FURTHER INVESTIGATIONS OF THE PREVULCANIZATION OF NATURAL RUBBER LATEX

by

AARON CHUN-PONG LOH, M.Sc.

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Sponsoring establishment: The Polytechnic of North London,
Holloway Road,
London N7 8DB

Collaborating establishment:
LRC Products Ltd.,
North Circular Road,
Chingford,
London E4 8QA

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ABSTRACT

A comparison has been made of the vulcanization of NR in the latex form and in the dry form. In latex form, NR was found to vulcanize at a much faster rate than in the dry form. The faster rate of reaction in latex prevulcanization is attributed to the presence of the aqueous phase which acts as a medium for the dissolution of ZDBC and sulphur, and provides a suitable environment for the two vulcanizing ingredients to react to form the active sulphurating agent.

A comparison has also been made of the prevulcanization behaviour of NR latex and synthetic cis-polyisoprene latex. It has been suggested that the indigenous vulcanization accelerators and activators present in NR latex act as additional vulcanizing accelerators and therefore increase the rate of prevulcanization.

Experiments have been carried out to determine the solubilities of sulphur and ZDBC in the aqueous phase of the latex during prevulcanization. Sulphur was found to dissolve to an appreciable extent; ZDBC was found to have a solubility of ca. 0.011%.

The effects of varying the levels of sulphur and ZDBC upon NR latex prevulcanization was investigated. The variations of the following properties with time of prevulcanization were investigated: free and network-combined sulphur, disappearance of ZDBC, crosslink insertion, and tensile strengths of cast films. Information was also obtained concerning the polymer-solvent interaction parameter for the cast films swollen in n-decane at 23°C.

Investigations of the different types of sulphidic crosslinks as a function of prevulcanization time for vulcanizate obtained from prevulcanized latex have also been carried out. The crosslinks were found to be mainly of the polysulphidic type.

The effect of varying the dialkyl chain-length and metal counterion of the dithiocarbamate accelerator upon NR latex prevulcanization have been studied. The molal effectiveness of the zinc dialkyl dithiocarbamates appears to pass through an optimum as the dialkyl chain-length of the accelerator is increased. PbDEC was found to be of very low activity as an accelerator and the water soluble SDEC has poor accelerating properties when compared to ZDEC. Plausible hypotheses to account for the observations have been postulated.

This thesis is dedicated to my parents and my three loving sisters; Poh Keng, Poh Wan and Poh Kuen. They have made many sacrifices to enable me to study in England (1976-1982); their love and patience will always be remembered.

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LIST OF ABBREVIATIONS AND SYMBOLS

The following abbreviations and symbols have been used in this thesis.

NR	natural rubber
HA	high-ammonia (latex)
pphr	parts per hundred rubber
RH	rubber hydrocarbon
ZDBC	zinc dibutyl dithiocarbamate
AR	analytical reagent
GPR	general purpose reagent
$[X]_{chem}$	concentration of chemically-crosslinked sites assuming tetrafunctional crosslinks
$[X]_{phys}$	concentration of physically-effective crosslink sites assuming tetrafunctional crosslinks.
G_{cs}	swollen compression stress-strain modulus
V_r	volume fraction of rubber
ZDEC	zinc diethyl dithiocarbamate
ZDMC	zinc dimethyl dithiocarbamate
ZDHC	zinc dihexyl dithiocarbamate
ZDOC	zinc dioctyl dithiocarbamate
ZDDC	zinc didodecyl dithiocarbamate
SDEC	sodium diethyl dithiocarbamate
PbDEC	lead diethyl dithiocarbamate
SeDEC	selenium diethyl dithiocarbamate
TeDEC	tellurium diethyl dithiocarbamate

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INTRODUCTION

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INTRODUCTION

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CHAPTER 1

INTRODUCTION

1.1. Natural Rubber Latex

Dry natural rubber has been established as a versatile material for almost two centuries. It is therefore perhaps surprising that the material from which it is derived, natural rubber latex, has been used industrially for a relatively short period only. Malaysia (then Malaya), first exported latex in commercial quantities (ca. 20,000 tonnes) in 1922.(1) Today, Malaysia is still the largest exporter country, exporting over 200,000 tonnes of natural rubber latex per year(2).

The utilisation pattern for natural rubber latex has changed over the years because of fierce competition from synthetic latices and synthetic polymers in other forms. Today, the main application of NR latex is for the production of dipped good, followed by extruded threads, adhesives, carpet-backing (including underlays), and moulded foams(3).

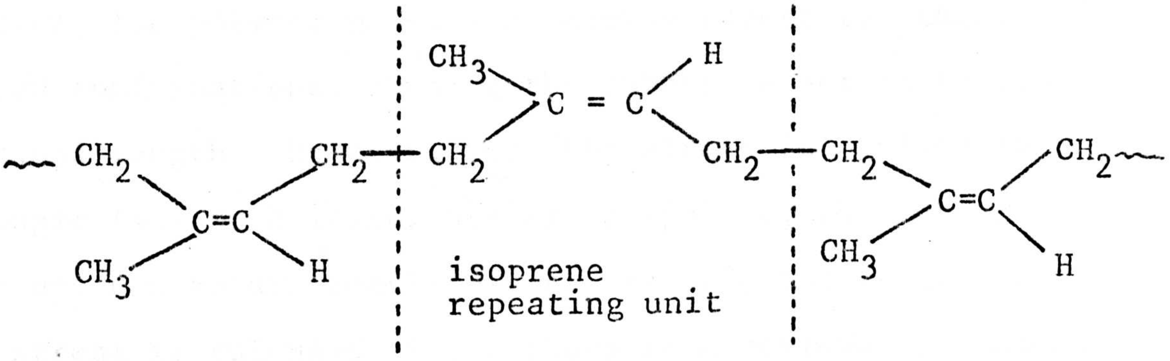
1.2. Production of Natural Rubber Latex Concentrate

Natural rubber (NR) latex is obtained from Hevea brasiliensis, a tree which was originally found growing in the Amazon basin of South America but which is now grown in plantations of the rubber-producing nations such as Malaysia, Indonesia, Thailand, Sri Lanka and Liberia. NR latex as it occurs in the Hevea brasiliensis tree is a slightly viscous juice comprising a dispersion of particles of a hydrocarbon polymer in an aqueous medium which contains the enzymes and co-enzymes necessary for the biosynthesis. The latex is found in a network of interconnected cells which are located just below the bark of the rubber tree. It is in these cells that the biosynthesis of the latex takes place. The latex may be obtained by tapping the tree. In this process, a cut is made in the bark of the tree; through this cut the latex exudes, being forced out by the hydrostatic pressure of the vessel contents. When the latex vessels have emptied, they then take up water and the biosynthesis of the hydrocarbon polymer and the non-rubber constituents starts again. It takes only a day for the latex to regenerate; therefore, the tree can be tapped on alternate days. The productive life-time of the Hevea brasiliensis tree is often as long as 30 years.

In a rubber plantation, the latex is usually collected very early in the morning and transported to centralized plants for processing. Plantation latex intended to be used as such is normally concentrated by centrifuging in order to increase the rubber content from 35% to around 60%. A preservative, usually ammonia, is added to the latex concentrate before the latex is transported to the user.

1.3. Shortcomings of Raw Natural Rubber in Latex

The rubber molecules which occur in the particles of natural rubber latex are linear hydrocarbon polymer molecules of the following structure:



The molecular weights of the polymer molecules varying widely from 100,000 to 4,000,000. At room temperature, these molecular chains are coiled up and become tangled with one another as shown in Fig. 1.1. The ordered regions shown

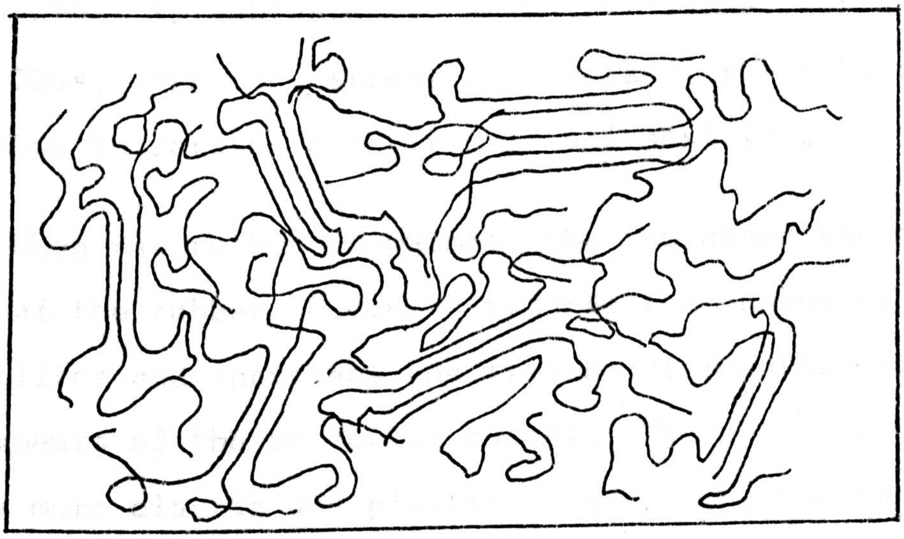


Fig. 1.1. Arrangement of rubber molecules at room temperature

in Fig. 1.1., in which sections of the molecular chains are orientated parallel to one another are known as crystallites. The coiled up conformation of the rubber molecules are responsible for the phenomenon of elasticity in rubber; when the rubber is stretched, the polymer molecules uncoil under the stress, thus allowing the rubber to extend by as much as 1000%. On release of the tension, the polymer molecules quickly revert to their coiled conformations, causing the rubber to return to its original length. However, when the stress is applied for a longer time or a larger stress is applied, the rubber does not now return completely to its original length when the stress is released, i.e., there is a residual permanent deformation. This phenomenon is a consequence of the viscoelastic nature of the material. It is explained by the rubber molecules physically sliding past each other after uncoiling under the large stress; process also occurs when a rubber is subjected to a smaller stress for a long time. Thus, when the stress is released, the rubber molecules are unable to return to their original positions.

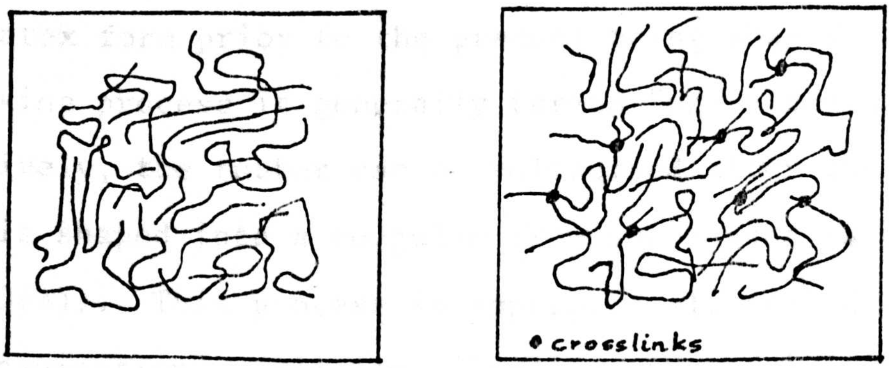
When raw rubber is warmed, the increased thermal motion of the rubber molecules reduces the number of crystallites and increases the freedom of rotation of the segments of the molecular chains. Thus, the material becomes more elastic and plastic. On cooling the same rubber down to room temperature, the converse behaviour occurs; more crystallites begin to form and the rubber becomes less elastic as a consequence. On further lowering the temperature to below the freezing temperature of water, the extent of crystallization can be such as to cause the rubber to become comparatively inextensible and even brittle.

The rubber molecules, being purely hydrocarbon, are very susceptible to dissolution in hydrocarbon solvent, therefore, it is not surprising that raw rubber readily swells and dissolves in benzene or toluene.

Raw rubber therefore has certain inherent undesirable properties which make the stabilized NR latex from the plantation unsatisfactory as a material from which to make rubber articles. These undesirable properties can be summarised as low tensile strength, sensitivity to temperature changes owing to the mobility of the molecules at high temperatures, and crystallization at low temperatures, and very poor resistance to organic solvents. Fortunately, however, these shortcomings of natural rubber can be greatly reduced by the process known as vulcanization.

1.4. Vulcanization of Rubber

Vulcanization involves the chemical crosslinking of the long linear and flexible rubber molecules to produce a three-dimensional network. Fig. 1.2. shows rubber molecules before and after vulcanization. The crosslinks



a) before b) after

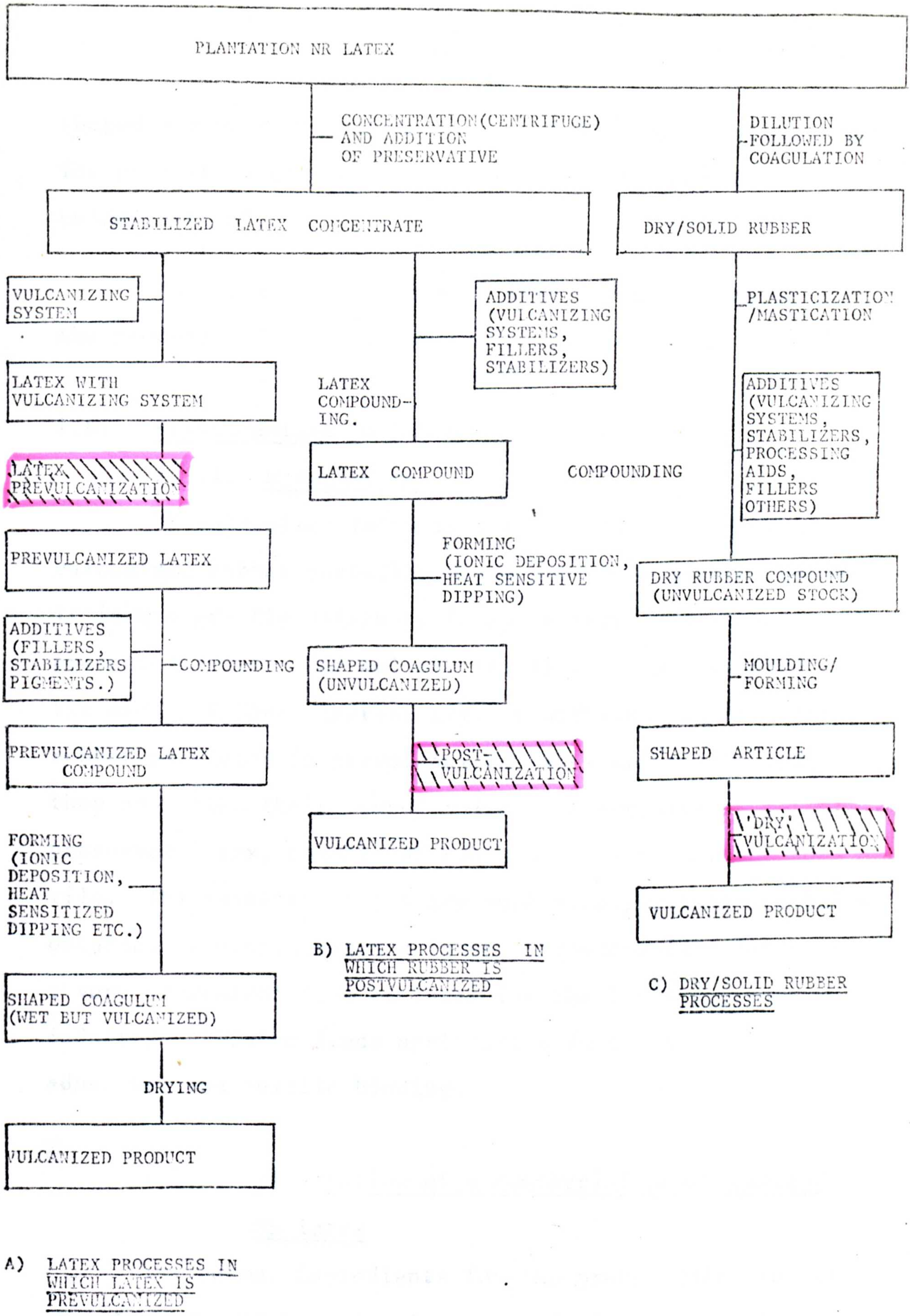
Fig. 1.2. Rubber molecules before and after vulcanization

prevent disentanglement of the polymer chains which is involved in dissolution and flow processes. Hence, vulcanization renders the rubber insoluble in organic solvents (although it nevertheless swells), imparts resistance to permanent deformation, and reduces sensitivity to temperature changes. However, the individual segments of the rubber molecules can still move freely. These segmental motions permit a vulcanized rubber to undergo large deformations without rupture and to return spontaneously to its original dimensions upon removal of the deforming force.

1.5. Forms of Rubber Vulcanization

Most rubber products are subjected to a vulcanization process. This may take place before, after or during the process by which they were shaped. Fig. 1.3. shows a flow chart which illustrates the technology of natural rubber, in both latex and dry rubber forms, with emphasis upon the point at which the process of vulcanization takes place.

It is seen (Fig. 1.3(A)) that rubber can be vulcanized in its latex form prior to the product being shaped. This crosslinking process is generally termed "prevulcanization". Alternatively, the rubber can be vulcanized after the product is shaped into a coagulum from compounded latex (Fig. 1.3(B)). This process is appropriately called "postvulcanization". Finally, there is the long-established and conventional crosslinking process for dry rubber (Fig. 1.3(C)). In this process, the product is often



A) LATEX PROCESSES IN WHICH LATEX IS PREVULCANIZED

B) LATEX PROCESSES IN WHICH RUBBER IS POSTVULCANIZED

C) DRY/SOLID RUBBER PROCESSES

Fig. 1.3. Illustrating the technology of natural rubber in both latex and dry rubber forms

shaped during or simultaneously with the crosslinking reaction. The process is conveniently known as "dry rubber vulcanization".

This thesis is concerned with an investigation into the process of latex prevulcanization.

1.6. Prevulcanized NR Latex

1.6.1. Description

Prevulcanized latex is a colloidal suspension of vulcanized rubber particles,dispersed in an aqueous medium. It is not greatly different in appearance from normal preserved latex. The colloid stability is approximately the same. Rather surprisingly, notwithstanding that the rubber particles in prevulcanized latex are vulcanized, they are, like their unvulcanized counterparts in normal preserved latex, capable of cohering to form a continuous film. The resultant films are much stronger than are those obtained from unvulcanized latex. Prevulcanized latex is a very convenient form of latex for the latex dipping industry. It also finds application in the fields of adhesives and textile binding.

1.6.2. Preparation of a commercial prevulcanized NR latex

The normal ingredients for the prevulcanization of NR latex are sulphur, accelerator and zinc oxide. In order to obtain homogeneity in the latex mix, these materials are first finely ground and dispersed in water with appropriate dispersing agents. It is usually necessary to grind the sulphur in ball mills for periods of at least 72 hours in order to obtain the best results. A typical formulation for a commercial prevulcanized latex is as follows[4]:

Ingredient	pphr dry	pphr wet
natural rubber as latex (60%)	100	167.0
potassium hydroxide solution (10%)	0.4	4.0
potassium caprylate solution (20%)	0.5	2.5
sulphur dispersion (50%)	0.5	1.0
zinc diethyldithiocarbamate dispersion (50%)	0.6	1.2
antioxidant dispersion (50%)	1.0	2.0
zinc oxide dispersion (50%)	0.25	0.5

The reaction is normally carried out by heating the mixture to a temperature between 70-80°C. Once the temperature is reached, it is maintained for an hour with slow stirring in a stainless steel jacketed vessel. After the reaction, the vessel is cooled and the latex strained through fine gauze to remove any coagulum which may be present. Sometimes, for special purposes, the prevulcanized latex is centrifuged to remove excess vulcanizing ingredients. For control of the degree of prevulcanization of the latex, various methods of assessment can be used. These include determination of the so-called "chloroform number" of the latex itself, and measurement of the equilibrium swelling and tensile properties of films dried down from the latex. One particular tensile property which is used is known as the "Prevulcanizate Relaxed Modulus" (PRM). These methods have been reviewed recently by Gorton and Pendle(5).

1.6.3. Advantages of prevulcanized latex compared to unvulcanized latex.

The greatest advantage of vulcanizing rubber in bulk in the form of latex as compared with postvulcanization is convenience compared to the trouble and expense of vulcanizing an equivalent amount of rubber in the form of thin deposits. Frequently, articles with very good physical properties are made from partially prevulcanized latex, and then the vulcanization completed by postvulcanization. Compared to a straightforward postvulcanization of coagulum obtained from unvulcanized latex, the earlier method represents a great saving in terms of energy and time. More consistent products are produced from the uniformly-prevulcanized latex than by the individual postvulcanization of products which may have non-uniform thickness. Latex-coated fabrics and paper, carpet backings, etc., can be merely dried after coating. Not only is the process simpler and quicker; there is also reduced risk of scorching heat-sensitive substrates. A further advantage of prevulcanized latex lies in the possibility of removing excess vulcanizing ingredients by centrifugation, so that the latex then contains almost nothing but particles of vulcanized rubber hydrocarbon.

Articles made from such a latex have a degree of transparency not easily obtained otherwise. Finally, before use, the prevulcanized latex can be compounded with fillers, colouring agent, etc., these ingredients are best added after the prevulcanization process. In this way, not only is the quantity of material to be heated reduced, but also heat-sensitive ingredients, such as colouring agents, are not subjected to heating.

1.7. Objectives of the Present Investigation

Whereas the sulphur-vulcanization of dry natural rubber has been thoroughly investigated and documented, very few studies on the prevulcanization of rubber latex have been published. Such publications as have appeared are mostly confined to improvements of industrial processes and formulations, and are often found in the patent literature. Very little work has been published in scientific journals on the systematic investigation of the prevulcanization of natural rubber latex. For these reasons, notwithstanding that the process was discovered in 1921, relatively little is known concerning the characteristics and mechanism of the prevulcanization of latex.

The objectives of the present investigation were therefore as follows:

(1) to discover more of the basic facts pertaining to the prevulcanization of natural rubber latex than are known at present;

(2) thereby to deepen understanding of the processes which occur during the prevulcanization of natural rubber latex.

Included within the scope of both these objectives are the studies on the following:

a) the fate of vulcanizing ingredients during prevulcanization;

b) the effects upon prevulcanization of varying the nature of the dithiocarbamate accelerator in respect of:

  (i) the alkyl chain-length of zinc dialkyl dithiocarbamate

  (ii) the nature of the metal counterion;

c) the effects upon prevulcanization of varying the levels of sulphur and zinc dialkyl dithiocarbamate accelerator in the prevulcanization recipe;

d) the kinetics of the disappearance of the vulcanization accelerator;

e) the nature of the crosslinks which are produced under various conditions of reaction;

f) the physical properties of films dried down from the latex.

CHAPTER 2

REVIEW OF LITERATURE PERTAINING TO PREVULCANIZATION OF NATURAL RUBBER LATEX

CHAPTER 2

REVIEW OF LITERATURE PERTAINING TO PREVULCANIZATION OF NATURAL RUBBER LATEX

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CHAPTER 2

REVIEW OF LITERATURE PERTAINING TO PREVULCANIZATION OF NATURAL RUBBER LATEX

2.1. Discovery of Latex Prevulcanization

Although there is uncertainty as to whether Goodyear or Hancock was the first to discover the sulphur-vulcanization of dry rubber, there is no doubt that Philip Shidrowitz was the discoverer of latex prevulcanization. His discovery was published in 1921.(7) It was made when Shidrowitz was attempting to improve an existing method for manufacturing cellular rubber products from NR latex. Together with Goldsborough,(6) he had earlier invented a method for manufacturing cellular rubber products (sponges) from NR latex. The sponges produced were postvulcanized. It occurred to Shidrowitz that if the starting NR latex were a dispersion of vulcanized rubber, subsequent vulcanization of the sponge would not be necessary. This would reduce the time required for the production of the sponges. However, it was found that it was still necessary to postvulcanize the sponges in an autoclave in order to impart the desired properties. Hence Shidrowitz failed to achieve his primary objective of improving the method of production. Nevertheless, he did succeed in prevulcanizing NR latex.

Shidrowitz then turned his attention to latex prevulcanization. He was subsequently granted a patent covering the process in 1921.(7) The patent describes how the latex could be prevulcanized by heating with sodium polysulphide, colloidal sulphur and zinc oxide. The reaction was carried out for 30-45 minutes at 145°C, the latex being heated by steam. However, it was necessary to reduce the steam pressure very slowly after the reaction in order to prevent the latex from boiling over. The method was improved by adding a water-soluble accelerator. This enabled prevulcanization to be carried out at much lower temperatures (70-80°C), thereby eliminating the need to use steam under pressure to heat the latex. This new method was also patented by Schidrowitz.(8)

2.2. Mechanism of Latex Prevulcanization

Although some 60 years has elapsed since the discovery of latex prevulcanization, little has so far been elucidated concerning the mechanism of the reaction. A reason often given for this is that such investigations as have been carried out were carried out in industrial organisations. The primary aims of such investigations have been to improve the quality and to reduce the price of the product. Very little fundamental research has been carried out having the objective of understanding how the process takes place. The small number of investigations of this latter type are reviewed in this chapter.

2.2.1. Early views of Hauser and Bender

One of the earliest discussions of the mechanism of latex prevulcanization occurs in a paper by Hauser and Bender presented at a rubber technology conference held in 1938.(9) These workers studied the electrophoretic behaviour of prevulcanized NR latex and compared it with that of an unvulcanized latex. No significant difference in ζ-potential was observed between the two latices. The surface tension, pH and specific conductance were also unaffected by prevulcanization. The absence of any apparent significant changes in surface properties of the latex particles after prevulcanization led the authors to conclude that during latex prevulcanization, adsorption phenomena are unlikely to be of primary importance in the mechanism of the reaction. These workers considered two possibilities for the mechanism of latex prevulcanization. According to the first mechanism, the vulcanizing ingredients, or possibly highly-reactive products formed from them, are retained in the dispersion until brought into close contact with the rubber particles during drying. The second mechanism is one in which the reactive reaction product of the vulcanizing ingredients are directly assimilated by the rubber hydrocarbon, without the surface condition of the particles being affected.

In the present writer's view, the first possibility is completely ruled out. The reason is because it suggests that the latex is not vulcanized until it is dried, which is not the case as it is known today. Nevertheless, the second possibility remains to be proven until today.

2.2.2. Subsequent views of Hauser, Le Beau and Kao

Four years after the rubber conference at which the earlier paper was presented, Hauser published a second paper,(10) this one being in collaboration with Le Beau and Kao. In this paper, an entirely different theory of latex prevulcanization was put forward. Rather surprisingly, the earlier work with Bender is not mentioned in this second paper. Hauser, Le Beau and Kao made a comprehensive study of the effects of the following prevulcanization variables upon the physical properties of, and amounts of combined sulphur in, both the latex and dry films from the latex: a) time, b) temperature and c) levels of zinc oxide, sulphur and accelerator. It was observed that when only sulphur was added, there was an increase in "sulphur combination" with time and temperature. This was interpreted as indicating that adsorption of the sulphur at the surfaces of the rubber particles occurred first, and was then followed by diffusion into the rubber particles. In the presence of an accelerator, the sulphur was thought to become activated in the rubber particles, thereby causing vulcanization to occur within the rubber particles. They also suggested that it was reasonable to suppose that vulcanization proceeds from the surface of the latex particle inwards. Furthermore, they considered that the formation of a crosslinked network within the particles would cause the diffusion of sulphur into the interior of the particle to become increasingly more difficult.

However, in the present writer's view, in spite of the many experimental data on physical properties and combined sulphur which these workers have published, these data do not convincingly support the theory which was put forward. Hence, their view that sulphur is initially adsorbed on to the particle surfaces and subsequently diffuses into the interior of the particles is no more than mere speculation. There was no discussion as to what were the forms of the adsorbed sulphur and accelerator. Neither was sufficient evidence given to support the view that the sulphur is first adsorbed and later activated by the accelerator on the surface of the rubber particles.

2.2.3. Theory of van Dalfsen

van Dalfsen(11) published a detailed study of the differences between the prevulcanization behaviours of fresh and purified latex. From his observations, he proposed a mechanism for latex prevulcanization in which sulphur first dissolves in the serum and then diffuses into the rubber particles where vulcanization takes place. He provided the following experimental evidence for this theory: Ammoniated latex was divided into two portions. The first portion was heated for 30 minutes with sulphur. The other portion was heated similarly without any sulphur having been added. After cooling, zinc oxide and accelerator (SDEC) were added to the first portion. To the second portion, sulphur, zinc oxide and accelerator were added. Both latices were then prevulcanized and films cast from them. The results of the analysis of the dried films for combined sulphur are given in Fig. 2.1. The results showed that preheating the latex with sulphur will subsequently give a higher rate and extent of sulphur combination during prevulcanization compared to prevulcanization of latex preheated without sulphur. This evidence led van Dalfsen to suggest that sulphur has first dissolved during preheating and diffused into the particles. However, in the view of the present writer, there is also another possibility which may happen during the preheating of latex with sulphur; i.e., the sulphur may react with the non-rubber substances present in the latex during preheating giving a more reactive product than the sulphur itself. Nevertheless, the evidence of van Dalfsen is not convincing enough to show any diffusion of dissolved sulphur into rubber particles.

2.2.4. Concept of partitioning of compounding ingredients between aqueous phase and rubber particles

Humphreys and Wake(12) attempted to study the structure of the films obtained by drying down prevulcanized latex. For their investigations, they wished to use prevulcanized latex having a high combined sulphur content. They soon realized that, no matter how much sulphur was added to the latex initially, the final combined sulphur did not exceed 1.8%. In order to explain this limiting

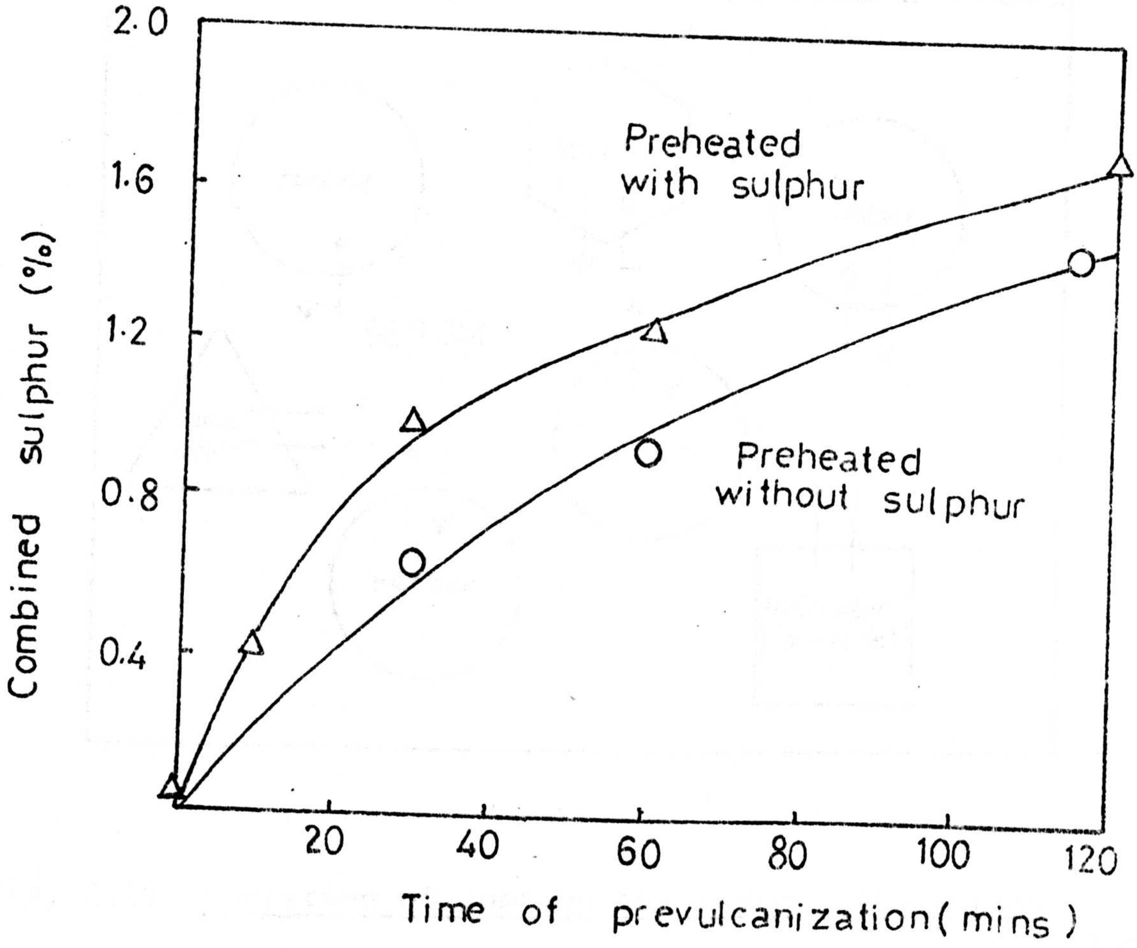


Fig. 2.1. Effect of preheating with sulphur upon prevulcanization of latex[(11)]

combined sulphur content, Blackley[(13)] suggested that the vulcanizing ingredients are partitioned between the serum and the rubber particles, as indicated in Fig. 2.2. The partitioning of the sulphur was believed by Blackley to be strongly in favour of the rubber phase, whilst the serum will be kept saturated with the vulcanizing ingredients as long as they are available as particles. It is important to note that the partitioning as proposed by Blackley is essentially a physical phenomenon. However,

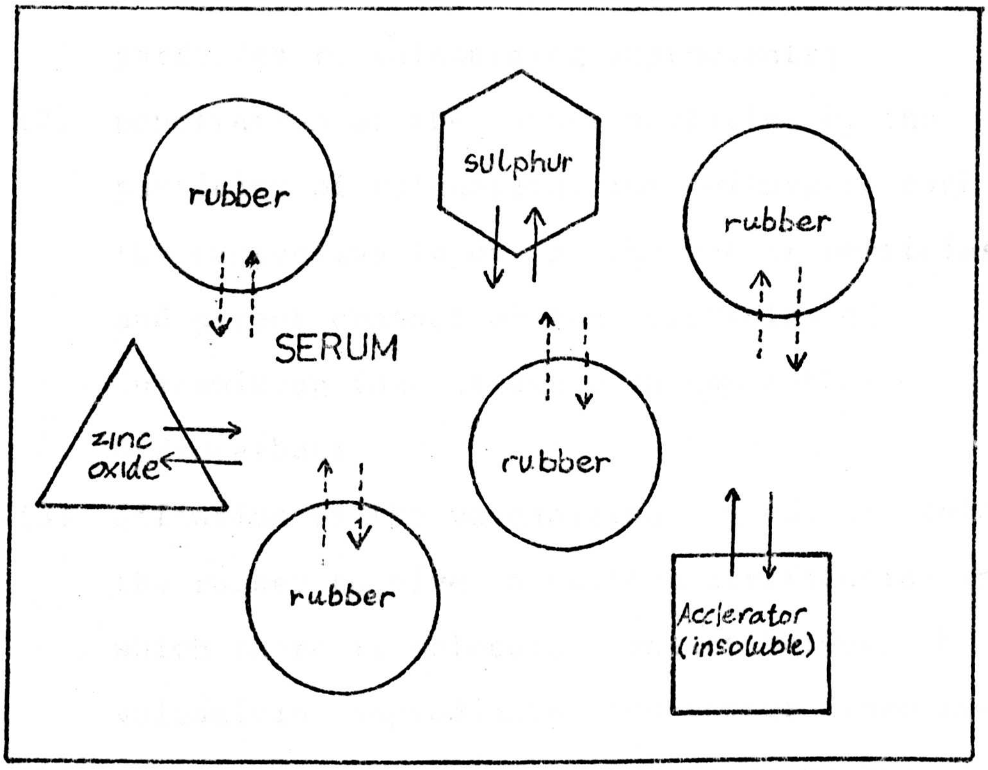


Fig. 2.2. Partition of compounding ingredients during latex prevulcanization according to Blackley(13)

the theory may be extended to cover the partitioning of reactive species which might be formed in the serum from reactions between the dissolved vulcanizing ingredients.

2.2.5. The collision theory

A very different mechanism from those discussed so far has been proposed by a group of Russian workers. This mechanism postulates direct contact between particles of vulcanizing ingredients and the rubber particles. Geller *et al.*(14) proposed that the mechanism of latex prevulcanization comprises a number of stages, the most important of which are the following:

(1) Collision of rubber particles with the particles of vulcanizing ingredients;

(2) penetration of the rubber particles by the particles of vulcanizing ingredients through the protective layers of the rubber particles, and direct contact of the particles of vulcanizing ingredients with the rubber hydrocarbon;

(3) diffusion of the vulcanizing ingredients into the rubber to give a uniform distribution in which there is molecular contact between the vulcanizing ingredients and rubber hydrocarbon;

(4) crosslinking reactions between the rubber hydrocarbon and the molecules of the vulcanizing ingredients.

In seeking support for their theory, they investigated the effect upon the kinetics of sulphur combination of various factors which increase the number or effectiveness of collisions between the particles in the prevulcanization system. They argued that, if their theory is true, these factors should accelerate the prevulcanization reaction. The factors investigated were:

a) concentration of vulcanizing ingredients;

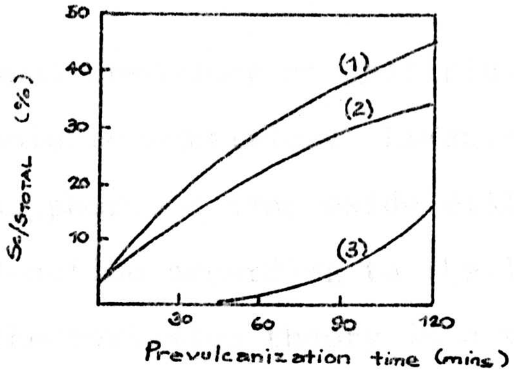
b) temperature;

c) the amount of protective substances;

d) preliminary treatment of latex mixtures.

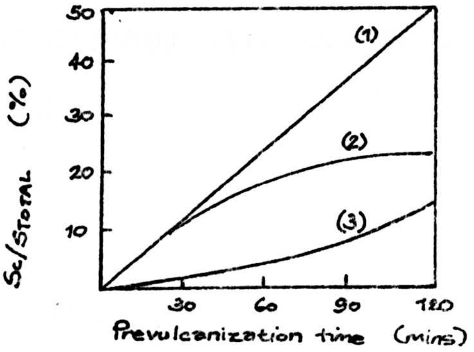
For the purpose of factor (c), latex from which some of the protective substances adsorbed on the rubber particle surfaces which had been previously removed by dialysis was used. The preliminary treatment of latex, (d), was carried out by adding zinc oxide and the water soluble accelerator in the latex and kept at room temperature for some time. Sulphur was then added and the mixture was prevulcanized. The idea for this investigation was to support their suggestion that latex prevulcanization may occur as a result of either simultaneous collision between three different types of particles or consecutive collision between two types of particles. In the latter case, the first collision would be between a rubber particle and a particle of one of the vulcanizing ingredients, say zinc oxide. Then the resultant double particle is envisaged as colliding with a particle of the other vulcanizing ingredient. Since simultaneous collisions between three particles are less probable than collisions between two, anything which increases the relative proportion of the latter should, they argue, accelerate the combination of sulphur to rubber.

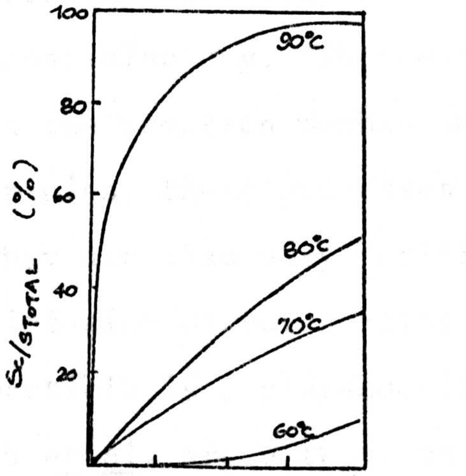
The results of the investigation are shown in Fig. 2.3(a-d). Even though all the results seem to support their collision theory, in the opinion of the present writer, the evidences also suggest other possibilities. Supposing there is a chemical reaction between the aqueous soluble accelerator sulphur and zinc oxide in the aqueous phase of the latex to form vulcanizing active species; temperature would then have a significant effect upon the chemical reaction apart from the effect



a) effect of increasing concentration of ZnO upon prevulcanization
(1) 3.0% ZnO
(2) 2.0% ZnO
(3) 0.0% ZnO

b) effect of increasing sulphur upon prevulcanization
(1) 1.9% sulphur
(2) 1.72% sulphur
(3) 1.00% sulphur





c) effect of temperature upon prevulcanization

d) effect of amount of protective substances upon prevulcanization
(1) dialysed latex
(2) ordinary latex

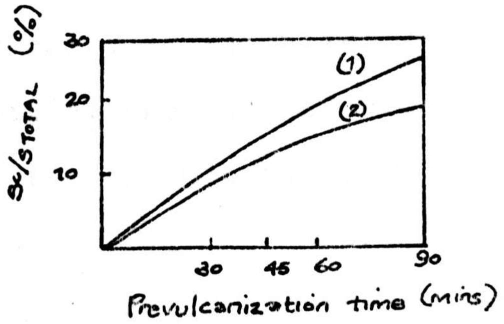


Fig. 2.3 Experimental data of Geller et al.[14] in support of their collision mechanism for latex prevulcanization

upon frequency of collision of the various non-aqueous soluble particles. Likewise, varying amounts of added sulphur and zinc oxide will also vary rate of the chemical reaction according to the law of mass action. Nevertheless, the collision theory is a very unique theory and worthy of consideration especially when non-aqueous soluble accelerator such as the zinc salt of dialkyl dithiocarbarmate are used during latex prevulcanization.

2.2.6. Views of Hu *et al.*

A group of Chinese workers, namely Hu *et al.*(15), believe the theory proposed by Geller *et al.* to be unsatisfactory. They disagreed with the Russian workers on the reaction mechanism having various stages. In their opinion, these processes are simultaneous and not separate. They are also very critical of the requirement that the diffusion of vulcanizing ingredients into the rubber particle is a prerequisite for prevulcanization to occur. Hu *et al.* argue that, as diffusion is a physical process whilst prevulcanization is a chemical process which takes place at a comparatively faster rate, it is unlikely that a uniform distribution of vulcanizing ingredients will persist throughout the course of the prevulcanization reaction. Hu *et al.* have proposed their own theory in which the vulcanizing ingredients, upon incorporation into the latex, first become adsorbed on the outer layers of the rubber particles by way of diffusion. Because the rate of prevulcanization is considerably greater than the rate of diffusion, the vulcanizing ingredients bring about prevulcanization almost immediately they diffuse into the rubber particles. Hu *et al*. further propose that the crosslinked structure formed on the outer layer of the particles during prevulcanization gradually moves into the particles through intensive motion of the rubber molecules within the particles. When further amounts of the vulcanizing ingredients diffuse into the rubber phase, a new crosslinked structure is formed in the new rubber molecular chain segments. Consequently, in the course of latex prevulcanization a motion occurs within the rubber particles owing to gradual redistribution of the crosslinked structure from the outer layer of the particles into the interiors of the particles. This motion is produced as a result of the motion of rubber molecules and their chain segments, and is thought by the Chinese workers to occur regardless of the state of prevulcanization of the latex. In fact the prevulcanization reaction is envisaged as taking place during the course of such motions.

2.2.7. Summary

In summary, literature reviewed so far does not give a coherent and convincing view of the mechanism of latex prevulcanization. Some of the theories are contradictory to one another. For example, the adsorption theory of Hauser, Le Beau and Kao(10) conflicts with the electrokinetic studies by Hauser and Bender(9), in which adsorption of vulcanizing ingredients on to the rubber particles is thought to be unlikely. Also, the concept of partitioning proposed by Blackley(13) conflicts with the 'collision' theory of Geller *et al.*,(14) the latter mechanism involving direct contact between the particles of vulcanizing ingredients and the rubber particles. However, it must be noted that most theories reviewed so far, except those of Hu *et al.* and Geller *et al.*, have been proposed independently of each other. As far as is known, this is the first occasion where all the theories have been considered together.

The general course of latex prevulcanization has been discussed in the preceding section. The subject may be conveniently divided into three broad aspects for further discussion, namely a) the vulcanizing ingredients in the latex prior to entering the rubber particles, b) the diffusion of vulcanizing ingredients into the rubber particles, and c) the crosslinking of the rubber hydrocarbon by vulcanizing ingredients within the rubber particles. The topics are discussed in the following sections (Sections 2.3-2.5).

2.3. State of Vulcanizing Ingredients in Latex prior to entering Rubber Particles

Prior to latex prevulcanization, sparingly-water-soluble vulcanizing ingredients, such as sulphur, zinc oxide and zinc dialkyl dithiocarbamate accelerators, are added to the latex as dispersions. The particle sizes of these dispersed vulcanizing ingredients are usually of the same order of magnitude as that of the latex particles. Fig. 2.4 gives an enlarged schematic diagram of a compounded latex, showing the rubber particles and particles of vulcanizing ingredients. The question arises as to how these vulcanizing ingredients get into the rubber particles which are separated from them by the aqueous phase of the latex. Some of the workers$^{(11,15)}$ whose investigations have been discussed in the preceding section concluded that the vulcanizing ingredients must somewhow first dissolve in the aqueous phase and then become adsorbed onto the surface of the rubber particles by way of diffusion.

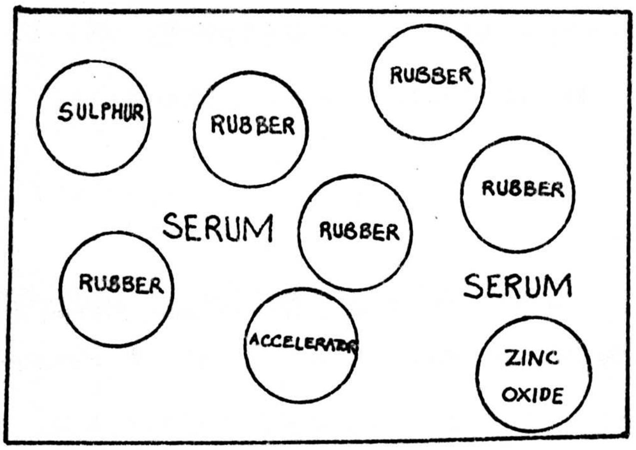


Fig. 2.4: Schematic diagram showing sparingly-water-soluble vulcanizing ingredients dispersed amongst rubber particles in compounded latex

2.3.1. Solubility of zinc oxide in latex

The dissolution of zinc oxide in ammonia-preserved latex is well documented(16,17). In the presence of water, zinc oxide behaves very much as though it were zinc hydroxide. In ammonia-preserved latex, the zinc ions are complexed by the free ammonia to give zinc-ammine complexes of various compositions. For this reason, zinc oxide dissolves in natural rubber latex to an extent of 0.18-0.30%.(16)

2.3.2. Solubility of sulphur in latex

Sulphur generally does not dissolve in water or in ammonia to any appreciable extent. However, the solubility of sulphur in latex has not been thoroughly investigated. van Gils(18) has recently claimed to have discovered that sulphur does actually dissolve in the serum of natural rubber latex in an amount sufficient for prevulcanization. He suggested that non-rubber substances in the latex, such as amino acids and proteins, may react with sulphur and bring it into the water phase. He studied the solubilization of sulphur in cystein solution, cystein being an amino acid which is found in natural rubber latex. Upon adding a cold 1% sulphur dispersion to a cold 1% cystein solution, he found that the turbidity (measured by an absorptiometer) fell sharply during the first three hours and then more gradually during the following 24 hours. On repeating the experiment with a warm solution (40-60°C), the turbidity was reduced much more rapidly.

2.3.3. Solubility of zinc dialkyl dithiocarbamates in latex

Unlike the alkali-metal and ammonium salts, all the zinc dialkyl dithiocarbamates are almost insoluble in water. A thorough search of the literature has failed to reveal any information concerning the solubility of these accelerators in latex.

2.3.4. Solubility of vulcanizing ingredients in latex and their effects upon prevulcanization of latex

It is difficult to determine with precision the solubilities of individual vulcanizing ingredients in natural rubber latex. This is because in order to analyse for the dissolved vulcanizing ingredient in the serum, it is usually necessary first to separate the rubber from the serum. The separation technique, such as ultracentrifugation or coagulation, inevitably mechanically entraps some of the dissolved vulcanizing ingredients amongst the rubber particles. Hence, the results are often dubious and unreliable. Besides, whether there is any dissolution of vulcanizing ingredients and how much is dissolved is one factor; more importantly, how significant are the dissolved vulcanizing ingredients for latex prevulcanization is entirely another matter. With this in mind, Hu et al.(15) conducted a series of experiments to investigate the solubilities of vulcanizing ingredients and their effects upon latex prevulcanization. The vulcanizing ingredients investigated were sulphur and zinc oxide in the presence of sodium diethyl dithiocarbamate. The experiments involved first extracting the serum from latex by a freezing method. The vulcanizing ingredients were then added in different combinations into the serum, and the serum then heated for 30 minutes at 70°C. By using a centrifuge, undissolved vulcanizing ingredients were removed from the serum immediately after heating. The serum was then added to the latex and prevulcanization attempted. The results are tabulated in Table 2.1.

Types of vulcanizing ingredients added to serum	Types of vulcanizing ingredients added to latex	Effects upon prevulcanization
Sulphur	Zinc oxide + SDEC	Very slight prevulcanization
Zinc oxide	Sulphur + SDEC	Normal prevulcanization
Sulphur + zinc oxide	SDEC	No prevulcanization
Sulphur + SDEC	Zinc oxide	No prevulcanization
Zinc oxide + SDEC	Sulphur	Normal prevulcanization
Sulphur + zinc oxide + SDEC	-	No prevulcanization
SDEC	Zinc oxide + sulphur	Normal prevulcanization

Table 2.1: Results of Hu *et al.*(15) for the solubilities of vulcanizing ingredients in latex serum, and effects upon prevulcanization

Hu et al. concluded that the solubility of sulphur in the serum is very low, because the dissolved sulphur in the serum caused only slight prevulcanization of the latex in the presence of zinc oxide and the SDEC accelerator. These workers also confirmed from the results that sufficient zinc oxide is dissolved in the serum to effect prevulcaniation. However, it is interesting to note, that when the three vulcanizing ingredients were added to the serum together, they lost their ability to prevulcanize the latex. The authors attributed this interesting observation to chemical interactions between the dissolved vulcanizing ingredients in the serum, with a consequent loss of the activity essential for latex prevulcanization.

2.3.5. Conclusion

It is clear that most of the vulcanizing ingredients are either almost insoluble or soluble to only a very low extent in the latex serum. In view of this, it is reasonable to suppose that any satisfactory mechanism of latex prevulcanization must involve more than mere physical dissolution of the vulcanizing ingredients in the serum, followed by diffusion of the dissolved ingredients into the rubber particles.

2.4. Diffusion of Vulcanizing Ingredients into Rubber Particles

There is no clear-cut evidence in the literature concerning the mechanism by which the vulcanizing ingredients of low water solubility enter the rubber particles during latex prevulcanization. However, it is certain that during the reaction the rubber hydrocarbon within the rubber particles is gradually vulcanized. This observation has been established by experiments reported by Freundlich and Hauser(19), by Green(20), and by Hauser and Bender(9). These workers confirmed that vulcanization took place within the rubber particles whilst they are still dispersed in the latex, and not, as has been suggested by some workers during the drying of the latex. Hence, most theories of latex prevulcanization require that at some stage the vulcanizing ingredients diffuse from the surface of the rubber particles into the core. Some workers, for example, van Dalfsen(11), have suggested that, as in the case of the vulcanization of dry rubber, the vulcanizing ingredients have first to be uniformly distributed within the rubber particle by way of diffusion before vulcanization can take place. On the other hand, Hu *et al.*(15) consider that diffusion is a much slower process compared to the vulcanization reaction. Hence, immediately the vulcanizing ingredients diffuse into the rubber particles the vulcanization of the rubber hydrocarbon begins.

However, a more important question concerns the importance of the role which the diffusion of the vulcanizing ingredients into the rubber particles plays in latex prevulcanization. Hu *et al.*attempted to answer this question by a series of experiments in which they investigated the effect of the maturation of a partially-compounded latex upon the rate of prevulcanization. They assumed that the longer the time of maturation, the greater were the amounts of vulcanizing ingredients which would have diffused into the rubber particles. In their experiment, sulphur and zinc oxide were initially compounded into the latex under ambient conditions. The compounded latex was then matured for different lengths of time at 23°C. After maturation, the compounded latex was prevulcanized by adding sodium diethyl dithiocarbamate. The results are shown graphically in Fig. 2.5. The results indicate that the rate of diffusion of the vulcanizing ingredients in to the rubber particles is not significant as far as the prevulcanization of latex is concerned.

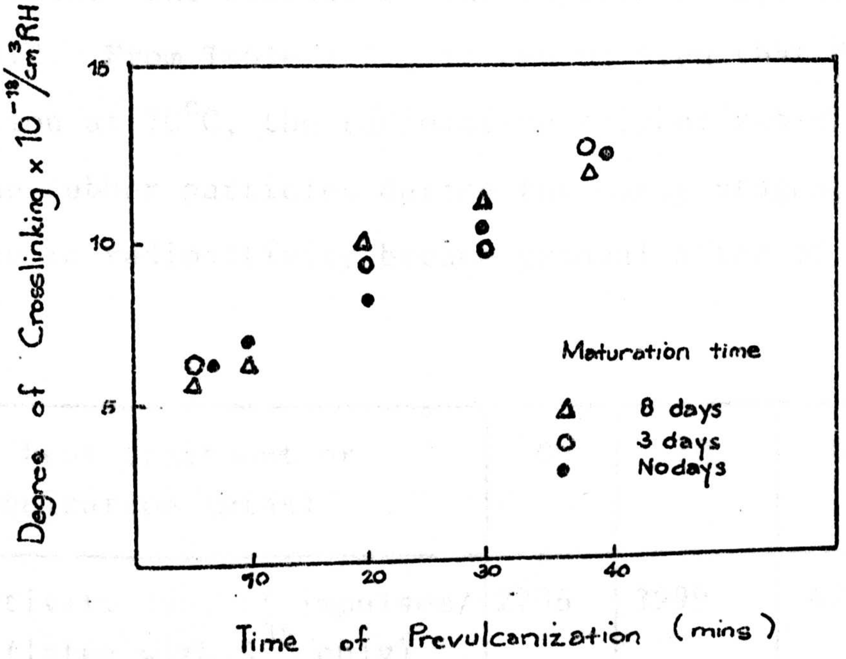


Fig. 2.5. Effect of maturation upon the rate of latex prevulcanization.(15)

In another series of experiments, the diffusion of vulcanizing ingredients into the rubber particles was studied by the same workers(15) using radioactive sulphur,

S^{35}. In this experiment, radioactive sulphur was compounded into the latex and the mixture matured without any prevulcanization at 70°C. Another latex compound consisting of radioactive sulphur, zinc oxide and sodium diethyl dithiocarbamate was prevulcanized at 70°C. The diffusion rate of radioactive sulphur in the rubber particles during both heat-treatment and prevulcanization were determined by sampling the latex at regular intervals, removing the serum, and then investigating the radioactivity changes after coagulation. The results of the experiment are shown in Table 2.2. From Table 2.2., it can be seen that during maturation at 70°C, the radioactive sulphur rapidly diffused into the rubber particles during the early stages, but the increase in radioactivity became gradual after 30 minutes

Time of heat treatment or prevulcanization (mins)	0	30	60	90
Radioactivity (no. of impulses/ 5 min) (latex with S^{35} only)	2736	3999	4243	4322
Radioactivity (no. of impulses/ 5 min) prevulcanized latex (S^{35} + ZnO + SDEC)	3021	3095	3229	3382

Table 2.2: Radioactivity changes in coagulum of unvulcanized and prevulcanized latex with time of prevulcanization/heating(15)

of heating. When prevulcanization and diffusion proceeded at the same time, the increase of radioactivity in the coagulum was found to be very slight. From the results, it was concluded that, in the case where sulphur alone was present, the sulphur can diffuse steadily into the rubber particles, whereas when zinc oxide and accelerator are also present, only negligible quantities of radioactive sulphur diffuse in. Hence, these workers concluded that during latex prevulcanization, there is limited diffusion of vulcanizing ingredients into the rubber particles even though merely heating the latex with sulphur alone has caused the sulphur to diffuse to a considerable extent into the rubber particles.

