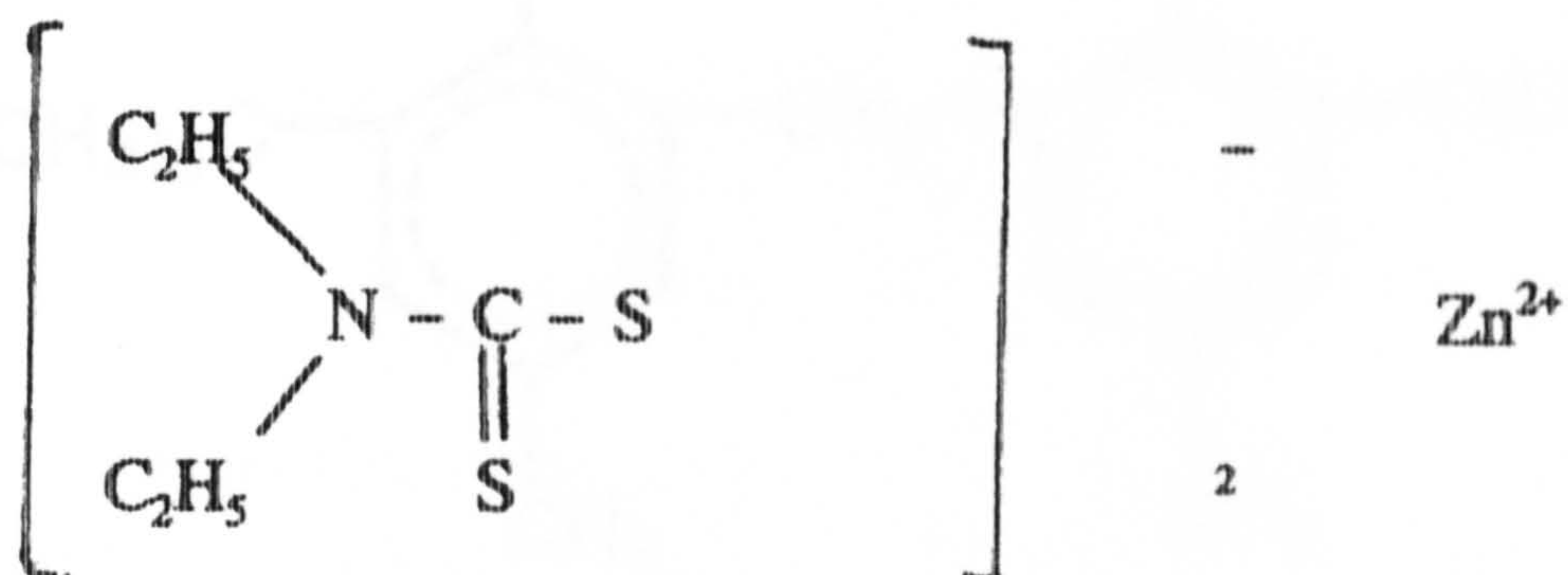
Figure38 Plot of Interaction between Maturation Time and Cure Time (AC) for Tensile Strength