2.5. Crosslinking of Rubber Hydrocarbon within Rubber Particles

It is well established that vulcanization of the rubber hydrocarbon takes place within the rubber particles during latex prevulcanization. There is also no doubt in the minds of most workers that the chemical reactions between the rubber hydrocarbon molecules and the vulcanizing ingredients to give crosslinked structures are of a similar nature to those which occur during the vulcanization of dry rubber. However, it has been noted that there is one important difference between dry rubber vulcanization and latex prevulcanization. In the case of dry rubber vulcanization, the vulcanizing ingredients are uniformly distributed amongst the rubber hydrocarbon molecules before chemical reaction between them is effected by heat. In latex prevulcanization, the distribution of the vulcanizing ingredients in the rubber particles occurs by way of diffusion, and the prevulcanization reaction is normally carried out simultaneously. Hence, it is not surprising that some investigators on this subject have speculated that latex prevulcanization proceeds from the surface of the rubber particles inward, and that the formation of crosslinked structures in the outer layers of the rubber particles impedes further diffusion of vulcanizing ingredients into the interior of the particles.(10) If this speculation is true, then prevulcanized latex would consist of rubber particles which comprise a soft core of unvulcanized rubber molecules surrounded by an outer layer of vulcanized rubber, as shown in Fig. 2.6.

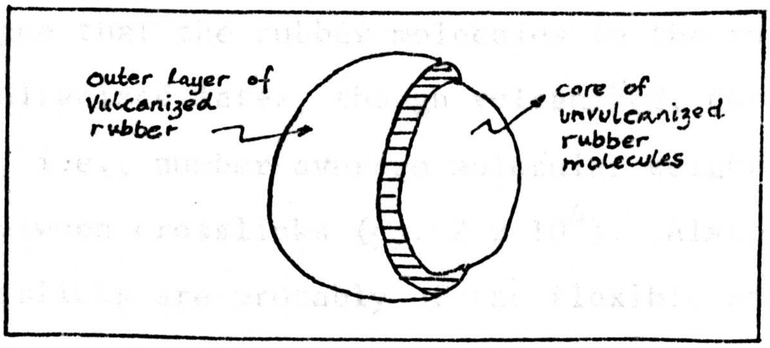


Fig. 2.6. Rubber particle in prevulcanized latex, as pictured by some research workers.

There are no investigations recorded in the literature which throw light upon this aspect of crosslinking within the rubber particles. One of the main reasons is perhaps the formidable experimental difficulties involved in studying the changes in the inner structure of rubber particles during latex prevulcanization.

Hu, Y.-M et al.* have noted an interesting observation(25) which has led them to propose the theory that during latex prevulcanization the crosslinked structures redistribute within the latex particle. They have concluded from NMR half-line width data that the molecular motion of the rubber molecules in the rubber particles of latex is much greater than that of rubber molecules in dry rubber. They suggest that the greater molecular motion of the rubber molecules in latex particles is probably a consequence of the presence of non-rubber substances and water dispersed in the rubber particles. Kemp(26) and Blackley(27) both state that there is approximately 10% of water dispersed in the rubber particles in natural rubber latex. Hu et al. also made observations on the molecular motions of rubber molecules in the rubber in prevulcanized latex. They argue that the rubber molecules in the rubber particles of prevulcanized latex, though vulcanized, normally have a high Mc, i.e., number average molecular weight of network chain between crosslinks (ca. 2 x 10^4). Also, the type of the crosslinks are probably of the flexible polysulphidic type. Hence the molecular motion of the rubber molecules in the rubber particles are unlikely to be impeded to any great extent by prevulcanization. To confirm their idea, they conducted an experiment in which they investigated

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*This is the same group of Chinese workers who have been referred to several times before in this review. They have carried out numerous investigations of latex prevulcanization. Unfortunately, most of their literature is still not translated from the Chinese(15,21-24).

the NMR half-line width of prevulcanized latex. The results are shown in Table 2.3. As can be seen from Table 2.3,

Time of prevulcanization (mins) @ 70°C	0	15	30	60	120
Crosslink density x $10^{-18}/cm^3$ of RH	-	-	11.0	16.4	23.5
Half-line width (Gauss)	0.0541	0.0546	0.0618	0.0618	0.0628
(ppm)	5.76	5.82	6.58	6.58	6.68

Table 2.3: Changes of NMR half-line width during latex prevulcanization.(25)

there is a slight increase in half-line width, which is interpreted as implying a decrease in the molecular motion. Hence, the molecular motion of the rubber molecules in the rubber particles of prevulcanized latex is slightly reduced as expected during prevulcanization. However, according to the investigators the decrease in molecular motion over the whole period of prevulcanization does not appear to be substantial.

Hu *et al*. were able to confirm these conclusions by an investigation of the changes in half-line width of a radiation-prevulcanized latex. Table 2.4 shows the results. Comparing the results in Table 2.3 with those in Table 2.4, it is seen that radiation-prevulcanization affects the NMR half-line width considerably more than does prevulcanization with sulphur. This is interpreted as implying that the

Radiation Dose (rad)	1×10^6	2.5×10^7	3.2×10^7
Crosslink density $\times 10^{-18}.cm^3$ of RH	-	17.4	20.8
Half-line width (Gauss)	0.0541	0.0722	0.0748
(ppm)	5.76	7.67	8.12

Table 2.4: Changes in NMR half-line width during radiation-prevulcanization of latex(25)

molecular motions are reduced to a greater extent in radiation-prevulcanized latex than in sulphur-prevulcanized latex. According to these workers, this interpretation is consistent because radiation prevulcanization is expected to result in a more compact crosslinking (higher crosslink density) than is sulphur prevulcanization. Also, the crosslinks are of the carbon-carbon type, which are less flexible than are the polysulphidic crosslinks which they presume form during sulphur prevulcanization. Both the factors reduce the ease of motion the rubber molecules have in the rubber particles of radiation prevulcanized latex.

Thus Hu *et al.*(15,25) proposed their theory that redistribution of crosslinked structures occurs because of the mobility of the rubber molecular chain segments and the crosslinked structures. In this theory, the diffusion of vulcanizing ingredients and the motion of rubber molecular main segments are assumed to occur at similar rates, so that after the entry of the vulcanizing ingredients into the rubber particles, it is likely that the crosslinked structures will be displaced as a consequence of the motions of rubber molecular chain segments before further vulcanizing ingredients diffuse into the rubber particles. Temperature plays a triple role in the theory: it promotes diffusion of the vulcanizing ingredients into the rubber particles; it effects the prevulcanization reaction between the rubber hydrocarbon and vulcanizing ingredients; and it increases the molecular motion of the rubber chain segments and crosslinked structure within the rubber particles to give uniformly crosslinked rubber particles.

The theory that mobility of crosslinked structure and rubber molecular chain segments plays an important part in latex prevulcanization can also explain the continuous enhancement of degree of prevulcanization during ageing. The residual vulcanizing ingredients can continuously enter into the particles to participate in the prevulcanizing reaction.

It is also interesting to note how the theory is employed to explain why there is no reversion during latex prevulcanization. The absence of reversion is characteristic of the prevulcanization of latex, and contrasts with the vulcanization behaviour of dry rubber. It is suggested that when the degree of prevulcanization has reached a certain extent, the restriction of the molecular motions by the presence of the crosslinks becomes greater. There will now be reduced opportunity for any further prevulcanization which might otherwise lead to over-prevulcanization or even reversion. The present writer agrees with Blackley(49) who finds this explanation of absence of reversion during latex prevulcanization using the above theory quite unsatisfactory. The behaviour of reversion in vulcanization of dry rubber implies the degradation of crosslinks which have already formed. It is difficult therefore to see why restriction of the molecular motions should prevent reversion. A more likely reason for absence of reversion in latex prevulcanization is probably the low temperature at which the reaction is carried out.

Fig. 2.7 gives results for the changes in crosslink density which occur during storage or maturation of prevulcanized latex(15). It can be seen that the latex

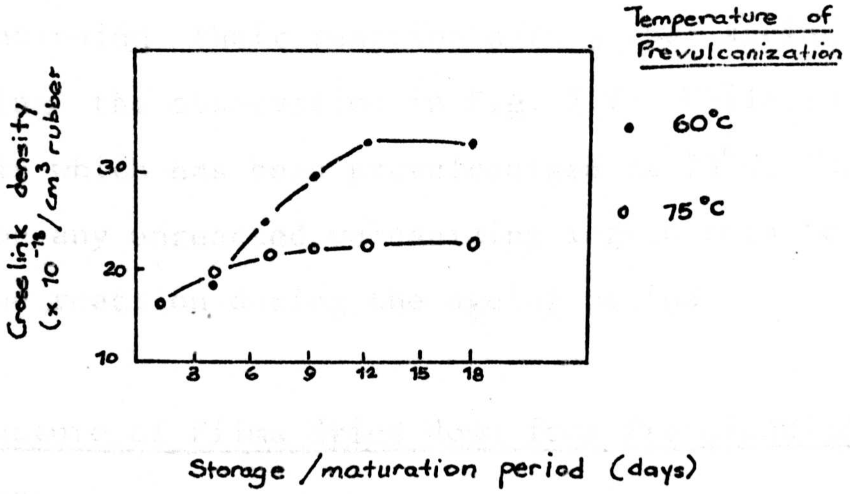


Fig. 2.7: Changes in crosslink density during storage/maturation of latex vulcanized at two temperatures(15)

which was prevulcanized at the higher temperature, and which therefore presumably had the higher degree of prevulcanization, showed less changes during ageing. This is one piece of evidence which Hu et al.(15) used to support their theory of the mobility of crosslinked structure and the continuous enhancement of degree of prevulcanization during ageing. In the view of the present writer, apart from the theory of Hu et al. there is also another possibility to the observation illustrated by the results in Fig. 2.7. Since there is no mention in the literature whether any purification to remove unreacted vulcanizing ingredients has been carried out in the two prevulcanized latices; presumably the latex prevulcanized at 75°C would have more of the added vulcanizing ingredients consumed during prevulcanization than that prevulcanized at 60°C. Therefore, it is perhaps the unreacted vulcanizing ingredients in the sample prevulcanized at 60°C continuing their reaction during the ageing period, hence, giving the observation in Fig. 2.7. While in the other sample which has been prevulcanized at 75°C, there might not be any unreacted vulcanizing ingredients to continue the reaction during the ageing period.

2.6. Structure of Films dried down from Prevulcanized Latex

It is well known that when rubber is vulcanized it loses its tackiness. Hence at first sight it seems unlikely that the rubber particles in prevulcanized natural rubber latex will coalesce together to form a continuous film when the prevulcanized latex is dried down. Even more unlikely is the fact that the resultant films have physical properties which are superior to those obtained by drying down unvulcanized natural rubber latex (see Fig. 2.9). In view of this, the structure of these films and the nature of the forces which hold the individual rubber particles together have been a topic of interest to several investigators. Several theories have been proposed to account for the nature of these forces and the structure of the dried films. Some of these theories have since been shown to be incorrect, whilst others remain purely speculative and unconfirmed.

2.6.1. Theory that strength and coherence are consequences of primary valence bonds

This is probably the earliest theory proposed to account for the formation and strength of films dried down from prevulcanized latex. This theory attributes the formation and strength of the films to the formation of inter-particle primary valence bonds. These bonds are presumed to be further crosslinks which form between the rubber particles during the drying period. This theory has been disproved because strong, coherent films are still formed even though the films are dried under conditions such that further vulcanization is not expected. More convincingly the theory has been shown to be incorrect by swelling experiments(12). Films dried down from prevulcanized latex under conditions such that further vulcanization is unlikely to occur are sufficiently crosslinked to prevent dissolution when immersed for prolonged periods in a solvent such as benzene, but collapse into a mass of very small separate particles when a shearing force is applied. Hence it is concluded that primary valence bonds or crosslinks do not exist between the particles, but do exist within the particles.

2.6.2. The 'cement' theory

The view of workers such as Hauser(29) and Flint(28) was that when water is removed during drying, the adsorbed layer of proteins and other non-rubber substances remains as a coating on the particles which acts as a cement holding the particles together. This theory has also since been disproved by experiments(12) which showed that strong films are still formed even although the latex was repeatedly creamed in the presence of a soap to displace the protein layer.

2.6.3. Theory that strength and coherence are consequences of secondary valence bonds

The theory that the strength and coherence of films from prevulcanized latex are consequences of secondary valence bonds was first formulated by van Dalfsen(31). It was subsequently demonstrated experimentally by Humphreys and Wake(12). The theory proposes that the cohesion between rubber particles during the drying of unvulcanized and prevulcanized latex is a consequence of the formation of the secondary valence bonds between the rubber molecules. These bonds are also known as van der Waal's forces. Although these forces between two molecules are known to be weak, the theory depends upon the fact that in one rubber particle there may be as many as 10^6 rubber molecules, (as would be the case for a rubber particle of diameter 1 μ which contained rubber of number-average molecular weight 300,000). Hence, the sum of the van der Waal's forces between two rubber particles can be appreciable, since the force between two individual molecules is multiplied by a factor of the order of 10^6.

Humphreys and Wake(12) demonstrated the secondary valence bond theory by a swelling experiment. They used benzene to swell films obtained by drying down prevulcanized latex. The results showed that the films swelled to a limited extent but the swollen films could not be extended by any measurable amount. When a shearing force was applied to the swollen film, it collapsed into a mass of small separate particles. It was concluded from this experiment that, firstly, the swelling in benzene is limited because the crosslinks within the particle limit the solvent uptake. Secondly, it was concluded that the imbibtion of benzene weakens the secondary valence bonds and destroys the cohesion between the rubber particles, and hence the swollen sample cannot be extended because of the loss of cohesion. This argument is supported by the observation that the strength of swollen films is recoverable when the benzene is removed from the film.

Blackley(32) has given a diagrammatic illustration of the secondary valence bond theory for a pair of latex particles. This is shown in Fig.2.7 for particles from unvulcanized latex. It is suggested that, when a latex is dried down, the rubber particles cohere together to give regions of overlap between the particles. In these regions of overlap, secondary valence bonds between the rubber molecules of different particles are formed. According to Blackley(32), the theory is consistent with observed mechanical properties of films dried down from both unvulcanized and prevulcanized natural rubber latex. For example, when a tensile stress is applied to a dried film, the initial extension leads to a rearrangement

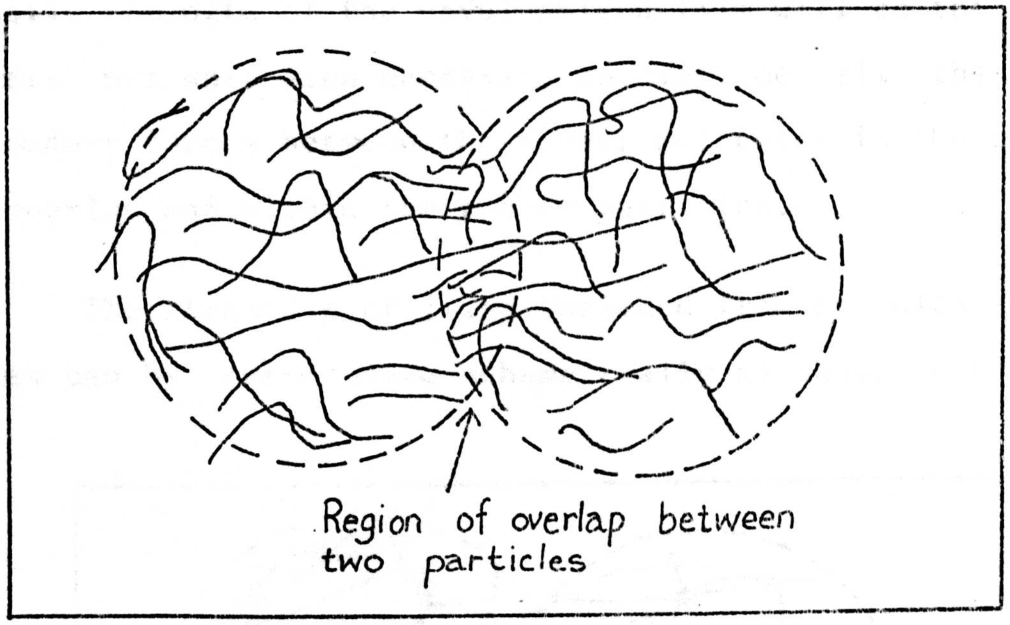


Fig.2.7 Schematic representation of the secondary valence bond theory showing two rubber particles in a film obtained from unvulcanized latex(32)

of the molecules in the region of overlap between the particles. In the case of films obtained from unvulcanized latex, the molecules within and between the particles are able to move independently of each other. Hence the tensile strength of the unvulcanized film will be the stress per unit area necessary to overcome all the secondary forces between the rubber molecules in the region of overlap and within the rubber particles.

The structure of films obtained from prevulcanized latex can be represented schematically as shown in Fig.2.8.

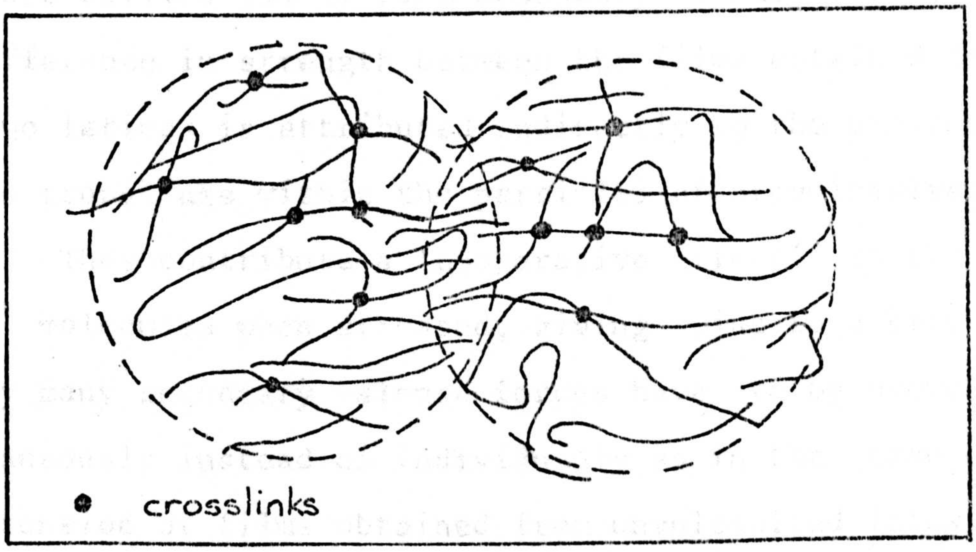


Fig.2.8 Schematic representation of the secondary valence bond theory showing two rubber particles in a film obtained from prevulcanized latex

When subjected to a tensile stress, the initial stage of the extension of the film will be similar to that of a film from unvulcanized latex film, the rubber molecules being able to rearrange in the region of overlap by moving independent of each other. But very soon after the rearrangement, the molecules are no longer able to move independently of each other because they are attached to a large number of other molecules by means of crosslinks as shown in Fig.2.8. Hence, in order to separate the particles, it is now necessary to overcome at the same time the secondary valence bonds which have formed between a large number of molecules.

According to this theory, the strengths of the dried films obtained from both unvulcanized and prevulcanized latex are derived solely from secondary valency forces. The difference in strength between the films obtained from the two latices is attributed indirectly to the presence of the crosslinks within the particles of prevulcanized latex. They contribute a 'cooperative effect' to the rubber molecules when stressed, giving rise to a situation whereby many secondary valence forces have to be overcome simultaneously instead of individually as in the case of the extension of films obtained from unvulcanized latex. The theory also predicts that the ultimate tensile strength of films obtained from prevulcanized latex will be intermediate in magnitude between the ultimate tensile strength of films obtained from unvulcanized latex and that of a postvulcanized latex film. The latter films are believed to contain inter-particle crosslinking.

Very recently, Merrill(33) has interpreted his tensile stress-strain results for films obtained from unvulcanized and prevulcanized latex (Fig.2.9) in terms of the secondary valence theory. According to Merrill$^{(33)}$, the

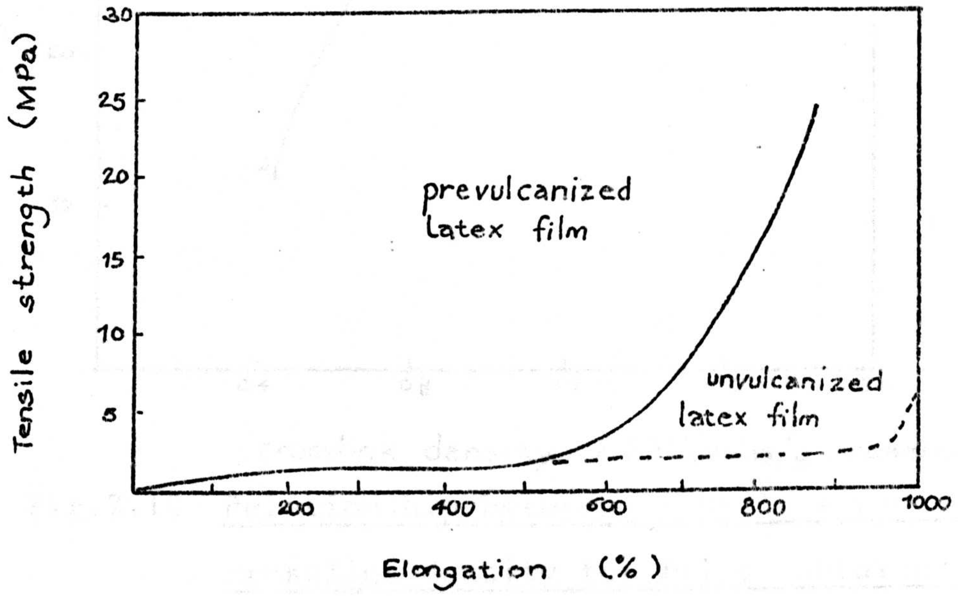


Fig.2.9 Stress-strain behaviour of films obtained from prevulcanized latex and unvulcanized latex (after Merrill$^{(33)}$)

initial flat region is associated with rearrangement of the rubber molecules independently of each other. The steep rise in stress on further extension is interpreted as the region where it is no longer possible for the rubber molecules in any given particle to move independently of each other, as they are all connected together.

Using the same theory, Merrill$^{(33)}$ also gave an explanation for the maximum which he observed in his results for tensile strength as a function of crosslink density (see Fig.2.10). Merrill argued that the initial increase of tensile strength is due to crosslink insertion.

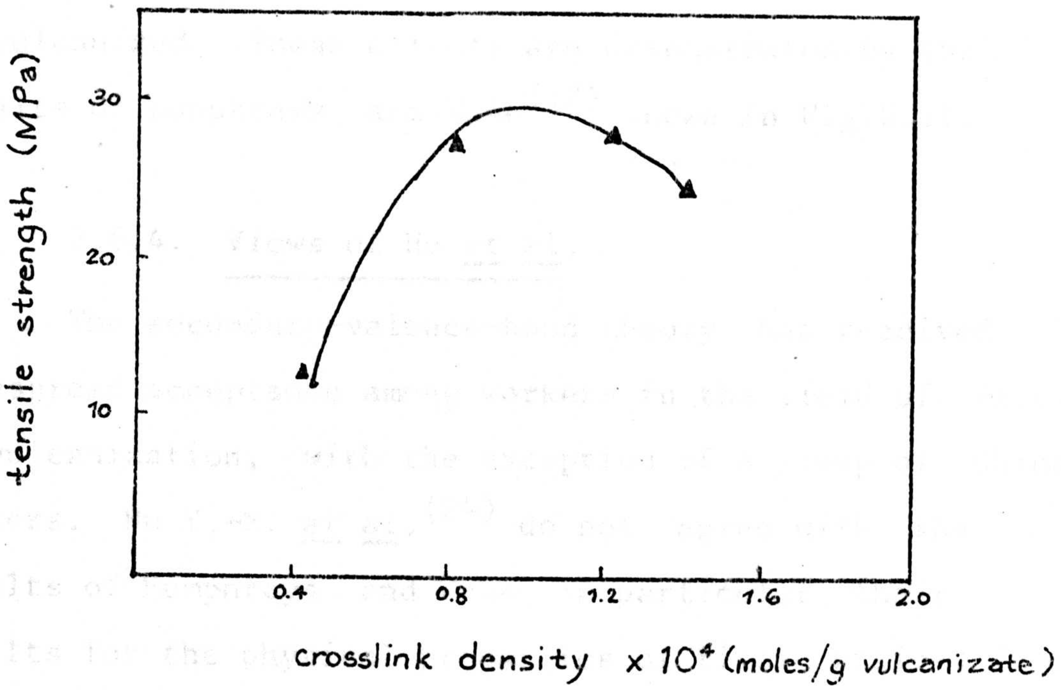


Fig.2.10 Relationship between tensile strength and crosslink density for films obtained from prevulcanized latex (after Merrill(33))

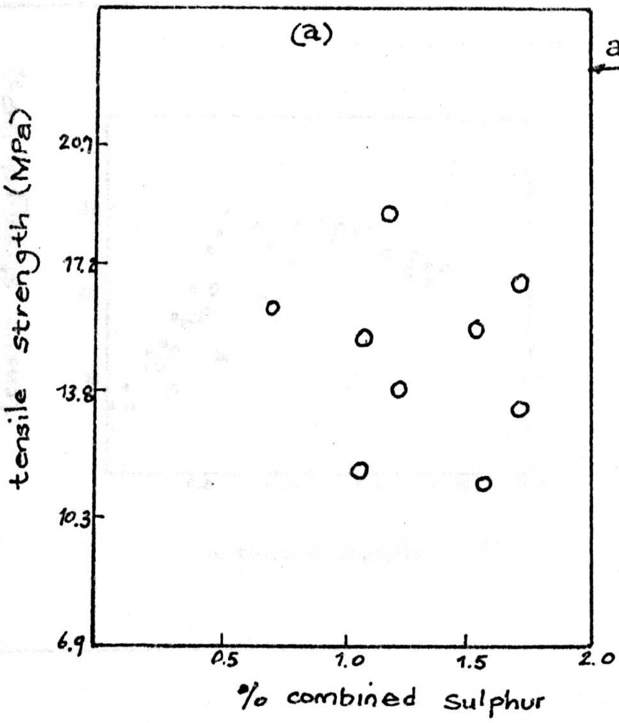
As the crosslink density increases, there comes a stage at which restriction of the mobility of the chains causes a decrease in the number of chain-ends which contribute to the secondary valence forces between neighbouring particles. There is consequently a reduction in the tensile strength.

It must also be pointed out that, because van der Waal's forces are essentially physical in origin, the physical properties of films obtained from prevulcanized latex tend to be independent upon the degree of prevulcanization of the latex. Hence, tensile strength of films obtained from prevulcanized latex are little dependent upon factors such as combined sulphur and crosslink density, and are insensitive to the temperature at which the latex is prevulcanized. These effects are demonstrated by the results of Humphreys and Wake(12) shown in Fig.2.11.

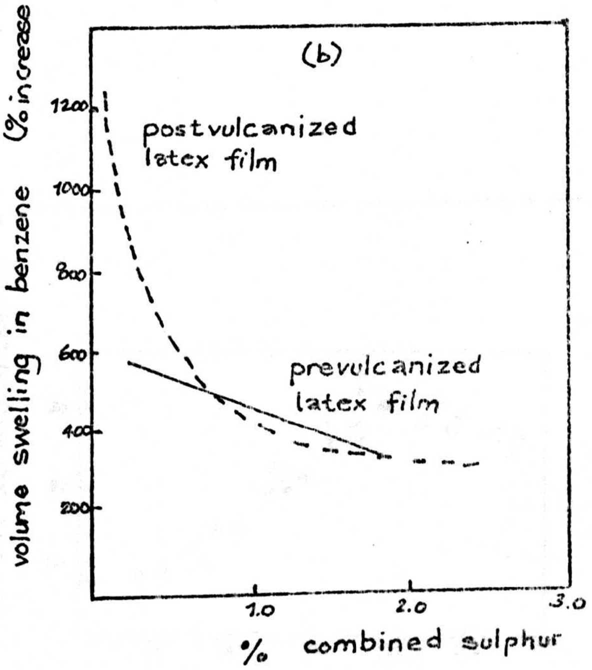
2.6.4. Views of Hu *et al.*

The secondary-valence-bond theory has received widespread acceptance among workers in the field of latex prevulcanization, with the exception of a group of Chinese workers. Hu Y.-M. *et al.*(24) do not agree with the results of Humphreys and Wake, in particular, their results for the physical properties of films obtained from prevulcanized latex. In the opinion of the Chinese workers, there is a definite relationship between the degree of prevulcanization and the properties of films dried down from the latex. In their results, shown in Fig.2.12, an interrelationship between the properties of dried film, combined sulphur and crosslink density was observed. These results are contradictory to those of Humphreys and Wake (see Fig. 2.11). Hu *et al.* were also critical of the experimental design used by Humphreys and Wake. They argued that the data of Humphreys and Wake represent the summation of different prevulcanization operations and therefore do not reveal much about the prevulcanization reaction itself.

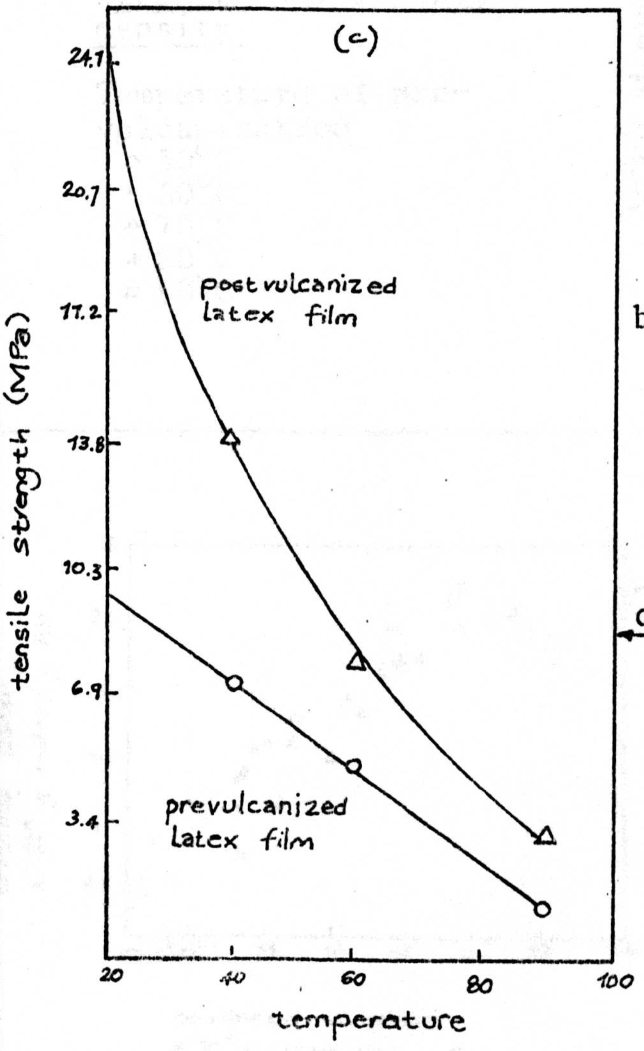
The Chinese workers have their own theory for the mechanism formation of films from prevulcanized latex. It is based on an extension of their idea that the crosslinked structures which form within the rubber particles during prevulcanization are mobile(15). (See



a) Showing that tensile strength is little dependent upon combined sulphur

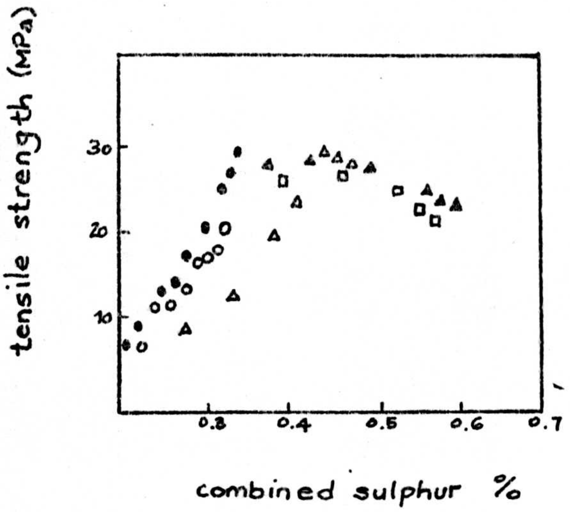


b) Showing that volume swelling is also little dependent upon combined sulphur



c) Showing that the tensile strength of films obtained from prevulcanized latex is insensitive to temperature of prevulcanization.

Fig.2.11. Results showing that physical properties of film obtained from prevulcanized latex are independent upon degree of prevulcanization of latex (after Humphreys and Wake(12)

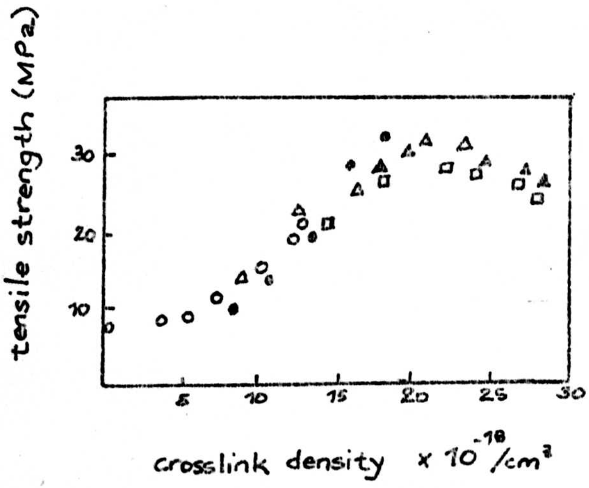


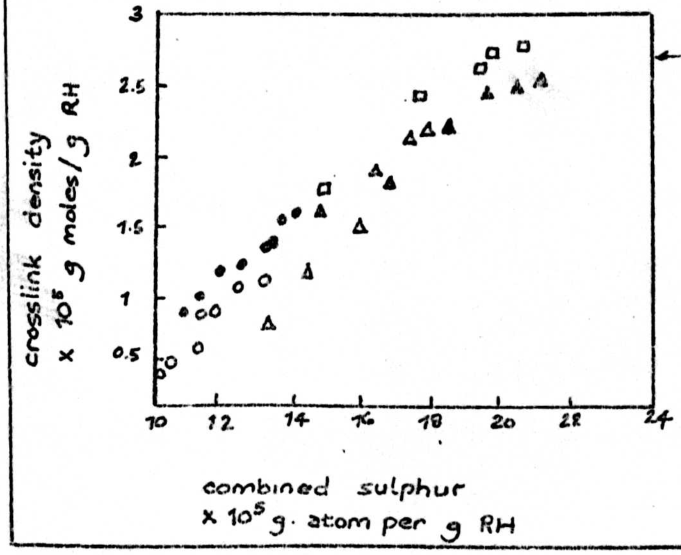
a) Results of tensile strength plotted against combined sulphur

Temperature of prevulcanization
- ○ 50°C
- ● 60°C
- △ 70°C
- ▲ 80°C
- □ 90°C

b) Relationship of tensile strength vs. crosslink density

Temperature of prevulcanization
- ○ 50°C
- ● 60°C
- △ 70°C
- ▲ 80°C
- □ 90°C





c) Crosslink density against combined sulphur relationship

Temperature of prevulcanization
- ○ 50°C
- ● 60°C
- △ 70°C
- ▲ 80°C
- □ 90°C

Fig.2.12. Results of Hu et al.(24) showing interrelationship between dried down film properties, combined sulphur and crosslink density

Sections 2.2.6 and 2.5 in this thesis). To support their initial idea, the Chinese workers investigated the physical properties of wet gels obtained by ionic deposition from prevulcanized latex(23). The results of this investigation are shown in Fig.2.13. The strengths of the wet gel obtained from prevulcanized latex were found to be dependent upon the time (and therefore presumably upon the degree) of prevulcanization. A similar trend was observed when the physical properties of films dried down from prevulcanized latex were studied. Fig. 2.14 shows typical results for the dependence of the tensile strength of dried films upon the time of prevulcanization of the latex.

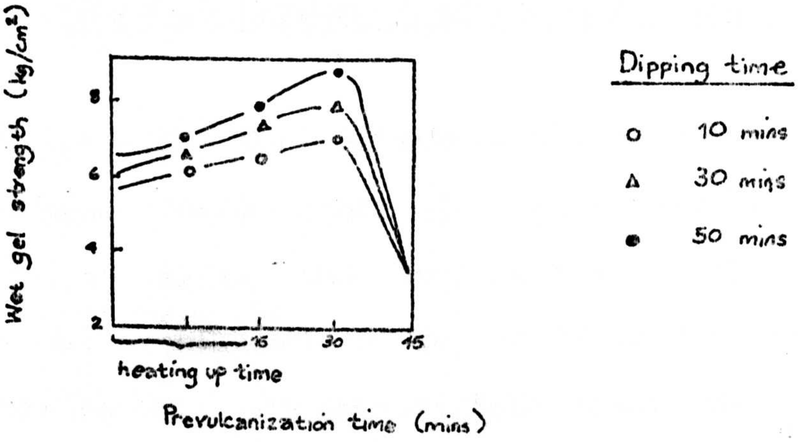


Fig.2.13. Variation of wet gel strength plotted with time of prevulcanization (after Hu et al.(23))

These results for the strengths of wet gels and dried films, together with those shown in Fig.2.12, have convinced Hu et al. that a crosslinked structure between

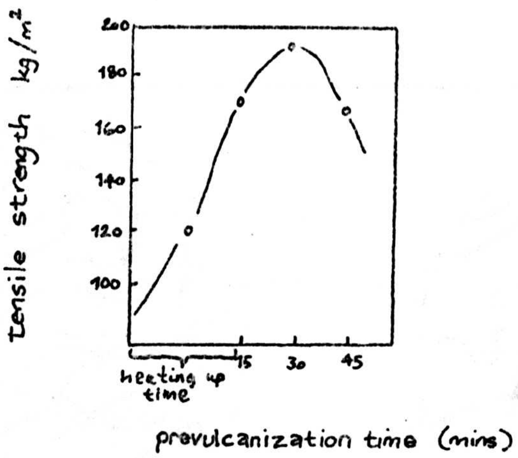
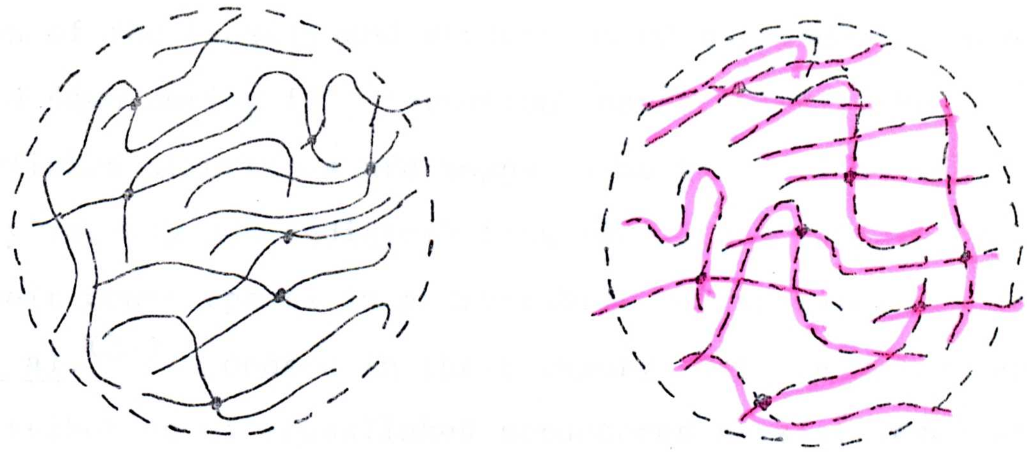
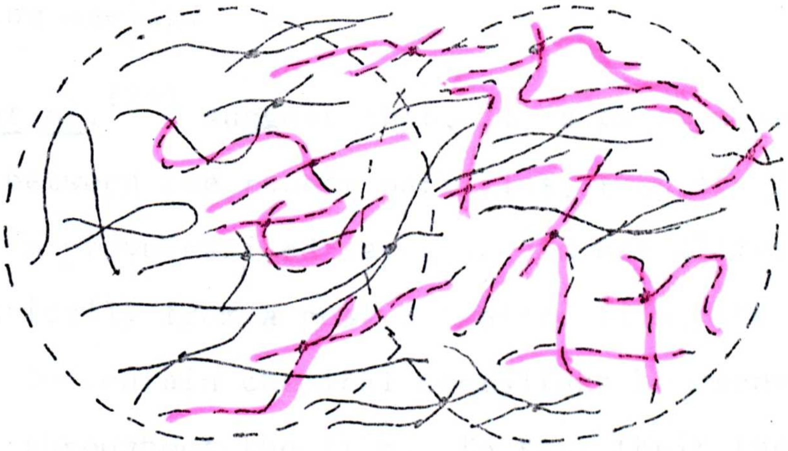


Fig. 2.14 Variation of tensile strength of dried films with time of prevulcanization(23)

the rubber particles comes into existence when a gel or dried film is formed. The presence of these crosslinked structures is said to explain the observed relationship between the physical properties and degree of prevulcanization. According to their theory, the crosslinked structures between the rubber particles are not formed by any chemical reaction during the drying or gelling process. Rather, they result from redistribution of crosslinked structures between particles during the formation of the gel or film. Fig.2.15 gives a schematic illustration of this theory. According to the theory, both the crosslinked networks and the uncrosslinked rubber molecules are always in a state of motion and change. The presence of a low crosslink density ($Mc \leq 2 \times 10^4$) does not impose any serious restriction on the motion. During the prevulcanization reaction itself, the motion between crosslinked structure and unvulcanized rubber molecules within the individual rubber



a) individual particles containing crosslinked structures in prevulcanized latex

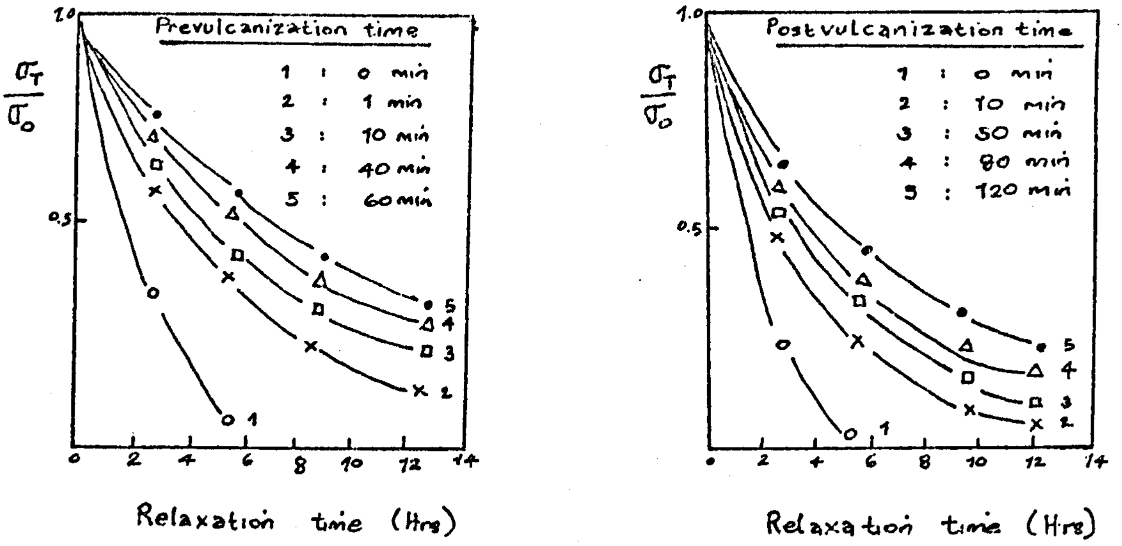


b) Redistribution of crosslinked structure between particles during film or gel formation

Fig. 2.15 Schematic illustration of the theory of redistribution of crosslinked structure between particles during film formation

molecules enables the vulcanizing ingredients to react with the rubber hydrocarbon continuously to give uniformly crosslinked rubber particles. This aspect of the theory has already been discussed in Section 2.5. Though this motion of the crosslinked structures must presumably have slowed down during film formation, nevertheless, the crosslinked structures are supposed to be still moving fairly rapidly and redistributing themselves rapidly compared to their counterparts in a dry-rubber vulcanizate. In fact, Hu _et al._(24) proposed in their theory that the motion and redistribution of crosslinked structures persist even after film formation. By this means, they explain why the properties of films from prevulcanized latex continue to change during ageing.

Hu _et al._(24) suggest that, if a crosslinked structure does exist between the rubber particles, then the film obtained from prevulcanized latex should not differ characteristically from a postvulcanized film, the latter being known to contain chemical crosslinks homogeneously distributed throughout the film. To test their theories they studied some of the mechanical properties of both postvulcanized films and films obtained from prevulcanized latex. Fig.2.16 shows the results of stress-relaxation experiments on the two types of film. It can be seen from these results that the stress-relaxation behaviours are very similar. Similar behaviours were also observed for intermittent stress-relaxation. Hu _et al._ regard these results as confirming their theory.



a) Stress relation of films obtained from prevulcanized latex

b) Stress relaxation of postvulcanized films.

(*Experiment conducted at room temperature in spindle oil).

Fig. 2.16. Stress relaxation behaviour of films obtained from prevulcanized latex and postvulcanized films$^{(24)}$

Although the Chinese workers lay great emphasis upon the existence of a crosslinked structure between the particles in films obtained from prevulcanized latex, they do not deny the importance of van der Waal's forces. They state that,

> "characteristically, cohesion between the particles of prevulcanized latex is neither a pure van der Waal's force type of bond nor a true chemical crosslinked bond. It rather resembles a transient-type bond in character, since the formation of a crosslinked structure between particles is caused by the redistribution of a crosslinked structure already existing within the particles instead of by the formation of a new crosslinked bond."

2.7. Physical Properties of Rubber Deposited From Prevulcanized Latex

There is considerable published information concerning the physical properties of vulcanized deposits from rubber latices.(34-48) However, more than half of the investigations reported(40-48) are concerned with the properties of post-vulcanized deposits, i.e., deposits obtained by vulcanizing the rubber dried down from compounded, unvulcanized latex or partially prevulcanized latex. In this section, only those studies of physical properties which refer to rubber deposited from prevulcanized latex will be discussed.(34-39) The common feature among the experiments reported in these studies is that significant chemical reaction took place during the aqueous prevulcanization stage only. Precautions were taken to avoid any further crosslinking reactions during the preparation of the test samples by drying down the prevulcanized latex at room temperature.

van Dalfsen(36) has investigated the physical properties of rubber deposited from prevulcanized fresh latex and from purified, aged latex. Fresh latex was obtained from the plantation, whilst the purified, aged latex was a normal preserved latex, kept longer than 4 days from time of tapping, and purified by repeated centrifugation and dilution. The results for physical properties are shown in Fig.2.17. The following observations are particularly interesting: Moist films, i.e., those exposed to high relative humidity, were shown to be weaker than dried films. It was also observed that moisture

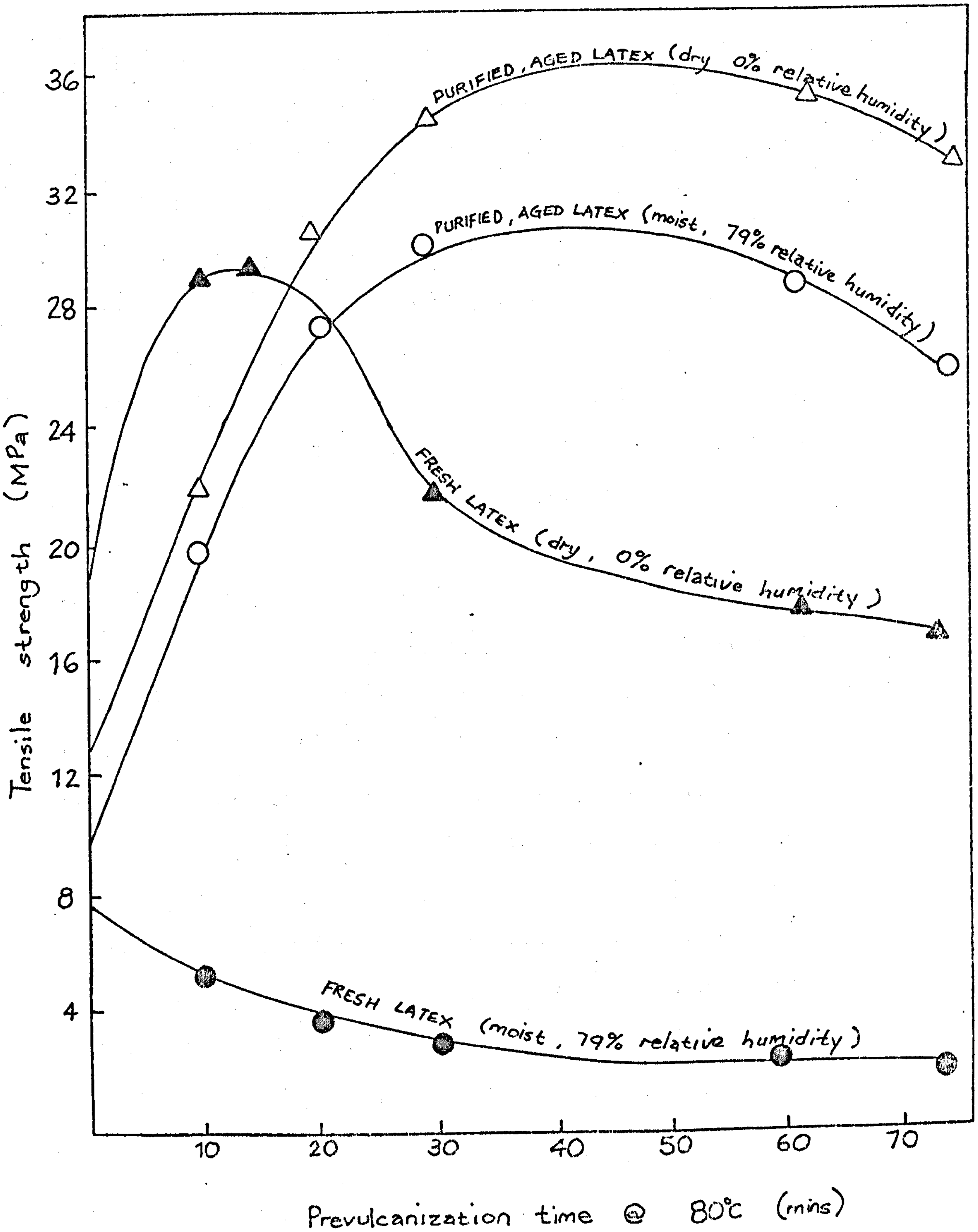


Fig. 2.17. Tensile strength vs. time of prevulcanization for dried films obtained from prevulcanized fresh latex and prevulcanized purified, aged latex, under both dry and humid conditions. After van Dalfsen(36).

content has greater effect upon the tensile strength of films obtained from prevulcanized fresh latex than upon the tensile strength of films obtained from prevulcanized aged, purified latex. In humid conditions, the films obtained from prevulcanized fresh latex were found to have very low tensile strength, also, the films obtained from prevulcanized, purified, aged latex had higher tensile strengths than the films obtained from prevulcanized fresh latex. van Dalfsen explained his results by assuming the presence of a thicker, largely unhydrolysed, adsorption layer in fresh latex compared to the smaller amount of non-rubber substances present in the purified, aged latex. He reasoned that the structure of film obtained from the two latices was probably rather different. According to van Dalfsen, during the drying of prevulcanized fresh latex, it is possible that the mutual approaches of the rubber particles are hindered by the thicker adsorption layer which is present around the fresh latex particles. This hindrance was thought to be responsible for the reduction in secondary forces between the rubber particles, and, consequently, for lower tensile strength according to the secondary-valence theory. In the opinion of van Dalfsen, the effect of moisture can be explained by the swelling of the adsorption layers which causes the particles to draw further apart.

The explanations given by van Dalfsen are consistent with the results obtained independently by Gorton(40) and by Merrill(33). Both these workers have shown that, by leaching the dried films before testing, increases in tensile strength can be obtained. Fig. 2.18 shows the results of Merrill(33) for the effect of leaching films obtained from prevulcanized latex in water and acetone upon tensile strength. The results evidently show that the removal of adsorbed non-rubber substances favours the formation of a more homogeneous film and hence results in increased secondary forces between the rubber particles, thereby giving higher tensile strength.

From Fig. 2.17, Fig. 2.18 and the results of other investigations of the physical properties of films deposited from prevulcanized latex(39-40), it can be seen that typically, when tensile strength is plotted as a function of time of latex prevulcanization, the tensile strength initially increases rapidly, passes through a maximum, and then decreases as prevulcanization proceeds. There has been a tendency to draw analogies with the phenomenon of 'reversion' or overvulcanization after optimum cure. This is a phenomenon which has been widely observed in dry rubber vulcanization. The reduction in physical properties which is observed after the optimum cure is exceeded is attributed to the fact that crosslinks are being destroyed at a faster rate than that at which they are being formed. However, it seems unlikely that reversion can occur during the prevulcanization of latex, because the crosslink density in films obtained from prevulcanized latex can be increased by merely postvulcanizing the film.

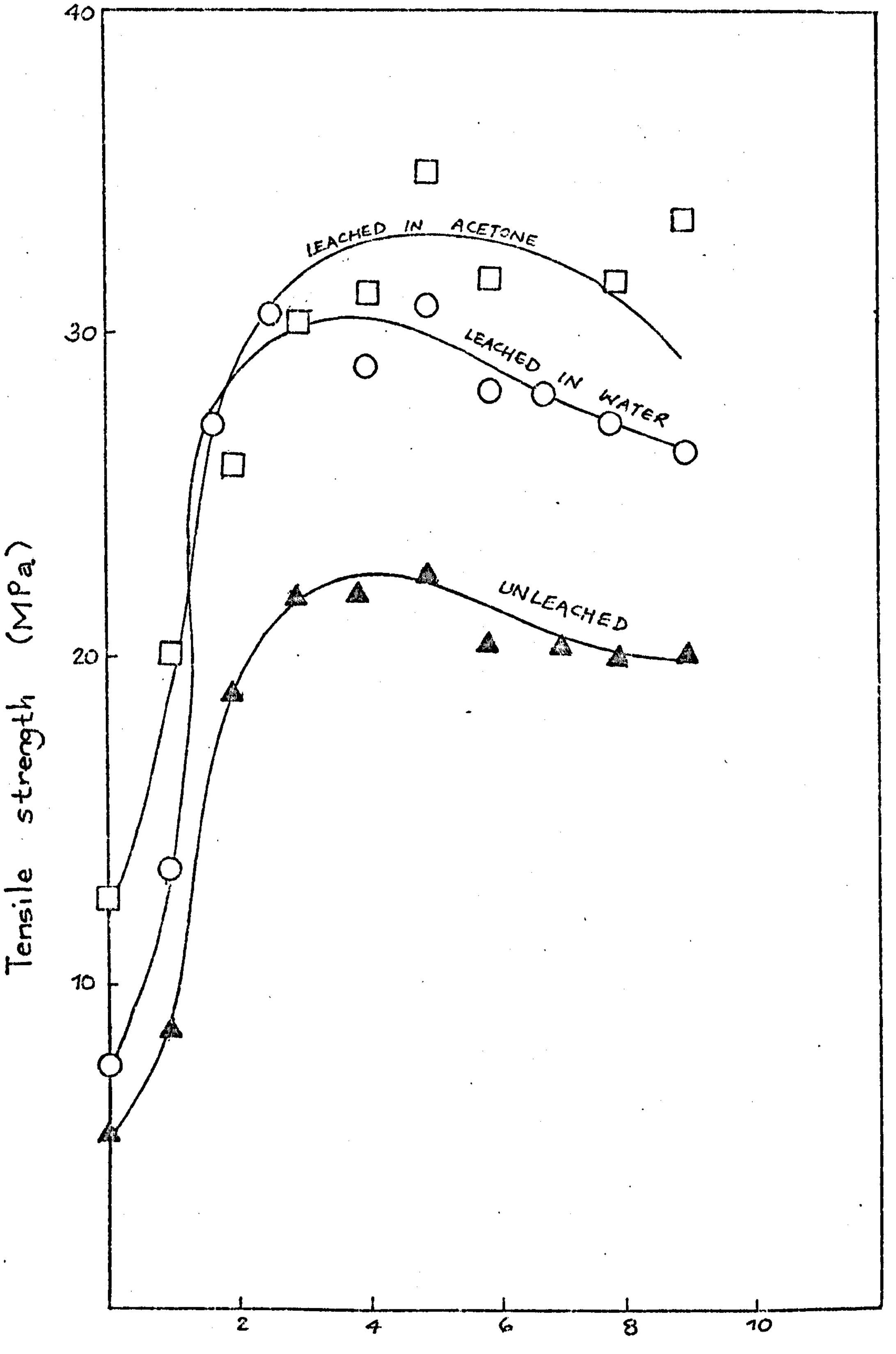


Fig. 2.18. Effect of leaching films obtained from prevulcanized latex in water and acetone upon tensile strength (after Merrill(33))

In the view of the present writer, the phenomenon of the tensile strength passing through a maximum and then decreasing as prevulcanization proceeds is consistent with both the secondary-valence theory as illustrated by Blackley(32) and the theory of redistribution of crosslinked structure proposed by Hu *et al.*(24) The initial increase in strength is undoubtedly due to the insertion of crosslinks within the rubber particles; a higher crosslink density within the particles means that higher secondary-valence forces have to be overcome simultaneously during extension of film. According to Blackley(49) as the crosslink density is further increased, restriction of the mobility of the chains causes a decrease in the number of chain ends contributing to secondary-valence forces, and hence causes a reduction in the tensile strength. On the other hand, according to the theory of redistribution of crosslinked structure of Hu *et al.*(24) the further increase in crosslink density has probably impeded the mobility of the crosslinked structures, thereby reducing their ability to redistribute between particles during and subsequent to film formation.