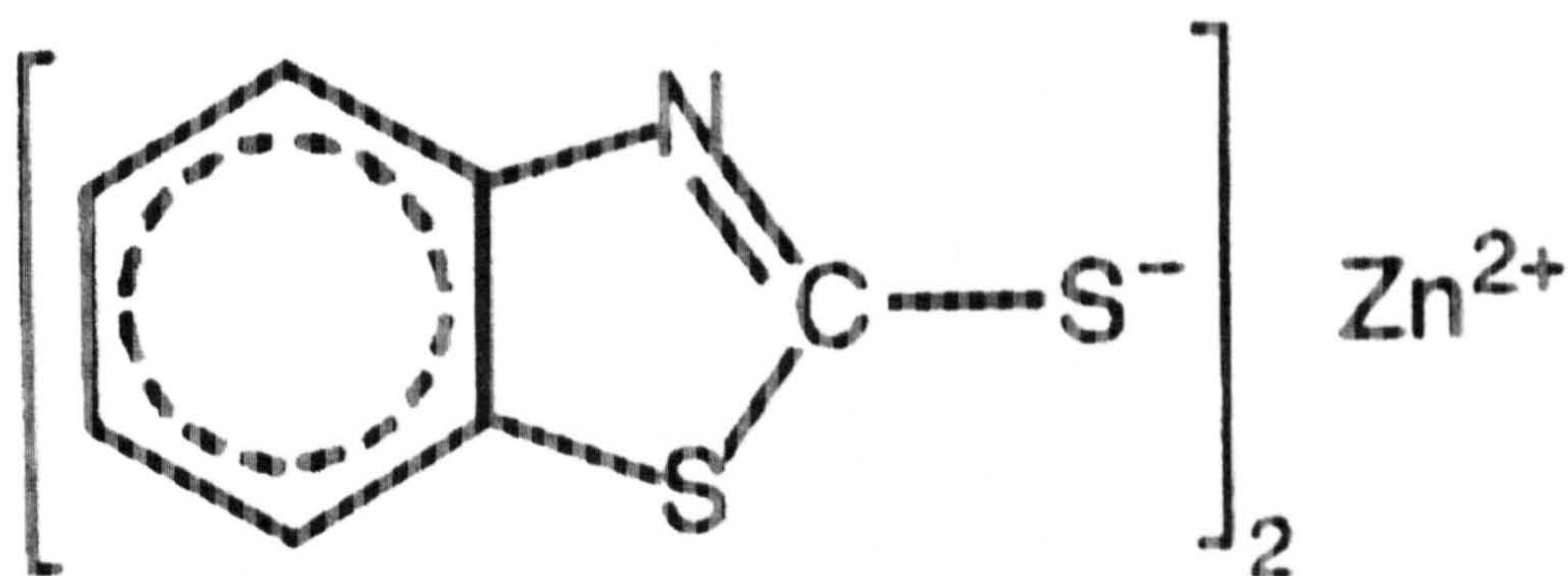
A = No Cure
B = 30 minute cure
C = 90 minute cure

1 = 30 minute maturation time
2 = 1 hour maturation time
3 = 2 hour maturation time
4 = 4 hour maturation time
5 = 16 hour maturation time
6 = 24 hour maturation time