2.8. Other Miscellaneous Investigations Relating to Latex Prevulcanization

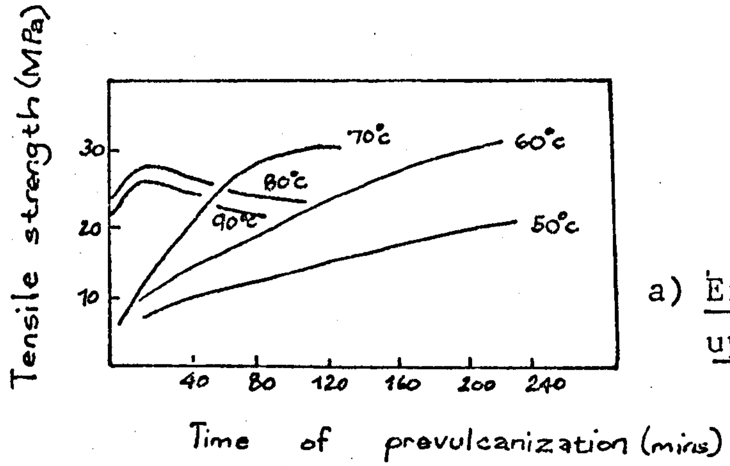
The literature reviewed so far has been concerned directly with the course or mechanism of the prevulcanization of natural rubber latex and with the structure and physical properties of films obtained by drying down the prevulcanized latex. There are also isolated investigations which provide information concerning other aspects of the process of latex prevulcanization. A summary of these investigations is given in this section.

2.8.1. Effects of different process and formulation variables upon latex prevulcanization

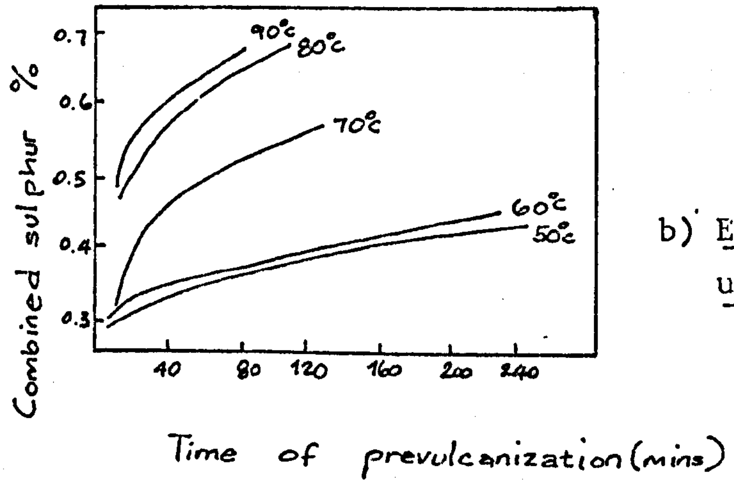
2.8.1.1. Effect of temperature of prevulcanization

Temperature has a very significant effect upon latex prevulcanization. The results of Hu et al.(25) for the effect of temperature of prevulcanization upon the mechanical properties of dried films, combined sulphur and crosslink density are shown in Fig. 2.19. It can be seen that, with increase in temperature of prevulcanization, the time required to reach an optimum state of prevulcanization (as judged by tensile strength) decreases. Fig. 2.19(a) also shows that, when the temperature of prevulcanization exceeded 70°C, the mechanical properties of films deposited from the prevulcanized latex deteriorated with prolonged prevulcanization.

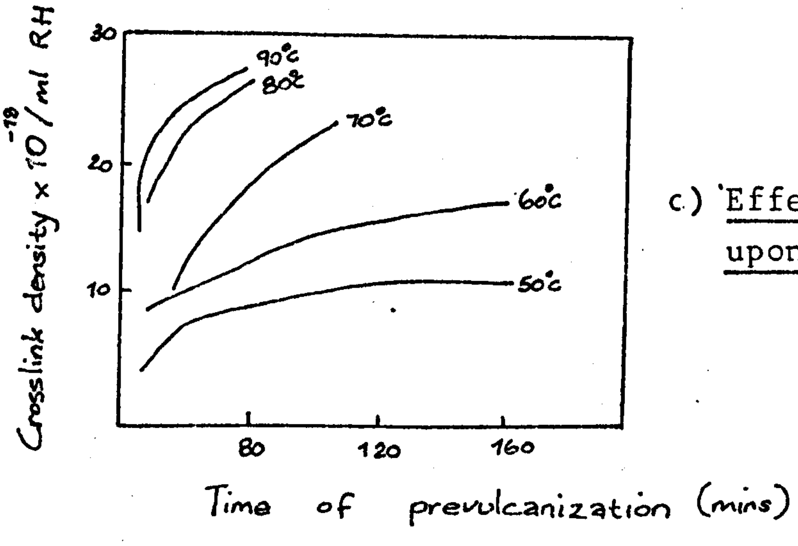
The experiments of Hu et al. described in the previous paragraph were based on a formulation which contained 1.0 pphr of sulphur and 1.0 pphr of the water-soluble sodium diethyl dithiocarbamate (SDEC) as vulcanizing system. Recently Merrill(33) has also investigated the effect of temperature upon latex prevulcanization. However, he used the water-insoluble zinc diethyl dithiocarbamate (ZDEC) instead of SDEC as



a) Effect of temperature upon tensile strength



b) Effect of temperature upon combined sulphur



c) Effect of temperature upon crosslink density

Fig.2.19. Effect of temperature of prevulcanization upon tensile strength of dried films, combined sulphur and crosslink density during NR latex prevulcanization (after Hu et al.,(25))

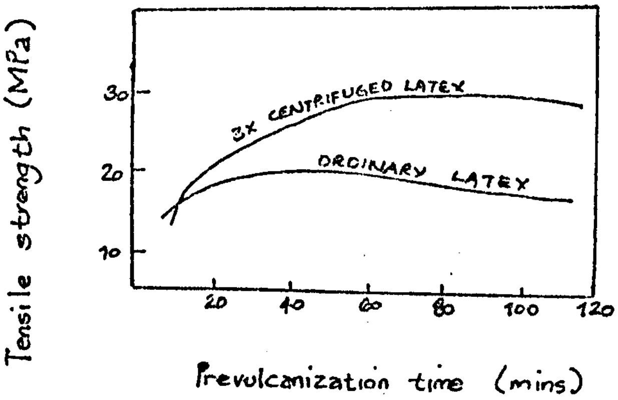
accelerator. The results obtained by Merrill are similar to those of Hu *et al.*, in that the time required to reach an optimum state of prevulcanization reduced sharply with increasing temperature of prevulcanization. Merrill(33) also studied the rate of disappearance of both ZDEC and sulphur during prevulcanization at various temperatures of prevulcanization (50-90°C). He found the rate of disappearance of ZDEC to be zero-order with respect to ZDEC concentration, and the rate of disappearance of sulphur to be first-order with respect to sulphur concentration. The activation energies of the disappearances of ZDEC and sulphur have also been estimated.

2.8.1.2. Effect of non-rubber substances in latex

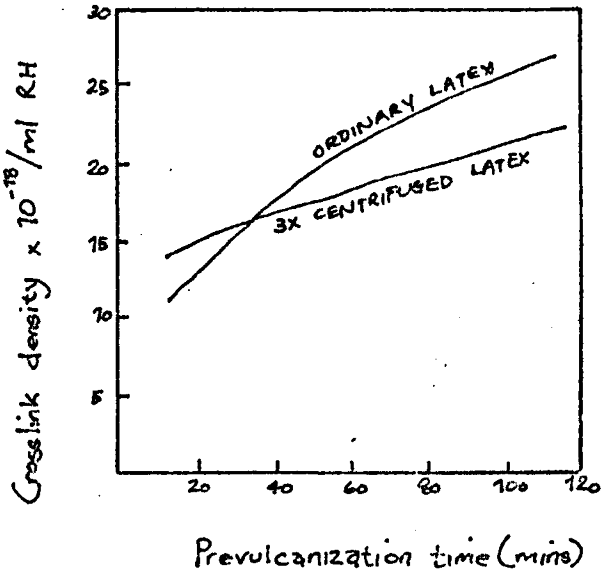
Apart from the investigation of van Dalfsen(36), discussed in Section 2.7, on the difference between prevulcanized fresh latex and purified latex in relation to the tensile strength of films dried down from them, there have not been many studies of the role played by the non-rubber substances in the latex during prevulcanization. The Chinese workers, Hu *et al.*(25) have reported an investigation of the prevulcanization of multiple-centrifuged natural rubber latex. The prevulcanization of a thrice-centrifuged latex was compared with the prevulcanization of an ordinary latex which had been centrifuged once. It was found that the ordinary latex contained three times more non-rubber substances than did the thrice-centrifuged latex. Fig. 2.20 shows the results of the investigation. The results for the mechanical properties of dried films agree with those of van Dalfsen(36) and Gorton(40), in that the non-rubber substances are detrimental to the tensile strength of the dried film. On the other hand, the results for crosslink density and combined sulphur indicate that a high concentration of non-rubber substances in the latex initially caused a slower rate of sulphur combination and crosslink insertion, but as prevulcanization progressed, seemed to have the reverse effect in that a higher concentration of non-rubber substances gives a higher rate of crosslink insertion and sulphur combination.

On the basis of these results, Hu et al.(25) proposed that the non-rubber substances are initially mostly adsorbed at the surface of the rubber particles. The adsorption layer of non-rubber substances possibly hinders the assimilation of vulcanizing ingredients into the rubber particles for crosslinking reaction, thereby reducing the rate of prevulcanization. However, with the progress of the prevulcanization, the adsorbed non-rubber substances gradually decompose and pass into the aqueous phase, forming activators which promote and accelerate the prevulcanization reaction.

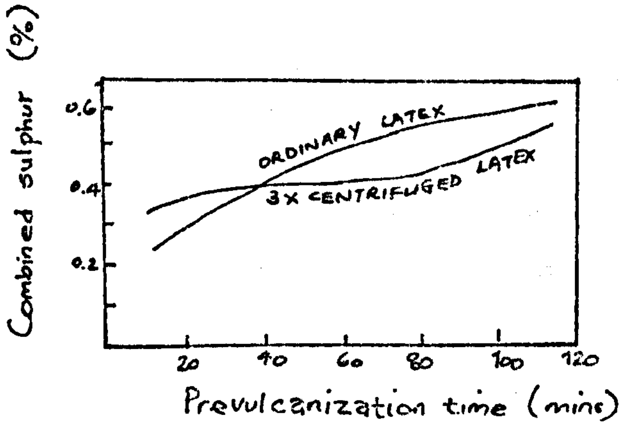
Merrill(33) in his study of the kinetics of the disappearance of ZDEC during prevulcanization observed that some of the ZDEC was apparently 'lost', possibly by reacting with non-rubber substances in the latex. However,



a) effect of non-rubber substances upon tensile strength of dried film.



b) effect upon crosslink density



c) effect upon combined sulphur

Fig. 2.20 Effect of non-rubber substances upon latex prevulcanization (after Hu et al.(25))

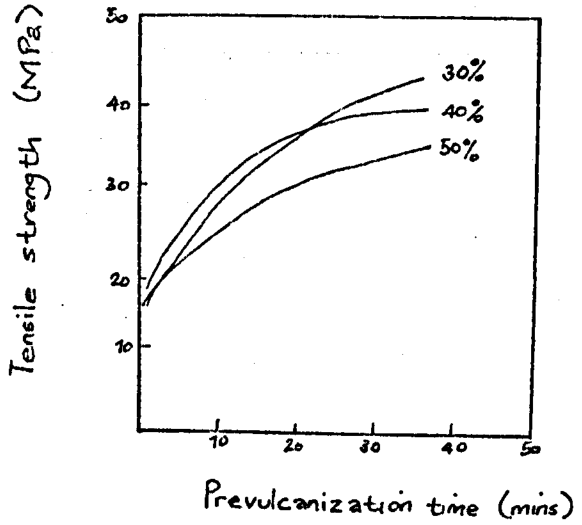
it has not been clarified whether the reaction products were themselves active in accelerating prevulcanization.

2.8.1.3. Effect of varying total solids content of latex

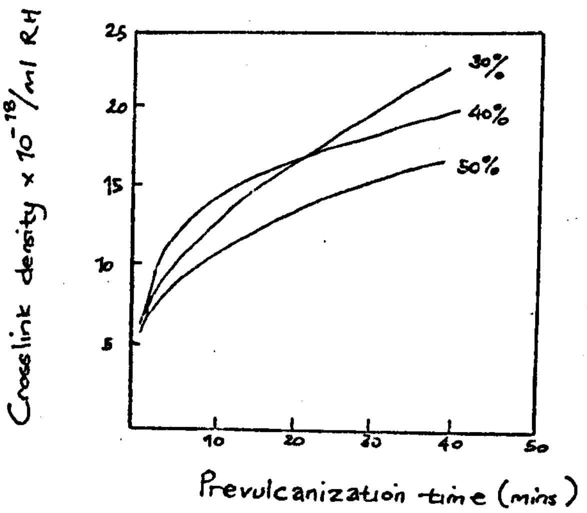
It is difficult to prevulcanize NR latex having a total solids content which exceeds 60%. This is because latex of such high solids content tends to destabilize during the prevulcanization reaction. So far, only the Chinese workers, Hu *et al.*(25) have reported the effect of dilution of latex upon prevulcanization. The results are shown in Fig. 2.21. It can be seen that decreasing the total solids content of the latex from 50% to 30% is accompanied by a slight, but significant, increase in the tensile strength of dried films, the combined sulphur, and the crosslink density. This effect may be associated with partial desorption of the adsorbed layer on the surfaces of rubber particles when the latex is diluted.

2.8.1.4. Effect of type of sulphur

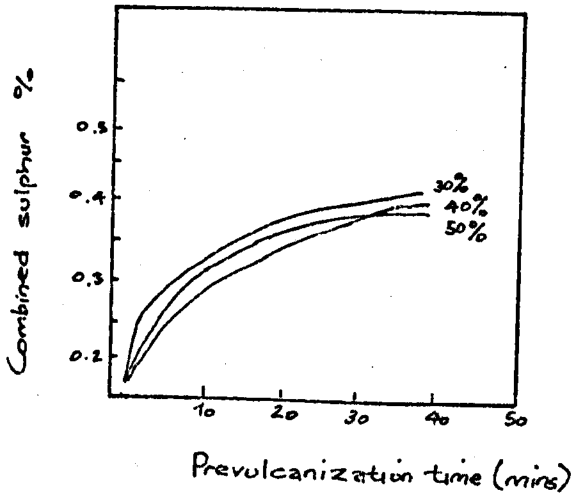
During the early days when prevulcanized latex was newly discovered, Davey(50), a contemporary of Schidrowitz, observed that different types of sulphur which differed in particle size differ in rate of combination during prevulcanization. Colloidal sulphur was found to combine more rapidly than precipitated sulphur, and the latter more rapidly than 'flowers of sulphur'. This phenomenon may be explained in the light of the theories of latex



a) Effect of dilution upon tensile strength of dried films



b) Effect of dilution upon crosslink density



c) Effect of dilution upon combined sulphur

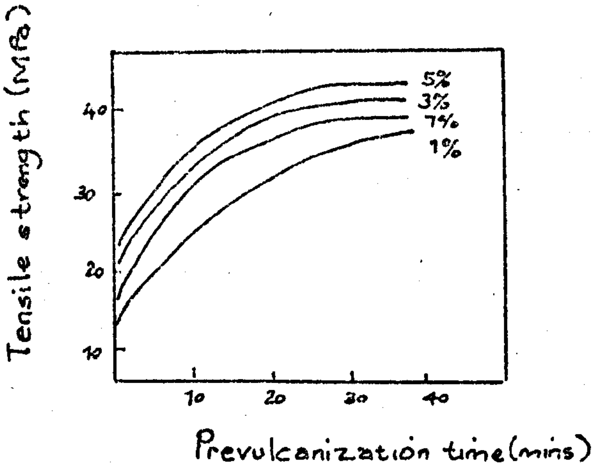
Fig. 2.21. Effect of dilution of latex upon prevulcanization behaviour (after Hu et al.(25)

prevulcanization which have been discussed in preceding sections. Firstly, according to the 'collision mechanism' proposed by Geller *et al.*(14), the smaller the particles of the sulphur, the greater would be the tendency for those particles to move about in the aqueous phase of the latex. Hence there would be more frequent collisions between the rubber particles and the sulphur particles, giving greater opportunity for crosslinking reaction.

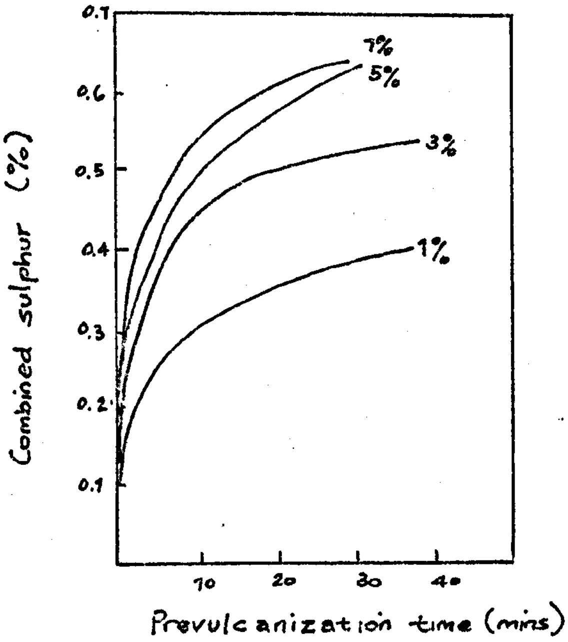
On the other hand, the diffusion theory predicts that the smaller the size of the sulphur particles, the greater will be their surface area. The rate of diffusion of sulphur into the aqueous phase and subsequently into the rubber particles should therefore increase with reduction in the size of the sulphur particles. Hence it is not unreasonable to suppose that the rate of prevulcanization might increase with reduction in the size of the sulphur particles.

2.8.1.5. Effect of varying levels of sulphur and SDEC in prevulcanization recipe

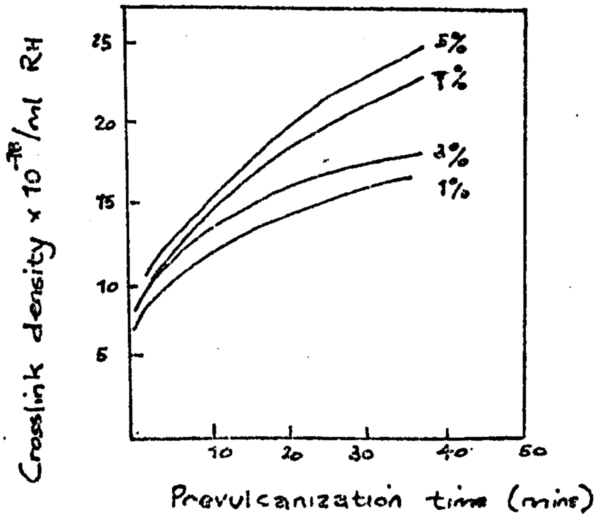
The influence of sulphur level upon latex prevulcanization has been reported by various workers, including Davey(50), Hauser *et al.*(10), Humphreys and Wake(12), Geller *et al.*(14) and Hu *et al.*(25) Of these reports, the most comprehensive is that of Hu *et al.*(25) Their results are shown in Fig. 2.22. Several interesting features are apparent from these results. With increasing level of sulphur, the tensile strength of dried films



a) Effect of sulphur level upon tensile strength of dried films



b) Effect of sulphur level upon combined sulphur



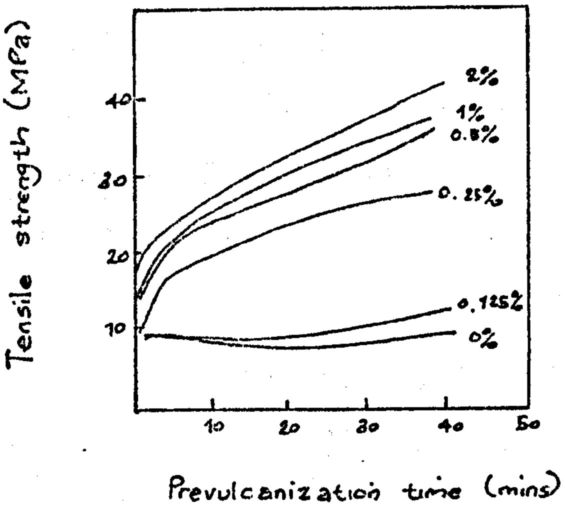
c) Effect of sulphur level upon crosslink density

Fig.2.22. Effect of sulphur level at constant SDEC level (1 pphr) upon the prevulcanization of NR latex (after Hu et al.(25))

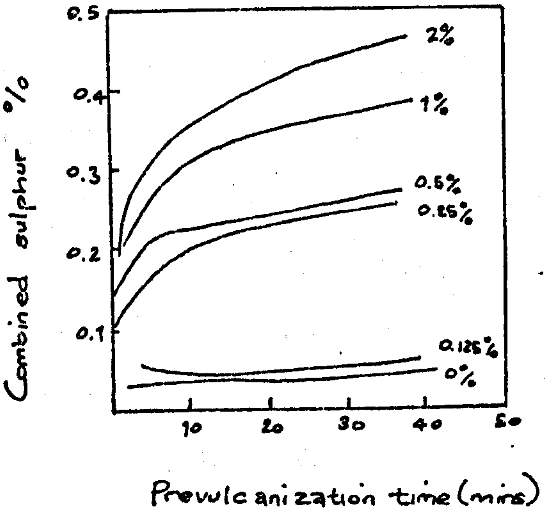
increases at first. However, when the level of sulphur exceeded 5%, the tensile strength begins to fall. Similar behaviour was also observed for crosslink density (Fig. 2.22(c)). On the other hand, the results for combined sulphur (Fig.2.22(b)), show that, as expected, the rate of combination of sulphur increased uniformaly with increasing level of sulphur. It is possible that the high rate of sulphur combination at high levels of sulphur causes excessive modification of the surface of the rubber particles. Over-prevulcanization of the surface of the rubber particles may well affect the cohesion of the rubber particles during drying, with consequent lowering of the tensile strength.

Another interesting observation from Fig.2.22(b) , is the extent of sulphur combination. At all times of prevulcanization and all levels of sulphur, it was well below the level of added sulphur. This observation is consistent with the results of Humphreys and Wake(12), who found that the maximum sulphur combined never exceeded 1.8%, even with 50% of sulphur added to the latex.

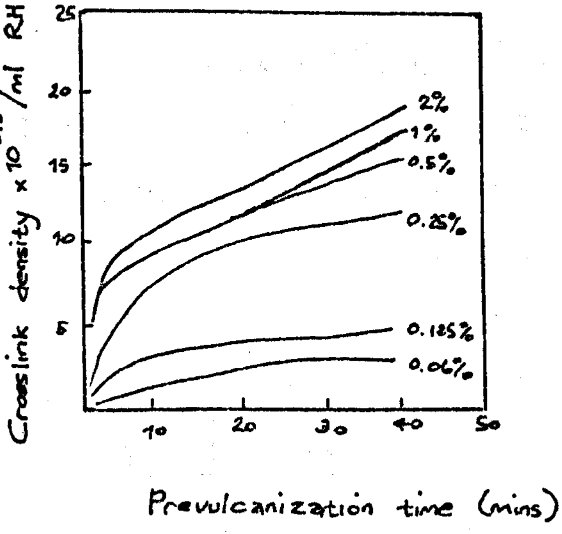
Hu et al.(25) also studied the effect of varying the level of SDEC. The results of this investigation are shown in Fig.2.23. Below 0.125% SDEC, there was negligible prevulcanization. From 0.25% to 2.0%, the rate and extent of prevulcanization increased with increasing level of SDEC. These results are at variance with those of Geller



a) Effect of SDEC level upon tensile strength of dried films



b) Effect of SDEC level upon combined sulphur



c) Effect of SDEC level upon crosslink density

Fig.2.23. Effects of varying SDEC level at constant sulphur level (1 pphr) upon the prevulcanization of NR latex (after Hu et al.(25)).

et al.(14), who studied the effect of varying the SDEC level between 0.5 and 1.5%. Geller *et al.* found that the level of SDEC had no effect upon the prevulcanization of NR latex.

2.8.1.6. Effect of particle size of vulcanizing ingredients

Gorton(51) has very recently published results for the effect upon latex prevulcanization of particle size of sulphur dispersions (7.0 μm to 1.4 μm) and of zinc dibutyl dithiocarbamate dispersions (2.3 μm and 3.1 μm). His conclusion is that the particle sizes of these dispersion has no significant effect upon latex prevulcanization, at least, not upon the tensile strengths of dried films. The explanation offered by Gorton is that these vulcanizing materials must have dissolved in the rubber before the onset of prevulcanization. This explanation possibly might apply to the postvulcanization of dried films, which is usually carried out at temperatures of 100°C or higher, at which perhaps the vulcanizing ingredients melt and dissolve in the rubber. This is probably not the case for latex prevulcanization, for which the temperature of reaction rarely exceeds 60°C.

2.9. Prevulcanization of Natural Rubber Latex by Irradiation

So far, the discussion of latex prevulcanization has been concerned with prevulcanization by reaction of the rubber with sulphur. NR latex can also be prevulcanized by the use of high-energy radiation. The use of γ-radiation to prevulcanize latex has been studied by Minoura and Asao(52), by Gregson et al.(53), and by Hu et al.(22). As this subject is not of direct relevance to the present research programme no discussion of these papers will be given here.

2.10. Prevulcanization of Synthetic Latices

Latex prevulcanization is not restricted to natural rubber latex. Synthetic latices can also be prevulcanized, both by reaction with sulphur and by irradiation with γ-rays. A group of Soviet workers, Lebedev et al.(54), have conducted a comprehensive investigation of this matter. Prevulcanization formulae and conditions were worked out for prevulcanization by sulphur and by irradiation with γ-rays for styrene-butadiene latex and styrene-acryolnitrile latex. Again, because of the limited relevance of this subject to the present research programme, this paper will not be discussed here.

CHAPTER 3

PROPERTIES AND BEHAVIOUR OF NATURAL RUBBER LATEX

CHAPTER 3

PROPERTIES AND BEHAVIOUR OF NATURAL RUBBER LATEX

3.1. High-Ammonia NR Latex.

3.2. Physical Properties of NR Latex

- 3.2.1. Appearance
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- 3.2.3. Total solids content and dry rubber content
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- 3.3.1. Chemical composition of NR latex
  - 3.3.1.1. Proteins
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- 3.3.2. Changes in composition of latex during ammoniation and storage

3.4. Colloidal Stability of NR Latex

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- 3.4.2. Stability of NR latex

CHAPTER 3

PROPERTIES AND BEHAVIOUR OF NATURAL RUBBER LATEX

This thesis is mainly concerned with the prevulcanization of natural rubber latex by reaction with sulphur. It is therefore necessary to describe the properties and behaviour of natural rubber latex. This will be the subject of this chapter. It is also necessary to discuss the vulcanization of natural rubber by sulphur. This will be the subject of the following chapter.

3.1. High-Ammonia Preserved NR Latex

All NR latex used today is in the preserved form. There are two reasons why preservation is necessary. Within hours of flowing out of the rubber tree, the latex separates into clots of rubber and a clear serum, and thus spontaneously destabilizes;at a later stage putrefaction sets in giving the latex a very unpleasant odour. It is to combat these two problems that preservatives are added to fresh latex.

The most widely-used preservative for NR latex today is still ammonia, although for some specialized applications, other preservatives such as tetramethyl thiuram disulphide/zinc oxide, boric acid and pentachlorophenol are used. Latices preserved solely by ammonia are known as high-ammonia (HA) latices; about 0.7% of ammonia based on the whole latex is present in such latices.

Since the programme of work reported in this thesis was concerned mainly with high-ammonia latex, the discussion of preserved latex in this chapter will be confined to latex which has been preserved solely by ammonia.

3.2. Physical Properties of Natural Rubber Latex

3.2.1. Appearance

Fresh, preserved and prevulcanized natural rubber latex are all milky-white fluids. Preserved latex may sometimes darken on standing because of the action of enzymes on the latex. When kept in iron containers for a long time, the action of hydrogen sulphide (which is often present in minute quantity in preserved latex) on the metal may also cause the latex to darken. Prevulcanized latex, on the other hand, tend to develop a slight pinkish colour when left undisturbed for some time. This is attributed to the residual zinc dithiocarbamate accelerator forming coloured complexes with certain non-rubber substances in the latex.

3.2.2. Odour

Latex fresh from rubber trees has a smell similar to that of milk. It soon develops an unpleasant, rancid smell if left unpreserved because putrefaction occurs.

Most preserved latex used today has a very strong ammoniacal odour because of the ammonia which is added as preservative. Prevulcanized latex may sometimes smell slightly of sulphides.

3.2.3. Total solids content and dry rubber content

The total solids content of fresh latex may vary from 30% to 40%, depending upon the source, the age of the tree, the season, and the particular part of the tree which was tapped. For economic reasons, and also for reasons of convenience during subsequent processing, plantation latex is concentrated to about 60% total solids content before it is transported to the manufacturer. Dry rubber content is distinguished from total solids content, being defined as the weight fraction of the latex which coagulates under controlled conditions. The value varies from 57.5% to 62.0% for a commercial concentrated latex, depending upon the method by which the latex was concentrated.

3.2.4. Density

The density of preserved latex is between 950 and 980 Kg/m^3. It is the resultant of two factors: the density of the rubber particles, and the density of the serum in which they are suspended. The former is between 900 and 930 Kg/m^3. The density of the serum depends upon the amount of dissolved materials. It is slightly greater than that of water. Since the rubber particles are lighter than the serum, it is therefore to be expected that they will tend gradually to rise to the surface of the latex, i.e., cream, if the latex is undisturbed for sometime.

3.2.5. pH

The pH of fresh latex varies between 6.5 to 7.0. The acidity of fresh latex increases somewhat during the first few hours after tapping. Eventually the latex coagulates unless ammonia is added. Normal ammonia-preserved latex has a pH value of between 10.2 to 10.5.

3.2.6. Viscosity

The viscosity of ammonia-preserved latex is considerably lower than that of fresh latex. This is because viscosity depends upon the pH of the latex, and the minimum viscosity is reached at a pH value of about 10. This is the condition which exists in ammonia-preserved latex. Viscosity is also markedly influenced by the concentration of the latex. At approximately 55% total solids content, the viscosity rises rapidly. At 60% total solids content, the latex is creamy. It becomes a paste when the total solids content is higher than about 70%. The reason for this sharp rise in viscosity as the total solids content approaches 70% is that the latex particles are almost touching one another.

NR latex behaves in a 'non-Newtonian' manner when sheared. The ratio of shear rate to shear stress is not constant. Thus the apparent viscosity depends upon the stress at which it was measured.

3.2.7. Surface tension

The surface tension (or surface free energy) of a liquid affects its ability to wet and spread on surfaces. The higher the surface tension, the more non-wetting is the liquid. Wetting is normally facilitated by the presence of surface-active agents in the liquid. In latex, these are dissolved in the serum and adsorbed at the surface of rubber particles and at the interface between the aqueous phase and the air above the latex. Fresh latex has a surface tension of about 4×10^{-2} N/m. In preserved latex the value is lower because of the presence of ammonia. In comparison, it should be noted that pure water has a surface tension of 7.2×10^{-2} N/m.

3.2.8. The latex particles

The number of rubber particles present in even a small volume of latex is very large. Langland(55) determined that in a 35% latex, one cm^3 of the latex contains about 6.4×10^{12} rubber particles. Those particles which are sufficiently large to be visible through a microscope can be seen to exhibit the characteristic Brownian movement.

3.2.6.1. Particle shape, size, and size distribution

There have been differing views concerning the shape of the individual particles. It is now generally agreed that rubber particles are predominantly spherical in shape.(56) However, in latex from certain mature clones, those particles of medium and large sizes may be pear-shaped. The diameters of the latex particles vary widely between 20 and 2000 nm. Nevertheless, the majority of the particles are small. Less than 4% of the particles have diameters larger than 400 nm(57).

3.2.8.2. Particle structure

Like particle shape, much has been written concerning the structure of the latex particle. Again there are several opposing views. However, certain features of the particle structure are generally agreed. Fig. 3.1 shows a simplified representation of structure of NR latex particle(58). The inner core of the particle consists of rubber hydrocarbon. On the surface of the core of the particle is an adsorbed layer of phospholipids, sterols, sterol esters, fats and waxes. An outer adsorbed

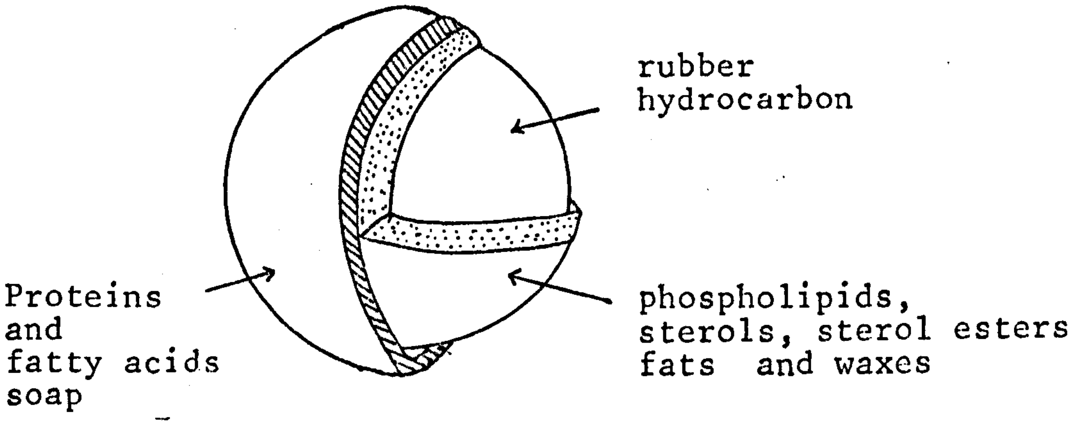


Fig. 3.1. Simplified representation of probable structure of natural rubber latex particle (after Blackley(87)

layer comprises proteins and fatty-acid soap, the latter replacing the protein to a large extent if the latex is made alkaline (e.g., by addition of ammonia) and allowed to age.

3.3. Chemical Properties of NR Latex

3.3.1. Chemical composition of NR latex

Other than the rubber hydrocarbon of the latex particles and the water of the latex serum, there are present in latex a great variety of chemical substances known collectively as non-rubber substances. A typical composition of fresh latex is given in Table 3.1.

Table 3.1. Typical composition of fresh latex

total solids content	36
dry rubber content	33
proteinaceous substances	1-1.5
resinous substances	1-2.5
ash	up to 1
sugars	1
water	to 100

The 'non-rubber substances' are distributed between the rubber particles, the so-called "Frey Wyssling" particles (the second most numerous particles in NR latex), the serum, and the so-called "bottom fraction". The "bottom fraction" is the heavy fraction which settles to the bottom after centrifugation. The manner in which the non-rubber substances so far detected in fresh latex are distributed is indicated in Table 3.2. Some of the non-rubber substances which are of particular significance are further considered in the following sections.

3.3.1.1. Proteins

The proteins are probably the most important non-rubber substances present in NR latex. Together with the phospholipids, they confer colloidal stability to the freshly-tapped latex when they are adsorbed on to the rubber particles(58). They may also act as vulcanization activators during dry rubber vulcanization(61,62) and during the postvulcanization of latex films(63). van Gils(64) has suggested that, during latex prevulcanization the proteins which are present in the latex serum may react with added sulphur, thereby bringing it into the water phase, from whence the dissolved sulphur can be transferred into the rubber phase.

In a recent study, Tata(65) has established that the total protein content in fresh latex is 0.95%. Of this, 27.2% is in the rubber phase, 47.5% is in the serum phase, and 25.3% is in the bottom fraction. Two of the major anionic proteins, α-globulin and hevein, have been isolated and studied in some detail(66). α-Globulin is made up of seventeen constituent amino acids, whereas hevein is made up of fifteen amino acids, one of which, cystine, contains a high sulphur content(67). These two proteins have similar isoelectric points. However, whilst α-globulin

Table 3.2. Distribution of non-rubber substances in freshly-tapped NR latex(60)

A) in rubber phase:-

- Proteins 0.5
- Lipids
  - Fats and waxes
  - Phospholipids
    - Lecithins 0.48
    - Cephalins 0.02
    - Metal phosphatides 0.10
  - Sterols and sterol esters
- Metals
  - Ca
  - Mg
  - Cu

B) in latex serum:-

- Inositols
  - Meso-inisitol
  - Quebrachitol 1.0-1.9
- Carbohydrates
- Proteins 0.5
  - Hevein
  - α-globulin
  - Basic protein
  - Enzymes
- Glutathione
- Free amino acid 0.08
  - Alanin, Tyrosine
  - Glutamic acid, glycine
  - Leucines, cysteine
  - Phenylalanine, valine
  - Cystine, proline
- Organic acid
- Nucleic acids
- Nitrogeneous bases 0.04
  - Methylarine
  - Stachydrine
  - Trigonelline
  - Tetramethylenediamine
  - Pentamethylene diamine
  - Alkaloids
- Pyrophosphate nucleosides
- Inorganic anions
- Metals

C) in bottom fraction:-

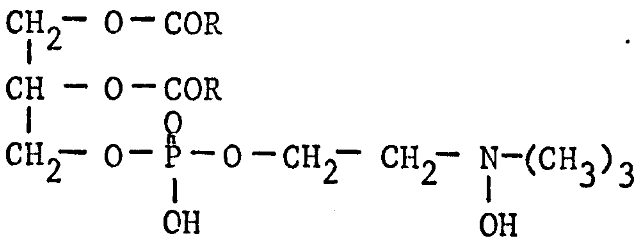
- Soluble protein
  - Basic proteins
  - Hevein
  - Other proteins
  - Enzymes
- Phospholipids
- Miscellaneous nitrogen compounds
- Rubber
- Metals
- Carotenoids

(The figure under a component indicates its approximate concentration in g/100g. latex).

is readily adsorbed at a water-oil interface with a resulting fall in the interfacial tension, hevein has very little surface activity.

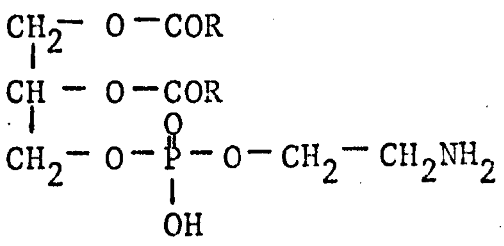
3.3.1.2. Lipids and carbchydrates

The total lipid content of fresh latex is about 0.9%. The lipid fraction is made up mainly of phospholipids amounting to about 60% of the total lipids), fats and waxes, sterols and sterol esters. Phospholipids are long-chain fatty-acid esters of glycerophosphoric acid in which the phosphate group are esterified with choline in the lecithins (structure A) with ethanolamine in the cephalins (structure B) and combined with a metal atom in the metal phosphatidates (structure C).



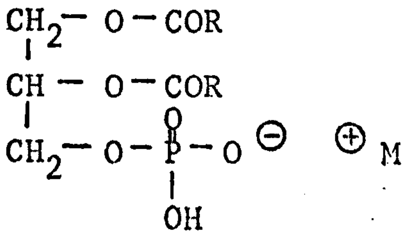
$$\begin{array}{l} CH_2-O-COR \\ | \\ CH-O-COR \\ | \\ CH_2-O-\overset{O}{\overset{\|}{P}}-O-CH_2-CH_2-N-(CH_3)_3 \\ \qquad\qquad | \qquad\qquad\qquad\qquad | \\ \qquad\quad\ OH \qquad\qquad\qquad\ \ OH \end{array}$$

(structure A)



$$\begin{array}{l} CH_2-O-COR \\ | \\ CH-O-COR \\ | \\ CH_2-O-\overset{O}{\overset{\|}{P}}-O-CH_2-CH_2NH_2 \\ \qquad\qquad | \\ \qquad\quad\ OH \end{array}$$

(structure B)



$$\begin{array}{l} CH_2-O-COR \\ | \\ CH-O-COR \\ | \\ CH_2-O-\overset{O}{\overset{\|}{P}}-O^{\ominus} \quad {}^{\oplus}M \\ \qquad\qquad | \\ \qquad\quad\ OH \end{array}$$

(structure C)

The phospholipids also contribute to the stability of the latex because they are adsorbed at the surface of the rubber particles. The choline compounds are vulcanization accelerators and show antioxidant properties in raw rubber(67).

The carbohydrate which is present in the greatest quantity in NR latex is quebrachitol. It occurs to an extent of about 1% in latex. Because of its high solubility in water, it is present exclusively in the serum phase. Apparently, the carbohydrates in natural rubber latex are unimportant as far as the colloidal and prevulcanization behaviour of the latex is concerned. However, they are metabolized by the bacteria in commercial latex concentrates, and in the process become oxidized to volatile fatty acids (VFA)(68). These acids (mainly acetic) are not present in fresh latex. Hence, the concentration of VFA in commercial latex gives a measure of the degree of bacterial decomposition which the latex has undergone.

3.3.1.3. Inorganic ions and other minor non-rubber substances

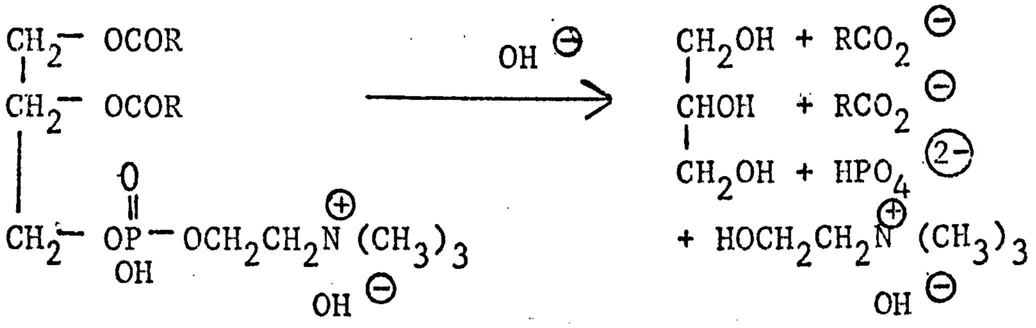
There is present in latex about 0.5% of inorganic ions. The principal ions are potassium, magnesium, copper iron, sodium, calcium and phosphate. The relative proportions of these ions may have a marked influence upon the colloidal stability of the latex concentrate; for example, a high ratio of magnesium to phosphate ions is often found in latices of low stability.

Choline and methylamine are amongst the other minor non-rubber substances which are present in the latex.

Being free nitrogenous bases, these substances are thought to play an important role during latex prevulcanization. It is possible that they act as ligands for the formation of accelerator complexes.

3.3.2. Changes in composition of latex during ammoniation and storage

When ammonia is added to fresh latex as preservative, there are profound changes in the composition of the latex both immediately and during subsequent storage. The phospholipids, for example, the lecithins, rapidly hydrolyse to glycerol, fatty-acid anions, nitrogenous bases and phosphates anion:



Some of the fatty-acid anions, being surface-active, partially displace the proteins at the surface of the rubber particles, thereby bringing about increased colloidal stability of the latex due to their charges. The remainder of the fatty-acid anions and other products of hydrolysis pass into the serum phase. A dynamic equilibrium is established between the fatty-acid anions in the serum and those adsorbed on the surface of the rubber particles.

In the case of the proteins, hydrolysis occurs gradually throughout the storage period. Polypeptides and amino acids are formed; these pass into the serum phase.

Hence ammoniation is accompanied by a decrease in the quantities of proteins and resinous substances, whilst there is an overalll increase in the concentration of ions in the serum. Listed in Table 3.3 are the distribution of non-rubber substances present in ammonia-preserved latex.

3.4. Colloid Stability of NR Latex

3.4.1. General theories of colloid stability

A colloidal system is one that contains particles of one substance dispersed in a continuous phase of another substance. The dimension of these dispersed particles are roughly between 1 nm and 1 μm. They are called lyophobic colloids if the system cannot be made by dissolution of the colloidal material in the dispersion medium. A colloidal system is said to be stable when the individual particles remain dispersed in the continuous phase. When a colloid becomes destabilized, the particles tend to coalesce or aggregate together. All lyophobic colloids are generally considered to be thermodynamically unstable. The reason for the instability is that the coalesced state is one of lower free energy than the dispersed state; for when the particles aggregate or coalesce, there is a reduction in the specific area of the colloidal system, and hence, in the interfacial free energy per unit volume of dispersed polymer.

Table 3.3. Distribution of non-rubber substances in ammonia-preserved NR latex(60)

A) in rubber phase:-

- Proteins 0.25
- Lipids
  - Fats and waxes 0.17
  - Phospholipids
  - Sterols and sterol esters
- Higher fatty acids 0.36
- Nitrogeneous bases
- Metals
- Carotenoids

B) in latex serum:-

- Choline 0.06
- Quebrachitol
- Free phosphate 0.1
- Glycerophosphate
- Fatty acids 0.4
  - Higher fatty acids 0.4
    - Palmitic
    - Stearic
    - Arachidic
    - Linoleic
    - Oleic
  - Volatile fatty acids 0.02
    - Formic
    - Acetic
    - Propionic
- Nitrogeneous bases 0.04
- Other organic acids
  - Oxalic
  - Tartaric
  - Citric
  - Malic
  - Malonic
  - Succinic
  - Fumeric
  - Oxalacetic
  - Glyoxylic
  - α-Ketoglutaric
- Proteins 0.25
- Free amino acids 0.14
  - Alanine, Aspartic Acid
  - Arginine, Histidine
  - Cystine, glutamic acid
  - Dihydroxyphenylalanine
  - Glycine, Hydroxyproline
  - Leucines, Methionine
  - Lysins, Phenylalanine
  - Ornithine, Proline,
  - Tryptophan, Valine,
  - Tyrosine, Cysteine
- Polypeptides
- Metals

C) in the sludge:-

- $MgNH_4PO_4$
- Sterol glycosides

It is now commonly believed that the stability of lyophobic colloidal dispersion is imparted by four principal factors, namely,

1) electrostatic stabilization,
2) steric stabilization,
3) stabilization by solvent binding and
4) depletion stabilization

The concept of electrostatic stabilization was first introduced by Helm-hotz and later modified by Gouy, Chapman and Stern(69-73). The stabilization is due to the presence of bound charge at the particle surface that leads to the formation of a diffuse counterion cloud in the dispersion medium. When two particles approach each other closely, their counterion clouds interpenetrate strongly. Because these clouds are of the same electrical polarity, interpenetration increases the potential energy of the pair of particles, i.e., work has to be done to bring about interpenetration of these counterion clouds. Hence interpenetration is an energetically unfavoured process, and therefore the effect is to provide a barrier which tends to keep the particles apart, thereby giving a stable colloidal dispersion.

The second factor which contributes to colloid stability is termed steric stabilization. This term was first adopted by Heller and Pugh(74) for a theory which describes the effect of adsorption of non-ionic surfactants and macromolecules at the surface of colloidal particles upon the ability of the particles to approach one another closely. Adsorbed surfactants or macromolecules extend an appreciable distance into the continuous phase. The chains projecting from the surfaces of different particles interact with each other when the particles approach one another. These interactions prevent the particles from entering one another's effective spheres of attraction. Fig. 3.3. illustrates a colloidal particle which is sterically stabilized.

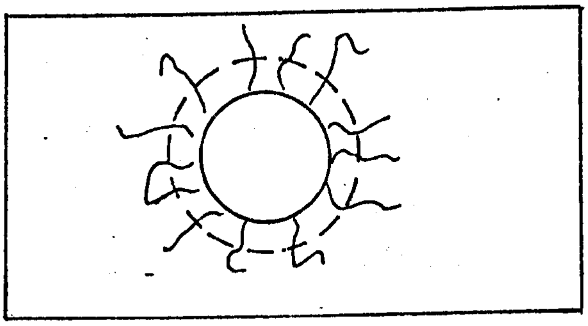


Fig. 3.3. Illustration showing colloidal particle with adsorbed macromolecules as steric stabilizer.

The third factor is stabilization by solvent binding(75-78). In this theory, a layer of solvent, several molecules thick, is thought to be 'bound' at the interface, thereby promoting colloid stability by a mechanical 'buffer' action during collision of the particles.

The fourth factor which is thought to contribute to colloid stability is known as depletion stabilization(79); this is a concept which has been developed very recently. Non-ionic unadsorbed polymers in solution in the dispersion medium are thought to be able to contribute to the stability of a lyophobic colloid. This effect contrasts with steric stabilization, where the stabilising effect is imparted by adsorbed or attached polymer. Stabilization by 'free' polymer is termed "depletion stabilization" because the stabilizing effect arises from the depletion of the concentration of segments of the free polymer near to and between the surfaces of the colloidal particles.

3.4.2. Stability of NR latex

Not all the theories of colloid stability discussed in the previous section are applicable to a particular lyophobic colloid such as NR latex. However, at least three of the four factors which contribute to colloidal stability are relevant to NR latex. As has been pointed out in earlier sections, proteins and phospholipids (especially their hydrolysis products such as fatty-acid soap anions in ammonia-preserved latex) form an adsorbed layer around the surface of the rubber particles at the interface which separates the rubber particles from the serum. It has been suggested(80) that ionization of part of the proteins and fatty-acid soaps gives rise to electric charges at the surface of the rubber particles and to part of the diffuse counterion cloud around the particles in the serum. Therefore, it is believed that NR latex partly derives its colloidal stability from electrostatic repulsion between the diffused counterion clouds which are associated with the individual particles.

Steric stabilization is also probably very important in the case of NR latex. This is again because of the proteins and protein degradation products which are adsorbed at the surface of the rubber particles.

It has also been proposed(77,80) that proteins and fatty-acid soap anions are probably able to bind a layer of water molecules near to and between the surfaces of the rubber particles. The presence of these tightly-bound water molecules around the particles is thought to act as a mechanical 'buffer', physically preventing coalescence or aggregation of the particles when they collide.

It is therefore apparent that the colloidal stability of NR latex, although usually considered to be a physical property of the latex, is determined primarily by the chemical nature of the latex. It is therefore possible to explain on the basis of the theory of the stability of NR latex physical phenomena such as why latex is less stable at high temperature and when it is subjected to mechanical agitation. In both the instances, there is an increase in the kinetic energy of the rubber particles and the frequency of the collisions between the particles. Both these factors lead to a reduction of colloid stability.

CHAPTER 4

VULCANIZATION OF NATURAL RUBBER AND THE CHARACTERIZATION OF RUBBER NETWORK

CHAPTER 4

VULCANIZATION OF NATURAL RUBBER AND THE CHARACTERIZATION OF RUBBER NETWORK

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CHAPTER 4

VULCANIZATION OF NATURAL RUBBER AND THE CHARACTERIZATION OF RUBBER NETWORK

4.1. Historical Development

Vulcanization is a key process in the technology of rubbers. Prior to the discovery of vulcanization in 1839, rubber was used in a very unsatisfactory manner for balls in playing games, waterproofing cloth and for footwear.(81) These articles had a tendency to soften in the summer heat and to freeze hard in the winter cold. They also became sticky when exposed to certain organic solvents.

It was during the search for a means of solving these problems that Charles Goodyear accidentally found that rubber could be 'cured' or changed by heating it with sulphur and white lead so that it was less affected by heat, cold and solvent. In his patent(82), he described a typical composition of 20 parts of sulphur, 28 parts of white lead and 100 parts of rubber, mixed together into turpentine. The mixture was then spread to form a sheet, followed by heating to obtain the desired product.

At about the same time that Charles Goodyear was working in America, Thomas Hancock working in England independently discovered that rubber when immersed in melted sulphur gave a product which did not stiffen when left on ice(83). In his patent(84), he described how the molten sulphur slowly migrates into the rubber until the rubber is saturated, giving a hard horny material which is known to us today as ebonite. Thomas Hancock is also credited with contributions to the industrial application of vulcanization. He discovered the efficient mastication and compounding process using roll mills, a process which is still practised today. He was also the first to vulcanize rubber in steel moulds.

Although both Goodyear and Hancock are credited with the discovery of rubber vulcanization, it was a colleague of Hancock's by the name of William Brokedon who first used the term 'vulcanization'. He named it after Vulcanus, the Greek God of fire and sulphur-bearing volcanoes.(85)

Since its discovery, there have been many improvements in the sulphur-vulcanization process. One of the greatest improvements was the discovery of organic vulcanization accelerators and activators(86). The properties of the rubber vulcanizates are very much enhanced by the discovery of these vulcanization accelerators and activators because they help in reducing the time of vulcanization and contribute to efficient use of sulphur in crosslinking.

Many non-sulphur-containing vulcanizing agents have also been discovered, e.g., organic peroxides, quinones and their oximes and imines, polynitrobenzenes, bisazodicarboxylic esters, diazoaminobenzenes. Natural rubber can also be vulcanized by exposure to high-energy radiation. However, none of these methods of vulcanizing natural rubber has been used widely industrially. For this reason, and also because the present research is concerned exclusively with vulcanization by reaction with sulphur the subsequent discussion of vulcanization is restricted to vulcanization by sulphur and by reagents which act as sulphur donors, such as the tetraalkylthiuram disulphides.

4.2. Features of Natural Rubber Vulcanization

4.2.1. Effects upon physical properties of rubber

Vulcanization involves the chemical interlinking or crosslinking of linear rubber molecules at relatively few sites along their length, thereby producing a 3-dimensional molecular network. The effects of the crosslink density upon the physical properties of the rubber vulcanizate are illustrated schematically in Fig.4.1(87-92).

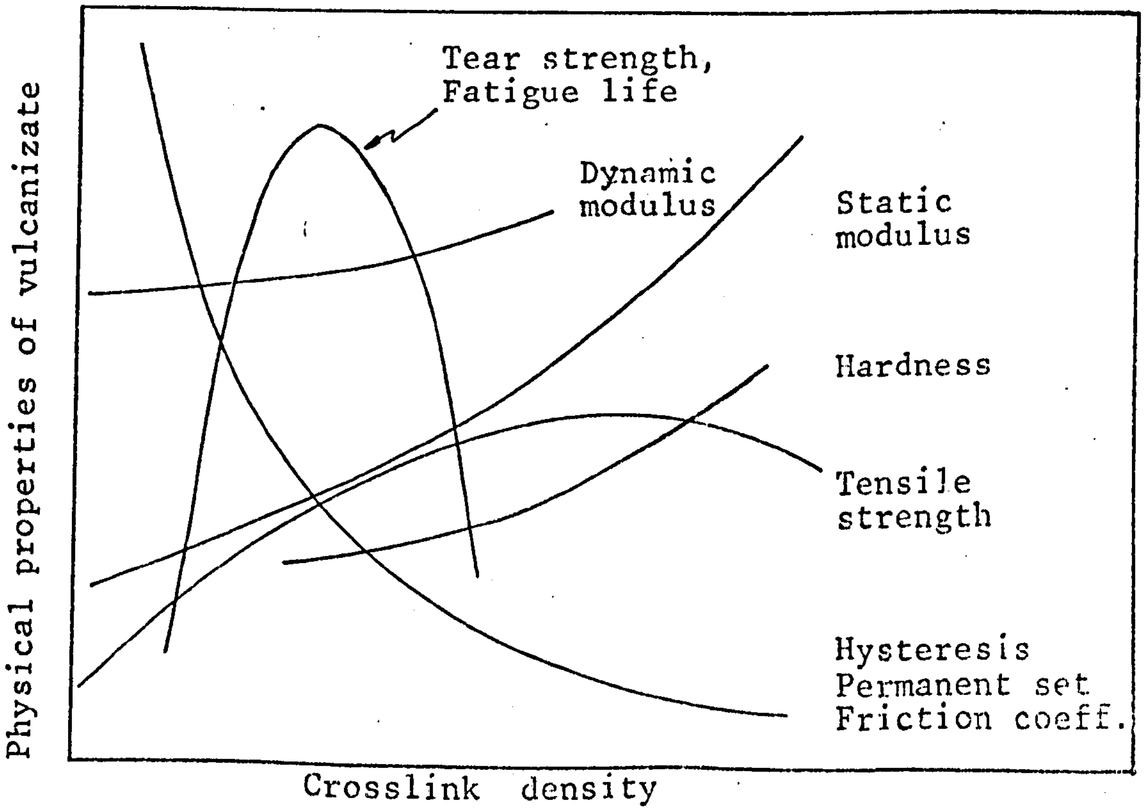


Fig. 4.1. Effects of vulcanization upon physical properties of natural rubber vulcanizates

The hysteresis, which is a measure of the proportion of the deformation energy which is not stored in the network but is dissipated as heat, diminishes with increasing crosslink density. Although properties such as tear strength and fatigue life initially increase with increasing crosslink density, then pass through an optimum value as crosslink density is increased. The decrease in these properties at crosslink densities above the optimum is a consequence of significant reduction of hysteresis with further crosslink insertion. An optimum tensile strength with increasing crosslink density is also observed. This phenomenon is usually attributed to the loss in ability of the chain segments to crystallize on the application of stress because of the high concentration of crosslinks.

The static modulus increases with crosslink density to a greater extent than does the dynamic modulus. Dynamic modulus is a composite of viscous and elastic components, whereas, static modulus is a measure of the elastic component alone. Thus, vulcanization causes a shift from viscous or plastic behaviour to elastic behaviour.

It should be noted that the properties illustrated in Fig. 4.1. are not only functions of crosslink density. They are also affected by the type of crosslinks, and by the type and amount of other compounding ingredients such as fillers.

4.2.2. Chemical structure of natural rubber vulcanizates

In defining the chemical structure of a rubber vulcanizate, the important characteristics are

(a) the chemical nature, concentration, distribution of the crosslinks;

(b) the nature and extent of any modification of the main rubber chains; and

(c) the nature and concentration of any substances which are not chemically attached to the network.

Application of the analytical methods (which will be described in the next section) to vulcanizates produced by a variety of accelerated sulphur-curing systems has shown that the generalized chemical structure of a natural rubber vulcanizate network can be represented as shown in Fig. 4.2. The vulcanizate comprises the network itself

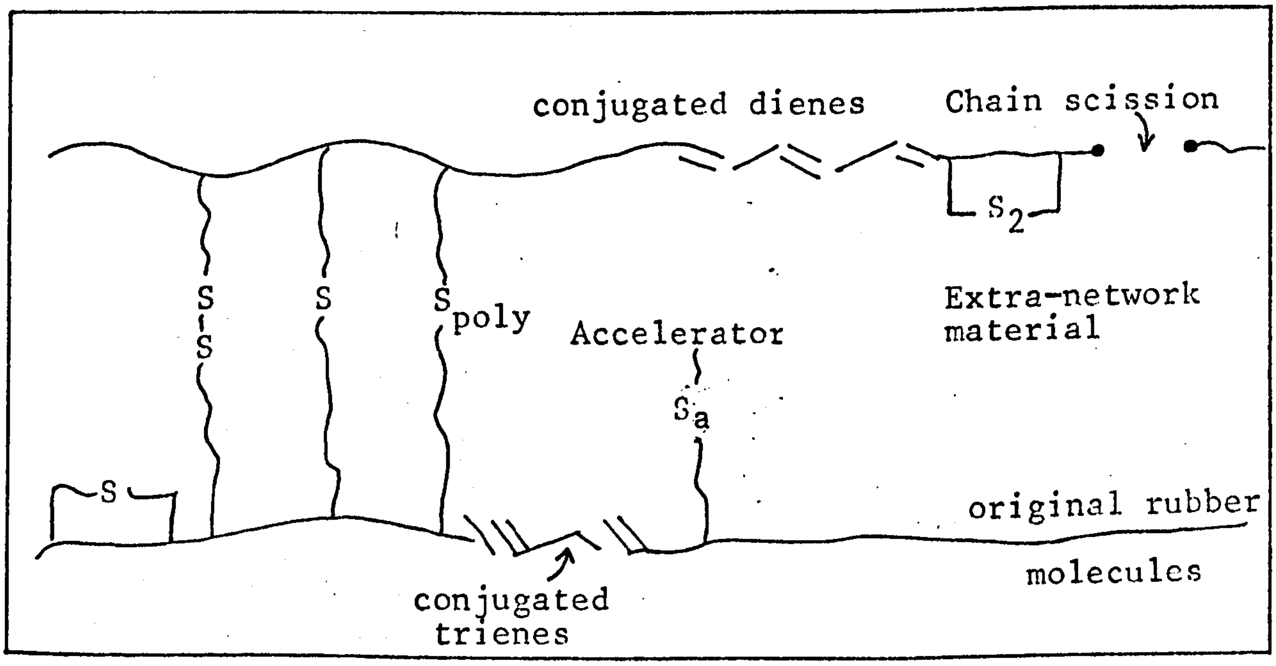


Fig. 4.2. Simple pictorial representation of structural features of an accelerated sulphur natural rubber vulcanizate(134)

and the extra-network materials. The latter comprise unreacted vulcanizing ingredients and products of vulcanization, such as zinc sulphide, which are not chemically bound to the network. The network consists of (a) the main chain of original rubber molecules; (b) the crosslinks, which can be mono-, di- or polysulphidic; and (c) structures produced by chemical modification of the main chain as a consequence of the vulcanization reactions, examples being cyclic mono- and disulphides, pendent sulphurated groups terminated by accelerator fragment, structures such as conjugated dienes and trienes, and the products of chain-scission.

The proportions of the various groupings in a given network generally depend upon the nature and concentration of accelerator used, and upon the temperature and time of vulcanization. Vulcanization activators or promoters such as zinc oxide and carboxylic acid also have some effect upon the vulcanizate structure produced.

The dependence of vulcanizate structure upon vulcanization recipe and conditions is illustrated in Fig.4.3. At very short times of vulcanization, both system A (high accelerator:sulphur ratio) and system B (low accelerator: sulphur ratio) form networks of the same type. The networks are made up of accelerator-terminated pendent groups. Relatively few crosslinks are present, these being of the polysulphidic type. As the time of vulcanization

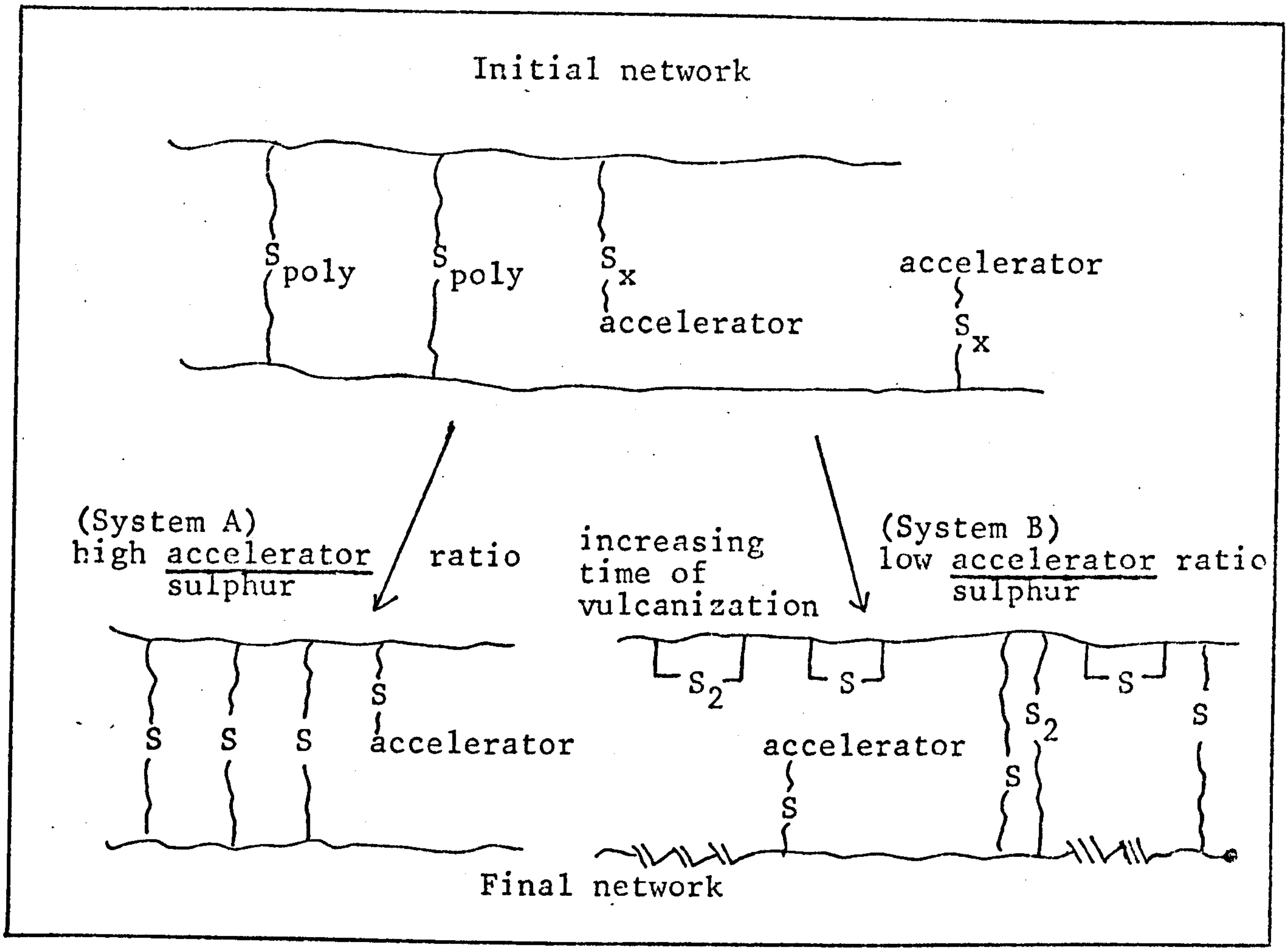


Fig. 4.3. Dependence of network structure upon vulcanization recipe and conditions(123)

is increased, so the network structures produced in the two cases become increasingly disparate. System A produces a simple network with a relatively high concentration of monosulphidic crosslinks and few residual pendent groups. On the other hand, the network from system B becomes increasingly more complex: polysulphidic crosslinks are replaced progressively by di- and mono-sulphidic crosslinks, and the main rubber chains become increasingly modified by olefinic and sulphur-containing groups. These differences in vulcanizate structure are also reflected in changes in physical properties and ageing behaviour(90).

4.3. Structural Characterization of Vulcanizate Networks

In the previous section, various qualitative aspects of vulcanizate network structure have been described. In the subsequent sections, ways in which quantitative information concerning rubber vulcanizate network will be considered.

4.3.1. Concentration of chemical crosslinks

4.3.1.1. Preliminary considerations

As a consequence of vulcanization, the following features are introduced into the vulcanizate structure: (a) crosslinks, (b) network chains, i.e., macromolecular segments bound at each end by a crosslink, (c) free chain ends, and (d) permanent chain entanglements. These features are illustrated in Fig. 4.4.

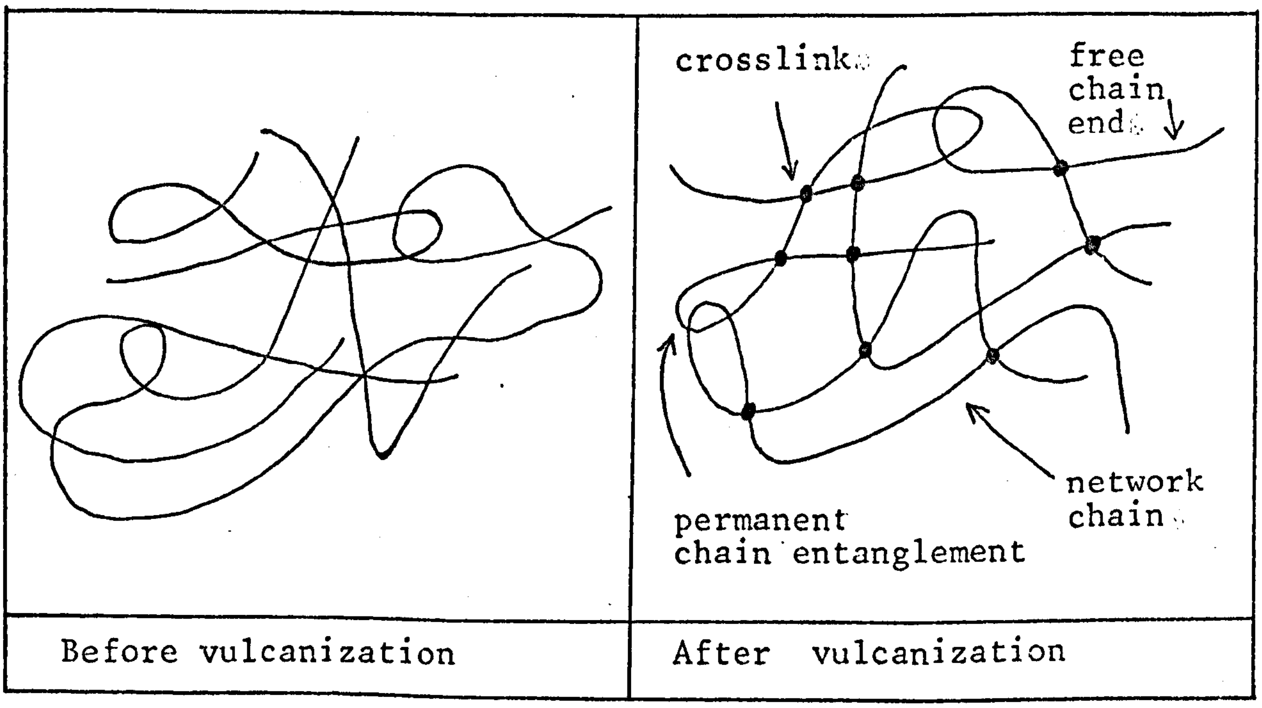


Fig. 4.4. Features introduced into rubber networks by vulcanization

In an ideal situation in which the network is free from free chain ends and permanent chain entanglements, the concentration of chemical crosslinks can be determined directly from the knowledge of functionality of the crosslinks i.e., the number of network chains terminated by each crosslink and M_c, the number average molecular weight of network chains between crosslinks. In the case of tetrafunctional crosslinking, each crosslink is associated with one half of the four network chain bound to it, as shown in Fig. 4.5. Therefore, if M_c is the number-average molecular weight of the network chains between crosslinks and N is the Avogadro number, each crosslink will be associated with on average $2M_c/N$ grams of rubber. One gram of rubber will therefore contain $N/2M_c$ crosslinks; or, more conveniently, one gram of rubber will contain $1/2M_c$ gmoles of crosslinks. $1/2M_c$ is therefore the concentration of crosslink. This is conveniently taken as a measure of the degree of crosslinking.

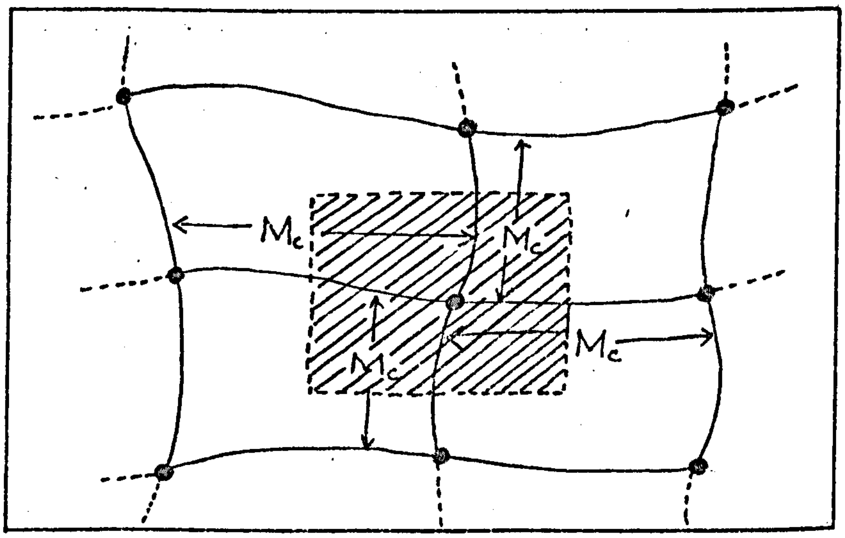


Fig. 4.5. Portion of tetrafunctional crosslinked rubber. M_c denotes the number average molecular weight of network chains between crosslinks

4.3.1.2. Determination of M_c from stress-strain measurements

M_c, the number-average molecular weight of network chains between crosslinks, can be determined experimentally from stress-strain measurements using a method which depends upon the statistical theory of rubber elasticity.(93,94) According to this theory, the stored energy function per unit volume of rubber, W, is given by

$$W = \frac{G}{2} \; (\lambda_1{}^2 + \lambda_2{}^2 + \lambda_3{}^2 - 3) \tag{4.1}$$

where G is the elastic constant, and λ_1, λ_2, λ_3 are the ratio of strained to unstrained dimension along the principal axis of X Y and Z. For simple extension, whereby there is no change in volume $\lambda_1 = \lambda$, and $\lambda_2 = \lambda_3 = \lambda^{-\frac{1}{2}}$ Equation (4.1) therefore becomes

$$W = \frac{G}{2} \; (\lambda^2 + \frac{2}{\lambda} - 3) \tag{4.2}$$

The equilibrium force per unit area required to extend an ideal network in the direction of λ is therefore given by

$$F = \frac{dW}{d\lambda} = G(\lambda - \lambda^{-2}) \tag{4.3}$$

Similar derivations lead to expressions for the compression and shear modes of deformation.

For ideal rubber networks which do not contain chain ends and permanent chain entanglements, G is related to M_c

by the equation

$$G = \frac{\rho RT}{M_c} \tag{4.4}$$

where ρ is the density of the network, R is the gas constant and T is the absolute temperature. Therefore equations (4.3) and (4.4) provide the basis of a method whereby stress-strain measurements can be used to obtain estimates of M_c, thus of degree of crosslinking, for real networks. However, in practice, stress-strain relationships are found to deviate from the ideal form predicted by equation (4.3). Some of the reasons for the deviations are that in ideal networks (a) no account is taken of the contribution made by chain entanglements to the concentration of elastically-effective network chains; (b) no allowance is made for chain ends which do not contribute to the stress; and (c) there is a finite extensibility of the network which is not taken into consideration.

4.3.1.3. Phenomenological Considerations

Mooney(95), Rivlin(96) and Saunders(97) obtained a more satisfactory description of the elastic behaviour of vulcanizate networks by an essentially phenomenological approach. Their empirical expression involves two elastic constants, C_1 and C_2. For simple extension and moderate strains, they find that

$$F = 2(C_1 + \frac{C_2}{\lambda})\ (\lambda - \frac{1}{\lambda^2}) \tag{4.5}$$

A linear relation may be obtained if results for simple extension are plotted in the form $F/2(\lambda - \lambda^{-2})$ against $1/\lambda$, because equation (4.5) can be rearranged to give

$$\frac{F}{2(\lambda - \frac{1}{\lambda^2})} = C_1 + \frac{1}{\lambda} C_2 \qquad (4.6)$$

C_1 and C_2 can then be obtained graphically. It has been established(98,99) for natural rubber vulcanizates that the C_2 term in equation (4.5) is almost zero for stress-strain data obtained using vulcanizates highly swollen with a liquid. In this case, equation (4.6) reduces to the form predicted by simple statistical theory (equation 4.3), provided that

$$C_1 = \frac{G}{2} = \frac{\rho RT}{2M_c} \qquad (4.7)$$

4.3.1.4. Relationship between concentration of physically-effective crosslinks, $[X]_{phys}$, and concentration of chemical crosslinks, $[X]_{chem}$

Mullins(98) has critically analysed C_1 data for many natural rubber vulcanizates in which known concentration of chemical crosslinks, $[X]_{chem}$, had been introduced. The concentrations of chemical crosslinks were accurately estimated from analysis of peroxide decomposition products and knowledge of the chemistry of the crosslinking reaction.

It was found that, in general, the concentration of physically-effective crosslinks, $[X]_{phys}$, determined by application of equation (4.7) to C_1 data, considerably exceeded $[X]_{chem}$. This was particularly apparent at low crosslink densities. This discrepancy is attributed to the effects of permanent chain entanglements. Therefore, in order to derive $[X]_{chem}$ for a network from $[X]_{phys}$, corrections must be applied for these effects. To date, the most reliable correlation between $[X]_{phys}$ and $[X]_{chem}$ is still the relationship proposed by Mullins$^{(98)}$. This relationship is

$$C_1 = \rho RT[X]_{phys} = \left[(\rho RT[X]_{chem} + 0.78 \times 10^5)\left(1 - \frac{2.3}{2[X]_{chem}\bar{M}_n}\right)\right] N/m^2 \qquad (4.8)$$

where the factor 0.78 x 10^5 is a correction which includes the maximum contribution of entanglements. In this equation, M_n is the number-average molecular weight of the rubber molecules before vulcanization.

4.3.1.5. Determination of M_c from measurements of equilibrium swelling

An alternative method to the use of stress-strain measurements for the determinatinon of $[X]_{phys}$ requires the determination of equilibrium swelling of the vulcanizate. The equilibrium volume fraction of rubber, V_r, in the swollen network is related to M_c, by the modified Flory-Rehner equation$^{(100)}$. This equation is as follows:

$$-\left\{\ln(1-V_r) + V_r + \chi V_r^{2}\right\} = \frac{\rho\nu_o(V_r^{\frac{1}{3}} - \frac{V_r}{2})}{M_c} \qquad (4.9)$$

where ν_o is the molar volume of the swelling liquid, and χ is the rubber-solvent interaction parameter. This relationship, which is derived from the molecular theory of rubber elasticity and from the theory of the thermodynamics of mixing of polymers and liquids, is again restricted to networks which are free from chain entanglements and chain ends. Therefore the M_c values and the derived values of $[X]_{phys}$ have again to be corrected if concentrations of chemical crosslinks are required.

Experimentally there are difficulties in using equation (4.9), in that χ must first be determined by using M_c values obtained for vulcanizates of the same type by an independent method. Also, it has been shown(101, 102) χ changes both with level of vulcanizing ingredients and with time of vulcanization, because of alteration in the chemical constitution of the network chains.

Equations (4.9) and (4.7) can be combined to give

$$-\left\{\ln(1-V_r) + V_r + \chi V_r^{2}\right\} = \frac{2C_1\nu_o(V_r^{\frac{1}{3}} - V_r/2)}{RT} \qquad (4.10)$$

If the value of χ is known, equation (4.10) enables one to convert V_r data to values of C_1, which can then be converted to values of $[X]_{chem}$ by the Mullins procedure described above.

4.3.2. Concentrations of different types of chemical crosslinks

The previous section has been concerned with the determination of the overall concentration of chemical crosslinks by the use of physical methods in conjunction with the theory of rubber elasticity. All types of crosslinks in the vulcanizate, such as mono-, di- and poly-sulphidic crosslink, contribute to this overall degree of chemical crosslinking. "Chemical probe" reagents have been developed for estimating the individual contributions of each type of sulphidic crosslink to the overall degree of chemical crosslinking. These "probes" are reagents which selectively attack particular sulphidic groups in a manner which permits their quantitative determination. Several reagents have been used for this purpose. However, some of them are obsolete today, either because of their deficiency in some respect, or because of the development of more efficient probes.

4.3.2.1. Determination of contribution of polysulphidic crosslinks to overall concentration of chemical crosslinks using sodium sulphide as chemical probe reagent

Aqueous sodium sulphite reduces polysulphides to disulphides, in the process producing sodium thiosulphate as follows:

$$\sim\!\sim CH_2 - S - S_x - S - CH_2 \sim\!\sim + SO_3^{2-} \longrightarrow$$
$$\sim\!\sim CH_2 - S - S - CH_2 \sim\!\sim + xS_2O_3^{2-} \qquad (4.11)$$

The contribution of polysulphide crosslinks to the overall concentration of chemical crosslinks may thus be determined by iodiometric titration of the thiosulphate ions which are formed. Dogadkin and Tarasova(103) used this reagent to determine polysulphide groups in vulcanized SBR. This reagent has not, however, been used in the present investigation because of its poor solubility in solvents which swell rubber. Furthermore, there is no mention in the literature whether thiosulphate ions can also be formed from disulphide crosslinks, cyclic sulphides and sulphides in pendent groups.

4.3.2.2. Determination of contribution of poly- and di-sulphidic crosslinks to overall concentration of chemical crosslinks

a) Methyl iodide as a chemical probe reagent

Methyl iodide is one of the earliest reagents to have been used as a chemical probe reagent. Meyer and Hohenemser(104) first used it to cleave dialkenyl monosulphide crosslinks by the reaction

$$\begin{aligned}&\sim CH=CH-CH_2-S-CH_2-CH=CH\sim \; + \; 3MeI\\ &\longrightarrow 2(\sim CH=CH-CH_2-I) + Me_3SI \qquad (4.12)\end{aligned}$$

By determination of the quantity of network-bound iodine after treatment, an estimate of dialkenyl monosulphide crosslinks can be obtained. Selker and Kemp(105,106) claimed to have confirmed the above chemistry by isolating trimethyl sulphonium iodide from vulcanizates which had been treated with methyl iodide. Other workers$^{(107-109)}$, however, have found that trimethyl sulphonium iodide can also be formed from teralkenyl and diteralkyl monosulphides. These are mainly present in sulphur-vulcanized rubber as non-crosslinking sulphides such as cyclic sulphides or sulphides in pendent groups. Therefore if methyl iodide were to be used as a chemical probe reagent for determining the concentration of monosulphidic crosslinks, the result is likely to be an overestimate.

b) Lithium aluminium hydride as a chemical probe reagent

This probe reagent is unreactive towards monosulphides, but readily cleaves and reduces di- and polysulphides to thiols:

$$\sim CH_2 - S - S_x - S - CH_2 \sim \xrightarrow[\text{hydrolysis}]{LiAlH_4} 2(CH_2SH) + xH_2S \qquad (4.13)$$

Determination of network-bound thiol groups gives an estimate of the concentration of polysulphidic and disulphidic crosslinks in the vulcanizate, whilst quantitative determination of the hydrogen sulphide liberated provides an estimate of the polysulphide rank. Lithium aluminium hydride, does not, however, react only with crosslinks. Like methyl iodide, it may also react with non-crosslinking sulphide groups, such as those present in cyclic sulphides and pendent groups. Nevertheless, this reagent was found to give reliable results for the contribution of di- and poly-sulphidic crosslinks to the overall concentration of chemical crosslinks when used in conjunction with a physical method for crosslink concentration, by means of which the concentration of chemical crosslinks in the vulcanizate before and after treatment could be estimated(110).

c) Trialkyl phosphites as chemical probe reagents

Trialkyl phosphites act as chemical probes very much as lithium aluminium hydride, in that they cleave di- and poly-sulphidic crosslinks but leave the monosulphidic crosslinks unaffected. The relevant reactions are as follows:

$$\sim\sim CH_2-S-S_x-S-CH_2\sim\sim + x(RO)_3P \longrightarrow x(RO)_3PS + \sim\sim CH_2-S-S-CH_2\sim\sim \tag{4.14}$$

$$\sim\sim CH_2-S-S-CH_2\sim\sim + (RO)_3P \longrightarrow \sim\sim CH_2-S-R + OP(SCH_2)(OR)_2 \tag{4.15}$$

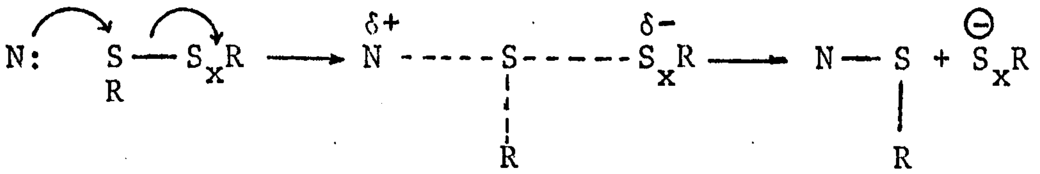
Determination of network-bound phosphorus following probe treatment gives an estimate of the contribution of di- and poly-sulphidic crosslinks to the overall concentration of chemical crosslinks(111,112).

Quite recently it was realized by Russell(113) that this particular reagent also damages the network in ways other than attacking di- and poly-sulphidic crosslinks.

This was evident when control samples of peroxide-vulcanized rubbers, which should not have been attacked by the reagent, were in fact found to be attacked as indicated by measurements of equilibrium volume swelling before and after treatment with the reagent.

4.3.2.3. Determination of contribution of di- and mono-sulphidic crosslinks to overall concentration of chemical crosslinks using propane-2-thiol and piperidine in *n*-heptane as a chemical probe reagent

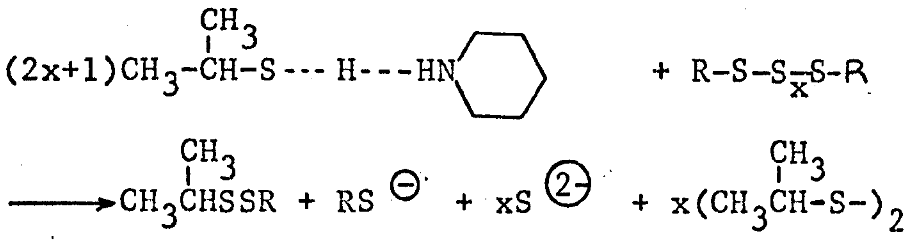
This probe reagent was developed by Campbell and Saville(114) with the aim of distinguishing between the contributions to the overall concentration of chemical crosslinks from disulphidic and polysulphidic crosslinks. This is a respect in which most of the other reagents described have failed. The combination of propane-2-thiol and piperidine acts in a manner which rapidly cleaves the polysulphide structure whilst reacting only slowly with corresponding disulphide. It does not react with monosulphides. The chemistry underlying the reaction was suggested by Saville(114) following observations on simple organic sulphides that, when the S-S bond of the organic sulphide is attacked by a nucleophilic reagent N:,the rate of substitution resulting from such attack is very dependent upon the stability of the leaving group anion $S_x^{\ominus}R$. Thus:



$$N: \ \underset{R}{S}-S_xR \longrightarrow \overset{\delta+}{N}\text{-----}\underset{R}{S}\text{-----}\overset{\delta-}{S_xR} \longrightarrow N-\underset{R}{S} + \overset{\ominus}{S_xR} \qquad (4.16)$$

When x = 1 (i.e., the sulphidic structure is a disulphide), the electron pair of the cleared S-S bond is associated entirely with a single sulphur nucleus. The resulting anion, $^{\ominus}$SR, is not very stable in this case, and thus substitution is not favoured. In the case of tri- and poly-sulphides, when x is 2 or more, the displaced electron pair is delocalized by association with the two or more sulphur nuclei. The anions produced are correspondingly more stable, and the substitution reaction is favoured. Therefore it was concluded that tri- and higher sulphides are more reactive towards nucleophilic reagent than di- and mono-sulphide. The prediction that polysulphidic crosslinks would be cleaved selectively was confirmed experimentally(114) using model compounds. Bis-(1,3-dimethyl but2-enyl) trisulphide and bis(2methyl pent-2 enyl) trisulphide were found to react with a solution of propane-2-thiol and piperidine in n-heptane within two hours at 20°C. However, under the same conditions, disulphide models were found to react at least 1000-fold more slowly, and are therefore essentially unaffected in the time required for complete decomposition of the trisulphides.

Propane-2-thiol and piperidine in n-heptane have been used by Trego(109) for the estimation of contribution of polysulphide crosslinks to the overall concentration of chemical crosslinks in sulphur vulcanizates produced using accelerators. The cleavage reaction is believed to be as follows:

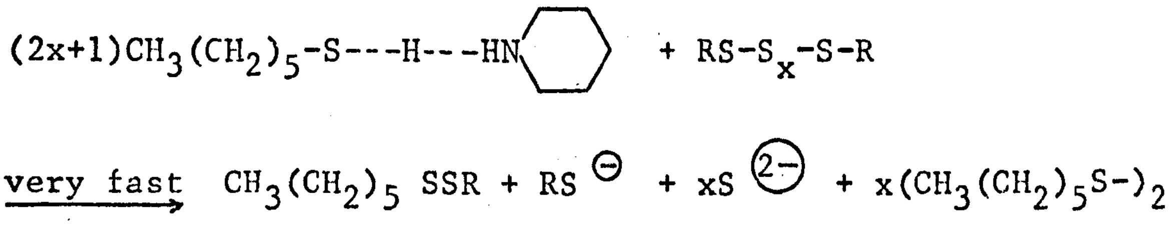


(4.17)

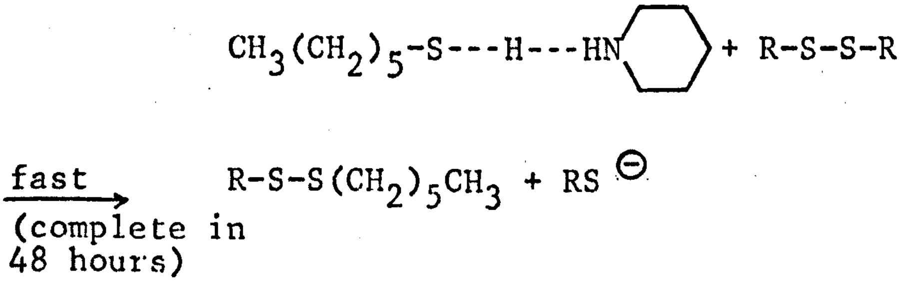
The concentration of chemical crosslinks was determined by means of C_1 measurements before and after treatment with the probe reagent. The concentration of chemical crosslinks after probe treatment is the concentration of di- and mono-sulphidic crosslinks. The difference between the crosslink densities before and after probe treatment gives an estimate of the concentration of polysulphidic crosslinks.

4.3.2.4. Determination of contribution of monosulphidic crosslinks to overall concentration of chemical crosslinks using n-hexanethiol in piperidine as a chemical probe reagent

This reagent selectively cleaves both di- and polysulphide crosslinks. The development of this reagent exploits the same principles as have been described for propane-2-thiol and piperidine in heptane. Campbell and Saville(114) reasoned that, in order to cleave the disulphidic as well as the polysulphidic crosslinks, it was necessary to increase the reactivity of the reagent by increasing the nucleophilicity of the thiol-amine combination. This increase in nucleophilicity was achieved by using a solution of alkanethiol in neat piperidine. Using this reagent, it was found that 94% of a model for disulphidic crosslinks was destroyed by n-butanethiol in less than 24 hours at 25°C. Russell$^{(113)}$, working with vulcanizates, also found that at 25°C, 48 hours was more than sufficient to ensure complete cleavage of di- and poly-sulphidic crosslinks in samples 1 mm or less thick. The chemistry which underlies the use of this probe reagent is believed to be as follows:



(4.18)



(4.19)

The contribution to the overall concentration of chemical crosslink made by monosulphidic crosslinks can then be determined from C_1 measurements made before and after treatment with the probe reagent.

4.3.3. Characterization of main-chain modifications using triphenyl phosphine as chemical probe reagent

So far, all the probe reagents described have been used for the determination of the types and concentrations of sulphidic crosslinks. Triphenyl phosphine, however, has been used to give information concerning sulphur combined in the network in the form of main-chain modification such as cyclic sulphides and as sulphidic pendent groups. This reagent has been shown by Trego(109) to reduce all dialkenyl disulphides and polysulphides to monosulphides. The monosulphides are unaffected. The desulphuration reaction is as follows:

$$\sim CH{=}CH{-}CH_2{-}S{-}S_x{-}S{-}CH_2{-}CH{=}CH\sim + (x+1)Ph_3P$$

$$\longrightarrow \sim CH{=}CHCH_2SCH_2CH{=}CH\sim + (x+1)Ph_3P{=}S \qquad (4.20)$$

Hence to obtain quantitative measure of sulphur combined in the main chain modification such as cyclic sulphide groups and pendent sulphidic groups, the vulcanizate is first treated with triphenyl phosphine, after treating with triphenyl phosphine, the E' value, which is the E value of the network after treatment with triphenyl phosphine is obtained. It represents crosslink contributions from crosslinks which contain only one sulphur atom per crosslink. Thus, the quantity E'-1 represents the average number of sulphur atoms per chemical crosslink combined in the network in the form of main-chain modification. This elegant technique also has the advantage of experimental convenience, in that the reagent is easily swollen into the vulcanizate. Unfortunately, however, there is a serious disadvantage associated with the use of this reagent, which was demonstrated by Watson(115) and confirmed by Moore(116), and which puts the usefulness of this probe reagent in doubt. Triphenyl phosphine was found to desulphurate some of the pendent group sulphides. The consequence of this is underestimation of main-chain modifications.

4.4. Chemistry of Sulphur Vulcanization of Natural Rubber

4.4.1. Chemistry of unaccelerated sulphur vulcanization

Understanding of the chemistry of unaccelerated sulphur vulcanization has been assisted by researches on low-molecular-weight olefins as model compounds for natural rubber(118-121). The model compounds were reacted with sulphur under typical vulcanization conditions, and the various reaction products identified.

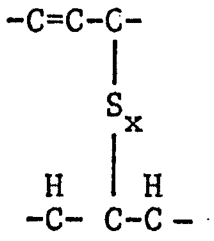
4.4.1.1. Reaction of sulphur with mono-olefins

The following features have been established for the reaction of sulphur with mono-olefins:

(i) Below 150°C, no hydrogen sulphide, thiol or other compounds with sulphurated functional groups have been observed. Therefore, the conclusion has been reached that the sulphuration of mono-olefins involves little or no dehydrogenation of the mono-olefins.

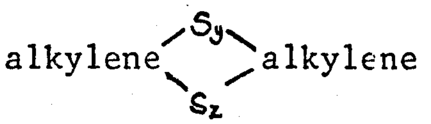
(ii) The principal products were a complex mixture of organic polysulphides having the following three structural types:

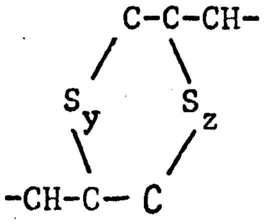
A) alkenyl-S_x-alkyl



(I)

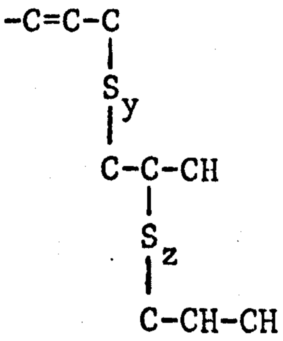
B)





(II)

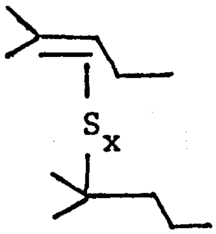
C) alkenyl-S_y-alkylene-S_z-alkyl



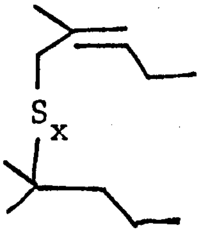
(III)

(iii) At short reaction times, (I) is the principal type of product, the average sulphur rank , (x), being about 4-5. At longer reaction times and with less substituted olefins (which have been shown to have a reduced reactivity towards sulphur(122)), the relative proportion of polysulphides having structures (II) and (III) increases and the sulphur rank of (I) reduces to approximately unity, i.e., the products of this type are mainly monosulphides. This observation has led to the conclusion(123) that polysulphides having structures (II) and (III) are secondary products which arise from further sulphuration of the alkenyl-alkyl polysulphides, (I).

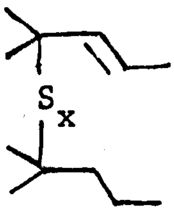
(iv) The alkenyl-alkyl polysulphides can be present as the following structures:-



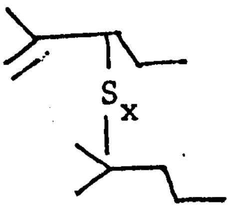
(IV)



(V)



(VI)

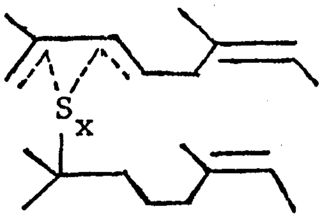


(VII)

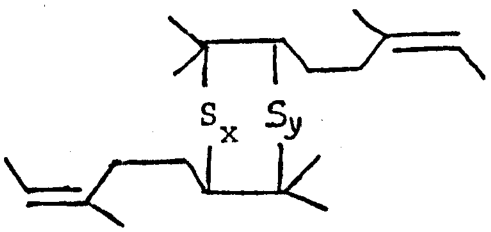
These structures are dependent on the degree of substitution at the olefinic double bond. Thus for the sulphuration of 2-methyl pent-2-ene,  , the main products are 1,3-dimethylbut-2-enyl 1,1-dimethylbutyl polysulphide (IV) and 1,1-dimethylbutyl-2-methyl pent-2-enyl polysulphides (V).

4.4.1.2. Reaction of sulphur with di-olefins

2,6-dimethyl octa 2,6 diene, whose simplified formula is  , has been used as a model compound for natural rubber(119). Crosslinked polysulphides, analogous to those described in the previous section, were again identified as products (structures (VIII) and (IX)).

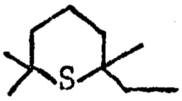


(VIII)

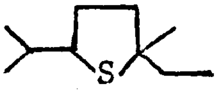


(IX)

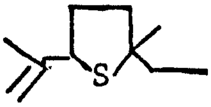
However, more significantly, a new type of organic polysulphide, which was not observed in the products of the reaction of mono-olefins with sulphur, was identified. The new products were cyclic monosulphides ((X), (XII), (XIII) and (XV). These structures were also found to appear in the crosslinked polysulphide products ((XIV) and (XV))



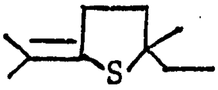
(X)



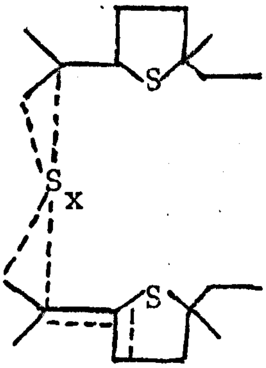
(XII)



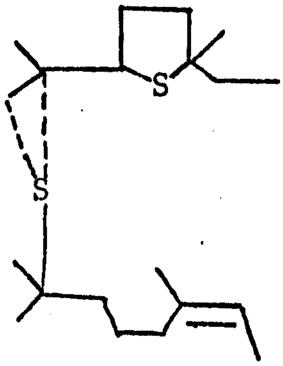
(XIII)



(XV)



(XIV)



(XV)

It has been reported(124-127) that the main products formed after short reaction times were (VIII) and (IX) but after prolonged reaction, products with structures (X) - (XV) were predominant, and the average length of the polysulphide chains decreased. It is also now believed(128) that all cyclic sulphides (X) - (XV) are formed as secondary reaction products from the primary products.

4.4.1.3. Kinetics and mechanism of unaccelerated sulphur vulcanization

In view of the multiplicity of species formed on sulphuration of even simple model compound of natural rubber, the kinetics of the process would be expected to be complex. This is indeed the case. Attempts to establish the mechanistic nature of olefin sulphuration by investigation of effects of additives upon the kinetics have not led to clear-cut results.(122)

Hence our knowledge of the mechanism of unaccelerated sulphur vulcanization is still somewhat confused. There are currently two main schools of thought. Some workers postulate a free radical-ionic mechanism(119,123,129). This is a two-part mechanism which involves homolytic dissociation of S-S bonds and the formation of an alkane perthiol, RS_aH, by a free-radical chain process. This is then followed by polar addition of the perthiol to the olefin in a non-chain process according to Markonikov's rule (equations 4.22-4.26).

$$TS_aS_bT \rightleftharpoons TS_a^{\bullet} + TS_b^{\bullet} \tag{4.22}$$

$$TS_a^{\bullet} + RH \rightarrow TS_aH + R^{\bullet} \tag{4.23}$$

$$R^{\bullet} + S_8 \rightarrow RS_a^{\bullet} \tag{4.24}$$

$$RS_a^{\bullet} + RH \rightarrow RS_a H + R^{\bullet} \tag{4.25}$$

$$RS_aH + RH \xrightarrow[\text{addition}]{\text{Markonikov}} R\,S_aRH_2 \tag{4.26}$$

(R = alkenyl; T = R or RH_2; a, b = 2-8)

The mechanism as formulated above yields the simple alkenyl-alkyl polysulphides (I), but can be extended to cover the formation of alkylene-alkylene polysulphides (II) and alkenyl-alkylene-alkyl polysulphides (III) by postulating an alternative step whereby the persulphenyl radical, $RS_a^{\bullet}$, adds to the olefin rather than abstracting hydrogen:

$$RS_a^{\bullet} + RH \rightarrow RS_aRH \xrightarrow{S_8,\text{etc.}} \text{(II),(III)} \tag{4.27}$$

This mechanism cannot readily explain the formation of cyclic monosulphides from the sulphuration of di-olefin compounds, but these are in any case now usually regarded as secondary products(128).

Other workers explain most of the features of olefin sulphuration by a polar-chain mechanism(122,126).

In this mechanism, initiation involves heterolytic S-S bond fission of initially-formed polysulphides to give incipient persulphenium ions ($TS_a^{\oplus}$) and persulphenyl ions ($TS_b^{\ominus}$). The former are postulated as the chain carriers, and the latter are postulated as the chain terminators. Reaction of the persulphenium ion at the olefinic double bond gives a cyclic persulphenium ion, $TS_aRH^{\oplus}$, which, depending upon its structure and that of the olefin, can either lose a proton to the olefin or gain a hydride ion from the olefin. In either case, a polysulphide and an alkyl, $RH_2^{\oplus}$, or alkenyl, $R^{\oplus}$, carbonium ion are formed. The latter can then react with sulphur to continue the chain. The proposed reactions can be summarised as follows:

Initiation $$TS_aS_bT \longrightarrow TS_a^{\oplus} + TS_b^{\ominus} \qquad (4.27)$$

Propagation $$TS_a^{\oplus} + RH \longrightarrow TS_aRH^{\oplus} \qquad (4.28)$$

$$TS_aRH^{\oplus} + RH \xrightarrow{H^{+}\ \text{transfer}} TS_aR + RH_2^{\oplus} \qquad (4.29)$$

$$TS_aRH^{\oplus} + RH \xrightarrow[H^{-}\ \text{transfer}]{} TS_aR + R^{\oplus} \qquad (4.30)$$

$$RH_2^{\oplus} + S_8 \longrightarrow RH_2S_8^{\oplus} \qquad (4.31)$$

$$(\hat{=} TS_a^{\oplus})$$

$$R^{\oplus} + S_8 \longrightarrow RS_a^{\oplus} \qquad (4.32)$$

$$\text{Termination}\quad \left.\begin{array}{l} RH_2^{\oplus} \\ \\ R^{\oplus} \\ \\ TS_a^{\oplus} \\ \\ TS_aRH^{\oplus} \end{array}\right\} + TS_b^{\ominus} \longrightarrow \text{inactive products} \qquad \begin{array}{r} (4.33) \\ \\ (4.34) \\ \\ (4.35) \\ \\ (4.36) \end{array}$$

The merit of this mechanism lies in its ability to explain consistently the detail structures of the products which are obtained from all types of mono olefins and diolefins. This mechanism has also been preferred to the free radical mechanism by some workers$^{(126)}$ because they believed that no examples of thermal homolytic scission of alkyl disulphides had been observed below 140°C at the time when their polar mechanism was proposed. Their conclusion is now thought to be in error. Tobolsky and coworkers$^{(130-132)}$ have shown that dimethyl tetrasulphide undergoes thermal homolysis at temperatures as low as 50-80°C. The homolysis produces two disulphenyl radicals, $MeS_2^{\bullet}$, by fission of the central S-S bond. Also, in order to have ionic initiation, polysulphenium ions must be generated. No evidence has so far been reported for the heterolytic thermal dissociation of a polysulphide bond.

Since the polar mechanism was proposed in 1958, very little additional evidence has been reported upon which a judgement might be based. It is therefore difficult to draw conclusions concerning the relative merits of the two mechanisms.

4.4.1.4 Chemical structure of vulcanizates produced by unaccelerated sulphur vulcanization

The crosslinking of natural rubber using sulphur without accelerators is very inefficient, it requires as many as between 40 and 55 sulphur atoms to combine with the rubber in order to produce one chemical crosslink(133). It is clear from this discussion why unaccelerated vulcanization is so inefficient. It is attributable to the incorporation of the sulphur in the form of long polysulphide crosslinks, cyclic monosulphides and vicinal or neighbouring crosslinks in which the two crosslinks act as a single crosslink.

The results from studies using model compound together with information concerning the extent of chain scission indicate that the structure of vulcanizate networks obtained by heating natural rubber with sulphur alone is of the general type illustrated in Fig.4.6.

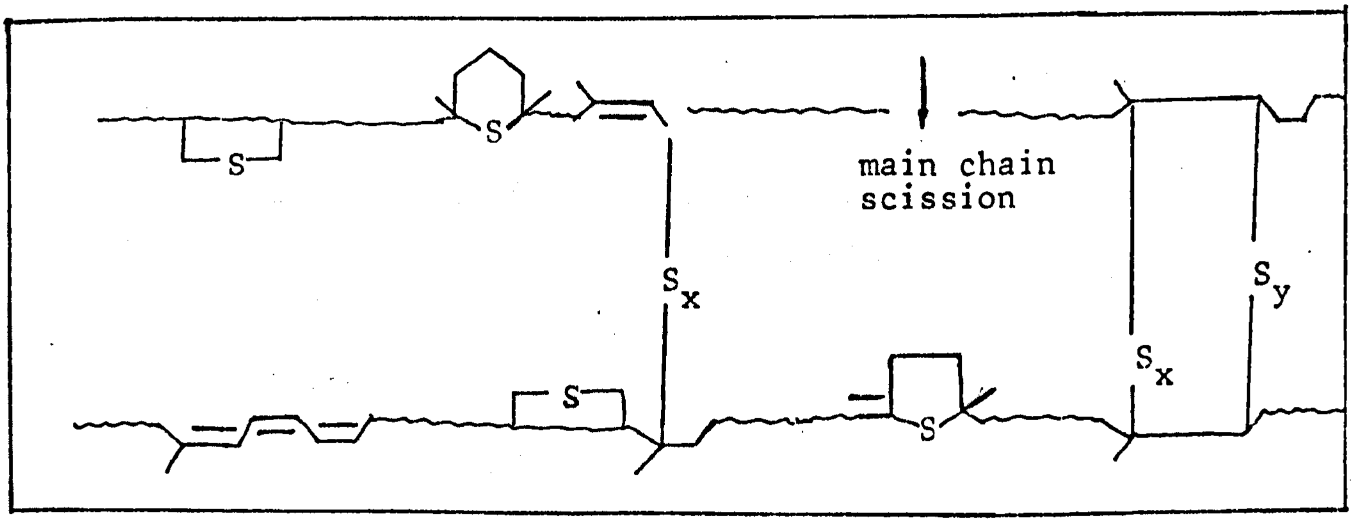
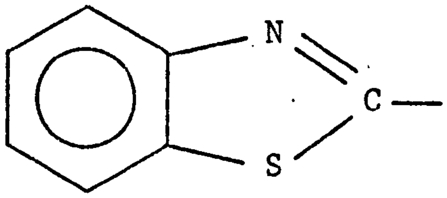


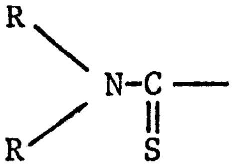
Fig.4.6. Pictorial representation of structural features of vulcanizates produced by unaccelerated sulphur vulcanization of natural rubber

4.4.2. Chemistry of accelerated sulphur vulcanization

Sulphuration of olefins in the presence of sulphur and an accelerator-activator system proceeds much more rapidly and leads to simpler products compared with systems in which sulphuration occurs by reaction with sulphur alone. Accelerated sulphur vulcanizing systems usually comprise sulphur (2-3 pphr), accelerator (0.5-1.0 pphr), zinc oxide (3-5 pphr), and a zinc soap (1-3 pphr). The zinc oxide and zinc soap together make up the activator system. The accelerator used most widely are derivatives of the benzothiazol-2-yl moiety (XVI), and of the dialkylthiocarbamyl moiety (XVII).



(XVI)

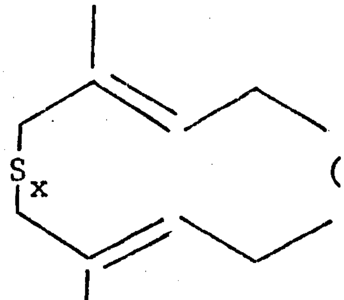


(XVII)

4.4.2.1. Studies using model compounds

The following features have been established from studies of the accelerated sulphuration of model compounds(117,124,128,135):

(i) The principal products are the disubstituted dialkenyl mono-, di- and poly-sulphides, (XVIII), compared to the combined substitutive/additive alkenyl-alkyl polysulphides produced by unaccelerated sulphuration of olefins.



(x varies from 1 to 6)

(XVIII)

(ii) The formation of saturated sulphide groupings and complex sulphide structures such as (II) and (III) is entirely suppressed.

(iii) Cyclic monosulphides and disulphides are formed to a lesser extent than in unaccelerated sulphuration.

(iv) Zinc sulphides and nitrogenous substances of the general type alkenyl S_x-Y (where Y is an accelerator fragment having structure (XVI) or (XVII)) are produced.

(v) The composition of the vulcanizing system affects the proportions of mono-, di- and poly-sulphides formed. Low accelerator:sulphur ratios lead to the formation of highly polysulphidic products. If the accelerator:sulphur ratio is high, di- and poly-sulphides are formed initially, but the products are mainly monosulphides over most of the reaction range (Figs. 4.7 and 4.8).

(vi) When the zinc activators are omitted entirely, the effect of the accelerator alone on the olefin-sulphur reaction is largely confined to increasing rate of sulphuration, with little effect upon the structure of the sulphuration product. On the other hand, zinc activators by themselves hardly affect the rate of sulphur

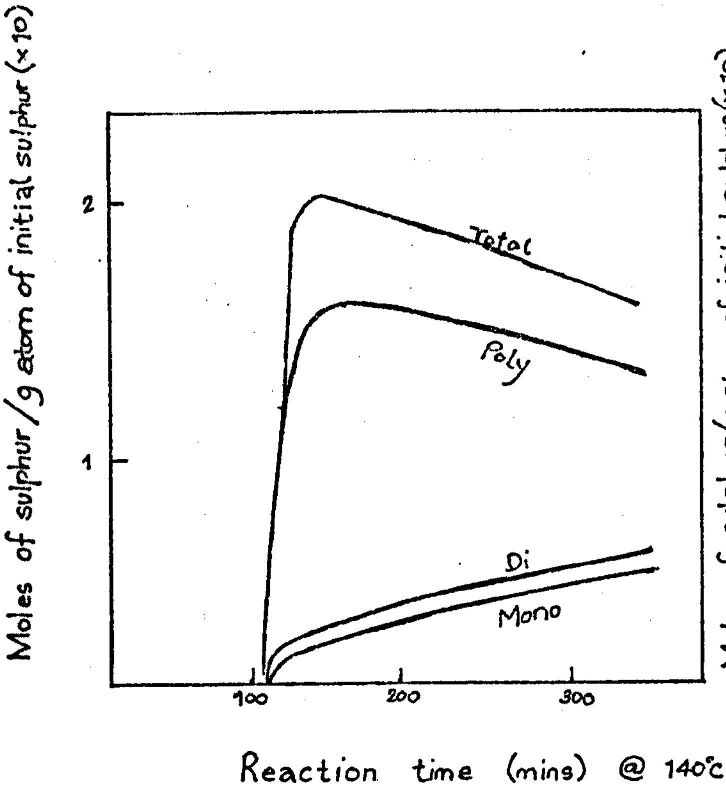


Fig.4.7. Course of sulphuration of 2-methylpent-2-ene with low accelerator: sulphur ratio (0.6: 2.5)(123)

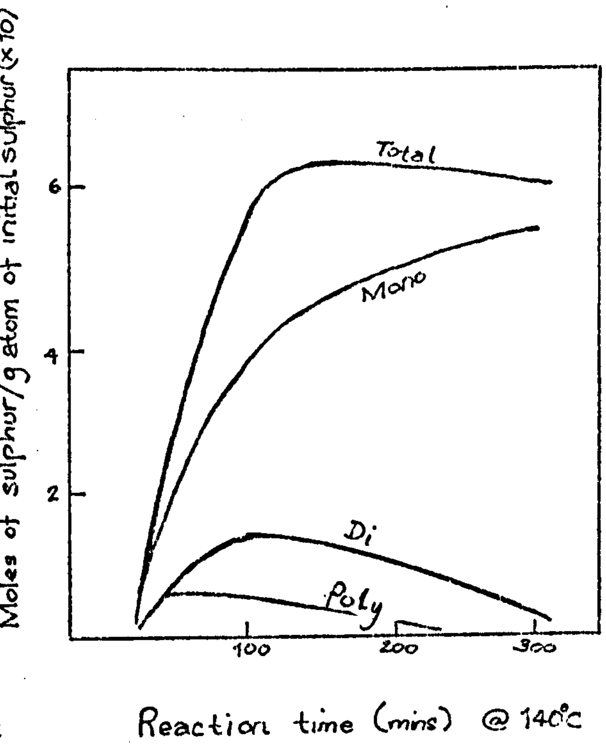


Fig.4.8. Course of sulphuration of 2-methylpent-2-ene with high accelerator: sulphur ratio (6.0:0.4)(123).

combination, but do exert a marked effect upon the structure of the sulphuration products produced, making sulphuration almost entirely a substitutive process rather than a combined additive-substitutive process, and thus eliminating complex sulphides such as (II) and (III). Only combinations of accelerators and zinc activators increase the rate of sulphuration.