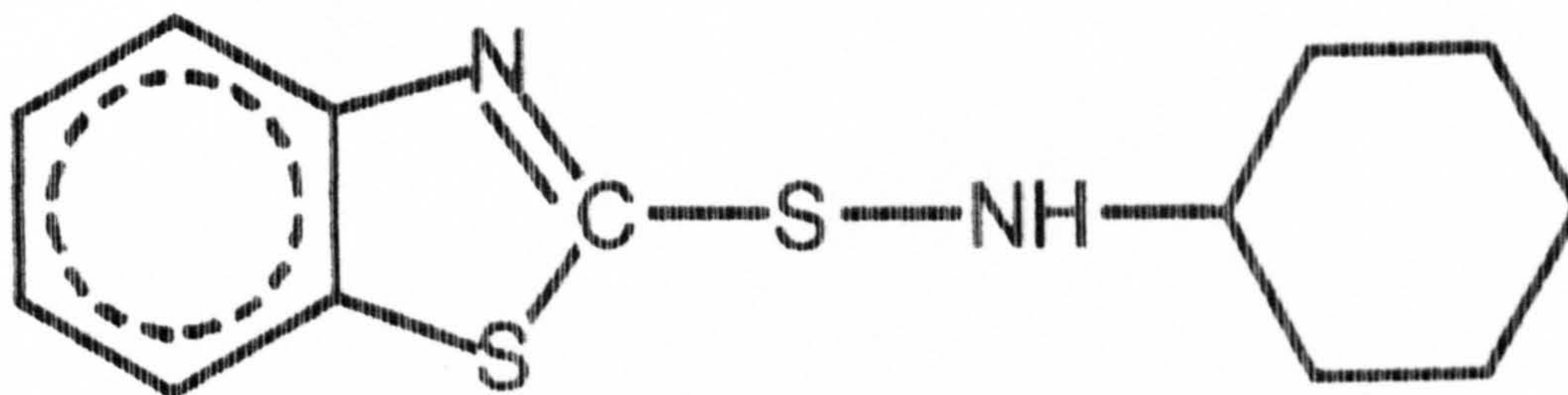
APPENDIX 2 STRUCTURES OF ACCELERATORS AND ANTIOXIDANT



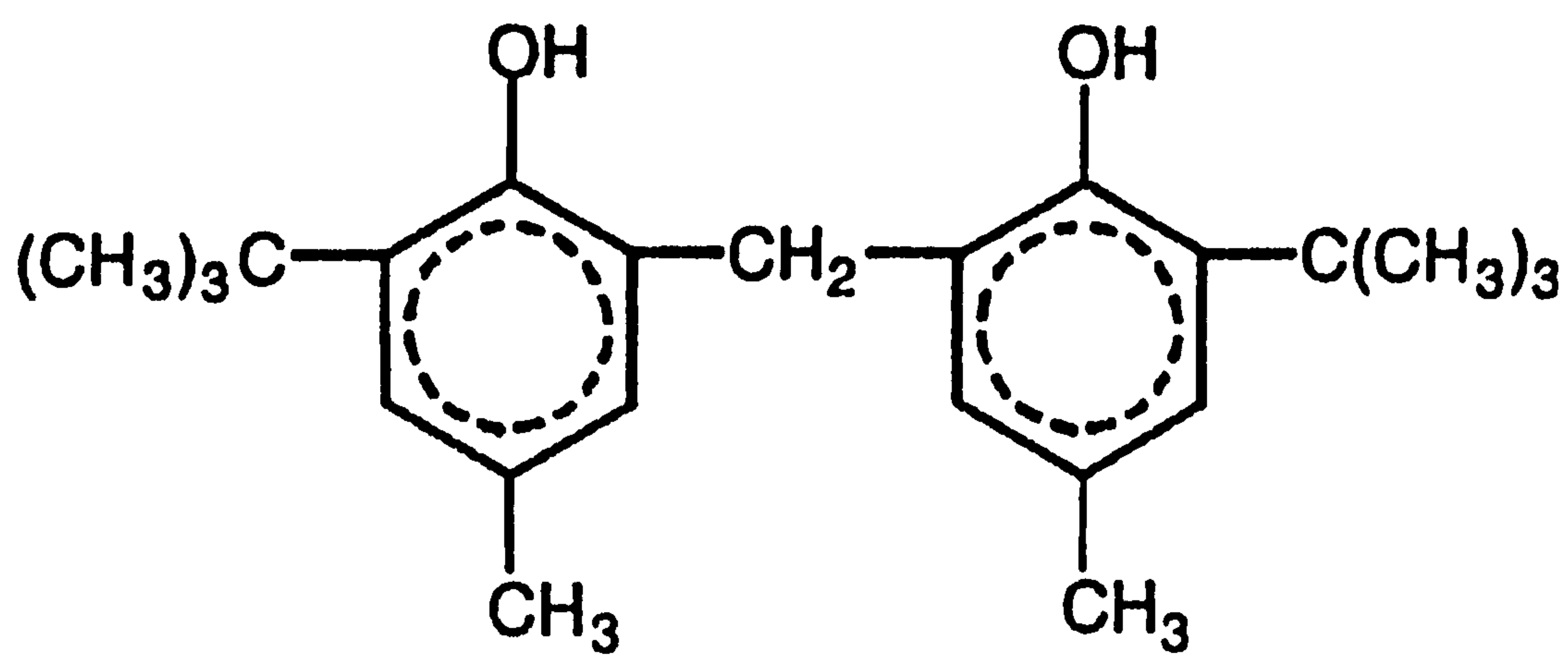
Zinc diethyldithiocarbamate (ZDEC)



zinc benzothiazole-2-thiolate (zinc mercaptobenzthioazole -ZMBT)



N-cyclohexylbenzothiazole-2-sulphenamide (CBS)



2,2'-methylene-bis-(4-methyl-6-tert-butylphenol) (Antioxidant 2246)

APPENDIX 3 PHYSICAL STRENGTH CALCULATIONS

Calculation of Tensile Strength

$$\text{Tensile strength} = \frac{F}{Wxt} \quad F = \text{maximum load (N)}$$

W = width of narrow portion of dumbbell (mm)

t = average thickness of narrow portion of dumbbell (mm)

Calculation of Modulus (Stress) (S)

The elongation must be specified

$$S = \frac{F_s}{Wxt} \quad F_s = \text{force at a given strain (N)}$$

W = width of narrow portion of dumbbell (mm)

t = average thickness of narrow portion of dumbbell (mm)

BS Type II Dumbbell



4mm narrow portion