4.4.2.2. Mechanism of accelerated sulphur vulcanization

The results of chemical studies with model compounds described earlier provide a fairly clear picture of the mechanism or pathway of vulcanization of accelerated sulphur vulcanization. Thus, it is generally accepted today that the main sequence of reaction is that generalized in Fig. 4.9. In Fig.4.9, the term "active sulphurating agent" denotes the species which interact with the rubber to form carbon-sulphur bonds. The products of this reaction are the rubber-bound intermediates, $-R-S_a-X$. These intermediates are identified as the species which contain the pendent sulphurated group terminated by accelerator fragment shown in Fig.4.2. Each of the steps in the sequence appears to consist of at least two consecutive or competing reactions, all of which involve equilibria.

(a) Formation of the active sulphurating agent

The sulphurating agent is itself produced by a multiple-step reaction. Firstly, a precursor, (XIX), is formed *in situ* in the rubber by a reaction which involves the accelerator, zinc oxide and fatty acid. The reaction is represented schematically as follows:

$$\left.\begin{matrix} XSH \\ XSSX \\ XSNR_2 \end{matrix}\right\} \xrightarrow[RCOOH]{ZnO} \underset{(XIX)}{XSZnSX} \qquad (4.37)$$

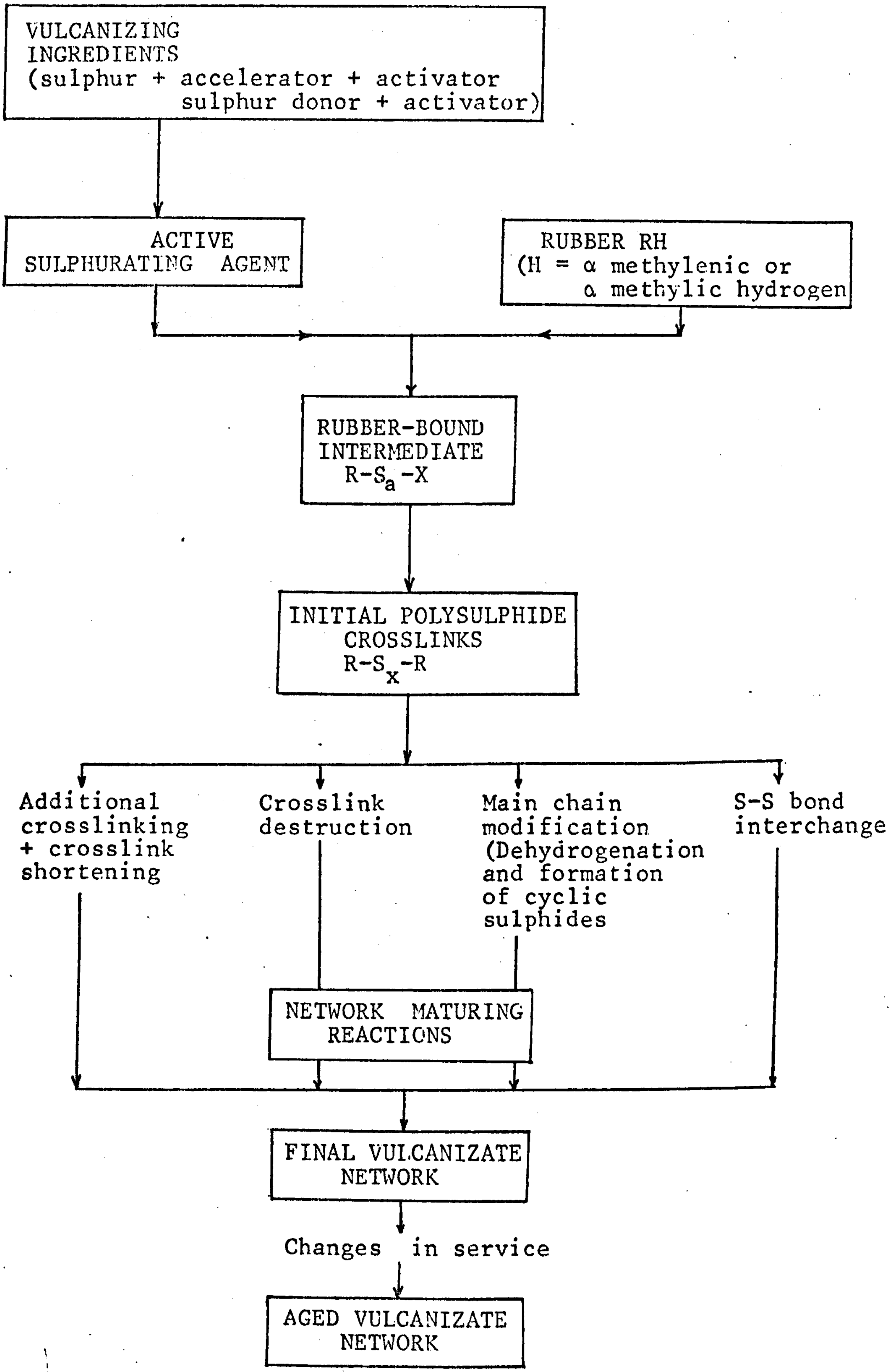
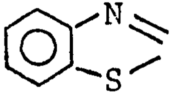
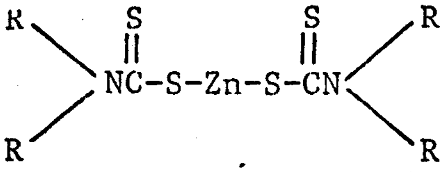
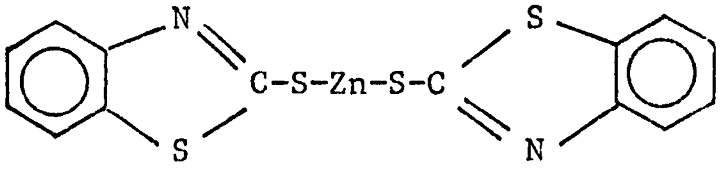


Fig.4.9. Overall course of sulphur vulcanization

In this reaction, the common accelerators, such as the thiazoles, thiurams and sulphenamides, are represented by XSH, XSSX, and $XSNR_2$ respectively, where X is $R_2N\overset{|}{C}=O$ or  C-. The precursor formed in these cases will therefore either be a zinc dialkyl dithiocarbamate (XXI) or zinc benzothiazole-2-thiolate, (ZMBT, (XXII)), depending upon the composition of the vulcanizing system.

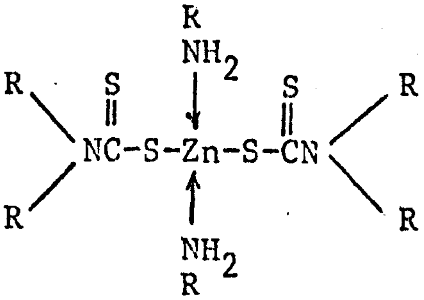


(XXI)



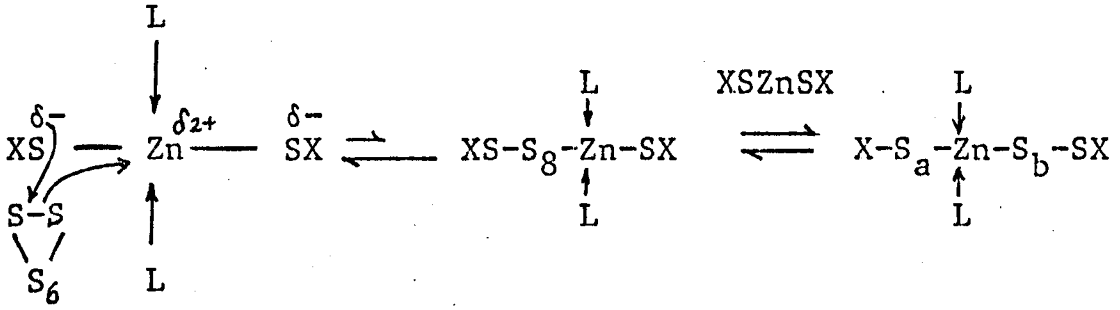
(XXII)

These precursors are only sparingly soluble in rubber. However, their coordination product with primary or secondary nitrogen bases as ligands are very soluble. The nitrogen bases either occur naturally in the rubber, or are deliberately added. The structure of a typical coordinated precursor is shown at (XXIII). Apart from



(XXIII)

making the precursor soluble in rubber, coordination with amine ligands also increases the polarization of the Zn---S bond of the precursor, thus, facilitating nucleophilic attack of the precursor complex(136). It is the nucleophilic attack of the precursor complexes on molecular sulphur that forms the active sulphurating agent, (XXIV), a perthiomercaptide. Thus,

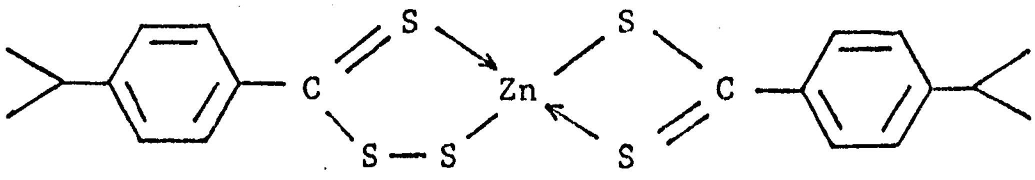


(4.38)

L = ligand

(XXIV)

This reaction is believed to comprise a series of equilibria which lie well to the left hand side. Support for the view has been provided by Milligan(136), who has shown that the precursor complex catalyses disulphide interchange reactions and the insertion of sulphur into diethyl disulphide. Even though no examples of the postulated active sulphurating species (XXIV) have yet been isolated, analogues such as (XXV) have recently been prepared and have been shown to contain rapidly exchangeable sulphur atoms(137-139). The precise mode of



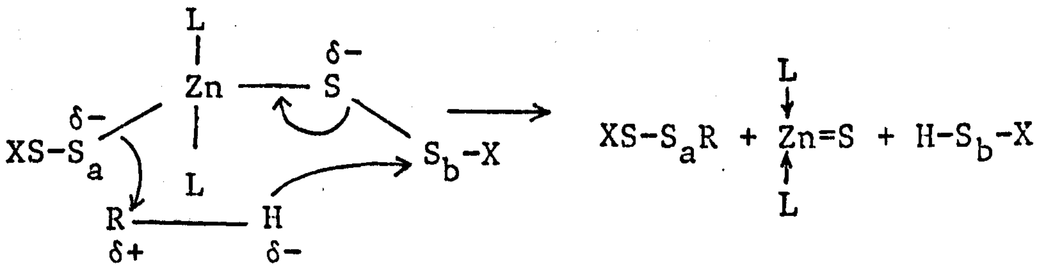
(XXV)

sulphur being 'activated' to an active sulphurating agent (XIV) is currently still under active investigation by a group of workers(143-146).

(b) Formation of rubber-bound intermediates

The rubber-bound intermediates are precursors to the crosslinks. Convincing evidence for the formation of such intermediates has been obtained(140-142). Nevertheless, the mechanism for formation of the rubber-bound intermediates is probably the least understood step in the whole vulcanization sequence. The mechanism involves the breaking of a C-H bond and the formation of C-S bond on the rubber molecules.

Based on observations made in experiments using model compounds, Bateman et al.(90) suggested a polar, largely concerted mechanism for the reaction between the active sulphurating agent (XXIV) and olefin or olefinic rubber, R-H, (where H is an α-methylene or α-methylic hydrogen atom). Nucleophilic attack on an allylic carbon atom by the sulphurating agent forms the intermediate (XXVI) directly:



(4.39)

(XXVI)

$$2H\text{-}S_b\text{-}X \xrightarrow{ZnO} XS_bZnS_bX + H_2O \qquad (4.40)$$

This mechanism explains satisfactorily the exclusive substitution of allylic hydrogen by sulphur, the absence of allylic rearrangement in the alkenethio groups, the influence of various ligands upon the ratio of substitution at the α-methylenic and α-methylic carbon atom, and the superiority of zinc over other metals in promoting vulcanization. Thus, the receipt of the displaced hydrogen by the other sulphur chain of the sulphurating agent (XXIV) is facilitated by the simultaneous formation of zinc sulphide. It is noteworthy that the presence of zinc oxide in the vulcanizing system brings about regeneration of the active sulphurating agent according to equation (4.40).

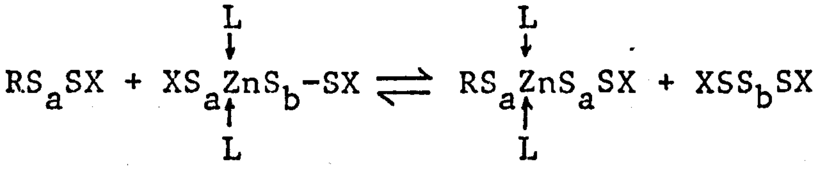
The rate of formation of the rubber-bound intermediate will be controlled by the relative energetics of C-S bond formation and C-H bond fission. Coordination of the zinc atoms by electron-donating ligands will increase the electron density on the XS_x moieties of the sulphurating agent, which in turn will facilitate C-S bond formation by increasing the nucleophilicity of the attacking XSS_a group, but hinder C-H bond fission by reducing the electrophilicity of the receiving XS_b group. The energetic contribution of bond formation will therefore increase relative to bond breakage. However, bond formation will also depend upon steric accessibility at the allylic carbon atom, i.e., it will be fastest at primary carbon atom, whereas bond fission will be fastest for a tertiary C-H bond. The enhancement of C-S bond formation relative to C-H bond fission will therefore increase substitution at primary α-carbon atoms. This is in fact the effect observed.

(c) Formation of initial crosslinks from rubber-bound intermediates

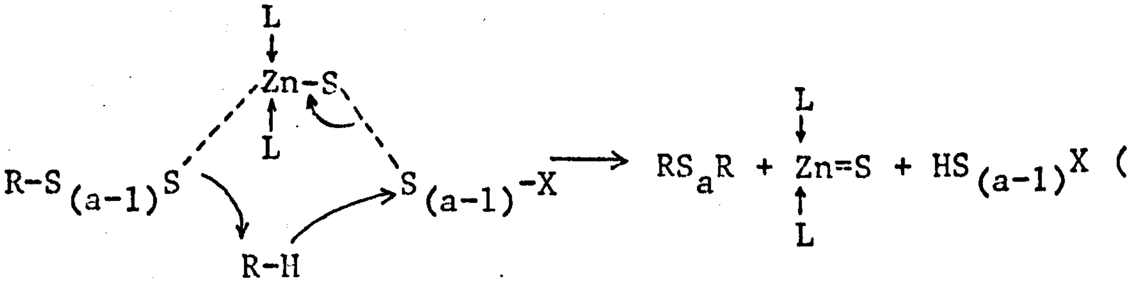
It has been suggested(90,123) that the rubber-bound intermediate (XXVI) is converted into crosslinks by two routes. The first is a simple disproportionation between two rubber-bound intermediates as follows:

$$2RS_aSX \longrightarrow RS_xR + XS.S_{(2a-x)}SX \qquad (4.41)$$

Alternatively, there could be an interchange reaction between rubber-bound intermediate (XXVI) and zinc perthiomercaptide (XXIV), followed by sulphuration of another rubber molecule:



$$RS_aSX + XS_a\underset{\overset{\uparrow}{L}}{\overset{\overset{L}{\downarrow}}{Zn}}S_b\text{-}SX \rightleftharpoons RS_a\underset{\overset{\uparrow}{L}}{\overset{\overset{L}{\downarrow}}{Zn}}S_aSX + XSS_bSX \qquad (4.42)$$



$$R\text{-}S_{(a-1)}S + \overset{\overset{L}{\downarrow}}{\underset{\overset{\uparrow}{L}}{Zn}}\text{-}S + S_{(a-1)}\text{-}X + R\text{-}H \longrightarrow RS_aR + \underset{\overset{\uparrow}{L}}{\overset{\overset{L}{\downarrow}}{Zn}}{=}S + HS_{(a-1)}X \qquad (4.43)$$

It is well established(103) that the crosslinks which form initially are mostly polysulphidic in nature, a few being disulphidic.

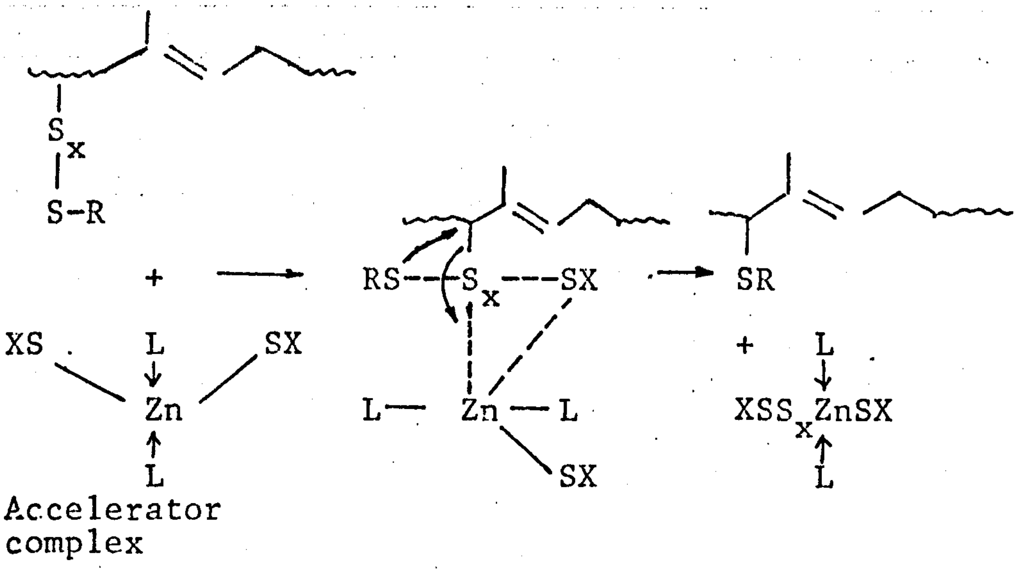
(d) Maturation of initially-formed crosslinks

The initial poly- and di-sulphidic crosslinks are subjected to further reactions in the presence of accelerators, activators and their transformation products. These reactions are known in the vulcanization sequence as network-maturing reactions. They occur during the later part of the vulcanization process and during subsequent service life, especially if the vulcanizate is subjected to elevated temperature. Hence, these reactions are important causes of changes in physical properties during service life, and affect the nature and ultimate length of service life. The most important of these network reactions are as follows:

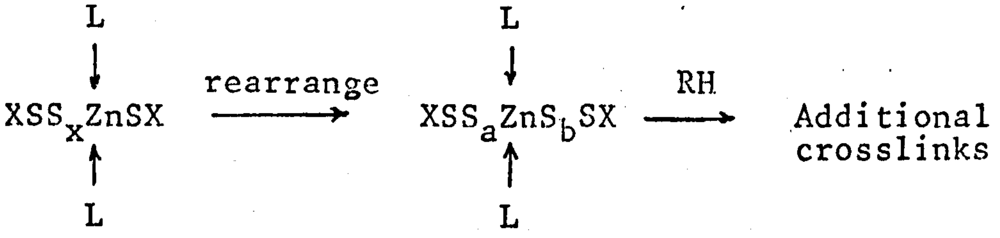
(i) crosslink shortening with additional crosslinking;
(ii) destruction of crosslink;
(iii) main-chain modification; and
(iv) S-S bond interchange.

(i) Crosslink shortening with additional crosslinking

In this reaction, sometimes known as desulphuration, sulphur is removed from the polysulphidic and disulphidic crosslinks without loss of the crosslink. This process takes place under the influence of accelerator complexes. The sulphur which is removed is available to be reutilized in the formation of new crosslinks. Thus:



(4.44)



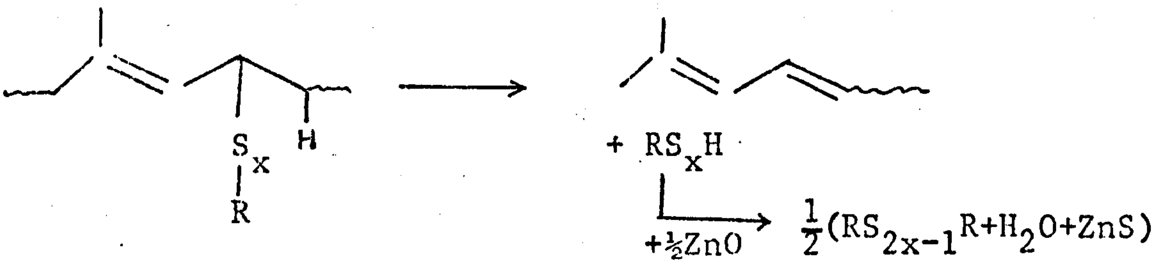
$$\overset{L}{\downarrow}\!\!\!\!\!\!\!\!\underset{\uparrow \atop L}{XSS_xZnSX} \xrightarrow{\text{rearrange}} \overset{L}{\downarrow}\!\!\!\!\!\!\!\!\underset{\uparrow \atop L}{XSS_aZnS_bSX} \xrightarrow{RH} \text{Additional crosslinks} \qquad (4.45)$$

In this reaction scheme, x is 1 to ca. 50, and L is the ligand of accelerator complex.

The environmental factors which favour desulphuration are a) long vulcanization times and high service temperatures, and b) high concentrations of zinc-accelerator complexes relative to crosslinks, i.e., high accelerator:sulphur ratio together with adequate activator concentration.

(ii) Destruction of crosslinks and (iii) main-chain modifications

Apart from desulphuration, the poly- and di-sulphidic crosslinks also undergo thermal decomposition, leading to the destruction of crosslinks during network maturation. Whereas in the case (i) above, the sulphur removed is reutilized in the formation of new crosslinks, in this process, the sulphur is irreversibly removed from crosslinks to form zinc sulphide as follows:



(4.46)

A consequence of this thermal decomposition of poly- and di-sulphides is that the main polymer chain becomes modified by the presence of conjugated diene, triene and cyclic sulphide groups. In practice, desulphuration competes with thermal crosslink destruction during the network-maturation process. Hence, because the monosulphidic crosslinks are thermally stable, rapid desulphuration leads to vulcanizates which have good heat-resistant properties. The factors which favour crosslink destruction and main-chain modification are therefore high vulcanization temperatures: and service temperatures, low accelerator: sulphur ratios, and inadequate concentrations of amine or carboxylate activators.

(iv) S-S bond interchange

This is a well-established dynamic process which occurs during the later stages of vulcanization and during service. The poly- and di-sulphidic crosslinks interchange dynamically with similar crosslinks and with sulphidic chains present in pendent groups or intramolecular loops. S-S bond interchange is not detectable in an undeformed vulcanizate since, it does not result in any change in overall concentration of crosslinks or in their average sulphur rank. However, if interchange occurs while the vulcanizate is deformed or swollen, the interchangeable crosslinks may slip into elastically-ineffective positions, resulting in creep, stress-relaxation, permanent set, or incremental swelling after removal of the deforming force or swelling liquid.

In summary, the maturing of the network which forms initially is seen to consist of a set of competing processes illustrated in Fig.4.10. The relative importance of the competing processes will depend upon the vulcanizing system, the reaction conditions, and the structure of initial network.

4.5. Main Differences between Latex Prevulcanization and Dry Rubber Vulcanization

The earlier part of this chapter has been concerned exclusively with the structure of the network in dry-rubber vulcanizates, and with the reactions of vulcanizing ingredients with dry rubber under the reaction conditions appropriate to dry rubber vulcanization. Surprisingly, very few similar studies seem to have been undertaken in order to understand the process of latex prevulcanization and the structure of the network which is present in vulcanized rubber obtained from prevulcanized latex.

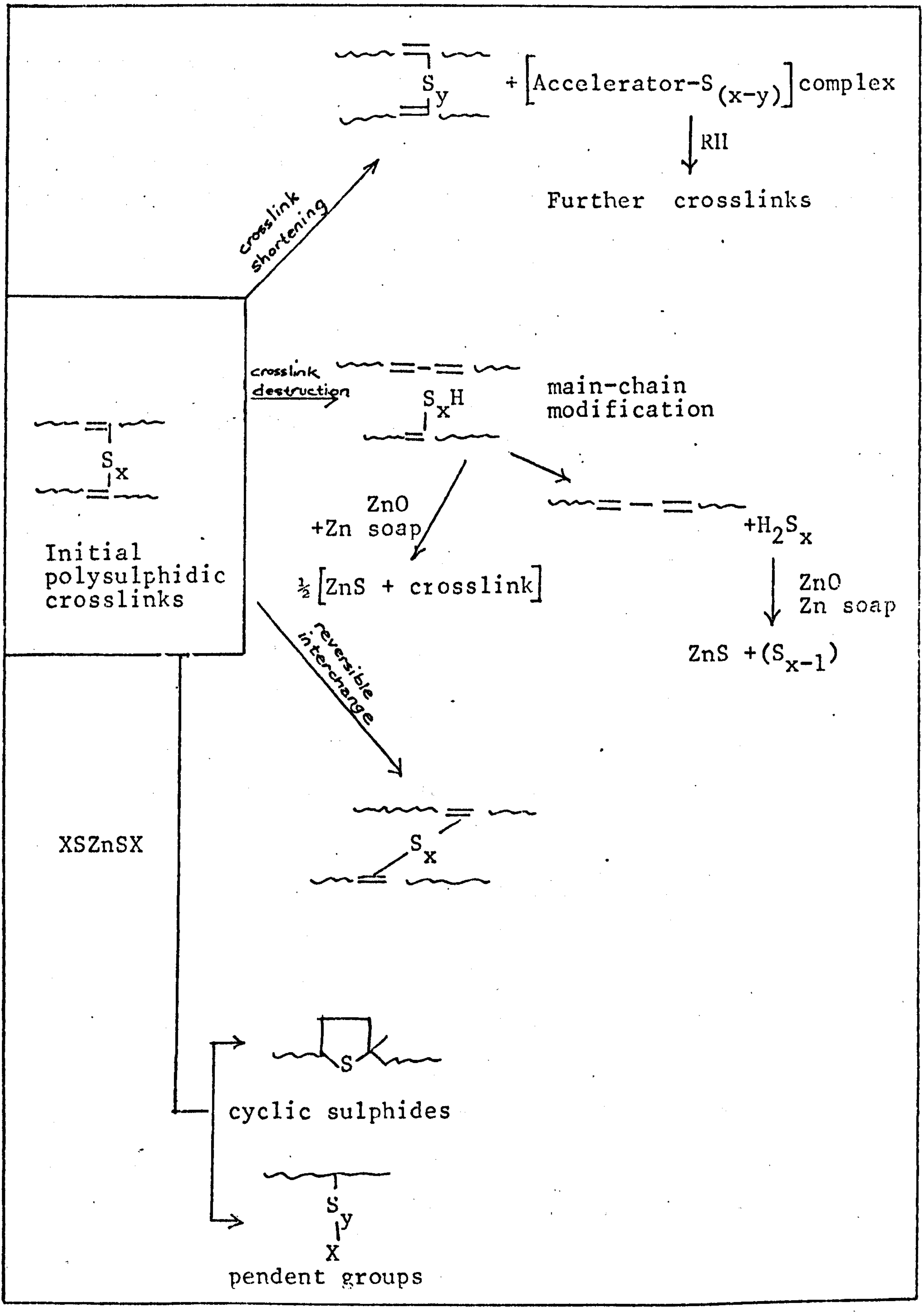


Fig.4.10. Illustrating the competing processes which occur during the maturing of an initial polysulphidic crosslinked network. (After Bateman et al. (90))

Very recently, Chong(63) has investigated the network structure of vulcanized rubber obtained from unvulcanized, vulcanizable latex deposits i.e., postvulcanized latex products. However as far as is known, no structural studies have been conducted on vulcanized rubber deposited from prevulcanized latex.

It is appropriate at this juncture to compare and contrast the process of latex prevulcanization and with that of conventional dry-rubber vulcanization. It is convenient to discuss the comparisons under the following headings:

(i) raw materials: (latex <u>vs</u>. dry rubber;)
(ii) compounding recipe and mixing processes;
(iii) reaction conditions and environment; and
(iv) the vulcanization reaction.

(i) <u>Raw materials: latex vs. dry rubber</u>

Most NR latex are preserved by ammonia. Hence not only is NR latex a liquid with <u>ca</u>. 60% rubber content, whereas dry rubber is a solid which contains almost 100% rubber hydrocarbon; there is also present in latex about 0.7% of ammonia which is not found in dry rubber. Also, amongst the non-rubber substances present in latex, there are some indigenous vulcanization activators and accelerators. During the coagulation process by which dry rubber is normally obtained, it is inevitable that some of these indigenous vulcanization accelerators and activators are removed during the separation process.

(ii) Compounding recipe and mixing processes

Although sulphur is used as the vulcanizing agent in both dry-rubber vulcanization and latex prevulcanization, the fatty acid (e.g., stearic acid) and zinc oxide which are commonly used as activators in dry-rubber vulcanization are not normally used in latex prevulcanization. Instead, very fast vulcanizing systems employing ultra-accelerators, notably the dithiocarbamates, are used for latex prevulcanization.

The vulcanizing ingredients for latex prevulcanization are generally blended into the latex in the form of dispersions. This differs from the compounding procedures prior to dry rubber vulcanization, in which the dry vulcanizing ingredients are mixed into the rubber matrix using two-roll mills or internal mixers. Almost all the vulcanizing ingredients are soluble in the dry-rubber matrix during the very early stages of dry-rubber vulcanization. This is not usually the case in latex prevulcanization. Sulphur and the zinc dialkyl dithiocarbamates are very sparingly soluble in the aqueous phase of the latex. Hence, the reaction is inevitably carried out heterogeneously.

(iii) Reaction conditions and environment

Unlike dry-rubber vulcanization which is normally carried out at *ca*. 150°C, latex is seldom prevulcanized at temperatures higher than 80°C. The actual temperature of prevulcanization depends upon several factors, including the vulcanizing system used; is in the range 50°C to 70°C. This low temperature of vulcanization may account for the many differences observed between the two types of reaction.

The reactions of dry-rubber vulcanization occur in a non-polar environment with the rubber hydrocarbon acting both as a reactant and the reaction medium. On the other hand, latex prevulcanization occurs in an environment, part of which is polar because of the presence of the water in the latex. It is quite possible that part of the prevulcanization reaction, such as the formation of the active sulphurating agent, may occur in the aqueous phase of the latex during prevulcanization. In addition, the presence of ammonia in the latex means the aqueous part of the prevulcanization environment is normally alkaline (ca pH 10.50) in nature.

(iv) The vulcanization reaction

It can be seen from this chapter that the process of dry-rubber vulcanization is quite well understood. Although the same cannot be said of latex prevulcanization it is believed that the chemical reactions which occur between the vulcanizing ingredients (and their reaction products) and the rubber in the form of latex cannot be very different from those which have been established for dry-rubber vulcanization. However, as can be seen from this section, there are several important differences between the two vulcanization reactions in terms of the form of the rubber, the non-rubber substances, the formulation, and the reaction conditions and environment. It is part of the objectives of the present programme to investigate how these differences affect latex prevulcanization.

CHAPTER 5

MATERIALS AND EXPERIMENTAL PROCEDURES

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5.1. Materials

5.1.1. Materials used in latex prevulcanization

5.1.1.1. NR latex

The NR latex chosen was a high-ammonia (HA) latex kindly supplied by LRC Products Ltd. To avoid batch-to-batch variations, precaution was taken to ensure that the same batch of latex was used throughout a particular series of experiments. The characteristics of a typical batch of latex used in the present programme,determined in duplicate according to the methods described in BS 1672: 1972,are summarised in Table 5.1.

Table 5.1. Typical characteristics of HA latex used in the present programme

Property	Value
Total solid content (TSC) (%)	61.73
Dry rubber content (DRC) (%)	60.26
Non-rubber substances (%)	1.47
Alkalinity (%) NH_3 on latex	0.76
(%) NH_3 on serum	1.97
Coagulum content (% of TSC)	0.0063
Mechanical stability time (secs)	920
pH	10.56

5.1.1.2. Synthetic *cis*-polyisoprene latex

Synthetic *cis*-polyisoprene latex supplied by an unknown Japanese source was kindly donated by Mr. A.D.T. Gorton of MRPRA. The *cis*-content of the contained polymer was stated by the supplier to be 97%. No information was available concerning the preparation and composition of this latex. The latex was found to have the properties summarized in Table 5.2. The characterization was carried out according to methods described in BS 1672:1972. Electron microscopic studies revealed that the sizes of the particles in this latex were generally comparable to those in the type of NR latex currently under investigation.

Table 5.2. Characteristics of synthetic *cis*-polyisoprene latex used in the present programme

Property	Value
Total solids content (%)	65.65
pH	10.20

5.1.1.3. Sulphur

Velvet sulphur, supplied by Anchor Chemical Co.Ltd., was used throughout the present programme. It was first sieved through a 200-mesh sieve before preparing into an aqueous dispersion by ball-milling.

5.1.1.4. Zinc dibutyl dithiocarbamate (ZDBC)

Industrial-grade ZDBC supplied by Robinson Brothers Ltd. was used without further purification unless otherwise stated. It was added to the latex as an aqueous dispersion prepared by ball-milling.

5.1.1.5. Dispersing agent

A common dispersing agent was used for the preparation of sulphur and accelerator dispersions, namely, a disodium salt of methylene di-napthalene sulphonic acid. It was supplied by Anchor Chemical Co. Ltd. as Belloid TD.

5.1.1.6. Other dithiocarbamate accelerators

a) Zinc dithiocarbamates of various alkyl chain lengths

The following zinc dithiocarbamates of various alkyl chain lengths were supplied by Robinson Brothers Ltd:-

zinc dimethyl dithiocarbamate	(ZDMC)
zinc diethyl dithiocarbamate	(ZDEC)
zinc diamyl dithiocarbamate	(ZDAC)
zinc dihexyl dithiocarbamate	(ZDHC)
zinc dioctyl dithiocarbamate	(ZDOC)
zinc didodecyl dithiocarbamate	(ZDDC)

Two of them, namely, the zinc dimethyl and zinc diethyl dithiocarbamate, were industrial grades. The zinc diamyl and zinc didodecyl dithiocarbamate, were specially prepared by Robinson Brothers Ltd. for the present programme. The zinc dihexyl and dioctyl were synthesized by the present writer in the laboratory. All the dithiocarbamates were used as supplied or prepared.

b) Dialkyl dithiocarbamates having counterions other than zinc

The following dialkyl dithiocarbamates with metal counterions other than zinc were used in the present investigation without further purification:

sodium dimethyl dithiocarbamate	(SDEC)
sodium diethyl dithiocarbamate	(SDMC)
sodium dibutyl dithiocarbamate	(SDBC)
lead diethyl dithiocarbamate	(PbDEC)
selenium diethyl dithiocarbamate	(SeDEC)
tellurium diethyl dithiocarbamate	(TeDEC)
copper diethyl dithiocarbamate	(CuDEC)

The sodium salts were supplied by Robinson Brothers Ltd. The others were supplied by Vanderbilt Inc., USA. All the dithiocarbamates were used without further purification.

c) Reagents used in the laboratory synthesis of zinc dihexyl and zinc dioctyl dithiocarbamates

The following reagents used in the laboratory synthesis of zinc dihexyl and zinc dioctyl dithiocarbamates were supplied by Kochlight Laboratories Ltd. All were of A.R. grade unless otherwise stated.

dihexylamine,
dioctylamine,
carbon disulphide (GPR grade),
sodium hydroxide, and
zinc sulphate

5.1.2. Materials used in sulphur analyses of films obtained from prevulcanized latex

5.1.2.1. Materials used in determination of free sulphur and ionic sulphides

copper gauze (40-60 mesh),
acetone AR,
cadmium acetate,
sodium acetate,
glacial acetic acid,
hydrochloric acid (SG 1.18)
potassium iodide AR,
iodine, AR
sodium thiosulphate, AR
starch indicator,
glycerol,
chloroform,
nitrogen gas.

All the reagents were GPR grade unless otherwise stated, and were supplied by Fisons Scientific Apparatus. Copper gauze was obtained from Scientific Supplies

5.1.2.2. Materials used in determination of total unextractable sulphur

The following reagents were used for the determination of total unextractable sulphur:

hydrogen peroxide (20 volumes),
methyl red and methylene blue indicators,
sodium hydroxide,
potassium hydrogen phthalate, and
phenolphthalein.

All the reagents were of AR grades, and were supplied by Fisons Scientific Apparatus.

5.1.3. Materials used in the determination of free (unreacted) zinc dialkyl dithiocarbamates in films obtained from prevulcanized latex

Chloroform, copper sulphate and anhydrous sodium sulphate were the reagents used in the determination of free zinc dialkyl dithiocarbamate accelerators. These reagents were all of AR grade, and were supplied by Fisons Scientific Apparatus.

5.1.4. Swelling solvent

n-decane of AR grade, supplied by Fisons Scientific Apparatus, was chosen as the swelling solvent for the vulcanizates.

5.1.5. Reagents used in determination of types of chemical crosslinks in films from prevulcanized latex

The following reagents were used, in conjunction with a physical method for determination of crosslink density for determination of types of chemical crosslinks present in the vulcanizates:

hexane-1-thiol,
propane-2-thiol,
n-heptane,
piperidine,
nitrogen gas.

All these reagents were of AR grade. The thiols were supplied by Eastman (Kodak) Ltd. *n*-heptane and piperidine were obtained from Fisons Scientific Apparatus.

5.2. Experimental Procedures

5.2.1. Prevulcanization of latex

5.2.1.1. Deammoniation of HA latex

In order to facilitate handling, HA latex (*ca*. pH 10.5) is normally partially deammoniated to *ca*. pH 9.8 prior to prevulcanization. For some of the experiments in the present programme, the initial HA latex was partially deammoniated prior to addition of the vulcanizing ingredients. Partial deammoniation was effected by maintaining the latex at 50°C and slowly stirring it whilst compressed air was blown over the surface of the latex.

5.2.1.2. Formulation

In order to avoid possible complications which might have arisen from the use of a complicated prevulcanization recipe, a simple formulation consisting of only the basic ingredients necessary to effect prevulcanization was used throughout the present programme. The reaction system normally comprised rubber in the form of latex and sulphur and dithiocarbamates in the form of aqueous dispersions. None of the reaction systems contained zinc oxide. A typical formulation is shown in Table 5.3.

Table 5.3. Typical prevulcanization formulation used in the present programme

Ingredient	Parts by weight dry
rubber as latex	100.0
33.33% sulphur dispersion	Normally 1.00 part. - varied when the effect of sulphur level was being investigated.
33.33% zinc dialkyl dithiocarbamate	Normally 1.00 part - varied when the effect of accelerator level was being investigated

5.2.1.3. Preparation of aqueous dispersion of sulphur and zinc dialkyl dithiocarbamate

A simple formulation which contained only the vulcanizing ingredient and dispersing agent was used for preparing aqueous dispersions of sulphur and accelerators. The composition of the dispersions are given in Tables 5.4 and 5.5. All the dispersions were prepared by ball

Table 5.4. Formulation for 33.33% aqueous sulphur dispersion

Ingredient	Parts by weight
sulphur (sieved)	33.333
disodium methylene dinapthalene sulphonic acid	4.999
deionised water	61.668

Table 5.5. Formulation for 33.33% aqueous zinc dialkyl dithiocarbamate dispersion

Ingredient	Parts by weight
zinc dialkyl dithiocarbamate	33.333
disodium methylene dinapthalene sulphonic acid	1.666
deionised water	65.001

milling. Sulphur was ball-milled for at least 72 hours. It also required higher amount of dispersing agent compared to dithiocarbamate dispersion. The reason is because it is difficult to break down sulphur aggregate and when broken down the particles have a tendency to re-aggregate. However, the zinc dialkyl dithiocarbamates only required 24 hours of ball milling in order to produce satisfactory dispersions.

During ball milling, the quality of the dispersion was checked using an optical microscope to study the particle sizes. The exact concentration of the dispersions was accurately determined using the method described in Sections 5.2.3.1. and 5.2.3.4. All the dispersions used in this investigation were freshly prepared.

5.2.1.4. Methods of carrying out prevulcanization reactions

Two different techniques were used to effect latex prevulcanization. In the first method, a 2-litre reaction vessel was used to carry out the reaction. In the second method, the reaction was carried out in separate 150-ml capped bottles. The reason for using capped bottles in some cases was that gradual escape of ammonia during prevulcanization could thereby be avoided.

a) Method using 2-litre reaction vessel

The apparatus for this method is shown in Fig.5.1. Partially-deammoniated NR latex was first weighed into the reaction vessel. The required amounts of sulphur and zinc dialkyl dithiocarbamate dispersions (see Table 5.3) were then added. The compound was then mixed at room temperature by gentle stirring. Before immersing the flask and its contents into a thermostatted water bath, a sample was taken from the well-mixed compound; this sample was regarded as representing the mixture at the beginning of the reaction. The timing for the prevulcanization reaction was started immediately the flask was immersed into the thermostatted water bath. Hourly

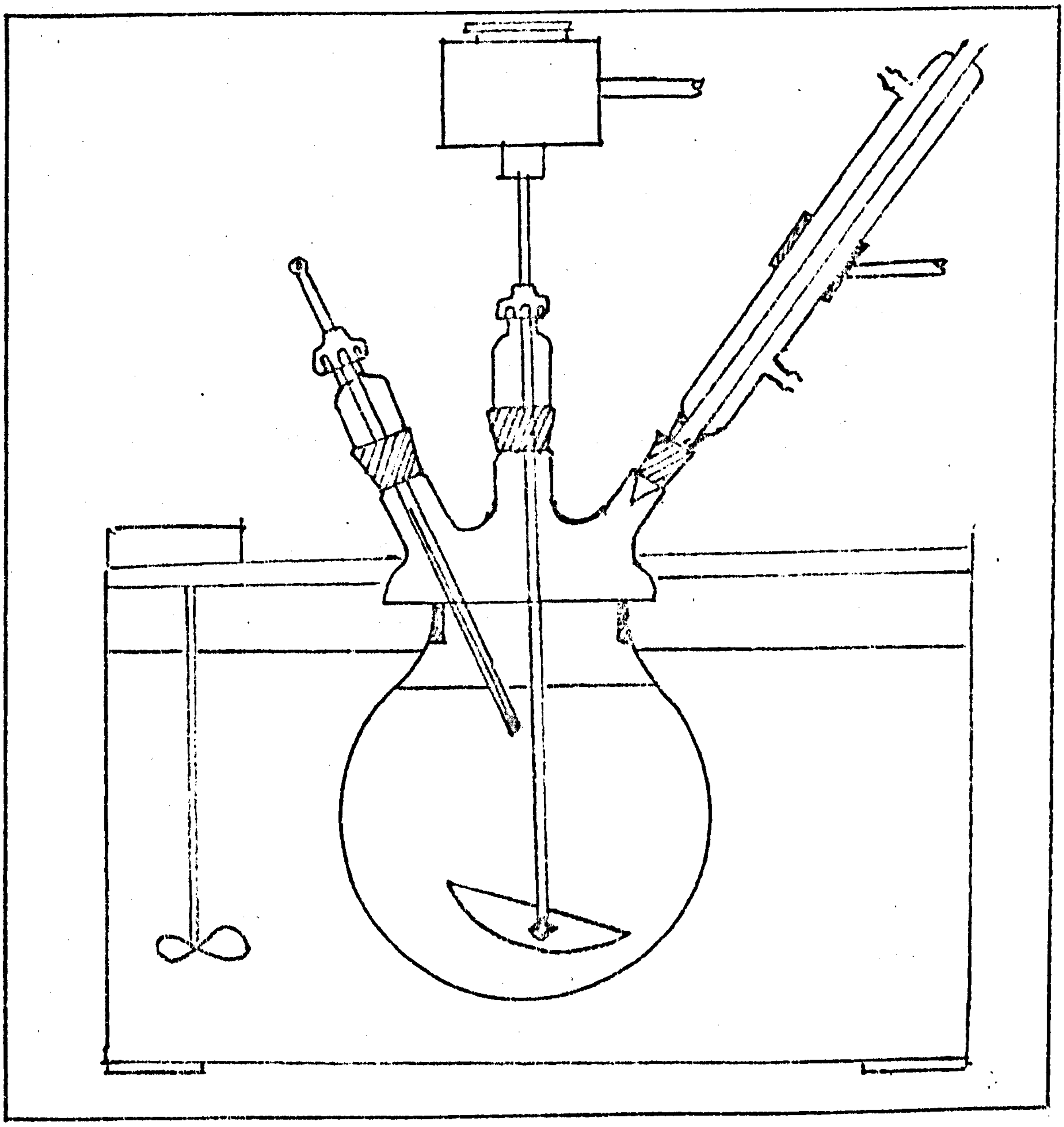

Fig. 5.1. Apparatus for prevulcanization of NR latex in a 2-litre reaction vessel.

samples were taken from the reaction vessel. To arrest the reaction after sampling, the prevulcanized latex sample contained in a glass bottle was chilled under cold running tap water for one hour, and then stored in a refrigerator at 5°C until required.

b) Method using capped bottles

In this method, the latex and dispersions of vulcanizing ingredients were weighed accurately into a 1-litre beaker initially. The latex compound was then stirred to give a homogeneous mixture, which was then divided between 10 150-ml glass bottles. These bottles were capped and then immersed in a thermostatted water bath. The bottles were gently shaken every 15 minutes whilst they remained submerged in the water bath in order to ensure that the contents remained reasonably homogeneous. One bottle was taken out of the bath every hour, and immediately chilled under cold running tap water. It was then stored in a refrigerator at 5°C until required.

5.2.1.5. Prevulcanization reaction conditions

Because ZDBC is a very fast accelerator, all the prevulcanizations using this accelerator were usually carried out at 50°C for a period of 8 hours. Prevulcanizations using less active accelerators compared to ZDBC were also investigated. Experiments using these accelerators were carried out at 70°C for a period of 10 hours.

5.2.2. Preparation of films and cast sheets from prevulcanized latex

Most of the investigations in the present programme were carried out on solid rubber deposited from the prevulcanized latices by evaporation. The rubber was usually deposited in the form of a very thin film (ca. 0.2 mm) or a slightly thicker sheet (ca. 1 mm). The thin films were used for chemical analysis for free sulphur, combined sulphur, unreacted zinc dialkyl dithiocarbamate, etc., and for the measurement of physical properties such as tensile strengths and elongation at break. The thicker sheets were used for the investigation of types of sulphidic crosslinks, and for the determination of swollen compression modulus, from which the crosslink densities were calculated. It was essential that virtually no further chemical reaction occurred during the casting of the films and sheets. Precautions were taken to achieve this objective.

5.2.2.1. Glass moulds used for preparation of films

Glass plates with fixed edges lined to give a well were used as moulds for the preparation of films. Fig. 5.2. gives a diagram of the plates together with the dimensions. 20 g of prevulcanized latex of TSC ca. 50% was required to be poured into these moulds in order to give a film ca. 0.2 mm thick.

For casting sheets, smaller moulds produced from glass plates having dimensions 60 mm x 60 mm were used.

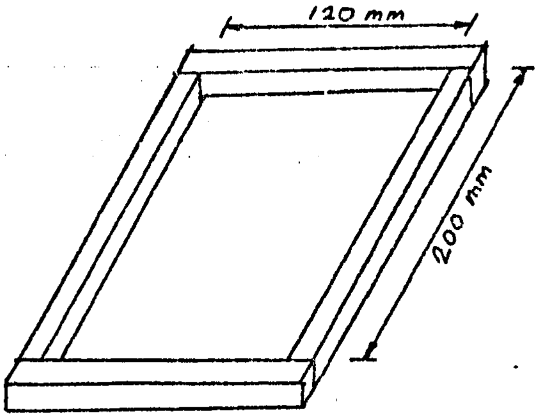

Fig. 5.2. Diagram of glass plates used for casting films and sheets

These smaller moulds also needed 20 g of prevulcanized latex of TSC *ca.* 50% in order to give sheets *ca.* 1.0 mm thick.

5.2.2.2. Procedure for preparation of films and sheets from prevulcanized latex

All films and sheets were cast on the same day the latex was prevulcanized. A set of glass moulds, previously cleaned and dried, were laid out flat on a large table top levelled using a spirit level and secured with plasticine. The required weight of prevulcanized latex (20 g) was filtered through a piece of muslin cloth into the well of the mould. Without disturbing the level of the glass plate, a glass rod was used to guide the latex gently in order that it covered the whole area of the mould. The latex was then left out in the open to dry under ambient conditions. It was established that the thin films (*ca.* 0.2 mm) dried by leaving overnight, whereas the thicker sheet (*ca.* 1 mm) required 36 hours.

5.2.2.3. Investigation of clarity of sheets obtained from prevulcanized latex

A simple method was used to provide an indication of the solubility of sulphur and ZDBC in the rubber. The method involved visual examination of the clarity of a standard, air-dried cast sheet obtained from prevulcanized latex. The cast sheets were prepared as described in Section 5.2.2.2. and were examined visually 36 hours after the sheets were cast. The test was very straightforward; giving the results as either clear (transparent) or opaque.

5.2.2.4. Storage of cast films and sheets

It was ascertained by preliminary experiments that changes occurred in the state of vulcanization of the films and sheets prepared from prevulcanized latex when they were left standing at ambient conditions over long periods, e.g., 3 months. However, the changes were found not to be significant within the first 15 days after the films and sheets were prepared. Hence, all tests and analyses on the films and sheets were carried out within 10 days of their being cast. Throughout this period, the films and sheets were stored in a refrigerator at -15°C.

5.2.3. Chemical analysis of cast films prepared from prevulcanized latex

5.2.3.1. Quantitative determination of free (elemental) sulphur by copper spiral method

a) Theoretical

The principle of the method is that, during soxhlet extraction of the cast films using acetone as the extraction liquid, a copper spiral is present in the round-bottomed flask, where it reacts with the free (elemental) sulphur as the sulphur is extracted from the rubber, copper sulphide being thereby produced. By treating the copper sulphide with an appropriate acid mixture, hydrogen sulphide is released. This is passed through a cadmium acetate solution, where it forms a precipitate of cadmium sulphide. The amount of cadmium sulphide formed is determined by iodometric titration.

b) Apparatus

A compact all-glass apparatus, developed by workers at MRPRA(147) was used. It is illustrated in Fig. 5.3. It is a modification of the apparatus which is described in BS903 1958. The apparatus was constructed for the present work by George Farley and Sons Ltd. The apparatus was mounted on a simple framework over a heating mantle in which the gas-generating flask, (A) was placed. All the ground-glass joints were lubricated with glycerol to prevent loss of hydrogen sulphide. The trap (C) contained buffered aqueous cadmium acetate solution (0.12 M).

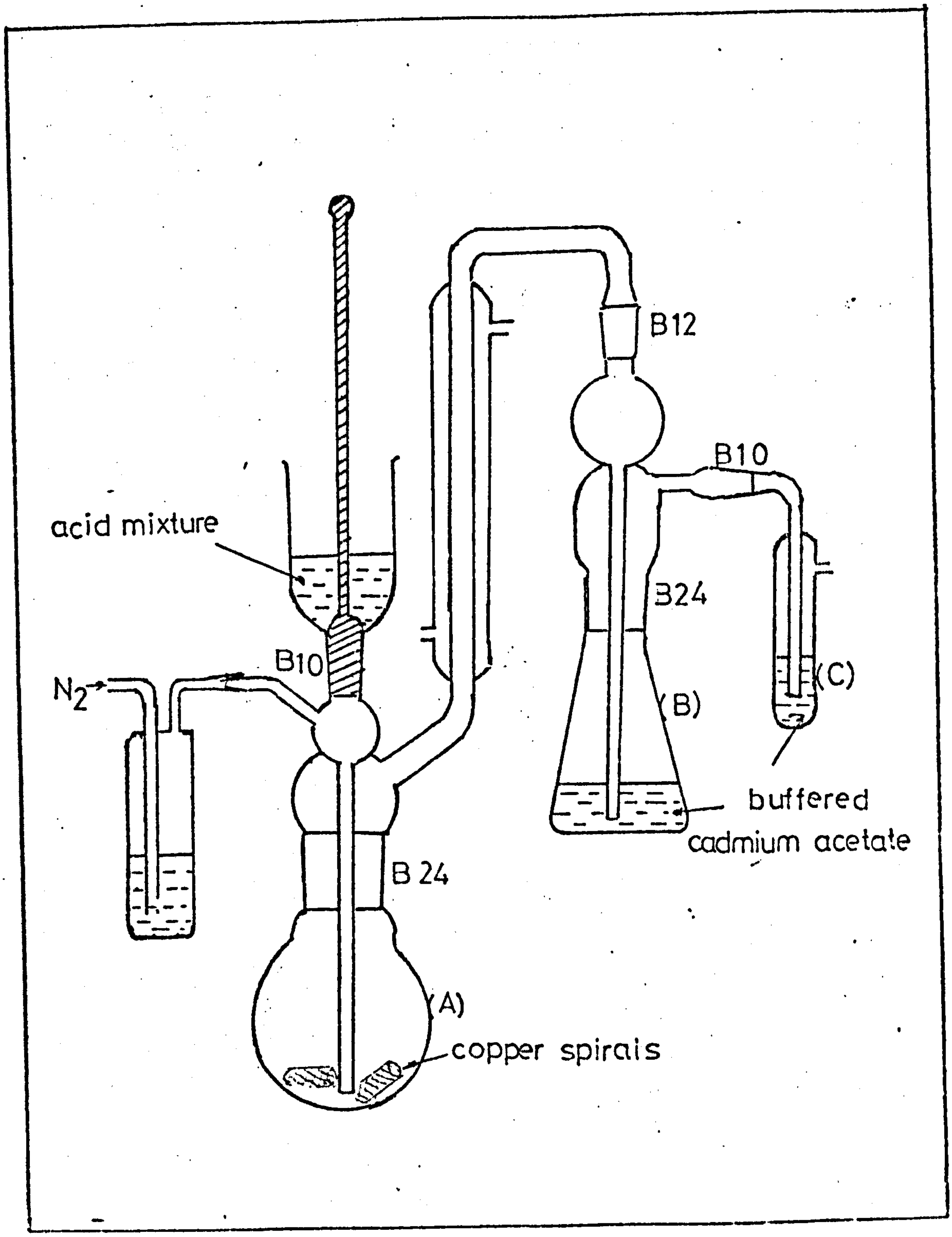

Fig.5.3. Apparatus for determination of free sulphur and ionic sulphides

c) Experimental procedure

Pieces of copper gauze, 7.5 cm long and 1.5 cm wide, were rolled up to form spirals. After cleaning in dilute nitric acid, two of these cleaned copper spirals were placed in an extraction flask containing about 80 ml of acetone. A piece of film cast from prevulcanized latex weighing between 0.1 - 0.5 g (depending upon the extent of prevulcanization) was continuously extracted in a Soxhlet extractor connected to the extraction flask which contained the copper spirals and acetone. Extraction was allowed to continue for at least 10 hours. At the end of the extraction period, the extraction flask was disconnected and the acetone decanted off through a glass fibre filter. The filter and the reacted copper spirals were placed back in the flask. The extraction flask with its contents were then connected to the remainder of the apparatus as in Fig. 5.3. so as to form the gas-generating flask, (A). 25 ml of 0.12 M cadmium acetate solution was placed in flask (B). Bubblers(C)and (D) were also quarter-filled with cadmium acetate solution. A stream of nitrogen was passed through the apparatus to sweep out the air, and was then adjusted to about one bubble per second in flask (B). 25 ml of acid mixture (composition acetic acid:hydrochloric acid:water, 5:1:1) was slowly introduced from the funnel into flask (A). The contents of flask (A) were then slowly heated to boiling, and were then refluxed continually for 30 minutes. At the end of the 30 minutes, the solution in bubbler (C) should still be clear. If not, a smaller film sample should be used, or, alternatively, the nitrogen flow rate should be reduced.

Sufficient 0.05 M iodine solution was added down the delivery tube into flask (B) to ensure that excess iodine was present. 5 ml was usually adequate. The cadmium sulphide reacted with the iodine to produce sulphur as follows:

$$\mathrm{Cd\,S} + I_2 \longrightarrow \mathrm{Cd}^{2+} + 2I^- + S.$$

The excess iodine was back titrated with 0.05 M sodium thiosulphate. To facilitate the titration to the true end point, 2 ml of chloroform was added to dissolve any iodine which may have become entrapped in the sulphur. A blank value was obtained by titrating 5 ml of iodine in 25 ml of cadmium acetate against the thiosulphate. The difference between the volume of sodium thiosulphate used in the blank and that used in the determination was equivalent to the iodine which had reacted with the cadmium sulphide, and hence to the free sulphur in the film sample. The free sulphur content of the rubber was calculated as

$$\%\ \text{free sulphur} = \frac{0.0802 \times (A - B)}{W}$$

where A is the blank titration (ml of 0.05 M $Na_2S_2O_3$), B is the sample titration, (ml of 0.05 M $Na_2S_2O_3$), and W is the sample weight in grams.

d) Precision of method

To determine the precision of the copper spiral method used in this work for the determination of free sulphur, cast film from a given sample of prevulcanized latex was analysed nine times over a period of three days. The results are tabulated in Table 5.6. The mean value was 0.994%, and the standard deviation of the individual results was 0.004%. This indicates that the method is sufficiently precise for results to be quoted to within 0.01%. All free sulphur results shown in the present work were average figures of duplicate determinations.

Table 5.6. Precision check on copper spiral method of free sulphur determination

Day	Free sulphur, %		
1	0.995	0.997	1.000
2	0.989	0.995	0.997
3	0.992	0.989	0.992

5.2.3.2. Quantitative determination of ionic sulphides

The same apparatus and reaction as for the determination of free elemental sulphur described previously was used for the determination of ionic sulphides. The only difference was that, in place of extraction in the presence of a copper spiral, unextracted, cast films from prevulcanized latex were reacted with the acid mixture, thus releasing hydrogen sulphide from any inorganic sulphides which were formed during prevulcanization. Duplicate determinations were carried out and the average figure taken as the result.

5.2.3.3. Determination of total unextractable sulphur by combustion method

a) Theoretical

Samples of the acetone-extracted dried latex films were burnt in a stream of oxygen. The oxides of sulphur thereby formed were passed into aqueous hydrogen peroxide solution, and the resulting sulphuric acid formed was estimated by acid-base titration.

b) Apparatus

The apparatus used was a slight modification of that described in BS 903 B6:(1958). The apparatus is shown in Fig. 5.4. It comprised an electric combustion furnace (A), a silica combustion tube fitted with a stirrer gland carrying a silica push rod (B), a silica combustion inner tube, a three-way tap for controlling the oxygen flow rate (C), a Rotameter used for measuring the oxygen flow rate (D), the U-tubes for the purification of the in-flowing oxygen, one of which (E) contained magnesium perchlorate, and the other (F) contained soda asbestos. The exit end of the combustion tube was connected to two absorbing vessels, (G) and (H), which contained aqueous hydrogen peroxide solution. This apparatus was constructed by George Farley and Sons Ltd.

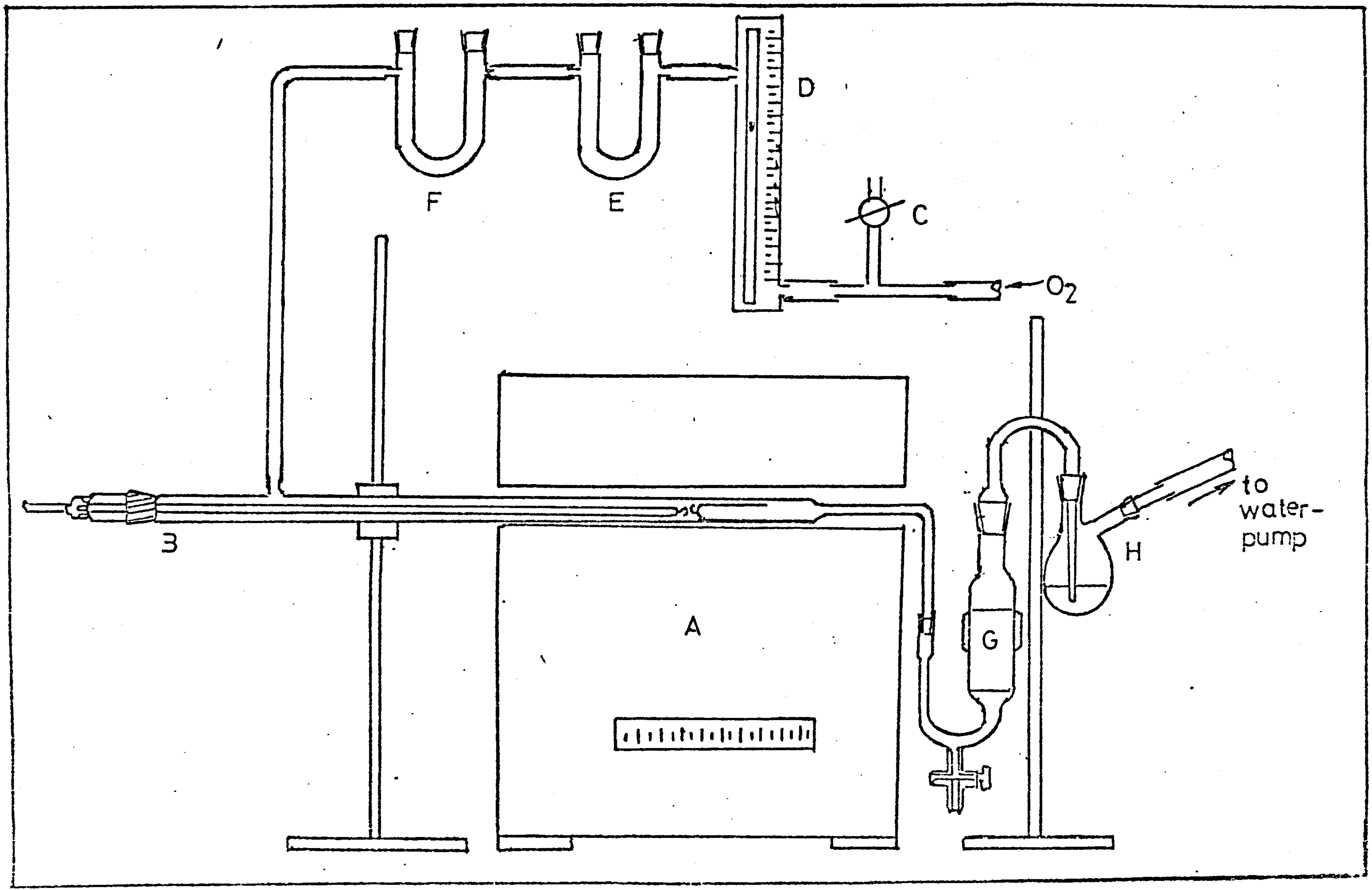

Fig. 5.4. Apparatus for determination of network-combined sulphur

c) Experimental procedure

The electric furnace was set to a temperature of 1000°C ± 20°C. About 500 mg of acetone-extracted dried latex film was accurately weighed and placed inside the silica inner tube. Using the silica push rod, the silica inner tube containing the test sample was pushed to a position approximately half-way into the tube but outside the furnace. After the combustion tube had been sealed by tightening the stirrer gland, the water pump was started and the oxygen-flow rate adjusted to about 60 ml per minute.

The method suggested by BS 903 B6: 1958 is gradually to move the combustion boat containing the test sample into the furnace to initiate combustion. However, the suggestion was found to be impracticable in the present work because of difficulty in controlling the combustion of the test sample in such a way that the sample did not burst into flame. To obtain reproducible results, it was realized that the combustion has to be very gradual. In particular, at no time during the combustion should the test sample catch fire. Satisfactory control of combustion was achieved in the present work by initially moving the furnace to a position such that the test sample in the inner tube was about 1 cm outside the entrance of the furnace. The furnace was then left in this position for about 30 minutes. During this period, the test sample was found to be gradually charred into a carbonaceous residue by the heat radiating from the furnace (ca. 500°C). After this period of initial combustion, the silica tube with its contents was very carefully pushed, using the push rod into the centre of the furnace over a period of 10 minutes. It was assumed that complete combustion had occurred after a further 10 minutes at the centre of the furnace at 1000°C. The assembly of absorbing vessels was then removed from the combustion tube and their contents blown through sintered-glass filters and out of the tap into a conical flask. The absorbing vessels were washed through with about 15 ml of water and the washings combined with the main solution. The acid present in the aqueous solution was then titrated with 0.02 M sodium hydroxide solution using a mixture of methyl red and methylene blue as indicator. The total unextractable sulphur content of the sample was calculated as

$$\% \text{ total unextractable sulphur} = \frac{V \times 0.032}{W}$$

where V is the volume (ml) 0.02 M sodium hydroxide solution required for the titration, and W is the sample weight in grams. The mean of duplicate determinations was taken for the result.

5.2.3.4. Determination of network-combined sulphur

Network-combined sulphur was calculated as the difference between the concentrations of total unextractable sulphur determined by the method described in Section 5.2.3.3. and the concentration of ionic sulphides determined by the method described in Section 5.2.3.2.

5.2.3.5. Determination of free (unreacted) zinc dialkyl dithiocarbamate

a) Theoretical

Reaction between the extracted zinc dialkyl dithiocarbamate and aqueous copper sulphate solution gives the corresponding copper dialkyl dithiocarbamate. Because the complex is strongly coloured and soluble in certain organic liquids, it can be estimated quantitatively spectrophotometrically.

b) Experimental procedure

The acetone extract from a 0.1-g latex film sample was evaporated to dryness using a rotary evaporator. The residue was treated with 60 ml of chloroform on a water-bath, and then made up to 100 ml with chloroform. A 10-ml aliquot of the solution was piepetted into a 100 ml separating funnel and diluted to 20 ml with chloroform. 5 ml of a 2% aqueous copper sulphate solution was then added. After shaking the contents of the separating funnel for 2 minutes, the chloroform layer was separated off and passed through a filter paper containing a little anhydrous sodium sulphate into a 25 ml volumetric flask. The filter was washed with 2-3 ml of chloroform, and the washings added to the volumetric flask. The contents of the flask were then made up to the mark with chloroform. The absorbance of this solution was measured by UV spectrophotometer at 435 nm.

The concentration of unreacted free dialkyl dithiocarbamate was determined by comparing the absorbance of the solution with the absorbance of standard solution of zinc dialkyl dithiocarbamate. The standard solutions were prepared by dissolving known concentrations of zinc dialkyl dithiocarbamate in chloroform followed by treatment with aqueous copper sulphate by the same procedure described previously.

The precision of the method was checked. The standard deviation of ten replicate determinations was found to be 0.006%. In the present work, the mean value of duplicate determinations was taken for the result.

5.2.4. Determination of degree of crosslinking of vulcanizates by swollen compression stress-strain measurements and the computation of γ

A description of the principles underlying the determination of concentration of chemical crosslinks in rubber vulcanizates, $[X]_{chem}$, has been given previously in Section 4.3.1. It has been noted in Chapter 4 that there are at least four methods available for the determination of the concentration of crosslinks, namely, those which use respectively unswollen tensile stress-strain measurements, swollen tensile stress-strain measurements, swollen compression stress-strain measurements, and simple swelling measurements. In the present investigation, the swollen compression stress-strain method was used in preference to the unswollen tensile stress-strain method after much consideration and experimentation. The reasons for the choice are explained in later sections of this chapter.

a) Theoretical aspects of swollen compression stress-strain method for the determination of concentration of crosslink

The elementary kinetic theory of rubber elasticity(94) predicts that in compression

$$f = {}^{F}/A_o = -G\ (\lambda - \lambda^{-2}) \qquad (5.1)$$

where f is the compressive stress, A_o is the unstrained area of the test-piece, G is the shear modulus and λ is the compression ratio. In contrast to results for uni-dimensional extension, i.e., tensile stress-strain data, it has been established by Treloar(148) that the uni-dimensional compression stress-strain behaviour of lightly vulcanized rubber is accurately represented by equation (5.1) for compressions of up to about 50% (i.e., $\lambda = 0.5$). Workers using the swollen compression modulus technique have found that their results can be fitted by the following modified expression

$$f' = {}^{F}/A_s = V_r^{1/3}\ G_{cs}\ (\lambda^{-2} - \lambda) \qquad (5.2)$$

where f' is the compressive stress, A_s is the unstrained area of the swollen test-piece, V_r is the volume fraction of rubber in the swollen vulcanizate, λ is the ratio of the thickness of the stressed swollen test piece to the thickness of the unstressed swollen test piece and G_{cs} is the swollen compression modulus.

It has been verified experimentally by Melly and Stuckey(149) and by Redding and Smith(150) that G_{cs} for highly swollen vulcanizates closely approximates to $2C_1$ (see Section 4.3.1.3.). In the present programme, G_{cs} obtained from compression stress-strain measurements was used to calculate the concentration of elastically-active chains in the network. For this purpose, the following expression was used.

$$\frac{G_{cs}}{\rho RT} = \text{concentration of elastically-active network chain} \qquad (5.3)$$

where ρ is the density of the rubber, R is the gas constant and T is the absolute temperature.

In a network formed by tetrafunctional crosslinks (which is assumed to be the case in the present study) each crosslink will terminate four network chains and therefore the number of elastically-active network chains will be twice the number of crosslinks. From this relationship, the physically-effective crosslink density, $[X]_{phys}$, was derived from the concentration of elastically-active network chains.

Using the Moore, Mullins and Watson calibration,(98) the concentration of chemical crosslinks, $[X]_{chem}$, was then obtained from $[X]_{phys}$. (See Section 4.3.1.4.).

b) Apparatus

Several workers(151-153) have devised methods by which the compression modulus of swollen vulcanizates can be determined. Of the various methods, the micro-compression-stress-strain method of Smith(153) was chosen. The method uses a so-called 'reticulometer'. This instrument is shown diagrammatically in Fig. 5.5. It is a modified Wallace microhardness tester constructed by the Wallace Instrument Company. A compression foot carried a load pan on a spindle, and is suspended from the head by leaf springs attached to the spindle. The foot moves only in a vertical direction, and its movement relative to the head is sensed by means of a plate attached to the spindle which forms a capacitor in conjunction with another plate attached to the head. This capacitor controls the frequency of a circuit oscillating at radio frequency. The output from this circuit is combined with that of a reference oscillator at an adjustable pre-set frequency, thus producing beats of an audible frequency which are amplified and heard as a whistle on headphones. Since the separation of the capacitor plates is controlled by the position of the foot, a position exists at which the frequencies of the two circuits are equalled and a null point is detected by a steady rise in the pitch of the whistle. The arrangement enables slight movement of the foot away from this reference position to be detected. A metal basin, through the jacket of which water at 25°C was circulated contained the test-piece and the swelling liquid, *n*-decane. When a load is placed

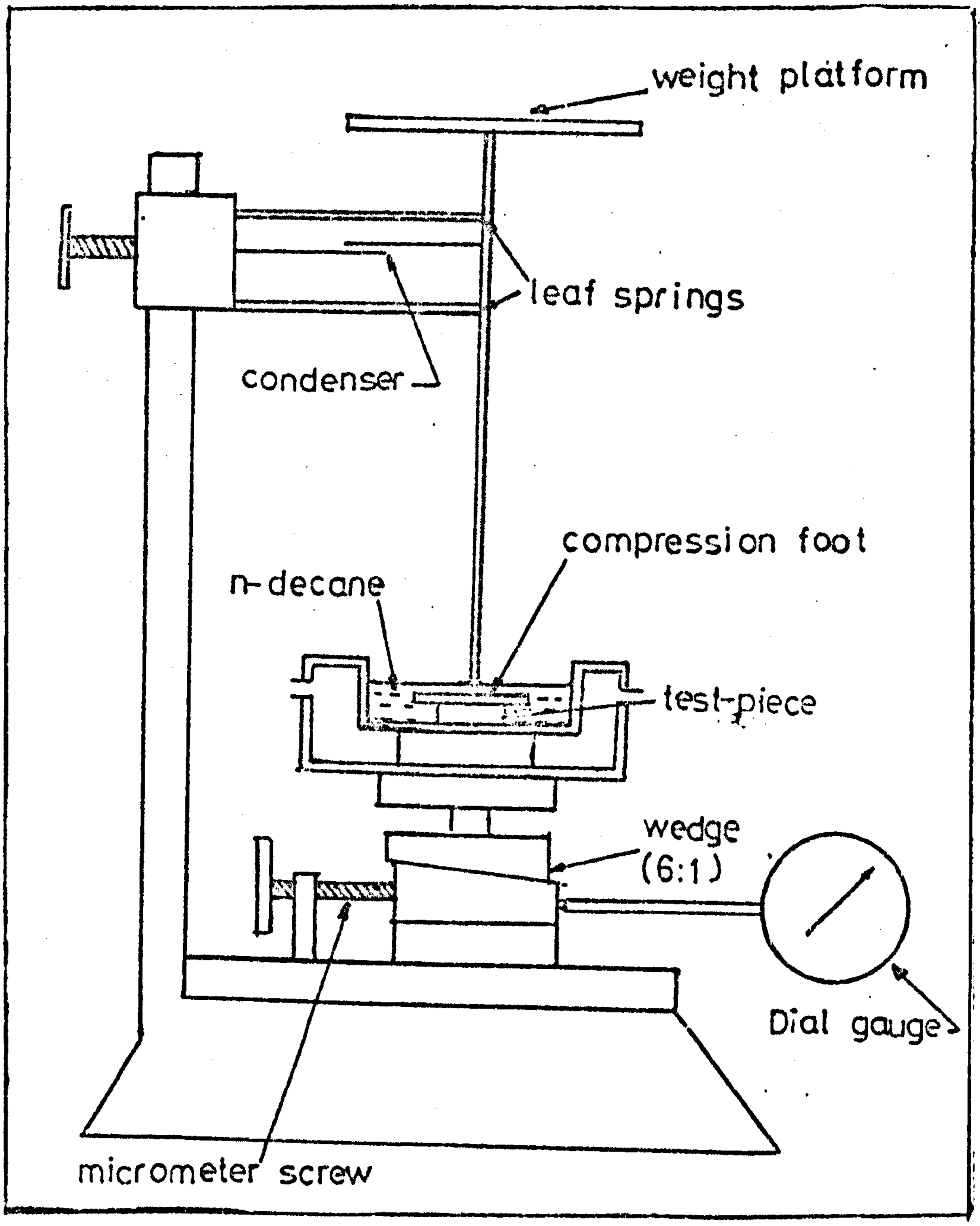

Fig. 5.5. Reticulometer used for compression stress-strain measurements for the determination of G_{cs}.

upon the pan, the compression of the specimen causes a displacement of the foot downwards from its position at the null point. By screwing in the wedge to raise the basin upwards, the null-point may be reattained. The compression of the test-piece is thus the distance by which the basin has been moved. This may be read directly from the Mercer dial gauge. The reproducibility of position of the foot at the null point is within 0.15% of the swollen unstressed thickness of the test piece.

c) Experimental procedure for determination of G_{cs}

An acetone-extracted test-piece having dimensions 6 mm x 6 mm x 1 mm was first swollen to equilibrium in n-decane. It was then placed in the metal basin, in which was also sufficient n-decane to cover the test-piece and the compression foot. The head of the instrument was then racked down until the compression foot touched the test sample, and was then slightly raised. The head was then clamped. By screwing in the wedge which raised the basin, the fine point of contact between the test-piece and the compression foot was then adjusted. The contact was detected by the steady rise in the pitch of an audible whistle. The Mercer dial gauge was then zeroed.

A load of slightly more than the maximum deflection to be used for the test (ca. 15% of the unswollen height) was used to pre-stress the sample. After 30 seconds, the load was removed and the dial gauge was allowed to recover to the zero position. For swollen samples, the recovery is usually almost instantaneous and always takes place within 20 seconds. A load sufficient to produce a compressive deflection of ca. 5% was applied, and the basin raised to attain the null point which was set prior to the loading. This was done by screwing in the Mercer dial. After 60 seconds, the deflection Δh_s was read from the Mercer dial gauge. The load was then removed and the basin lowered to its original null point. After allowing another 60 seconds for relaxation, the zero of the Mercer dial gauge was reset if necessary. This procedure was repeated for ten other loads, each of which exceeded the previous one by a constant increment. In this way was obtained a series of loads, W, in grams weight, and a corresponding series of compressive deflections, Δh_s. Using these results, together with the measured value of V_r, the volume fraction of rubber in the test-piece, the equilibrium swollen compression modulus, G_{cs}, was calculated using the following equation:

$$G_{cs} = \frac{F\, V_r^{1/3}}{A_o} \quad (\lambda^{-2} - \lambda)^{-1} \qquad N/m^2 \tag{5.4}$$

$$= \frac{W_g\, V_r^{1/3}}{A_o} \left[\left(1 - \frac{\Delta h_s}{h_o\, V_r^{-1/3}}\right)^{-2} - \left(1 - \frac{\Delta h_s}{h_o\, V_r^{-1/3}}\right) \right]^{-1} N/m^2 \tag{5.5}$$

where h_o is the thickness of unswollen test-piece and A_o the unswollen area of test-piece. Previously, approximation was used for the strain function $(\lambda^{-2} - \lambda)^{-1}$ by omitting the higher powers of the binomial expansion(151,154). It is not now necessary to use such approximations because of the ready availability of sophisticated calculational facilities. It is now possible readily to calculate G_{cs} without any approximations and without difficulty. In the present work, the calculations were accomplished using a hand-held programmable calculator, Commodore Model PR100. The programme used is given in Appendix A.

d) Computation of χ, the polymer-solvent interaction parameter from measurements of V_r and G_{cs}

It is interesting to note that the swollen compression stress-strain technique not only enables the degree of crosslinking of vulcanizates to be determined, it also incidentally, allows the polymer-solvent interaction parameter, χ, for a vulcanizate to be obtained from data for V_r and G_{cs}. Values of χ for vulcanizates from prevulcanized latex swollen in n-decane were computed using the following equation

$$\chi = \frac{\left[-\ln(1-V_r)-V_r\right] - \left[v_o \left(\frac{G_{cs}}{RT}\right) V_r^{1/3}\right]}{V_r^2} \qquad (5.6)$$

A programme for the computation of χ is given in Appendix B.

5.2.5. Determination of crosslinking efficiency, E

The crosslinking efficiency, E, is defined as the average number of atoms of combined sulphur per chemical crosslink. It is a measure of crosslinking inefficiency. The higher the E value, the more inefficient is the crosslinking process. E-value is obtained by dividing the combined sulphur (expressed in g atoms of sulphur per g of rubber) by the degree of chemical crosslinking (expressed in g moles per g of rubber).

5.2.6. Determination of contribution of mono-, di- and poly-sulphidic crosslinks to overall degree of chemical crosslinking

After considering carefully the advantages and disadvantages of the various probe reagents available, the thiol-amine reagents were selected for determining the contributions of mono-, di-, and poly-sulphidic crosslinks to the overall degree of chemical crosslinking.

The general procedure was first to determine the overall degree of chemical crosslinking, $[X]_{overall}$, before treatment with a probe reagent (see Section 5.2.4.). The test-piece was then treated with propane-2-thiol and piperidine in heptane to destroy all the polysulphide structures. Such chemical crosslinks as remained in the treated sample were therefore disulphidic or monosulphidic crosslinks. The concentration of monosulphidic and disulphidic crosslinks was denoted by $[X]_{S_1 + S_2}$. The difference between the concentrations of crosslinks before and after probe treatment gave the contribution of polysulphidic crosslinks to the overall degree of chemical crosslinking. This contribution is denoted by $[X]_{S_x}$. Another sample of the same vulcanizate was treated with *n*-hexanethiol in neat piperidine. This destroyed all the poly- and di-sulphidic structure, leaving only the monosulphidic crosslinks intact. Using the same principle of determining concentrations of chemical crosslinks before and after probe treatment, the concentration of monosulphidic crosslinks, $[X]_{S_1}$, could be obtained. The contribution of disulphidic crosslinks, $[X]_{S_2}$, to the overall degree of chemical crosslinking could then be obtained as the difference between $[X]_{S_1 + S_2}$ and $[X]_{S_1}$.

5.2.6.1. Experimental procedure for treatment with propane-2-thiol and piperidine in n-heptane

Acetone-extracted test-pieces cut to the size suitable for reticulometry and measurements of equilibrium swelling were marked using a ball-point pen for identification purposes. They were then swollen overnight in 25 ml of n-heptane at room temperature under an atmosphere of nitrogen in the apparatus illustrated in Fig. 5.6. Propane-2-thiol (1.85 ml) and piperidine (1.95 ml) made up to 25 ml with n-heptane were then added. The swollen samples were allowed to react with the probe reagent for two hours at room temperature under an atmosphere of nitrogen. After the treatment, the treated samples were washed five times with 100 ml of petroleum ether (30^o-40^oC boiling range) every half hour for 2 hours. All these procedures were carried out under an atmosphere of nitrogen and away from direct sunlight. The washed vulcanizate samples were then dried to constant weight in vacuo.

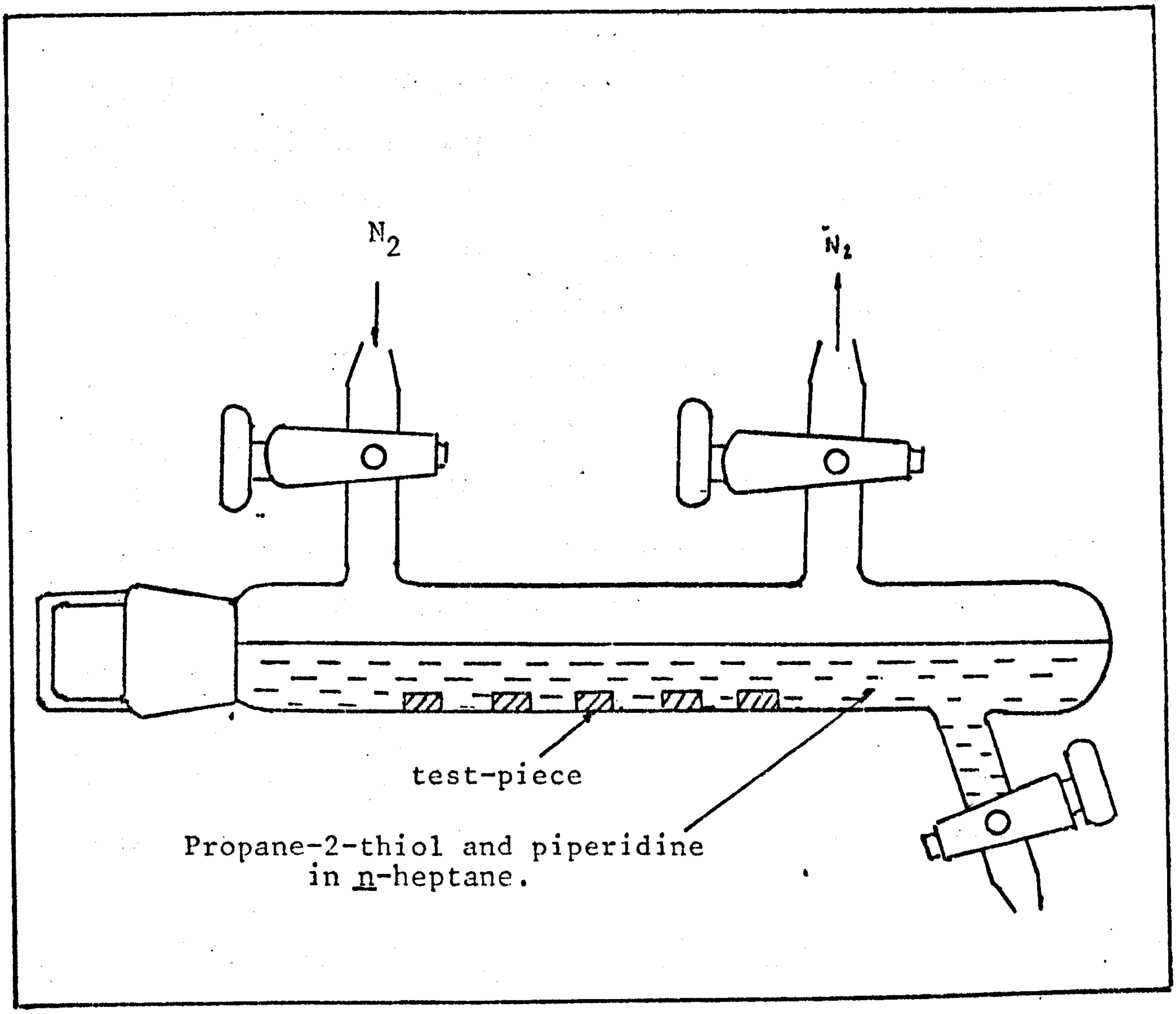

Fig.5.6. Apparatus used in the determination of contribution of polysulphidic crosslinks, $[X]_{S_x}$ to the overall degree of chemical crosslinking.

5.2.6.2. Treatment with n-hexanethiol in piperidine

Acetone-extracted test-pieces of size similar to those used for propane-2-thiol treatment were introduced into a glass ampoule with a 250-mm long neck carrying a B12 cone at one end. A constriction was created using a blow torch half-way through the neck of the ampoule after the introduction of the samples. 25 ml of a 1 M solution of n-hexanethiol in neat piperidine was then introduced. The ampoule containing the test samples and probe reagents was quickly frozen with liquid nitrogen. It was then connected to a high-vacuum unit (10^{-4} mm) and evacuated. After evacuation at 10^{-3} mm the pump was cut off from the ampoule by turning off the tap at the vacuum unit. The contents of the ampoule were then allowed to thaw. This freeze-evacuate-thaw cycle was repeated twice. The ampoule was then frozen again and sealed at the constriction under vacuum. The sealed ampoule was then left in a thermostatted water bath at 25°C for 48 hours. After the reaction, the treated samples were recovered from the ampoule and were washed and dried as described in Section 5.2.5.1.

5.2.7. Determination of solubilities of zinc dialkyl dithiocarbamates in various aqueous media by atomic absorption spectroscopy

a) Theory of atomic absorption spectroscopy

This instrumental method of analysis is usually used to detect very small concentrations (i.e. parts per million) of metal atoms. It is based upon the characteristic absorption of electromagnetic radiation by atoms. The solution containing the metal atom to be analysed is first aspirated into a hot flame. Within the flame is produced a gaseous solution or plasma containing a significant concentration of elementary particles. The flame here serves the same purpose as a cell or cuvette in an ordinary spectrophotometer, i.e., the flame can be considered to be a dilute gaseous solution of the atomized sample held in place by the aspirator-burner. Radiation from a suitable source is passed through the atomized sample and into the slit of a spectrophotometer. The absorption spectrum of an atomised element consists of a relatively limited number of discrete lines at wavelengths which are characteristic of the element. The concentration of metal atoms can be determined by measuring the intensity of the absorption spectrum under controlled conditions.

A Pye Unicam SP2900 atomic absorption spectrophotometer was used in the present work.

b) Experimental procedure

A calibration curve was first obtained by determining the absorbance obtained by vaporising a series of solutions of the metal of known concentrations. In like manner, a small quantity of the test solution was vaporised, and the absorbance measured. The calibration curve was used to read off the concentration of solution corresponding to the measured value of absorbance.

The procedure used in the preparation of solutions of dissolved zinc dialkyl dithiocarbamate in deionised water, in ammoniated-deionised water, and in dilute latex serum, will be described in Chapter 6, Section 6.3.

5.2.8. Preparation of dilute NR latex serum

Several attempts were made without success in the course of the present work, to obtain NR latex serum in sufficient quantity to be used for various experiments. However the following procedure, kindly suggested by Mr. A.D.T. Gorton of MRPRA, allowed a dilute form of NR latex serum to be obtained fairly easily.

A sample of 60% NR latex was first diluted 1:1 by weight with an aqueous solution having the following composition:

ammonia alginate	4.0
30% ammonia	51.0
water	945.0

The diluted latex was then centrifuged at 3000 rpm for 30 minutes, whereupon a cream layer was seen to separate clearly from the serum and the sludge. Serum obtained using this procedure contains about 28% of NR latex serum.

5.2.9. Synthesis of zinc dihexyl and dioctyl dithiocarbamates

The sodium salts of dihexyl and dioctyl dithiocarbamic acids were prepared by reacting carbon disulphide with the appropriate secondary amine in dilute aqueous sodium hydroxide solution. The following procedure was followed: Equimolar amounts of diamine and sodium hydroxide (in the form of aqueous solution) was first reacted in a separating funnel. The exact concentration of the sodium hydroxide solution was obtained through trial and error as that which gave a convenient concentration of the sodium salt. In the present work, a 45% solution was found to be a convenient solution. The requisite amount of carbon disulphide (1.0 M) was accurately metered using a burette. The corresponding zinc salt was obtained by diluting the sodium salt to 10% and then adding the requisite amount of zinc sulphate as a 10% solution. The zinc salt was formed as a dark heavy liquid. Purification of the zinc salt was carried out by extraction using chloroform. The chloroform was then removed from the purified zinc salt by rotary evaporation.

CHAPTER 6

INVESTIGATIONS OF CERTAIN ASPECTS OF PREVULCANIZATION OF NR LATEX

CHAPTER 6

INVESTIGATIONS OF CERTAIN ASPECTS OF PREVULCANIZATION OF NR LATEX

6.1. Comparison between Latex Prevulcanization and Dry-Rubber Vulcanization.

- 6.1.1. Comparison between NR latex prevulcanization and the dry vulcanization of NR
  - 6.1.1.1. Results
  - 6.1.1.2. Discussion
- 6.1.2. Comparison between synthetic *cis*-polyisoprene latex prevulcanization and the dry vulcanization of synthetic *cis*-polyisoprene
  - 6.1.2.1. Results
  - 6.1.2.2. Discussion

6.2. Investigation of Solubilities of Sulphur and ZDBC in Aqueous Phase of Latex During Prevulcanization

- 6.2.1. Solubilities of sulphur and ZDBC in the aqueous phase of NR latex during prevulcanization
  - 6.2.1.1. Results
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- 6.2.2. Solubilities of sulphur and ZDBC in the aqueous phase of synthetic *cis*-polyisoprene latex during prevulcanization
  - 6.2.2.1. Results
  - 6.2.2.2. Observations and discussion

6.3. Investigation of Solubility of ZDBC in Ordinary Deionised Water, Ammoniated Water and Dilute NR Latex Serum

- 6.3.1. Results
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6.4. Effect of Ammonia upon NR Latex Prevulcanization

- 6.4.1. Results
- 6.4.2. Discussion

CHAPTER 6

INVESTIGATIONS OF CERTAIN ASPECTS OF PREVULCANIZATION OF NR LATEX

6.1. Comparison Between Latex Prevulcanization and Dry-Rubber Vulcanization

In order to gain some insight into the characteristics of latex prevulcanization, it was considered appropriate initially to ascertain in what ways it differs from conventional dry-rubber vulcanization. Previously, in an attempt to understand the characteristics of the post-vulcanization of compounded latex films, a series of experiments were undertaken by Chong(63) in which he sought to compare the postvulcanization of latex films with dry-rubber vulcanization. However, as for comparisons between latex prevulcanization and dry-rubber vulcanization, it is rather surprising that there appear to be no reports of such studies in the literature as far as the present writer is aware.

6.1.1. Comparison between NR latex prevulcanization and the dry vulcanization of NR

In order to compare the prevulcanization of NR latex with the dry vulcanization of NR, the experimental procedure, illustrated schematically in Fig. 6.1. was carried out. A single batch of compounded latex, having composition as shown in Fig. 6.1, was divided into two

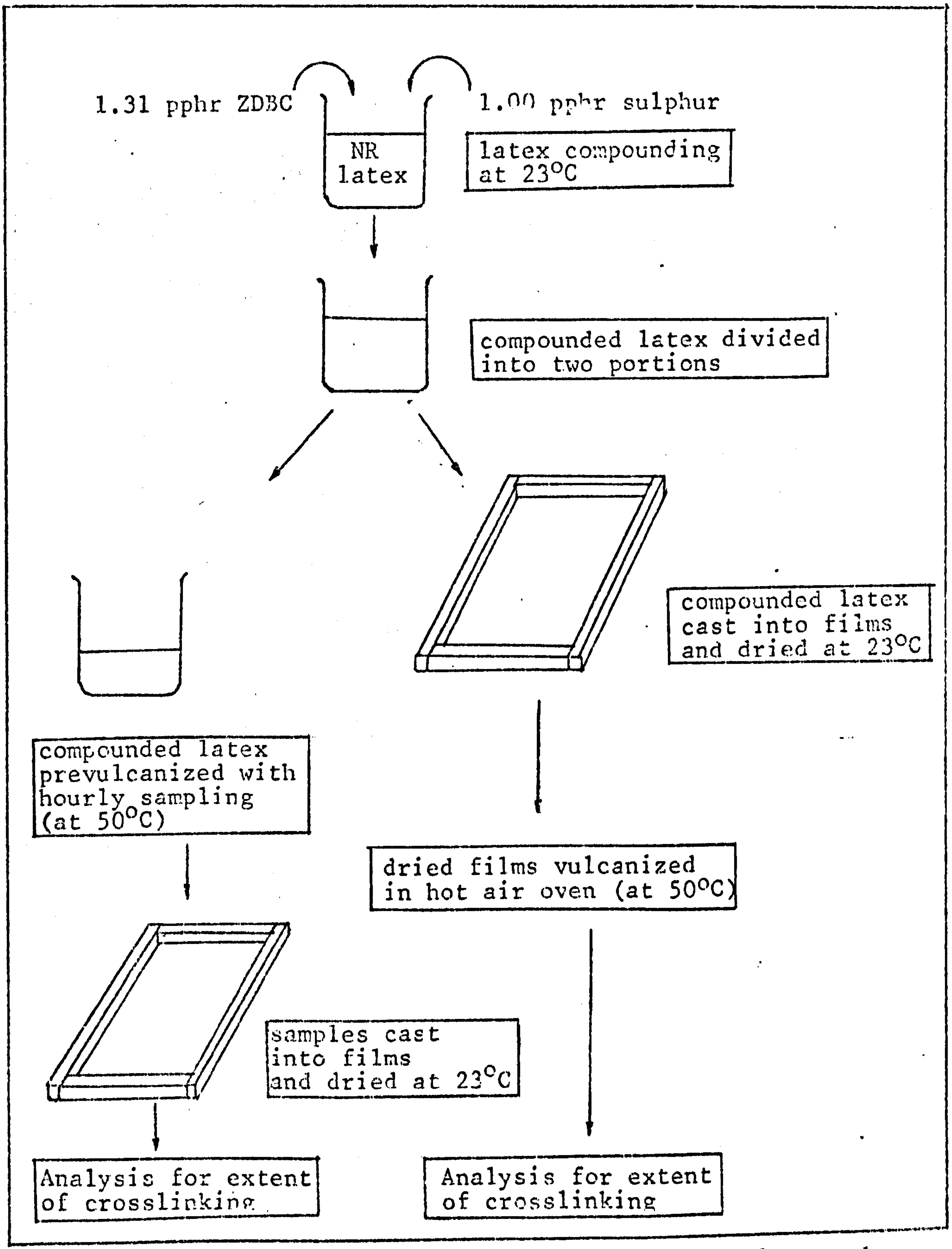


Fig. 6.1. Schematic representation of experimental procedure carried out to study the difference between latex prevulcanization and dry rubber vulcanization

portions. One portion of the compounded latex was prevulcanized in a water bath at 50^{o}C. The reaction mixture was sampled hourly, and the samples cast into films and dried in air at 23^{o}C. The other portion of compounded latex was cast into films without any prevulcanization. The dried films from the latter latex which was not prevulcanized were then vulcanized for various periods in a hot-air oven at a similar temperature as that at which the other portion of compounded latex was prevulcanized, i.e. 50^{o}C. The vulcanization times were also similar. The free sulphur contents, network-combined sulphur contents, and concentrations of chemical crosslinks were then determined on the two sets of film samples.

6.1.1.1. Results

Fig. 6.2 shows the change of free sulphur with time of latex prevulcanization or dry vulcanization. The results show that approximately 50% of the added sulphur was found to be unextractable in the film obtained from prevulcanized latex after 2 hours of prevulcanization. On the other hand, in the case of dried film samples subsequently vulcanized in an air oven, over the same period, only about 5% of the added sulphur was unextractable. At the end of the prevulcanization/vulcanization experiment,(i.e., after the 8th hour) only about 10% of the added sulphur could be extracted as free sulphur from the film sample obtained from drying down the prevulcanized latex. This result should be compared with that obtained in the case of

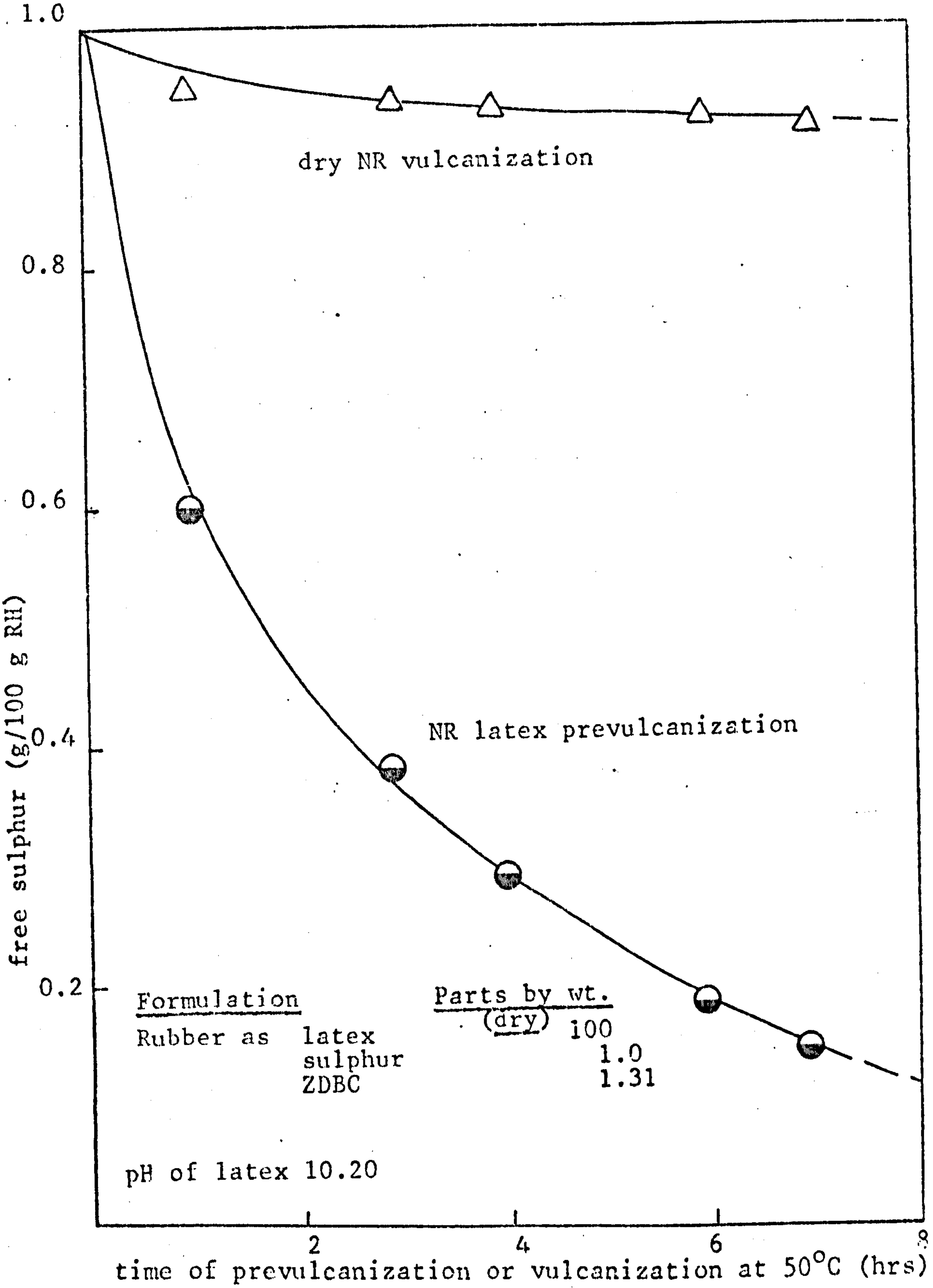


Fig. 6.2. Change in free sulphur during NR latex prevulcanization and dry NR vulcanization.

film samples subsequently vulcanized dry in an air oven, where in the 8-hour sample more than 90% of the added sulphur could be extracted as free sulphur.

Fig. 6.3. shows the results for the variation of network-combined sulphur of the films with time of latex prevulcanization or dry vulcanization. Comparing the results shown in Fig. 6.3. with those shown in Fig. 6.2., it can be seen that the unextractable sulphur was found to be present almost entirely as combined sulphur. No significant amounts of ionic sulphides were detected in any of the films. Fig. 6.3. shows that nearly all of the added sulphur (1.00 pphr) was combined after 8 hours of reaction in the case of the films obtained by drying down prevulcanized latex. By contrast, no more than 5% of the added sulphur was combined when dried films were vulcanized dry in an air oven.

The results for the variation of degree of chemical crosslinking, $[X]_{chem}$, with time of prevulcanization or dry vulcanization are shown in Fig. 6.4. Taken together with the results for free sulphur and network-combined sulphur, it is clear that at least some of the unextractable sulphur in the films had become combined in the form of crosslinks. Fig. 6.4. shows that the degree of chemical crosslinking gradually increases with time of latex prevulcanization. However there was almost no crosslinking at all during the dry vulcanization at the same temperature. This result is consistent with the very low network-combined

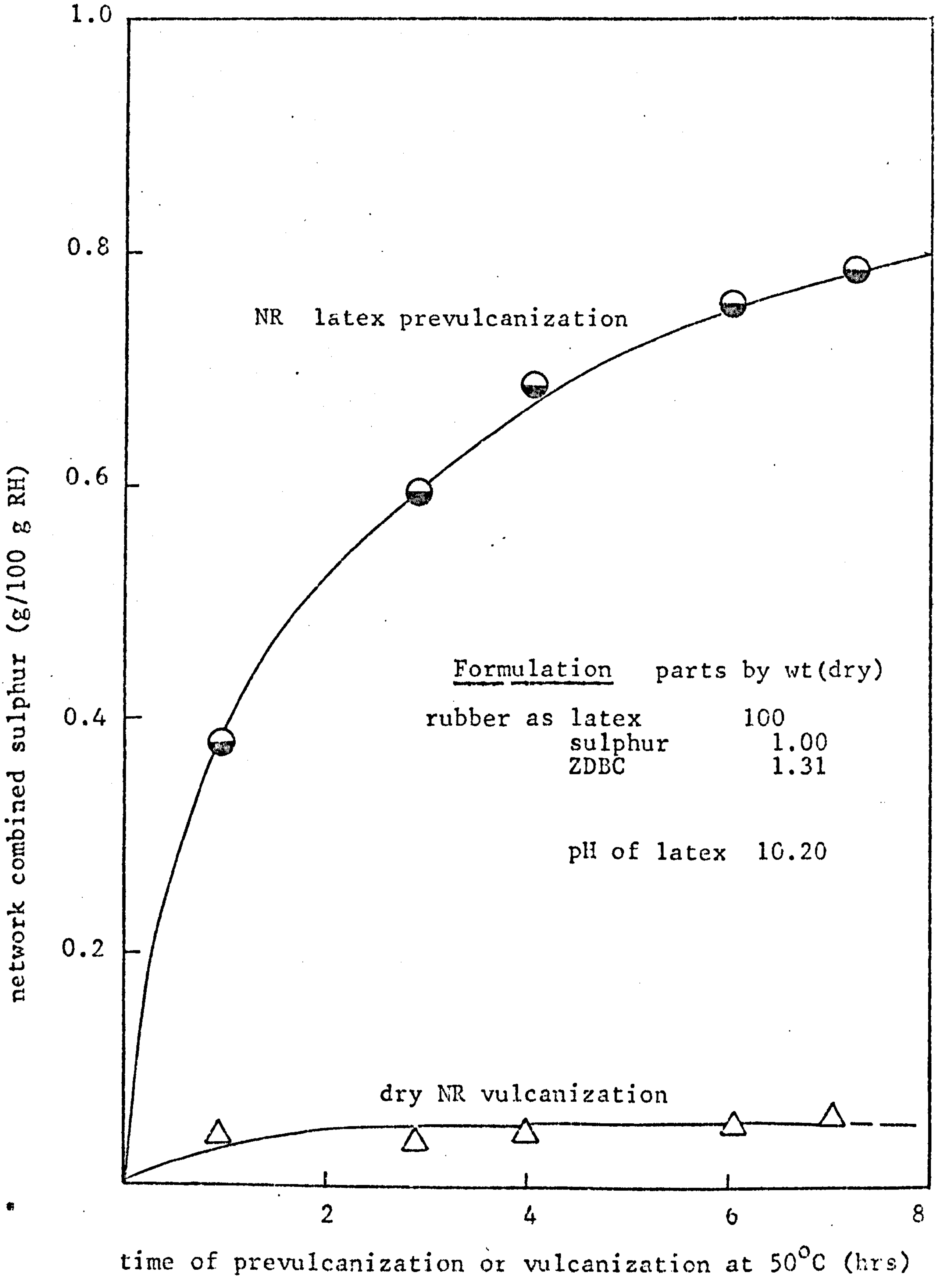


Fig. 6.3. Change in network-combined sulphur during NR latex prevulcanization and dry NR vulcanization

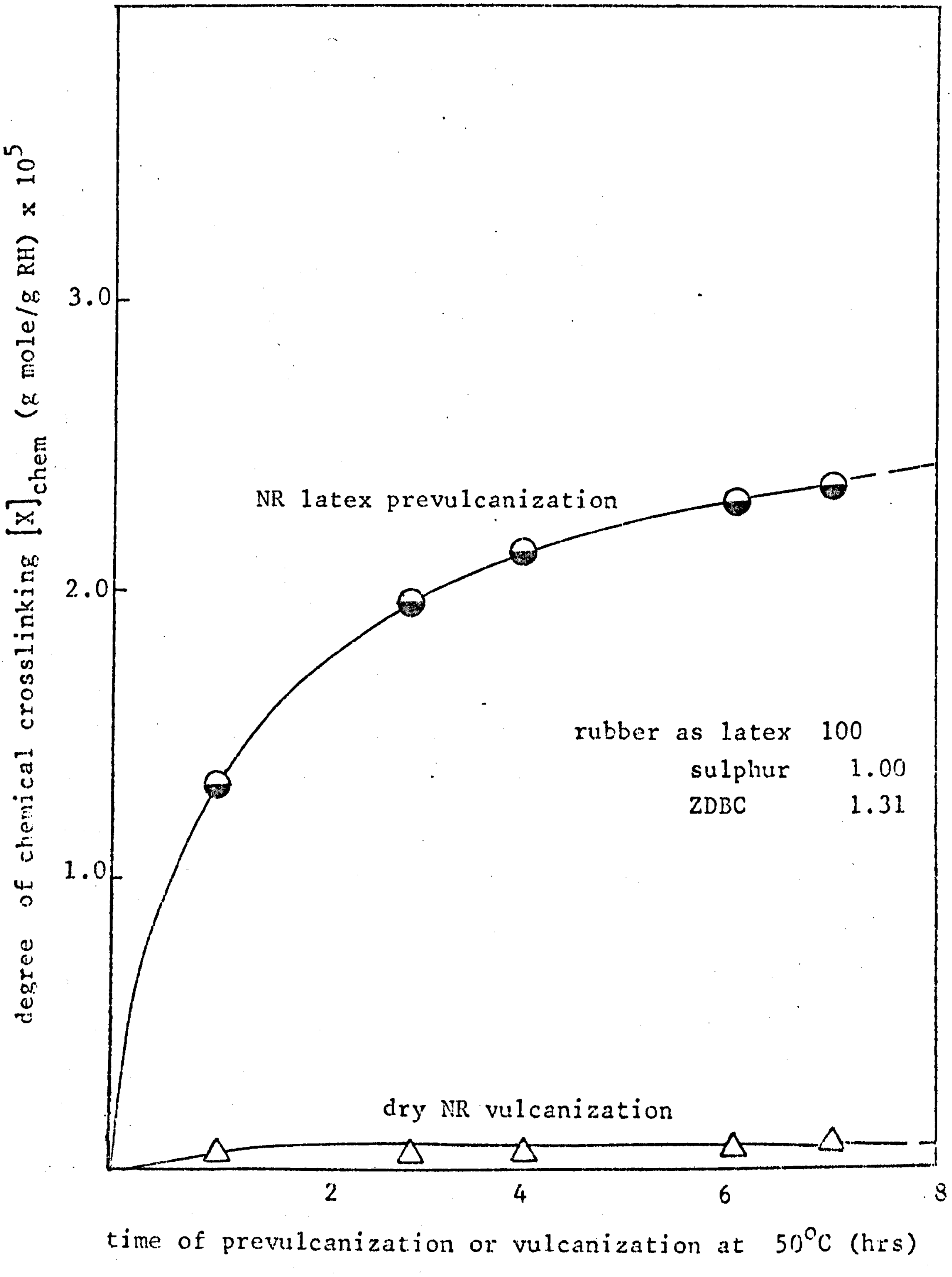


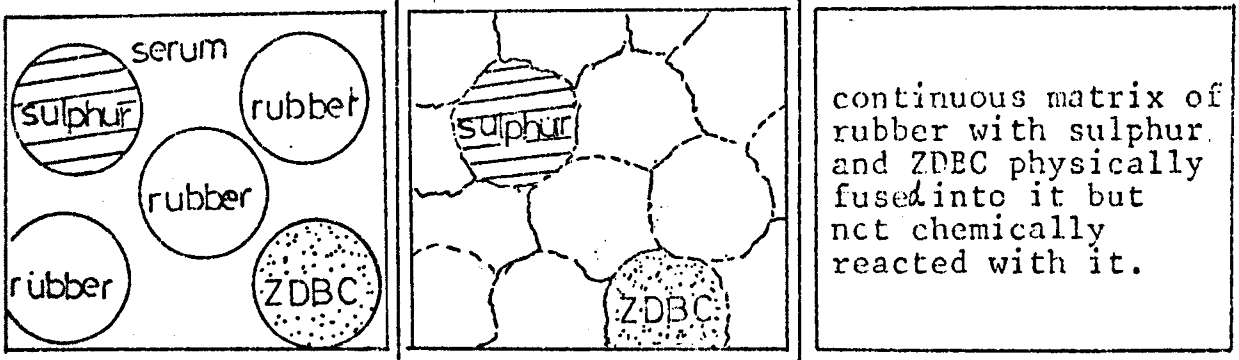
Fig. 6.4. Variation of degree of chemical crosslinking, $[X]_{chem}$, during NR latex prevulcanization and dry NR vulcanization

sulphur contents obtained for films vulcanized dry in an oven.

6.1.1.2. Discussion

From the results presented in Figs. 6.2-6.4, it is evident that under the conditions used in this investigation, rubber in the form of latex vulcanizes at a very much faster rate than it does at the same temperature when it is in the dry form and similarly compounded. In fact, the rate of vulcanization of dry rubber under the conditions used in the present programme was almost negligible.

Consider first the vulcanization of rubber in the dry form. Industrially, dry rubber compounds are generally vulcanized at temperatures between 140-150°C. At these temperatures, the vulcanizing ingredients first normally dissolve or fuse into the rubber matrix physically before chemically reacting with the rubber molecules. With the formulation and reaction conditions used in this work, namely, 1.00 pphr of sulphur (m.p. ca. 113°C), 1.31 pphr of ZDBC (m.p. ca. 103°C), and a vulcanization temperature of 50°C, it is perhaps not surprising that the reaction should be so slow. It is suggested that the sequence of events that take place when compounded latex is dried in air at 23°C, and vulcanized in an oven at 50°C may be as indicated in Fig. 6.5. When the film samples are dried from compounded (but unvulcanized) latex, the particles of sulphur and ZDBC probably maintain their discrete identities and are surrounded by rubber particles as shown in Fig. 6.5(b).



a) Compounded latex at 23°C

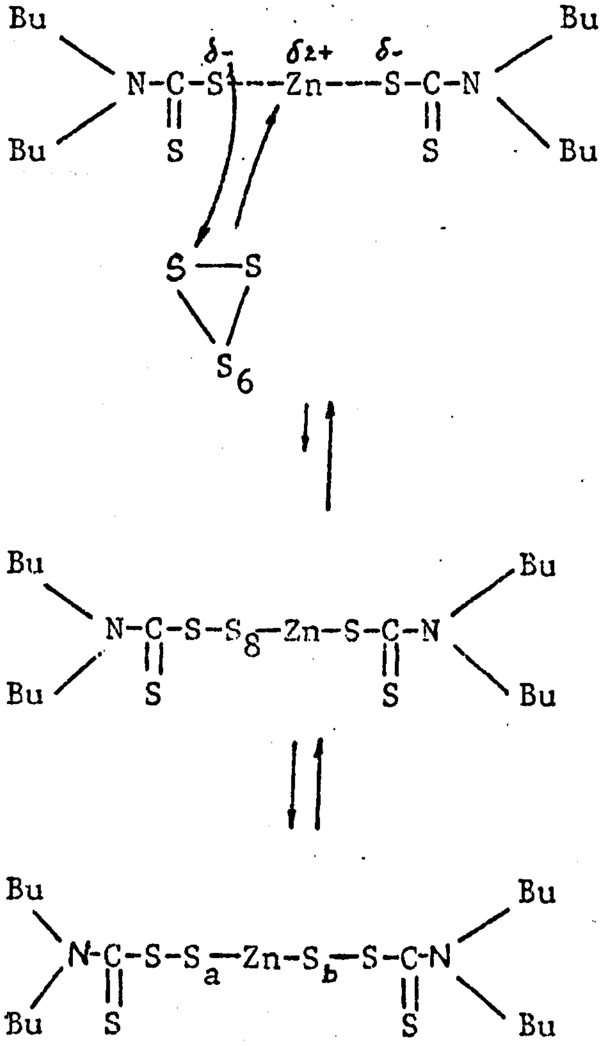
b) Film dried down from compounded latex showing particles of ZDBC and sulphur embedded in rubber matrix

c) Film vulcanized at 50°C in an air oven

Fig. 6.5. Schematic representation of sequence when compounded latex is dried in air and vulcanized in an oven at 50°C

During vulcanization at 50°C, it is very likely that all the sulphur and ZDBC particles become physically dissolved into the rubber matrix. That the sulphur and ZDBC did dissolve in the rubber is supported by the observation that the films became transparent when heated at 50°C, although they were opaque when first cast from the compounded latex. However the temperature of 50°C is probably too low to effect any significant sulphur combination or crosslinking.

In the case of latex prevulcanization, the higher rate of reaction compared to the vulcanization of rubber in dry form probably has much to do with the presence of the aqueous phase in the latex. This is a reasonable conclusion to draw from the observations because the experiment was designed so that the only difference between the two vulcanization procedures was the presence of the aqueous phase in the latex during prevulcanization. The question then arises as to why the aqueous phase of the latex has such an effect upon the rate of vulcanization as demonstrated by the results of Figs. 6.2-6.4. One possibility is that some chemical reactions between the sulphur and the ZDBC may have occurred in the aqueous phase during latex pre-vulcanization, and this may have resulted in the formation of an active sulphurating agent. One such reaction which can be envisaged is the following:

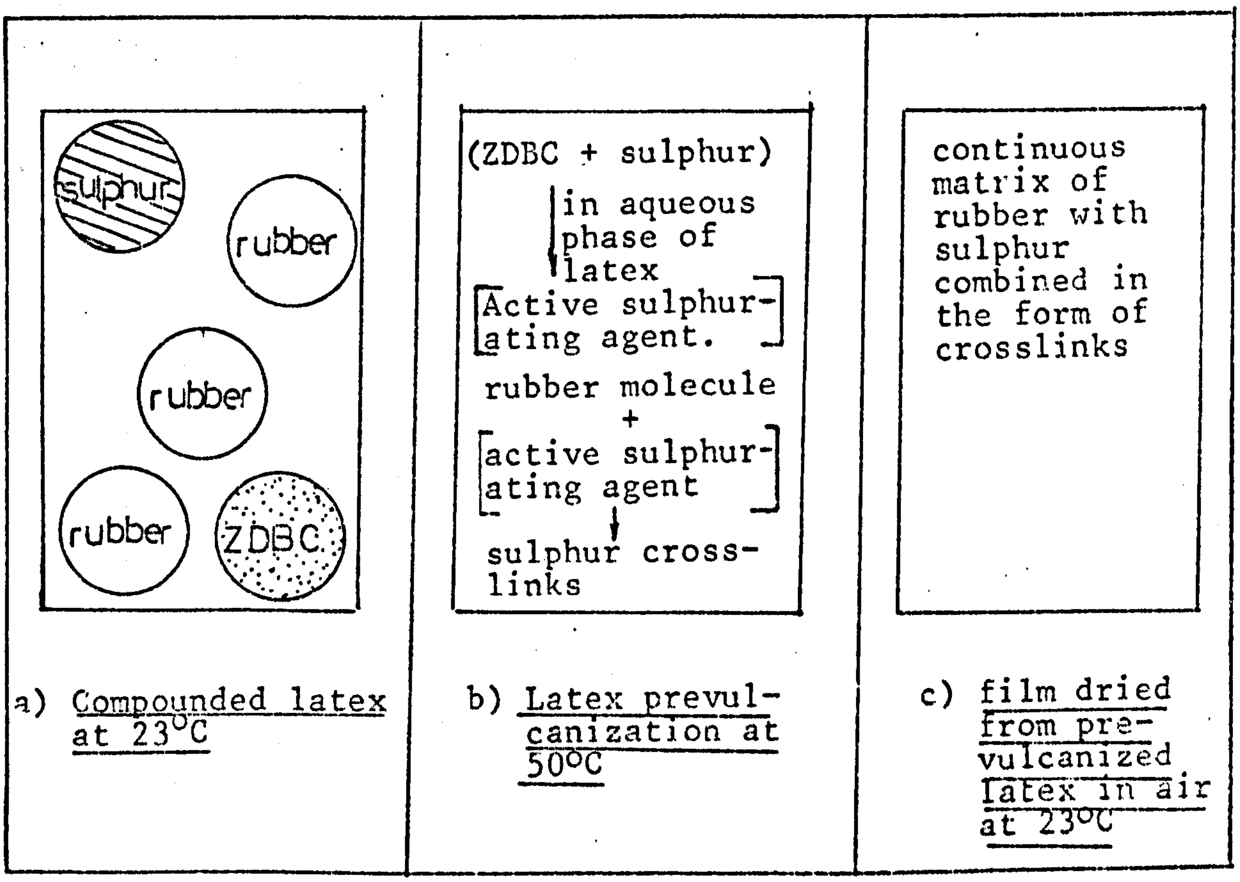


(6.1)

Active sulphurating agent

Since this reaction is a polar reaction, it may well have been promoted by the polar environment such as that presented by the aqueous phase of the latex. On the other hand, the same reaction in a non-polar environment, as in dry-rubber vulcanization, may not have been as easy and may therefore require a much higher energy compared to the reaction in a polar medium.

Hence, based on the results reported so far prevulcanization may proceed via an outline mechanism such as is illustrated in Fig. 6.6. During latex



a) Compounded latex at 23°C

b) Latex prevulcanization at 50°C

c) film dried from prevulcanized latex in air at 23°C

Fig. 6.6. Illustration of possible outline mechanisms for latex prevulcanization and nature of dried film.

prevulcanization at 50°C, some ZDBC and sulphur may dissolve molecularly into the aqueous phase. (The subject of the solubility of ZDBC and sulphur in the serum of NR latex will be discussed in more detail in the next section of this chapter.) In the aqueous phase of the latex, the ZDBC and sulphur may react with each other to form an active sulphurating agent according to a reaction such as that shown in equation (6.1). The resultant active sulphurating agent may then become partitioned into the rubber particles, perhaps by an adsorption mechanism. Reaction with the rubber molecules then follows to form sulphur crosslinks. It is also possible that some of the sulphur and ZDBC dissolved in the aqueous phase may partition into the rubber particles together with the active sulphurating agent. However, it is reasonable to suppose that these dissolved vulcanizing ingredients may be rather inactive at 50°C in a non-polar environment such as that presented by the rubber hydrocarbon, because of the evidence of the slow rate of the corresponding dry-rubber vulcanization discussed earlier.

It is therefore suggested that latex prevulcanization has a much higher rate of reaction than the corresponding dry-rubber vulcanization principally because of the presence of the aqueous phase of the latex. The presence of this aqueous phase may provide a medium in which the ZDBC and sulphur are dissolved to some extent. The polar nature of the medium may also promote reaction between the ZDBC and sulphur to form an active sulphurating agent which then partitions into the rubber particles, where it reacts with the rubber hydrocarbon to form sulphur crosslinks.

6.1.2. Comparison between synthetic cis-polyisoprene latex prevulcanization and the dry vulcanization of synthetic cis-polyisoprene

Following the comparison between latex prevulcanization and the corresponding dry-rubber vulcanization using NR latex, it was of interest to repeat the experiment using a different type of latex. The primary aim of this duplication was to confirm the effect of aqueous phase of the latex upon latex prevulcanization. Synthetic *cis*-polyisoprene latex was chosen for this second experiment. The following were the reasons for this choice: First, there is a close similarity between the polymer in this latex and that in natural rubber latex. This provides a better comparison than would be possible using, say, a styrene-butadiene rubber latex or polybutadiene latex. The second reason was relatively simplicity of the aqueous phase of synthetic *cis*-polyisoprene latex. The aqueous phase of NR latex is known to contain numerous non-rubber substances, some of which are known to be vulcanization activators in dry-rubber vulcanization.(61,62) Such substances are absent from the aqueous phase of synthetic *cis*-polyisoprene latex. Therefore, comparison of the prevulcanization behaviour of the two latices was expected to give an indication of the importance or otherwise of these non-rubber substances for NR latex prevulcanization. Thirdly, as far as is known, the prevulcanization behaviour of synthetic cis-polyisoprene latex has not so far been reported in the literature. Thus it was expected that this investigation would provide new information concerning the prevulcanization behaviour of synthetic cis-polyisoprene latex.

The experimental procedures were similar to those described in Section 6.1.1., except for the use of synthetic cis-polyisoprene latex in place of NR latex.

6.1.2.1. Results

Figs. 6.7-6.9 show the results obtained for the variation of free sulphur, network-combined sulphur, and degree of chemical crosslinking with time of latex prevulcanization and dry-rubber vulcanization. The trends shown by the results were generally similar to those observed in the experiment with NR latex.

6.1.2.2. Discussion

The results show that synthetic cis-polyisoprene latex can also be prevulcanized by reaction with sulphur and ZDBC. The results also confirm the observation made earlier concerning the effect which the presence of the aqueous phase of the latex seems to have upon the prevulcanization process. Hence, at 50°C, both NR latex and synthetic cis-polyisoprene latex prevulcanize reasonably well with progressive sulphur combination and crosslink insertion

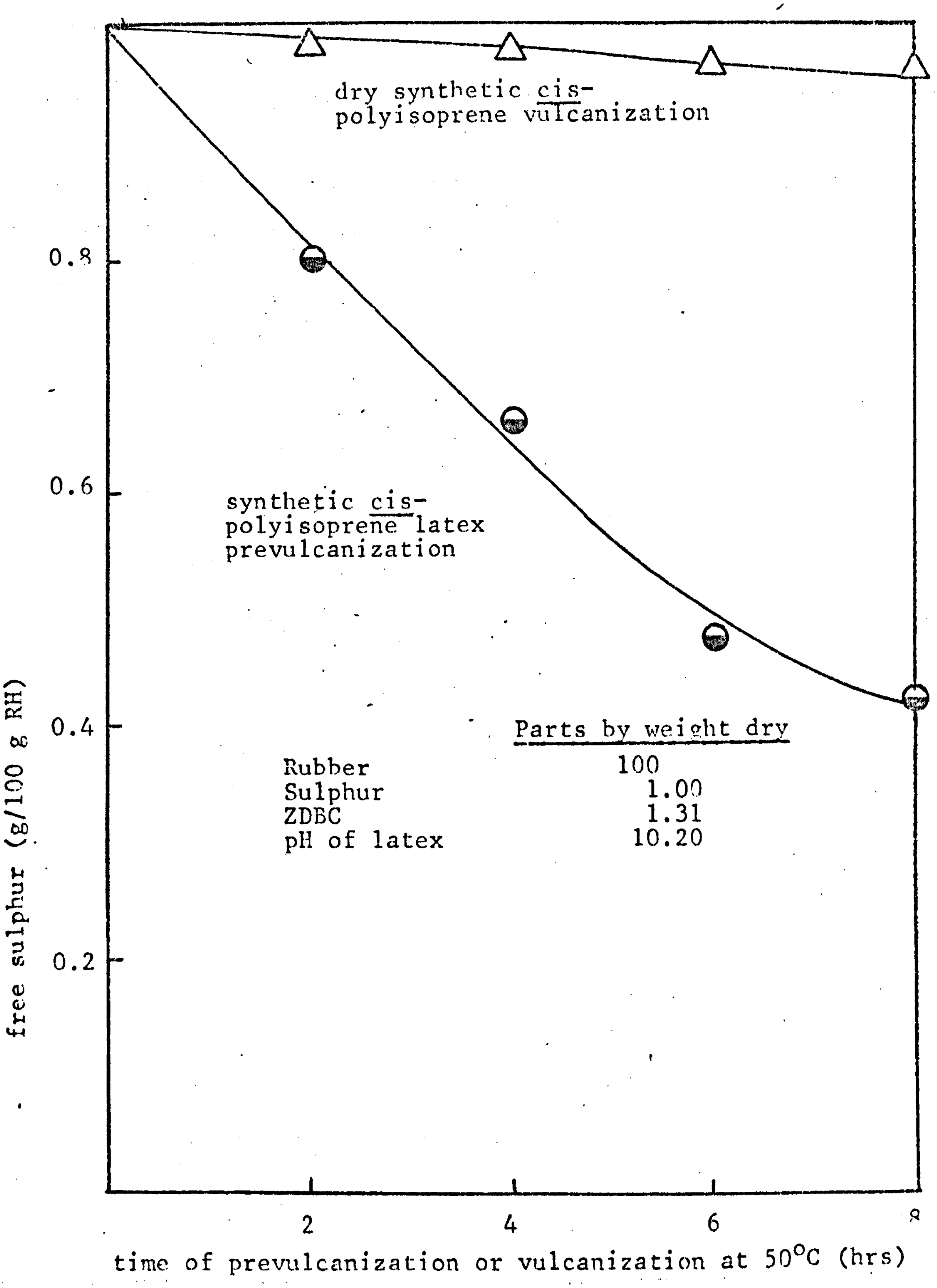


Fig. 6.7. Change in free sulphur during synthetic *cis*-polyisoprene latex prevulcanization and dry synthetic *cis*-polyisoprene vulcanization

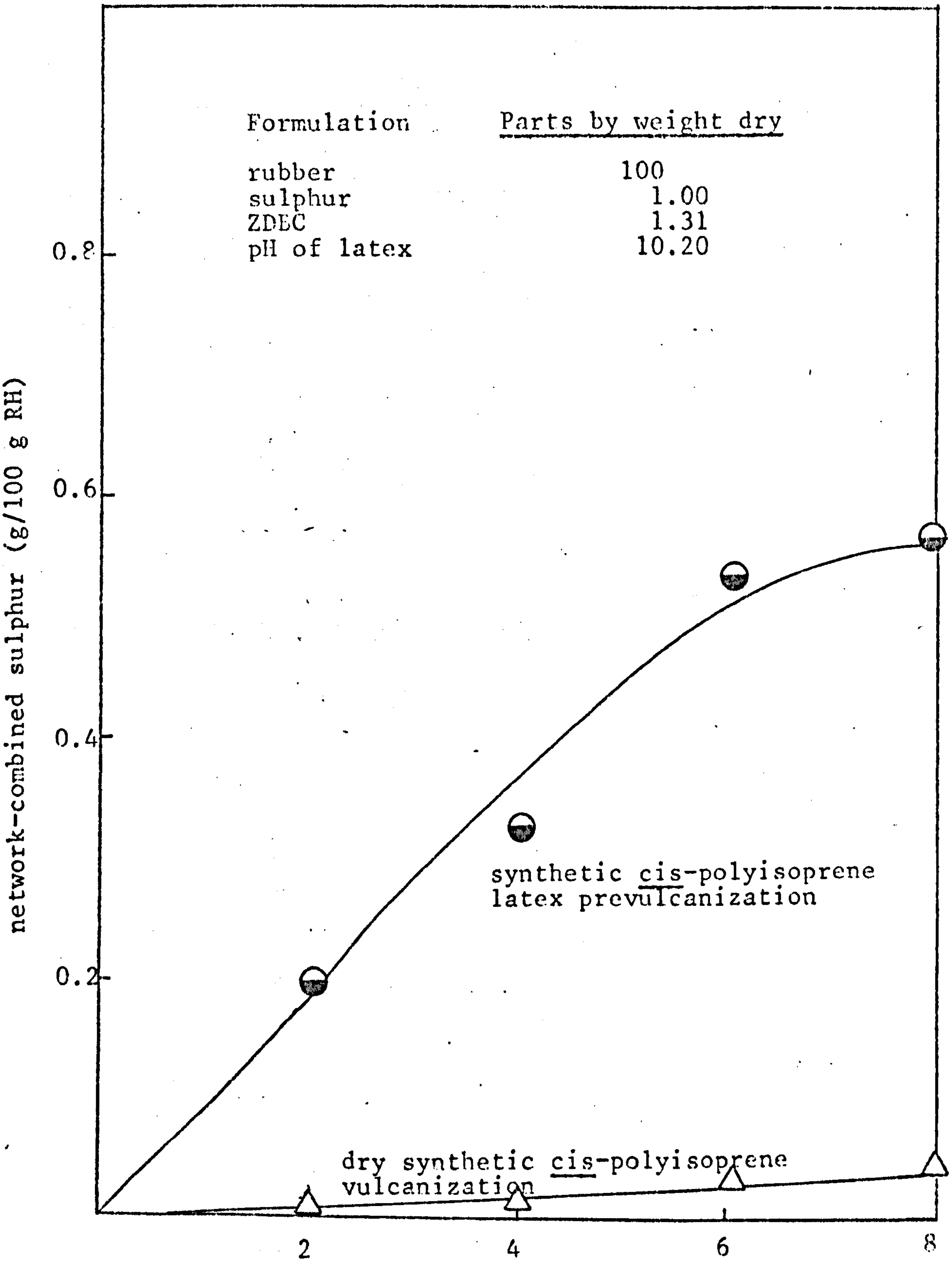


Fig. 6.8. Change of network-combined sulphur during synthetic cis-polyisoprene latex prevulcanization and dry synthetic cis-polyisoprene vulcanization

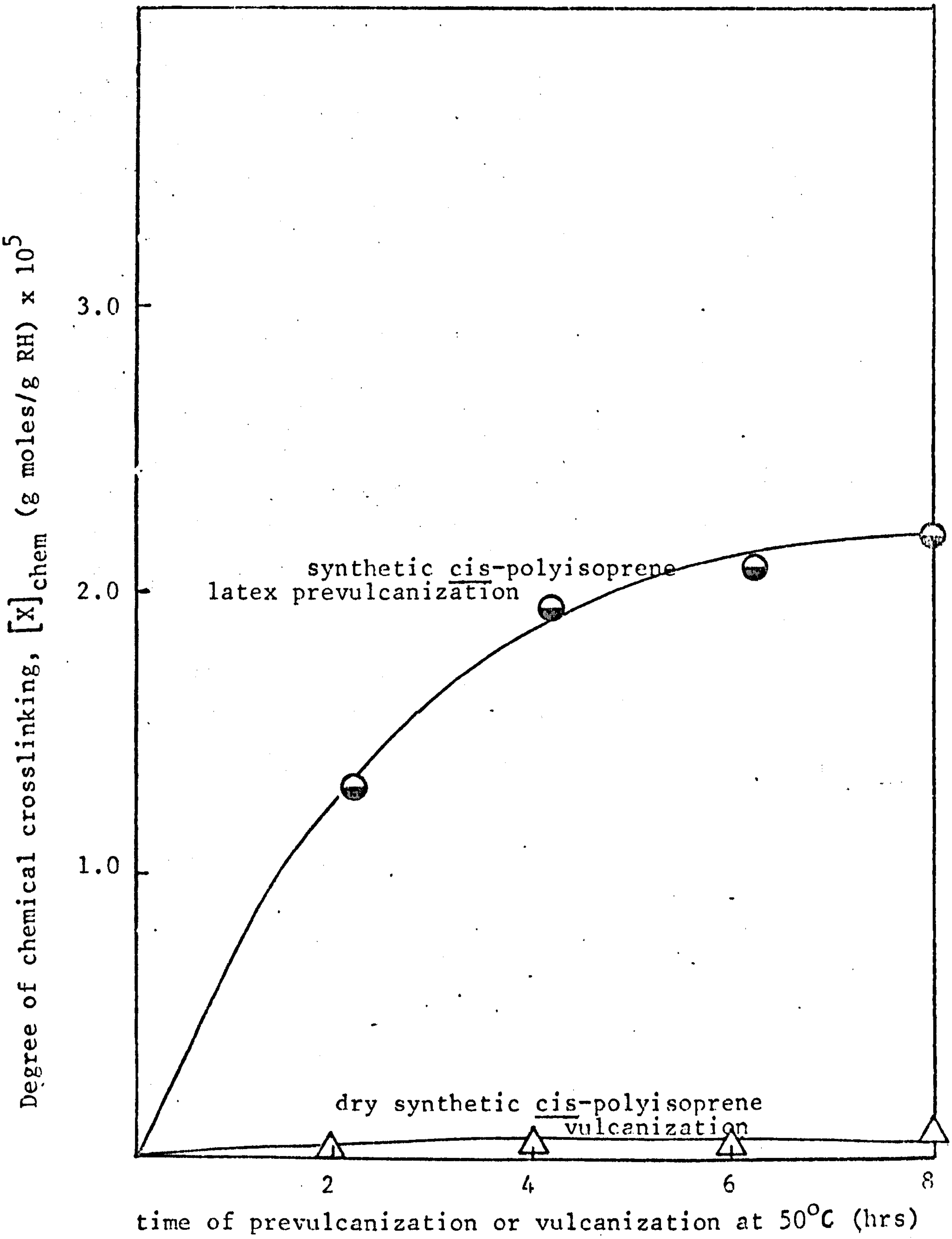


Fig. 6.9. Variation of degree of chemical crosslinking, $[X]_{chem}$, during synthetic cis-polyisoprene latex prevulcanization and dry synthetic cis-polyisoprene vulcanization

occurring. And in both cases there is negligible reaction when the unvulcanized compounded latex is dried down into films at 23°C and vulcanized in this form at 50°C in an air oven.

When the prevulcanization of synthetic <u>cis</u>-polyisoprene latex is compared with that of NR latex, both having the same reaction conditions, it is found that the two reactions differ somewhat as evidenced by the variation of free and network-combined sulphur with time of vulcanization. The two sets of results are compared in Fig. 6.10. The rates of crosslink insertion of the two reactions (shown in Fig. 6.4. and 6.8) are also found to be very different. The results show clearly that crosslink insertion occurs more rapidly in NR latex prevulcanization. These differences in the variation of free and network-combined sulphur and rates of crosslink insertion with time of vulcanization between the two prevulcanizations are presumably a consequence of the presence of indigenous vulcanization accelerators and activators in NR latex, but not in synthetic <u>cis</u>-polyisoprene latex. It is suggested that these indigenous vulcanization accelerators and activators act as additional accelerators and activators during NR latex prevulcanization. Hence, it is concluded that the contribution towards prevulcanization made by the naturally-occurring vulcanization accelerators and activators in NR latex is probably quite significant.

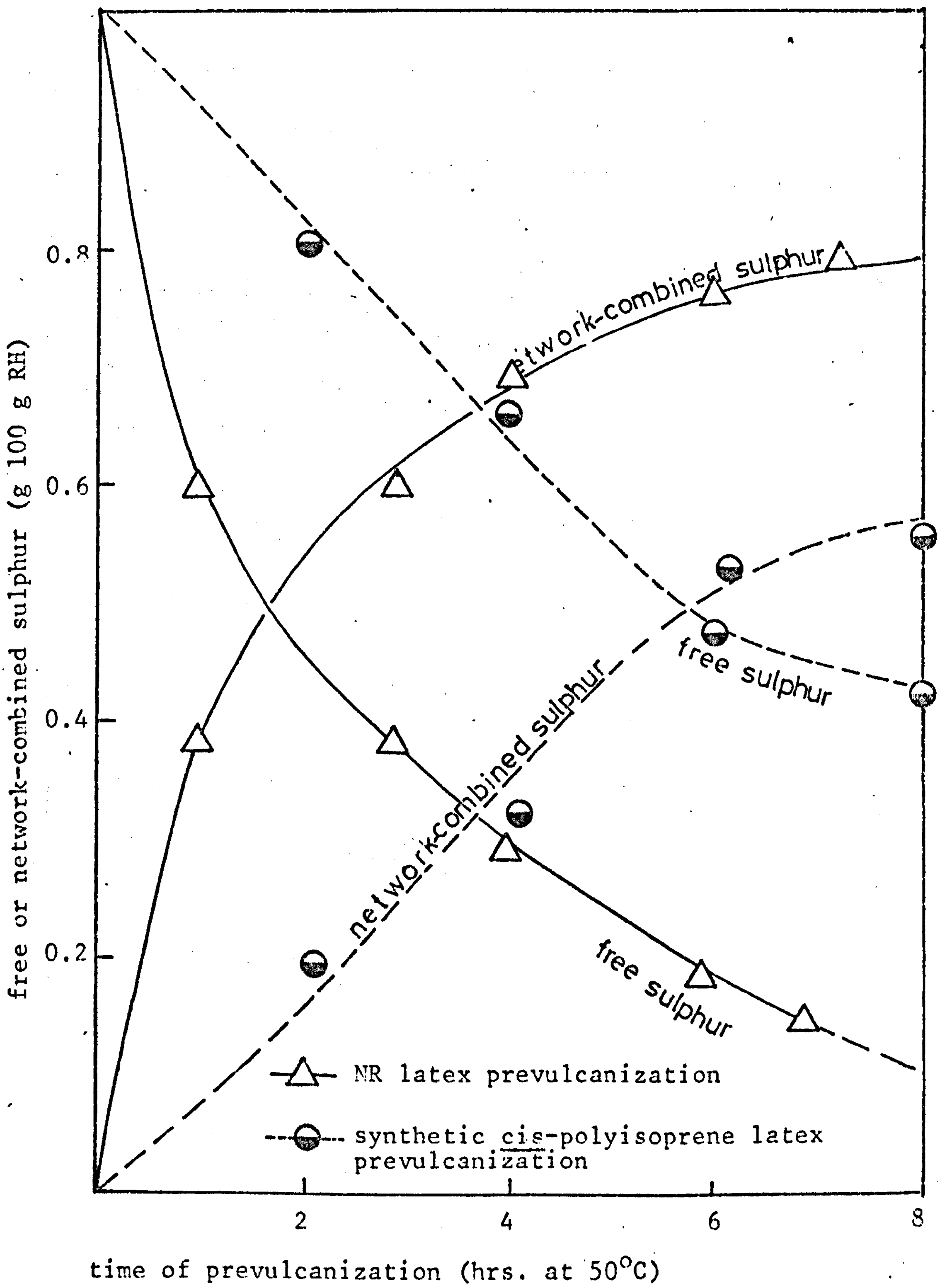


Fig. 6.10. Variation of free and network-combined sulphur during the prevulcanization of NR latex and synthetic cis-polyisoprene latex

6.2. Investigation of Solubilities of Sulphur and ZDBC in Aqueous Phase of Latex During Prevulcanization

When sulphur and ZDBC are added to latex, they are usually added in the form of aqueous dispersions. Under an optical microscope, the sulphur and ZDBC particles which are present in the dispersions are seen to be roughly similar in size to the larger of the rubber particles in NR latex. When the sulphur and ZDBC dispersions have been mixed into the latex, the system can be represented schematically as shown in Fig. 6.11. It is known that ZDBC and sulphur do not dissolve in water to any appreciable extent. Furthermore, it seems very unlikely that the particles of sulphur, ZDBC and rubber, being protected by their respective colloidal stabilizers, will react and

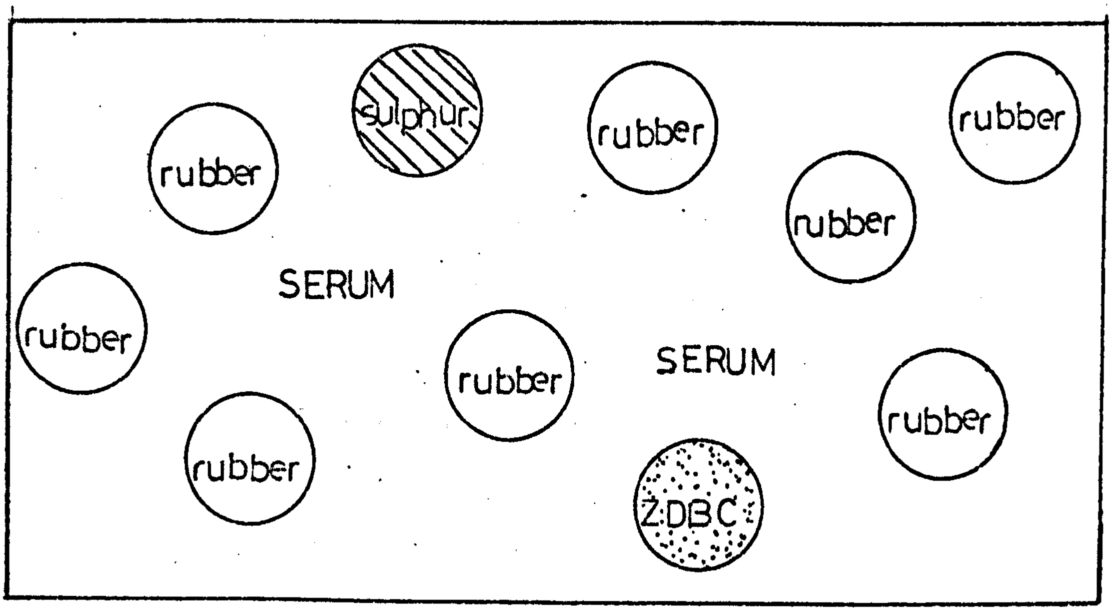


Fig. 6.11. Schematic diagram showing sulphur and ZDBC dispersed among rubber particles in compounded NR latex.

form sulphur crosslinks in the rubber as a consequence of collisions between themselves. The question then arises as to how the molecules of the vulcanizing ingredients make contact with the molecules of the rubber so as to effect prevulcanization.

It has already been proposed that the sulphur and the ZDBC in the aqueous phase of the latex react to form an active sulphurating agent. This active sulphurating agent is then partitioned from the aqueous phase into the rubber particles, where it can effect prevulcanization by reaction with the rubber molecules. It was therefore of considerable interest to attempt to determine the solubilities of sulphur and ZDBC in the aqueous phase of latex under conditions similar to those which prevail during latex prevulcanization. As far as is known, these solubilities have not been determined previously. This aspect of the investigation is described in the present section.

6.2.1. Solubilities of sulphur and ZDBC in aqueous phase of NR latex during prevulcanization

Initial attempts to investigate the solubility of sulphur in the aqueous phase of NR latex by a direct method failed. The method involved using an ultracentrifuge to separate the compounded latex into serum and rubber phases. The separated serum was then added to a fresh portion of latex. The idea was to use the rubber in the latex as a convenient "carrier" for the sulphur in the separated serum Films were cast and dried at 23 ± 1°C from this compound.

The film samples were then analysed for free and total unextractable sulphur to establish the amount of dissolved sulphur which was present in the separated serum. Unfortunately, the results obtained using this direct method were very erratic and unreproducible. Doubts were cast upon the efficiency of the separation process: In particular, it was possible that there might still be in the serum unseparated, minute particles of sulphur which would have been estimated as dissolved sulphur during the analysis. There was also doubt concerning the extent of mechanical entrapment of dissolved sulphur by the rubber particles during the vigorous centrifugation. The method was eventually abandoned after repeated attempts failed to give any sensible results.

It was then realized that, by visual observation of the clarity of dried 1.0-mm sheets, it was possible, rather surprisingly, to draw certain conclusions concerning the probable solubilities of sulphur and ZDBC in the aqueous phase of the latex during prevulcanization. This possibility was indicated by certain observations which initially were made accidentally. An experiment was therefore conducted to investigate more systematically the clarity of sheets dried down from NR latex compounds. The sheets were prepared in the usual manner using a standard amount of latex compound to give 1.00-mm thick sheets and air-dried under ambient conditions (23 ± 1°C). In order to ensure that the solubility phenomenon observed in these experiments is not the consequence of prevulcanization having occurred, in most cases the experiment conditions were such that little or no prevulcanization reaction would occur.

6.2.1.1. Results

Table 6.1 shows the various NR latex compounds, their treatment after compounding, and the results as indicated by the clarity of the sheets when dried.

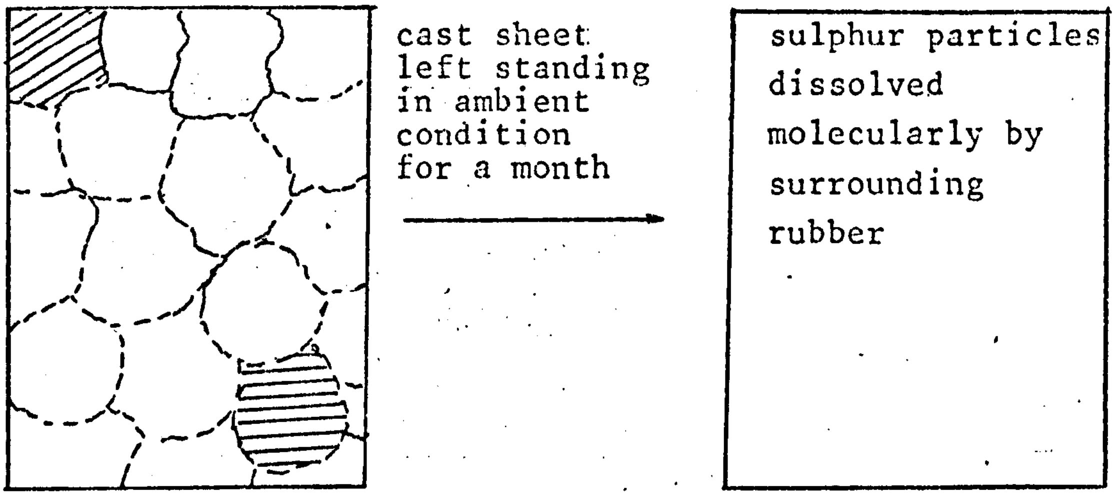
6.2.1.2. Observations and discussion

Cast sheets obtained from the control NR latex to which no ingredients had been added (Experiment 1) were transparent. When 1.00 pphr of sulphur was added to NR latex, without any further treatment after compounding (Experiment 2), the sheets prepared from this compound were opaque when dried. The obvious inference is that the opacity of cast sheet obtained from Experiment 2 is caused by the presence of particles of sulphur uniformly dispersed in the rubber matrix. These dispersed sulphur particles are presumably capable of scattering the incident light with the effect of causing the sheet to be opaque. When the opaque sheet obtained from Experiment 2 was heated in an air oven at 50°C over a period of 30 minutes, it gradually turned clear. The obvious explanation is that the sulphur dissolved molecularly in the rubber, and was no longer able to interfere with the transmission of light which passed through the rubber matrix. A similar effect was observed when the opaque sheet obtained from Experiment 2

Table 6.1. Results of investigation of clarity of cast sheets in the study of solubility of sulphur and ZDBC in NR latex

Experiment no.	Latex compound	Treatment of latex after compounding	Result (clarity of dried cast sheet)
1	NR latex (control)	None	clear
2	NR latex + 1.00 pphr sulphur	None	opaque
3	NR latex + 1.00 pphr sulphur	maturation of latex compound for one month at 23 ± 1°C	opaque
4	NR latex + 1.00 pphr sulphur	heated for 30 minutes at 50°C	clear
5	NR latex + 1.00 pphr sulphur	heated for 5 minutes at 50°C	opaque
6	NR latex + 1.00 pphr sulphur	heated for 5 minutes at 70°C	clear
7	NR latex + 1.00 pphr of sulphur and 1.31 pphr ZDBC	prevulcanized at 50°C for 10 hours	first 4 hours: opaque, 5th hour onwards: clear
8	NR latex + 1.31 pphr ZDBC	heated at 50°C for 10 hours	all samples opaque
9	NR latex + 1.31 pphr ZDBC	heated at 70°C for 10 hours	all samples opaque

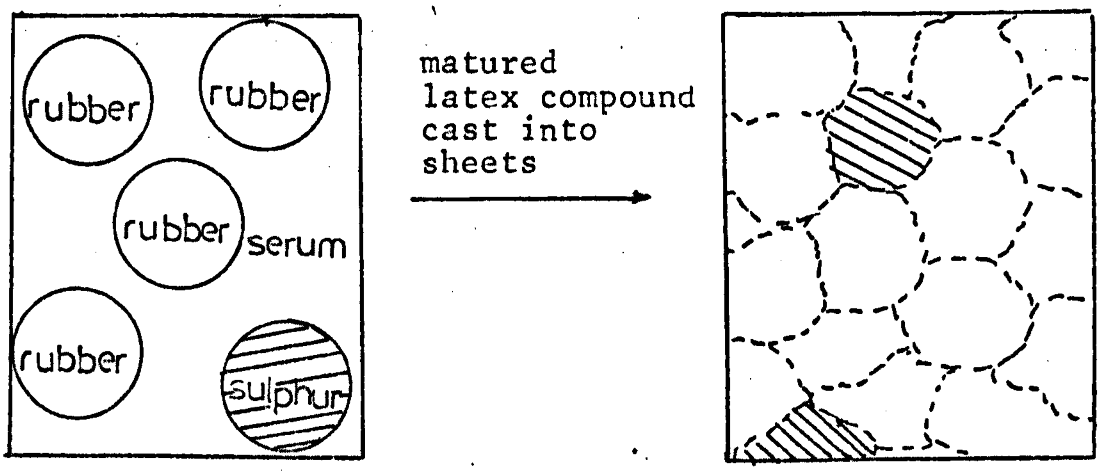
was left standing for one month at ambient conditions (23 ± 1°C). At the end of that period, the sheet was found to be clear. These phenomena were consistent with published results(155) for the solubility of sulphur in dry natural rubber. At 30°C the solubility is about 1.00 pphr. The solubility doubles when the temperature is raised to 50°C. While the opaque sheet obtained from Experiment 2 when left standing over a month at ambient conditions turned into a clear sheet, the latex compound itself when left standing over the same period and under similar conditions still gave opaque cast sheets when dried. An explanation for this observation is illustrated in Figs. 6.12 and 6.13. Fig. 6.12 shows the probable structure of the cast sheet with the dispersed sulphur particles which causes opacity embedded in the rubber matrix. (The sulphur particles are shown as spheres for convenience only; in reality, they are probably irregular in shape.) The opaque sheet turned clear after standing in ambient conditions for a month as a consequence of the physical contact which existed between the sulphur particles and the rubber matrix. The sulphur particles were able to dissolve molecularly in the rubber over the period of standing. Maturation of the latex compound under ambient condition for one month, on the other hand, did not seem to reduce the opacity of the cast film obtained from the latex. It is very likely that the sulphur particles were still dispersed and separated from the rubber by the serum in the latex (Fig. 6.13(a)) after the one month maturation. Hence when the



a) Cast sheet showing dispersed sulphur (shaded) embedded in rubber matrix.

b) transparent sheet of sulphur dissolved in rubber

Fig. 6.12. Illustrating changes in opaque cast sheet left standing for one month at ambient conditions (Experiment 2)



a) Sulphur particles still remain dispersed after one month maturation of compound

b) Opaque sheet showing dispersed sulphur (shaded) embedded in rubber matrix.

Fig. 6.13. Illustrating latex compound after maturation for one month at ambient conditions, and cast sheet obtained from it.

matured latex was cast into sheets, they were opaque because of the presence of discrete sulphur particles embedded in the rubber matrix (Fig. 6.13(b)).

One of the most interesting observations made in this series of experiments was that when NR latex containing 1.00 pphr sulphur added to it was heated for 30 minutes at 50°C (Experiment 5), the cast sheets obtained from this compound were clear. They were, in fact, as clear as sheets cast from the control NR latex which had no ingredients added to it. It thus appears that heating the compounded latex for a short while at a temperature some 25°C above ambient is sufficient to enable the sulphur to become molecularly dissolved in the rubber. Presumably this implies that the solubility of the sulphur in the aqueous phase of the latex was also increased to some extent by raising the temperature. It may be that, as a result of the increased solubility of the sulphur in the aqueous phase, all the sulphur in the latex is gradually partitioned into the rubber particles from the aqueous phase. Alternatively, and perhaps more probably, a dynamic equilibrium is established between sulphur dissolved in the aqueous phase and sulphur dissolved in the rubber phase of the latex. In either case, cast sheet from the compound would be clear because the sulphur has become molecularly dissolved during heating.

Experiments 5 and 6 show that the dissolution of sulphur in NR latex during heating depends upon the time and temperature of heating. In Experiment 5, where the NR latex with 1.00 pphr sulphur added was heated for only 5 minutes at 50°C, the resultant cast sheets were still opaque when dried. To obtain clear cast sheet, it was found necessary to heat the latex compound for at least 30 minutes at 50°C. Experiment 6, on the other hand, shows that 5 minutes was sufficient to produce clear cast sheets, if the same compound was heated at 70°C.

This investigation of the clarity of cast sheets was extended to a study of the effect upon the opacity of cast sheets of heating NR latex and sulphur in the presence of ZDBC. Some prevulcanization of the latex would have occurred during this treatment. Experiment 7 was carried out by heating NR latex with 1.31 pphr ZDBC and 1.00 pphr sulphur at 50°C over a period of 10 hours. Samples were removed at hourly intervals and cast into sheets which were dried at 23°C. It was found that the first four hourly samples gave opaque sheets when dried, whilst from the fifth hourly sample onwards, clear sheets were obtained. Having established earlier in Experiment 4 that clear sheets were obtained from NR latex containing 1.00 pphr sulphur alone heated for 30 minutes at 50°C, it was concluded that the opacity of the sheets obtained from the first four hourly sample in Experiment 7 was associated with the presence of the ZDBC. This conclusion was confirmed by Experiments 8 and 9, in which NR latex was heated with 1.31 pphr ZDBC alone. The cast sheets obtained from this latex compound were always opaque, regardless of the conditions of time and temperature under which the heating was carried out. It therefore seems that, when 1.31 pphr ZDBC alone is added to NR latex, it remains dispersed as particles, even after heating the latex compound. When cast into sheets and dried, the ZDBC particles dispersed in the continuous rubber phase are sufficiently large to scatter light, hence giving opaque sheets.

In order to account for the clarity of cast sheets obtained in Experiment 7 from latex samples which had been prevulcanized for 5 hours or longer, it is necessary to suppose that the size and number of the ZDBC particles were reduced, perhaps through reaction with the dissolved sulphur to form a rubber-soluble active sulphurating agent, to such an extent that they could no longer scatter light when the latex compound was cast into sheets.

Based on this investigation of the clarity of sheets cast from various compounded NR latices, the outline reaction scheme shown in Fig. 6.14 is proposed. It indicates in outline a sequence of processes which leads to the disappearance of particles of vulcanizing ingredients and to the formation of crosslinks in the rubber.

6.2.2. Solubilities of sulphur and ZDBC in the aqueous phase of synthetic cis-polyisoprene latex during prevulcanization

Having studied the clarity of sheets obtained from NR latex to which sulphur and ZDBC were added, it was of interest also to conduct a similar study using synthetic

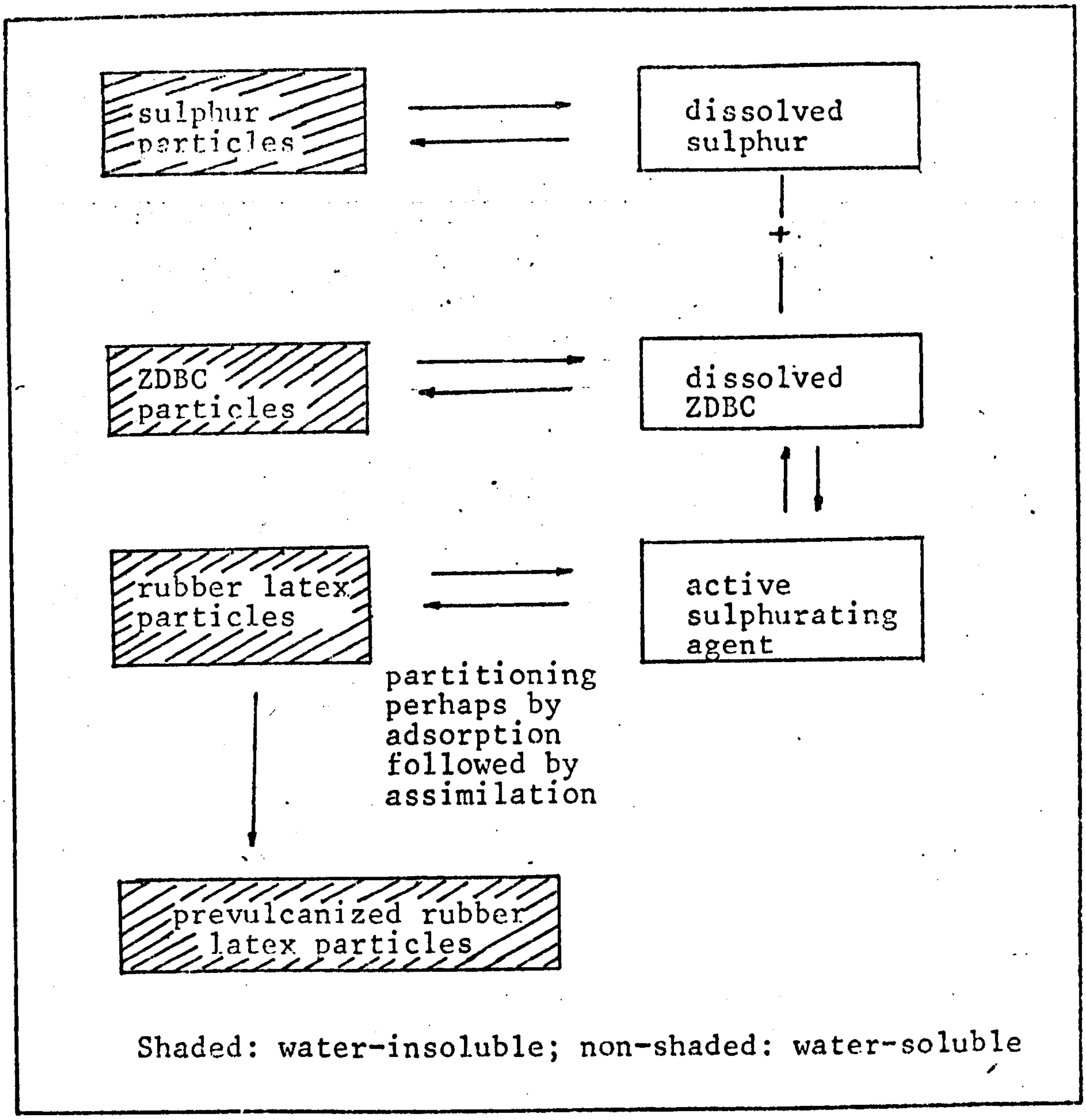


Fig. 6.14. Outline reaction scheme suggested by study of clarity of cast sheets leading to disappearance of particles of vulcanizing ingredients and to formation of crosslinks in the rubber.

cis-polyisoprene latex. As stated previously, in the serum of NR latex, there are numerous substances known collectively as non-rubber substances. These substances are not present in synthetic cis-polyisoprene latex. It was therefore thought that the differences between the two latices in this respect might provide evidence concerning the importance of the non-rubber constituents of NR latex in determining the clarity or otherwise of cast sheets obtained from latex compounds.

6.2.2.1. Results

Table 6.2. shows the details and results of the series of experiments which were carried out using synthetic cis-polyisoprene latex. The procedure was similar to that for the series of experiments using NR latex.

6.2.2.2. Observations and discussion

Unlike the cast sheets obtained from NR latex or its compounds, which all had a yellowish tinge, perhaps caused by the presence of yellow pigments which in the fresh NR latex were associated with the Frey-Wyssling particles, the dried cast sheets obtained from synthetic cis-polyisoprene latex and its compounds were either water-clear or white opaque. Very clear cast sheets were obtained from the synthetic cis-polyisoprene latex to which no ingredients had been added (Experiment 10). As in the case of NR latex, the synthetic latex also gave opaque cast sheets when 1.00 pphr of sulphur was added to the latex

Table 6.2. Results of investigation of clarity of cast sheets in the study of solubility of sulphur and ZDBC in synthetic cis-polyisoprene latex

Experiment no.	Latex Compound	Treatment of latex after compounding	Result (clarity of sheet when dried)
10	synthetic cis-polyisoprene latex (control)	None	clear
11	synthetic cis-polyisoprene latex +1.00 pphr sulphur	None	opaque
12	synthetic cis-polyisoprene latex +1.00 pphr sulphur	maturation of latex compound for one week at 23 ± 1°C	opaque
13	synthetic cis-polyisoprene latex +1.00 pphr sulphur	heated for 30 minutes at 50°C	opaque
14	synthetic cis-polyisoprene latex +1.00 pphr sulphur	heated for 5 minutes at 70°C	opaque
15	synthetic cis-polyisoprene latex +1.00 pphr sulphur	heated for 10 hours at 70°C	opaque
16	synthetic cis-polyisoprene latex +1.31 pphr ZDBC	heated for 10 hours at 70°C	opaque
17	synthetic cis-polyisoprene latex +1.31 pphr ZDBC + 1.00 pphr sulphur	prevulcanized at 50°C for 10 hours; samples removed at hourly intervals	First 6 hours: opaque 7th hour onwards: clear

(Experiment 11). Furthermore, the opaque cast sheet could be turned into a clear sheet by heating it in an air-oven at 50°C for 30 minutes. However, it is interesting to observe that, in contrast to Experiment 4 in the series of experiments using NR latex, when 1.00 pphr sulphur was added to synthetic <u>cis</u>-polyisoprene latex and the mixture heated for 30 minutes at 50°C, the resultant latex compound did not give a clear cast sheet when dried. Indeed, even heating the latex compound at a higher temperature (i.e., 70°C) for a longer period (i.e., 10 hours) did not bring about any reduction of opacity (Experiment 15).

ZDBC in synthetic <u>cis</u>-polyisoprene latex gave the same results as in NR latex. When added alone, it always gave opaque cast sheets. Experiment 16 shows that even heating at 70°C for 10 hours did not change the clarity of the resultant cast sheet.

It was found that, although 1.00 pphr sulphur and 1.31 pphr ZDBC when added individually to synthetic <u>cis</u>-polyisoprene latex always gave opaque cast sheets, even though the latex compound had been heated for 10 hours at 70°C, when both the vulcanizing ingredients were present together in the synthetic latex and the latex was prevulcanized at 50°C, the cast sheets obtained from the seventh hourly sample onwards were clear (Experiment 17).

From these observations, it may be surmized that the sulphur and ZDBC particles, when added alone to synthetic <u>cis</u>-polyisoprene latex, remained as discrete, dispersed particles even when the latex compound was heated for 10 hours at 70°C. The results obtained using synthetic cis-polyisoprene latex when compared to those obtained using NR latex, indicate that whilst ZDBC in both the latices has very low solubility in the aqueous phase, the sulphur particles on the other hand dissolve to some appreciable extent in NR latex but not to the same extent in synthetic cis-polyisoprene latex when the latex compound is heated. The obvious inference from this comparison is that the non-rubber substances present in NR latex are responsible in some way for bringing the sulphur molecules from the sulphur particles into the aqueous phase of the NR latex. This proposal is consistent with the findings of van Gils,(18) who has indicated similar results in his investigations.

The clear cast sheets obtained in Experiment 17 from latex samples which had been prevulcanized for 7 hours or longer indicated however that, even though the solubility of sulphur in the aqueous phase of synthetic cis-polyisoprene latex is insufficient for clear sheets to be obtained from latex + sulphur alone (even with heating), it is sufficiently soluble to permit prevulcanization to occur when ZDBC is present. This finding is interesting and significant because it lends credibility to the proposal that sulphur and ZDBC react together in the aqueous phase to form an active sulphurating agent which partitions advantageously in the rubber phase.

6.3. Investigation of the Solubility of ZDBC in Ordinary Deionised Water, Ammoniated Water and Diluted NR Latex Serum

Circumstantial evidence based on the clarity of cast sheets discussed in the previous section indicated that ZDBC has low solubility in the serum of NR latex during prevulcanization. In this section, attempts to determine the solubilities of ZDBC in ordinary deionised water, ammoniated water and dilute NR latex serum are described. It was hoped that the results from this investigation would provide new information concerning the solubility of ZDBC in the serum of NR latex during prevulcanization.

In contrast to the difficulties encountered in attempting to determine the solubility of sulphur in the serum of NR latex using conventional analytical techniques, reasonably accurate determination of the solubility of ZDBC in aqueous media is made relatively easy by using the instrumental technique known as atomic absorption spectroscopy. 3.00 g of ZDBC dispersion (33.33%) was added to 50.0 ml of ordinary deionized water. The suspension was heated with slow stirring at 50°C for 6 hours. Samples were taken at hourly intervals. The samples of ZDBC suspension were then centrifuged at 20,000 rpm for 20 minutes at 20°C. The supernatant liquid was carefully removed and analysed for dissolved zinc using an atomic absorption spectrometer. The same procedure was repeated using (a) deionised water which had been previously ammoniated to pH 10.20, and (b) diluted NR latex serum in place of water. (The concentration of the dilute latex serum is 28% and obtained by the procedure previously described in Section 5.2.7.). The atomic absorption spectrophotometer was first calibrated with standard zinc nitrate solution.

6.3.1. Results

The results for the calibration are shown in Fig. 6.15. The concentrations of zinc in the deionised water, ammoniated water and dilute NR latex serum were determined from the calibration graph in Fig. 6.15 using the appropriate measured values of absorbance. The results are given in Tables 6.3-6.5 and shown graphically in Fig. 6.16.

The average value of the solubility of ZDBC in ordinary deionised water was found to be 0.003% (Fig. 6.16). Heating at 50°C over a period of 6 hours did not have any significant effect upon the solubility. Fig. 6.16 also shows that the solubility of ZDBC increases slightly in ammoniated deionised water at room temperature. But when heated to 50°C, the solubility of ZDBC in ammoniated deionised water is almost double the solubility in ordinary deionised water, i.e., 0.005%. In diluted NR latex serum, the solubility of ZDBC was found to be markedly higher than in the other two media investigated, i.e., 0.011%. Heating at 50°C over 6 hours did not have any significant effect upon the solubility in diluted NR latex serum.

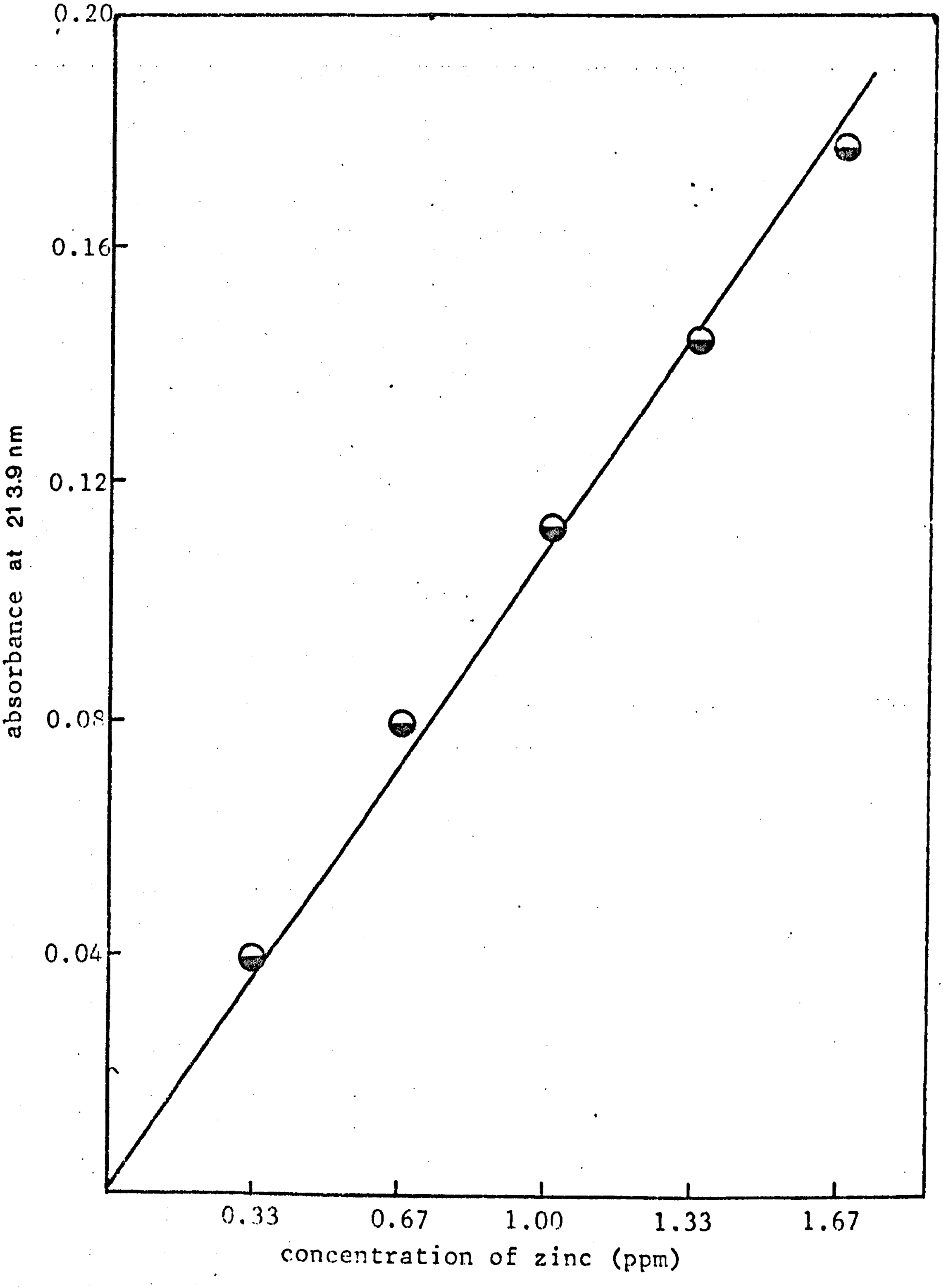


Fig. 6.15. Calibration curve for zinc using standard zinc nitrate solution

Table 6.3. Results for solubility of ZDBC in deionised water.

Time of heating at 50^{o}C (hrs)	Mean Absorbance	Concentration of zinc in 5x diluted sample (ppm)	Concentration of zinc in test sample (ppm)	Concentration of ZDBC in deionised water (ppm)	% solubility in deionised water (x10^{3}%)
0	0.093	0.82	4.10	29.89	2.99
1	0.087	0.72	3.60	26.24	2.62
2	0.088	0.73	3.65	26.61	2.66
4	0.089	0.75	3.75	27.33	2.73
6	0.097	0.83	4.15	30.25	3.03
8	0.091	0.76	3.80	27.70	2.77

Table 6.4. Results for solubility of ZDBC in ammoniated water (pH 10.2)

Time of heating at 50°C (hrs)	Mean Absorbance	Concentration of zinc in 5x diluted sample (ppm)	Concentration of zinc in test sample (ppm)	Concentration of ZDBC (ppm)	% solubility in ammoniated water ($\times10^{-3}$%)
0	0.105	0.91	4.55	33.17	3.32
1	0.157	1.44	7.20	52.48	5.25
2	0.163	1.51	7.55	55.03	5.50
4	0.162	1.49	7.45	54.30	5.43
6	0.166	1.53	7.65	51.74	5.17

Table 6.5. <u>Results for solubility of ZDBC in dilute NR latex serum</u>

Time of heating at 50^{o}C (hrs)	Mean Absorbance	Concentration of zinc in 10x diluted sample (ppm)	Concentration of zinc in test sample (ppm)	Concentration of ZDBC (ppm)	% solubility in dilute NR latex serum $(x10^{-3}\%)$
0	0.160	1.42	14.2	103.50	10.35
1	0.170	1.53	15.3	111.53	11.15
2	0.170	1.53	15.3	111.53	11.15
4	0.172	1.55	15.5	112.98	11.30
6	0.171	1.54	15.4	112.25	11.23

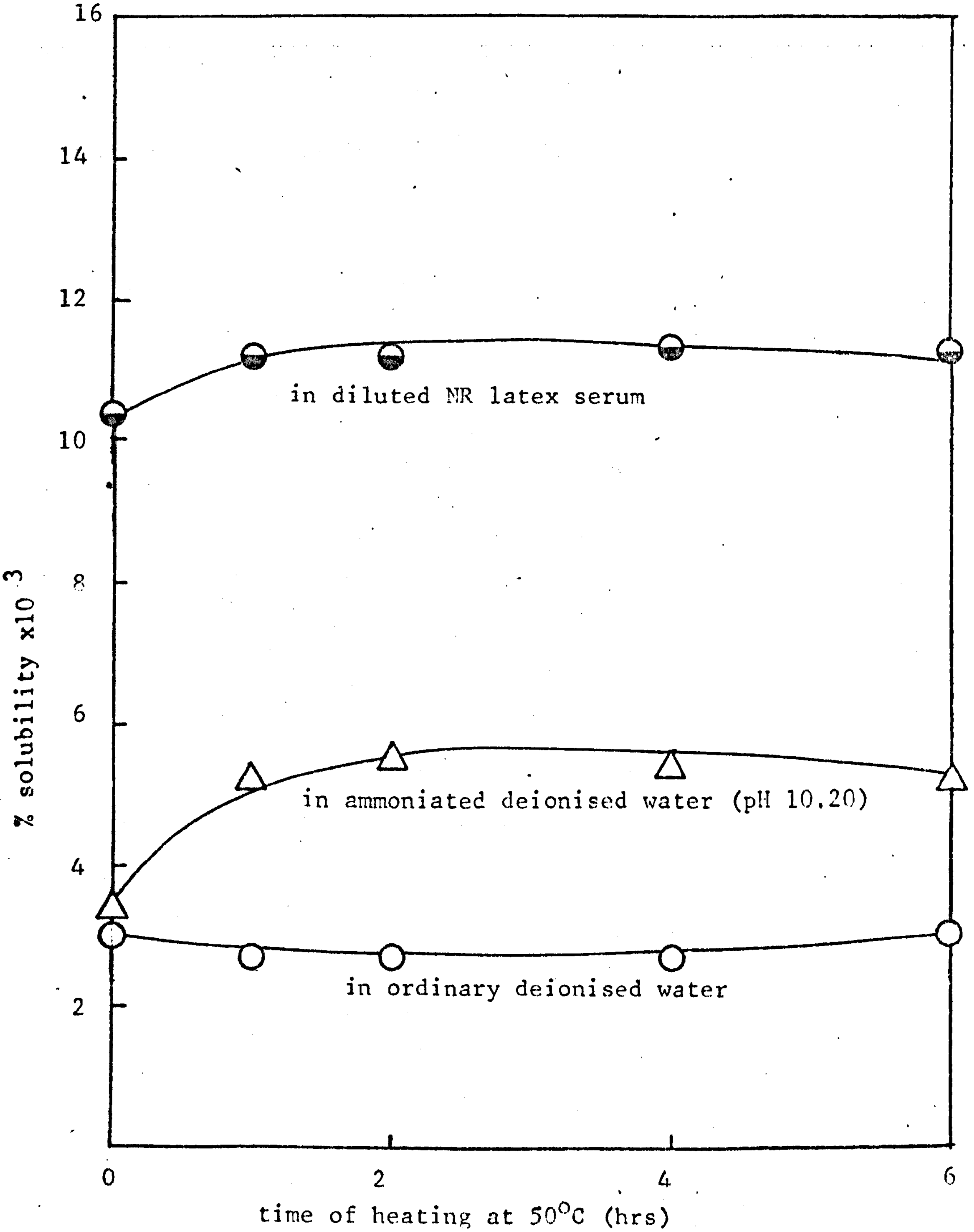


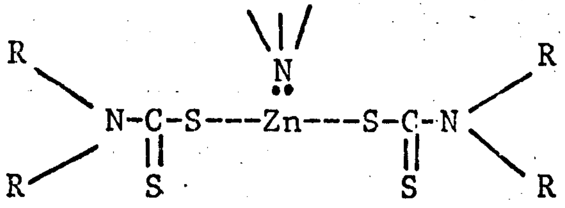
Fig. 6.16 Solubility of ZDBC in ordinary deionised water, ammoniated-deionised water and diluted NR latex serum plotted against time of heating at 50°C

6.3.2. Discussion

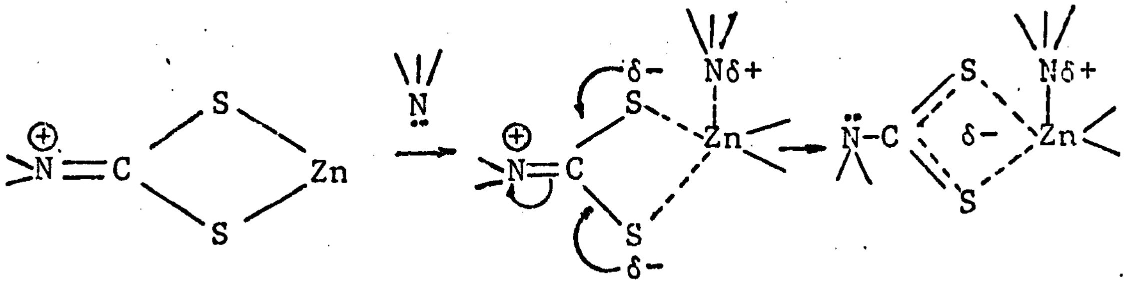
It would have been ideal if normal latex serum could have been obtained in sufficient quantity for this investigation of the solubility behaviour of ZDBC. However, experimental difficulties made this not possible. Therefore in place of normal latex serum, deionised water (pH 6.00), deionised water previously ammoniated to pH 10.20, and a dilute form of NR latex serum was used. Fig. 6.16 shows that ZDBC is soluble to a limited extent in each of the three media investigated. These results suggest that the solubility of ZDBC in normal latex serum is at least 0.011%, and may be somewhat higher. It is interesting to note that, although a solubility of 0.01% seems to be very small by conventional standards, nevertheless, it is of the same order as the solubility of styrene monomer in the aqueous phase of a styrene emulsion polymerisation system. Styrene has a solubility of 0.03%(156,157) in water at 15°C. A dynamic equilibrium is established in the aqueous phase between the styrene in droplets and styrene dissolved in the aqueous phase. During polymerisation, the dissolved styrene reacts with free radicals derived from the initiator in the aqueous phase, thereby forming oligomeric free radicals which possess surface-active properties. These oligomers then become entrapped in the micelles, and there initiating polymerisation of monomer molecules which are already solubilized in the micelles. More styrene dissolves from the monomer droplets into the aqueous phase to replenish the consumed dissolved styrene and thereby to re-establish equilibrium. In this way, the styrene monomer droplets are gradually depleted as polymerisation proceeds within the micelles.

It is tempting to draw an analogy between the disappearance of styrene monomer droplets during emulsion polymerisation and the disappearance of ZDBC during latex prevulcanization. In the latter case, it is possible that the estimated 0.01% ZDBC which is dissolved in the serum reacts with molecularly-dissolved sulphur (see Section 6.2.1.1.), thereby forming active sulphurating agents. As suggested earlier, these active sulphurating agents may then become partitioned into the rubber particles or adsorbed on to the rubber particles and further assimilated into the rubber phase, thereby starting the crosslinking reaction within the rubber particles. In the same way as the styrene monomer in a styrene emulsion polymerisation reaction system replenishes the styrene which has polymerised in the principal reaction loci, more ZDBC is then dissolved into the aqueous phase of the latex to re-establish the equilibrium.

Returning to Fig. 6.16, it is now necessary to account for the higher solubility of ZDBC both in dilute NR latex serum and in ammoniated water compared to that in unammoniated deionised water. It appears that the non-rubber substances (especially the nitrogenous bases) and ammonia present in the dilute NR latex serum, and the ammonia present in the ammoniated water, in some way assist the dissolution of ZDBC. The most likely explanation is that these substances complex with the zinc atoms of the ZDBC. Published literature(158,159) and patents(160-163) suggest that complexes of the following type are formed when ammonia or nitrogenous bases such as amines, are reacted with zinc dialkyl dithiocarbamate:



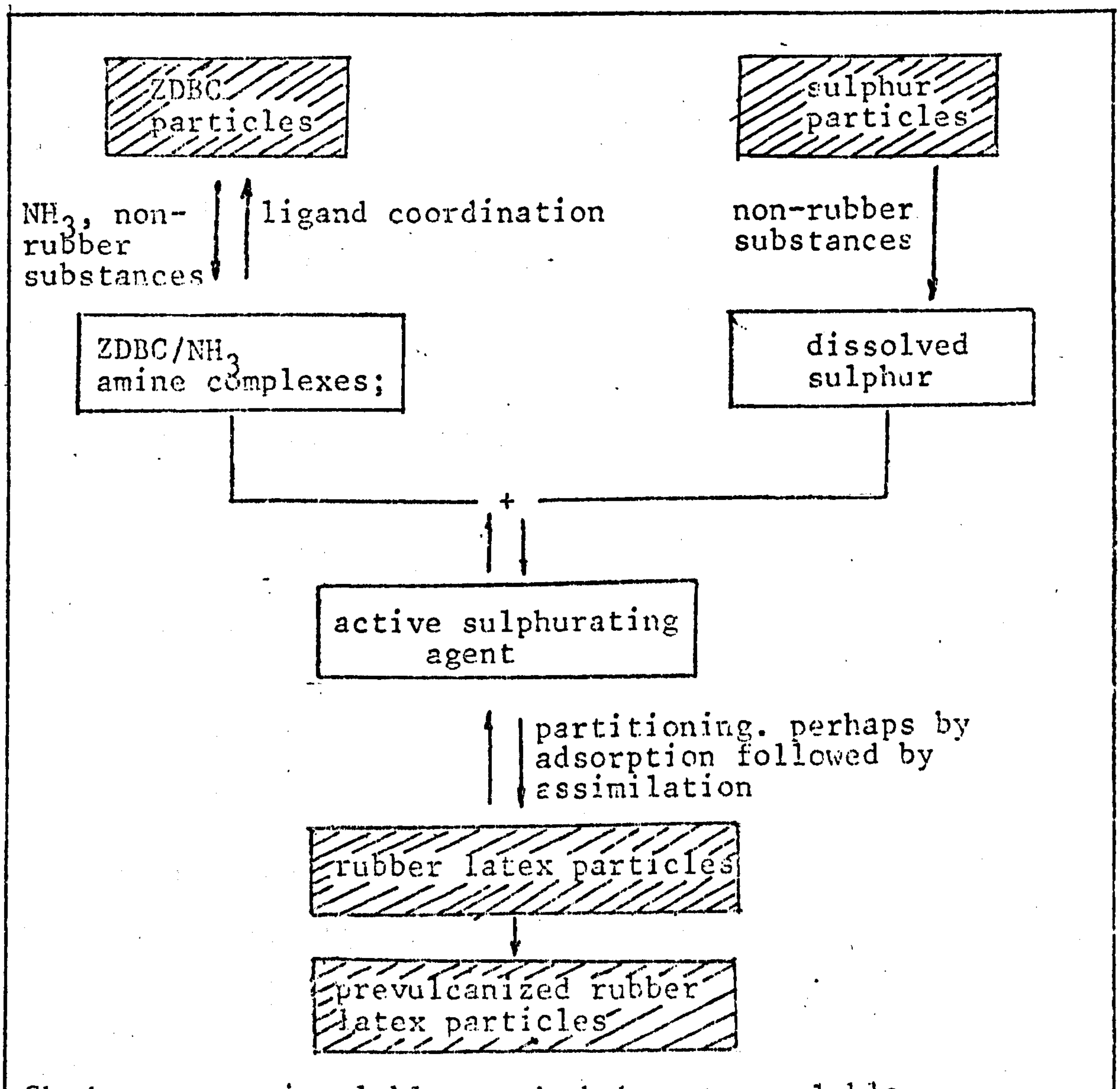
Such complexes are probably more soluble in aqueous media than is uncomplexed zinc dialkyl dithiocarbamate. Therefore in this context it is reasonable to suggest that, during NR latex prevulcanization, these ZDBC-ammonia (or amine) complexes, which are dissolved in the serum, will then nucleophillically attack the dissolved sulphur to form an active sulphurating agent. Indeed, it has been suggested by Higgins and Saville$^{(164)}$ that coordination of an amine molecule on to the zinc atom of the dithiocarbamate renders the zinc-sulphur bonds more ionic, as shown in the following scheme:



(6.2)

The sulphur atoms of the complexes carry higher negative charge densities and are therefore more nucleophilic than do those of the parent dialkyl dithiocarbamate. Hence, in the context of the present work they are therefore more effective in attacking the dissolved sulphur to form the active sulphurating agent during NR latex prevulcanization.

Based on the further information described in the present section, it is now thought necessary to modify the reaction scheme which has been proposed earlier to account for the disappearance of ZDBC and sulphur during NR latex prevulcanization (Fig. 6.14, Section 6.2.1.2.).
A revised reaction scheme for NR latex prevulcanization is shown in Fig. 6.17.



Shades: water-insoluble; unshaded: water soluble

Fig. 6.17. Revised reaction scheme for NR latex prevulcanization based upon results from study of clarity of cast sheets and solubility of ZDBC accelerators.

6.4. Effect of Ammonia upon NR Latex Prevulcanization

The results obtained for the solubility of ZDBC in aqueous media, given in the preceding section, raise the question of the possible effect of the ammonia present in NR latex as preservative upon the prevulcanization of NR latex. Hence a study was undertaken of the effect of ammonia upon NR latex prevulcanization. This is described in the present section. In order that the effect of ammonia could be studied satisfactorily, the prevulcanization reactions were carried out in sealed bottles to prevent loss of ammonia during the reaction. Some of the prevulcanization reactions carried out in the present programme were performed in a reaction vessel. In this technique, although the latex was first deammoniated to the desired pH prior to prevulcanization, there was no control of the further escape of ammonia during the reaction (see apparatus set up in Section 5.2.1.4(a).

6.4.1. Results

In an initial investigation, latex prevulcanization in a reaction vessel was compared to latex prevulcanization performed in sealed bottles. The results of this initial investigation are shown in Fig. 6.18. Further investigations were carried out on the effect of ammonia concentration upon latex prevulcanization. In these experiments, the initial ammonia concentration of the latex was varied. This was accomplished by deammoniating high-ammonia NR latex by slow stirring to the required ammonia concentration

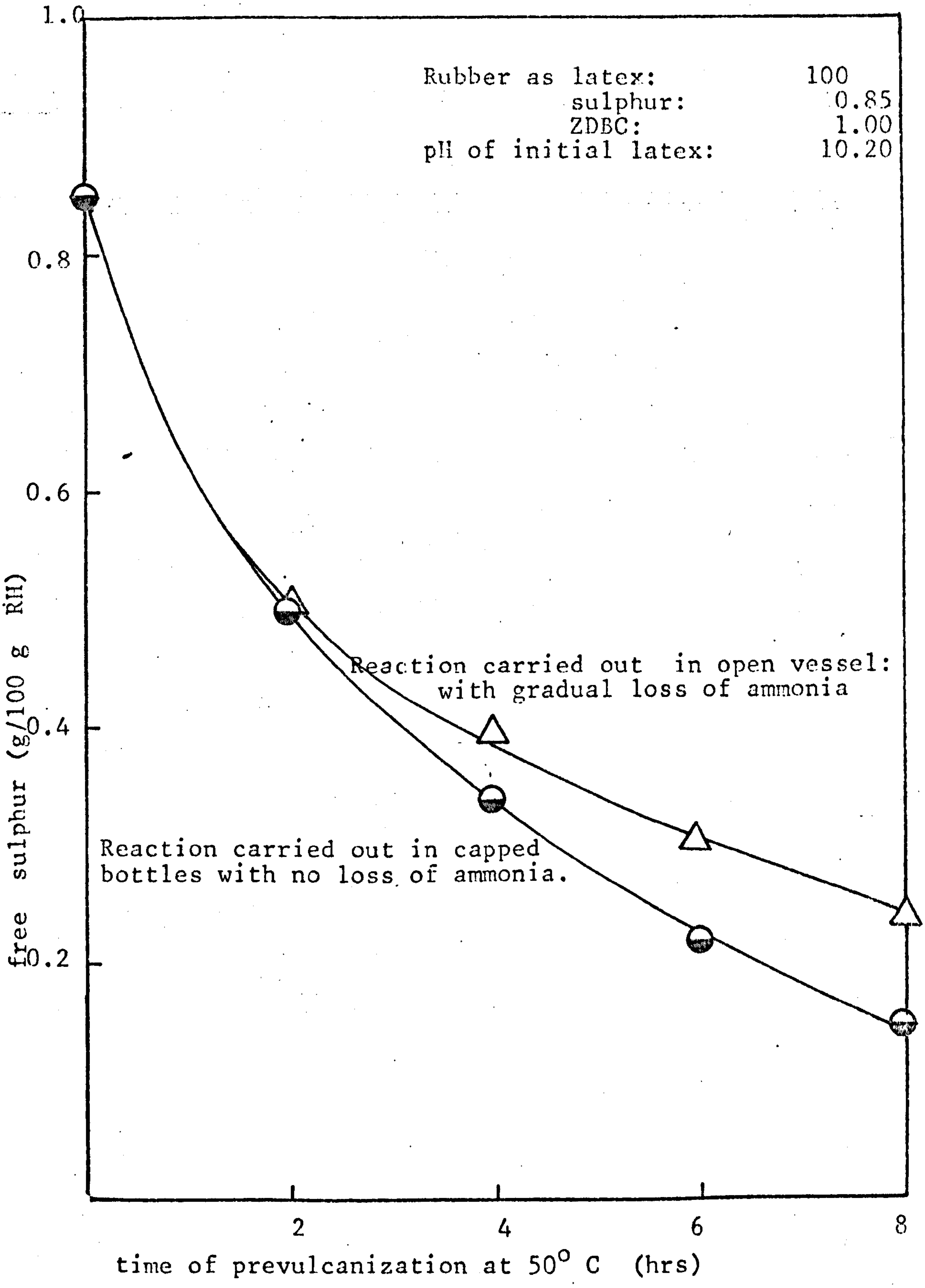


Fig. 6.18. Effect of loss of ammonia during NR latex prevulcanization in reaction vessel upon variation of free sulphur with time of prevulcanization

(see Section 5.2.1.1). All the prevulcanization reactions were carried out in sealed bottles. The results of this latter series of experiments are shown in Fig. 6.19.

6.4.2. Discussion

It is evident from Fig. 6.18 that loss of ammonia during latex prevulcanization by the reaction vessel method has a significant effect upon the rate of disappearance of free sulphur during the prevulcanization of NR latex. It is rather surprising that, as far as the present writer is aware, there is no published information on the effects of ammonia upon NR latex prevulcanization. Fig. 6.19 shows that, at high ammonia concentration (0.652% and 0.835%, based on the latex), rate of disappearance of sulphur is almost independent of the ammonia concentration. With decrease in ammonia concentrations down to 0.152% in the initial latex, the results show that the rate of prevulcanization becomes progressively slower as indicated by the free sulphur values. These results are consistent with the concept of ammonia behaving as a complexing ligand for ZDBC during NR latex prevulcanization. It is also probable that, at high ammonia concentrations, higher complexes such as a 1:2 ZDBC:ammonia complex may be formed. These higher complexes may have a higher solubility in the aqueous phase of the latex than does the normal 1:1 ZDBC:ammonia complex which has been previously discussed.

Fig. 6.19 also shows the results for the prevulcanization of NR latex which contained a very low

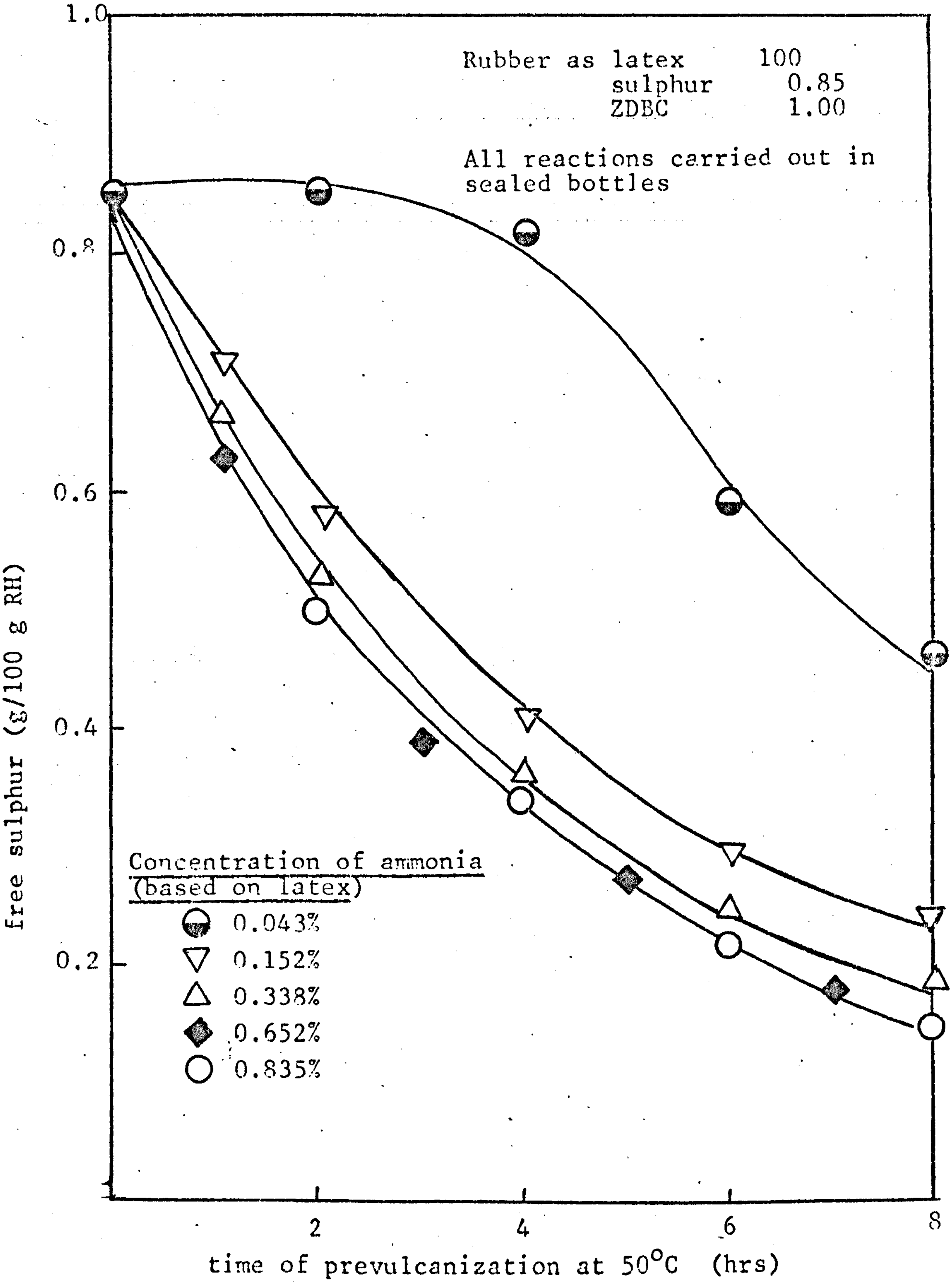


Fig. 6.19. Effect of ammonia concentration in NR latex upon variation of free sulphur with time of prevulcanization

concentration of ammonia (0.043%). An unexpected phenomenon was observed in this case. The curve of free sulphur <u>vs</u>. time of prevulcanization appeared to have a different shape to the others in the same series of experiment. The free sulphur results indicate that the onset of the prevulcanization is delayed, and that when the latex prevulcanizes, the extent of prevulcanization, as evidenced by the free sulphur results, is much lower compared to the others in the same series. One possible explanation for the delay in the onset of the prevulcanization of NR latex which has a very low ammonia concentration is that the reaction is inhibited by some substances. The inhibitor involved could be free fatty acids which are present in de-ammoniated ammonia-preserved NR latex. In fully-ammoniated NR latex, the ammonia has of course converted the free fatty acids to the corresponding ammonium salts. As the ammonia is removed, so the free fatty acids re-appear. In order to account for the apparent inhibition of prevulcanization, it is necessary to suppose that these free fatty acids react with the dissolved ZDBC or ZDBC/amine complex to produce inactive compounds. As for the eventual onset of prevulcanization the reasonable assumption is made that there is a dynamic equilibrium established in the aqueous phase of the latex between the dissolved ZDBC and the ZDBC particles. As the dissolved ZDBC reacts with the free acids, so the equilibrium readjusts itself to liberate more ZDBC into the aqueous phase. As a consequence of this process, the fatty acids will eventually all be consumed and the normal prevulcanization will begin when dissolved ZDBC is again available to react with dissolved sulphur to form the active sulphurating agent. This proposal is supported by the observation in the results that once the prevulcanization commences, free sulphur disappears at almost the same rate as when the ammonia content is higher. The lower extents of prevulcanization at any given time of reaction is noted to be primarily a consequence of the presence of the induction period.

An alternative explanation for the induction period when the ammonia content is very low is that under these conditions (i.e., low ammonia content and low pH), the latex does not initially contain sufficient suitable ligands to complex with the zinc atom of ZDBC. But heating for <u>ca</u>. 3 hours at 50°C creates sufficient ligands by hydrolysis of some of the non-rubber substances in NR latex.

In order to test the concept of fatty acids causing the delay in the onset of prevulcanization of NR latex which has a low concentration of ammonia, an ammoniated NR latex (pH 10.20) was deammoniated to pH 8.50, and the pH then re-adjusted to 10.20 using 0.02 M sodium hydroxide solution. The three latices were then prevulcanized in sealed bottles in the usual manner. The results for the variation of free sulphur content with time of prevulcanization are shown in Fig. 6.20. Delay of the onset of prevulcanization was again observed in the prevulcanization of the deammoniated NR latex. The extents of prevulcanization after any given time of reaction were also lower than during the

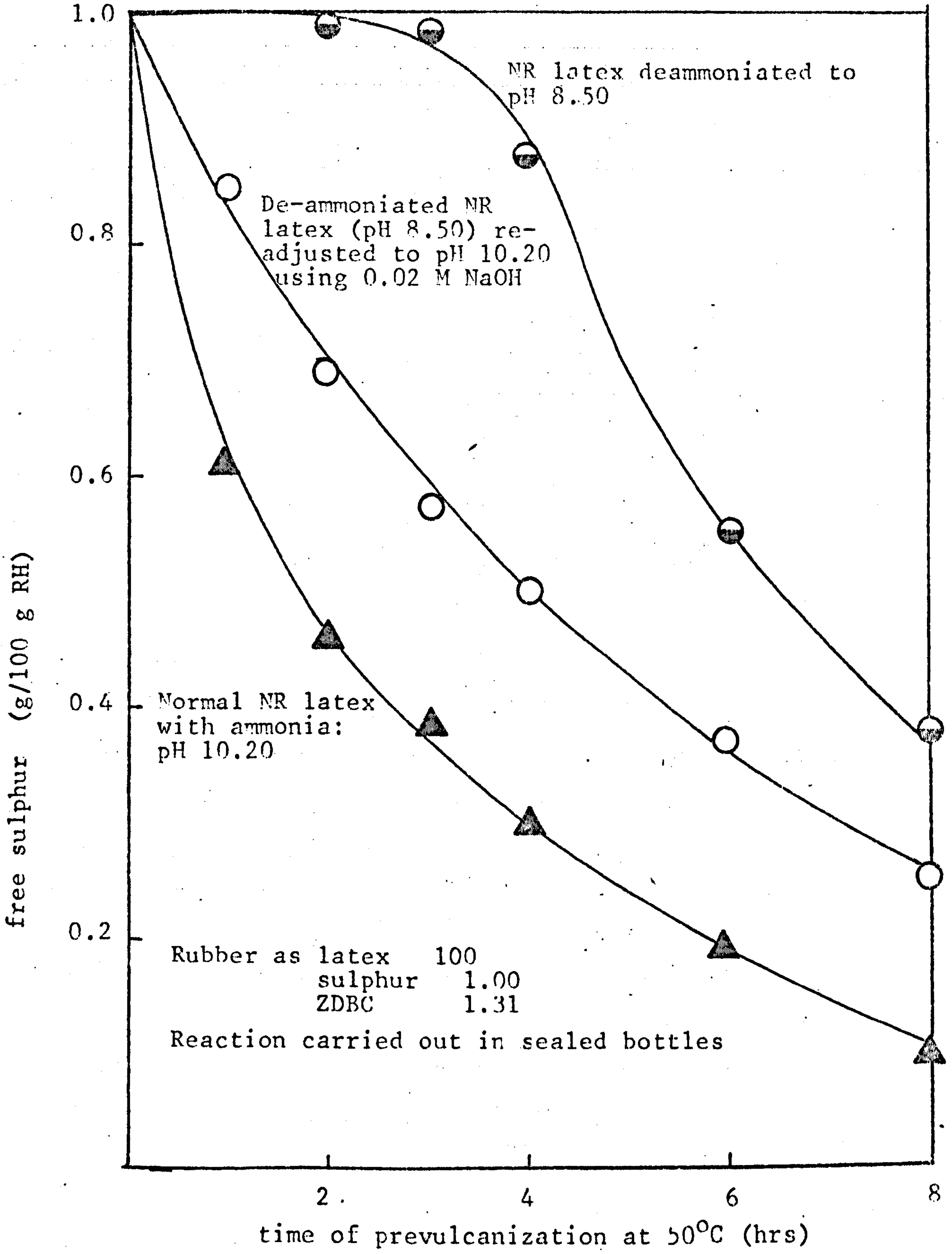


Fig. 6.20 Disappearance of free sulphur during prevulcanization of (a) normal HA latex (pH 10.20), (b) HA latex previously deammoniated to pH 8.50, and (c) HA latex previously deammoniated to pH 8.50 and readjusted to pH 10.20 using sodium hydroxide.

prevulcanization of normal HA NR latex, which has a pH of 10.20. When the alkalinity of the deammoniated latex was readjusted to pH 10.20 using sodium hydroxide, the prevulcanization of this latex shows no delay of the onset of prevulcanization. This is expected if the free fatty acids at low pH act as inhibitors of prevulcanization. It is also evident from Fig. 6.20 that the extents of prevulcanization of the NR latex which had been readjusted to pH 10.20 using sodium hydroxide lay between those for the normal HA latex and those for the deammoniated latex. This observation is consistent with the ideas which have been proposed previously in that, in a latex which has a very small ammonia concentration, the solubility of ZDBC in the aqueous phase of the latex is lowered and consequently the rate of prevulcanization is lower. Therefore the extents of prevulcanization at any given time of prevulcanization are lower.

Results were also obtained for the amounts of unreacted ZDBC in sheets cast from the latex obtained by prevulcanization of deammoniated NR latex. The results are shown in Fig. 6.21. From the results, it can be seen that free ZDBC disappears at a steady rate right from the beginning of the reaction although very little free sulphur disappeared during the early stages of the reaction using deammoniated latex (see Fig. 6.20 and 6.21). This indicates that ZDBC is disappearing by some reaction other than prevulcanization. The indication is consistent with the idea that when the pH is very low, the ZDBC reacts with free fatty acids.

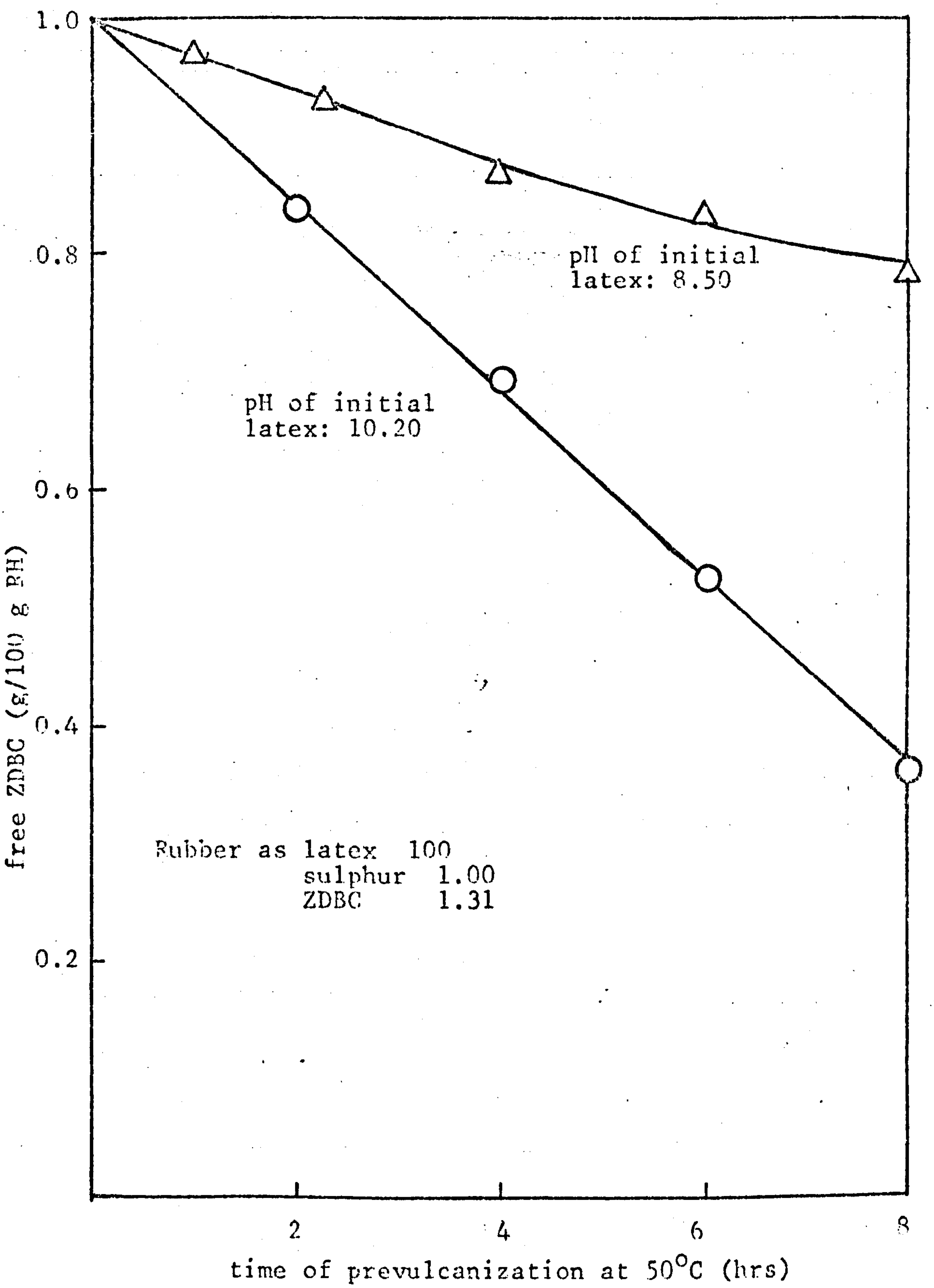


Fig. 6.21. Effect of pH of initial latex upon disappearance of ZDBC during NR latex prevulcanization

CHAPTER 7

DETAILED INVESTIGATION OF NR LATEX PREVULCANIZATION

CHAPTER 7

DETAILED INVESTIGATION OF NR LATEX PREVULCANIZATION

7.1. Effects of Levels of Sulphur and ZDBC upon Prevulcanization of NR Latex

7.1.1. Series A investigations: Effects of varying level of ZDBC with fixed 1.00 pphr sulphur

7.1.1.1. Prevulcanization recipe and reaction conditions

7.1.1.2. Other experimental procedures

7.1.1.3. Results and observations

7.1.1.4. Discussion

7.1.2. Experiments carried out to test possible explanations to account for apparent contradiction between zero-order and and first-order kinetics for disappearance of ZDBC reported in Section 7.1.1

7.1.2.1. Effects of various level of recrystallized ZDBC with fixed 1.00 pphr sulphur

a) Recrystallization of industrial-grade ZDBC

b) Prevulcanization recipe and reaction condition

c) Results and observations

- d) Discussion
- 7.1.2.2. Investigation of other factors which may have contributed to the apparent contradiction between zero-order and first-order kinetics for ZDBC disappearance observed in Section 7.1.1
  - a) Effect of varying amount of dispersing agent upon rate of disappearance of ZDBC during prevulcanization
  - b) Effect of varying number of particles of ZDBC upon rate of disappearance of ZDBC during prevulcanization
- 7.1.3. Series B investigation: Effects of varying level of sulphur with fixed 1.00 pphr ZDBC
- 7.1.3.1. Results and observations
- 7.1.3.2. Discussion
- 7.2. Polymer-Solvent Interaction Parameters, χ, for Vulcanizates Obtained from Prevulcanized Latex Swollen in *n*-Decane
- 7.3. Contribution of Monosulphidic, Disulphidic and Polysulphidic Crosslinks to the Overall Degree of Chemical Crosslinking for Vulcanizates Obtained from Prevulcanized Latex
  - 7.3.1. Prevulcanization recipe and reaction conditions

7.3.2. Other experimental procedures

7.3.3. Results and discussion

7.4. Effect of Varying Nature of Dithiocarbamate Accelerator upon Latex Prevulcanization

7.4.1. Effect of variation of alkyl chain length of zinc dithiocarbamate upon NR latex prevulcanization

7.4.1.1. Prevulcanization recipes and reaction conditions

7.4.1.2. Results and discussion

7.4.2. Effect of varying metal counterion of diethyl dithiocarbamate upon NR latex prevulcanization

7.4.2.1. Prevulcanization recipe and reaction conditions

7.4.2.2. Results and discussion

CHAPTER 7

DETAILED INVESTIGATION OF NR LATEX PREVULCANIZATION

The investigations reported in the previous chapter were aimed at answering some very basic questions pertaining to NR latex prevulcanization. Such question as have been dealt with are the following: How does the prevulcanizatin of NR latex differ from that of synthetic cis-polyisoprene latex and from the vulcanization of rubber in the dry form? What are the solubilities of sulphur and ZDBC in the aqueous phase of NR latex and synthetic cis-polyisoprene? What are the effects upon NR latex prevulcanization of the ammonia which is present in the latex as a preservative? It was hoped that the answers to these questions would lead to some initial ideas concerning the mechanistic aspects of the prevulcanization of NR latex, as well as providing useful basic information.

The present chapter reports a more detailed investigation of the prevulcanization of NR latex. In particular, it describes and discusses the effects of some of the more obvious variations which can be made in respect of the prevulcanization recipe. The variations in recipe consisted of different levels of sulphur and ZDBC (ZDBC was used instead of the more popular ZDEC because it gives faster prevulcanization reactions), the use of various levels of a purified ZDBC with constant level of sulphur; variation of the alkyl chain length of the zinc dialkyldithiocarbamate, and variation of the metal counter-ion of the dialkyldithiocarbamate. The aspects of the prevulcanization of NR latex which were investigated included the following: free and network-combined sulphur; rate of ZDBC disappearance as a function of prevulcanization time; variation of degree of chemical crosslinking and types of sulphur crosslinks as prevulcanization progressed and variation of tensile strength of cast films as a function of prevulcanization time. As far as is known, systematic investigations of this nature have not so far been reported in any published literature. Therefore, the present investigation has provided very useful information concerning the sulphur prevulcanization of NR latex using metal dialkyldithiocarbamates as accelerators. Apart from the usefulness of the information which has become available from this study, it was also hoped that a better understanding of the subject of NR latex prevulcanization would be achieved through interpretation of the results, perhaps in drawing upon the concepts and theories which have been developed from the investigations reported in the previous chapter.

7.1. Effects of Levels of Sulphur and ZDBC upon Prevulcanization of NR Latex

Two series of experiments, Series A and B, were carried out. In Series A, the prevulcanization behaviour of NR latex systems which had a fixed level of sulphur (1.00 pphr) but different levels of ZDBC was investigated.

In the Series B experiments, the prevulcanization behaviour of NR latex systems which had a fixed level of ZDBC (1.00 pphr) but different levels of sulphur was investigated.

7.1.1. Series A investigations: Effects of varying level of ZDBC with fixed 1.00 pphr sulphur

The primary aim of this series of experiments was to study the effects of different levels of ZDBC upon the prevulcanization behaviour of NR latex keeping the level of sulphur fixed.

7.1.1.1. Prevulcanization recipe and reaction conditions

HA latex was first deammoniated to pH 9.8 as described previously in Chapter 5. It was then used without further treatment in four prevulcanization recipes. The recipes for the four separate experiments in the series are shown in Table 7.1.

Table 7.1. Recipe of experiments in Series A investigation

	parts by weight(dry)			
Ingredient Experiment No.	1	2	3	4
Rubber as 50% latex	100	100	100	100
Potassium Oleate(added as 10% solution before deammoniation of latex)	0.75	0.75	0.75	0.75
Sulphur (33.33%)	1.00	1.00	1.00	1.00
ZDBC (33.33%)	0	0.30	1.00	2.00

The compounded latex contained about 50% total solids. The prevulcanization was carried out in a 2-litre reaction vessel at 50±0.5°C, the temperature being maintained constant by immersing the reaction vessel in a thermostatted water bath. Samples were taken from the reaction vessel at hourly intervals. To arrest the reaction after sampling, the prevulcanized latex samples in glass bottles were immediately chilled in ice water for one hour and were then stored in a refrigerator at 0°C awaiting further use.

7.1.1.2. Other experimental procedures

To assist presentation of the sequence of experiments carried out in the present investigation, a simplified flow chart is given in Fig. 7.1. All the experimental procedures for, and the principles underlying, the experiments such as film and sheet casting, determination of degree of cross-linking by reticulometry, analysis for network-combined and free sulphur and free ZDBC, have been described in detail in Chapter 5.

7.1.1.3. Results and observations

The results for the variation of free sulphur with prevulcanization time in recipes containing different levels of ZDBC, are shown in Fig. 7.2. The results of the reaction system which did not contain added ZDBC are omitted. This is because the reaction was very slow and appeared to be non-existent even up to 12 hours of prevulcanization. At any given ZDBC, the free sulphur decreased progressively with increasing prevulcanization time. The decrease was very

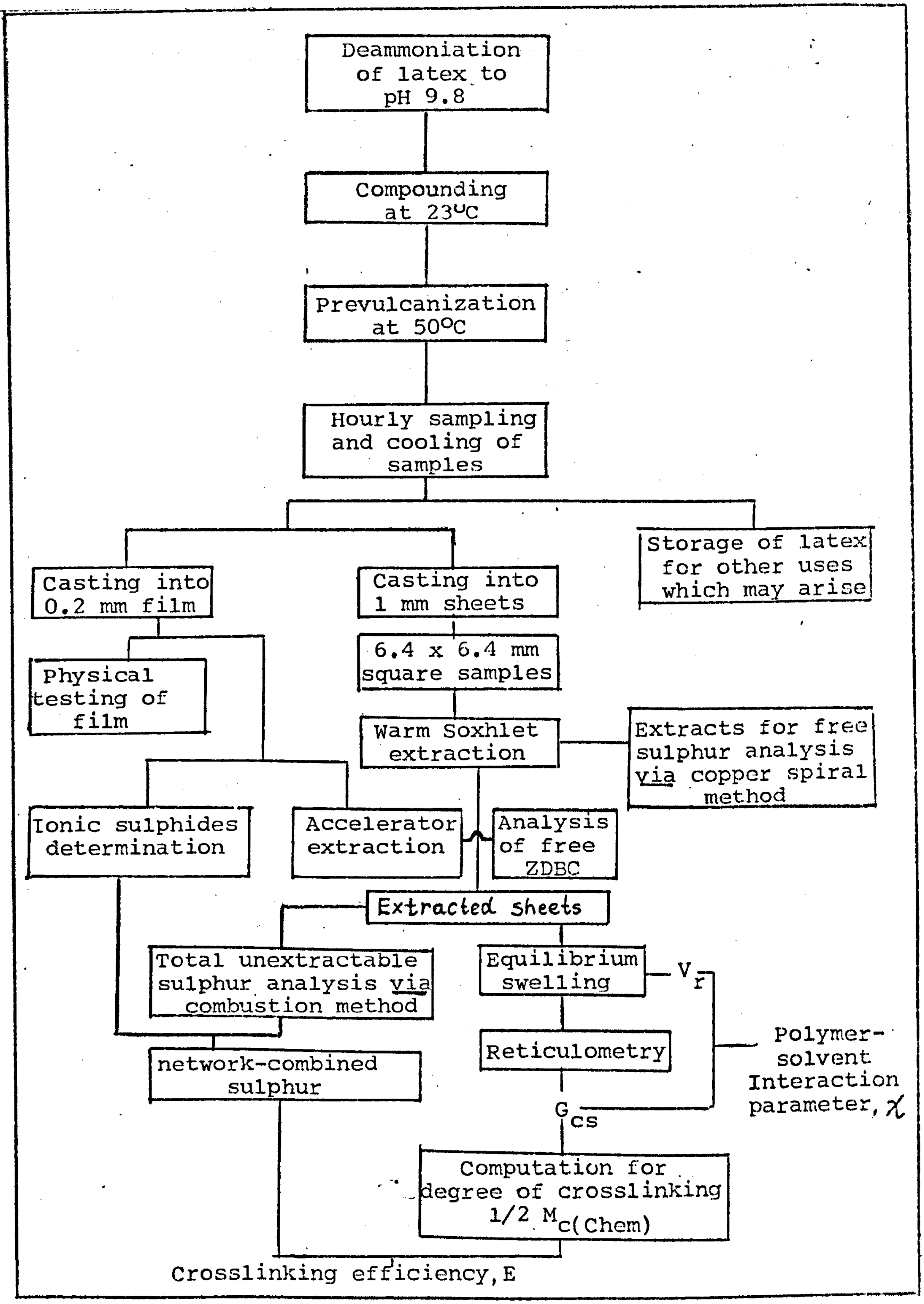


Fig. 7.1 Simplified flow chart showing experimental procedures for series A and series B experiments

rapid over the first two hours of prevulcanization, after which, the decrease gradually slowed down. In the case of the system which contained 0.30 pphr ZDBC. 50% of the added sulphur was found to have reacted only after about 8 hours of prevulcanization. This contrasts with the system which contained 1.00 pphr ZDBC, for which it took less than 2 hours for the same amount of added sulphur to be reacted. It is interesting to note that system which contained 2.00 pphr ZDBC behaved contrary to expectation, in that the free sulphur was higher than in the system which contained 1.00 pphr ZDBC at any given prevulcanization time.

Results for network-combined sulphur are shown in Fig. 7.3. They indicate that almost all the added sulphur which did not appear as free sulphur in Fig. 7.2 was chemically-combined with the rubber. This finding is also supported by the negligible amounts of ionic sulphides which were found in all the samples in which analysis for ionic sulphides was carried out. It can also be seen from Fig. 7.3 that the system which contained 2.00 pphr ZDBC gave lower values of network-combined sulphur after any given time of prevulcanization than did the system which contained 1.00 pphr ZDBC. This is consistent with the observations made concerning the free sulphur results.

Fig. 7.4 shows the results for the variation of degree of chemical crosslinking with prevulcanization time at different levels of ZDBC. The results are in general

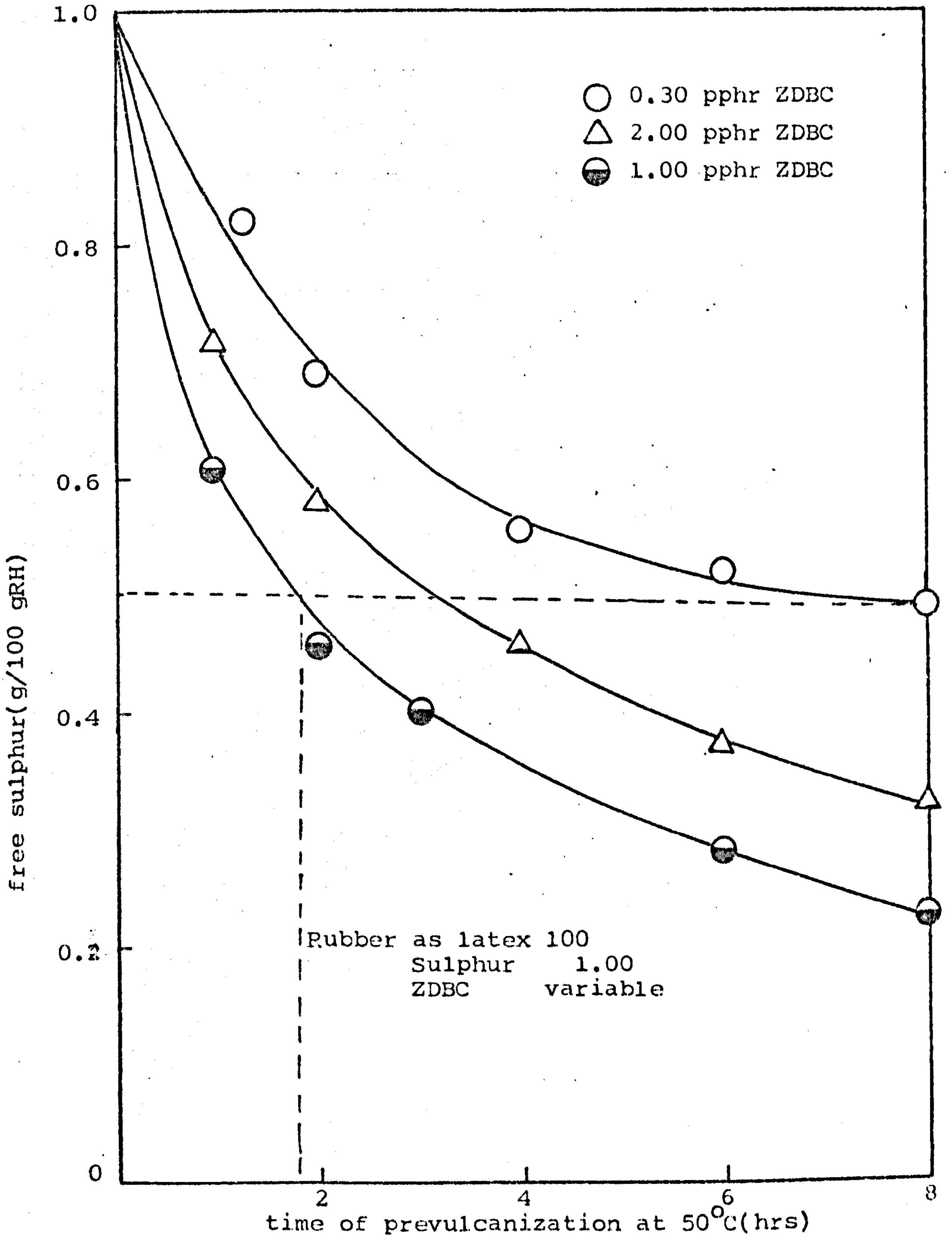


Fig. 7.2 Effect of different levels of ZDBC upon free sulphur as a function of time of prevulcanization (sulphur level constant at 1.00 pphr)

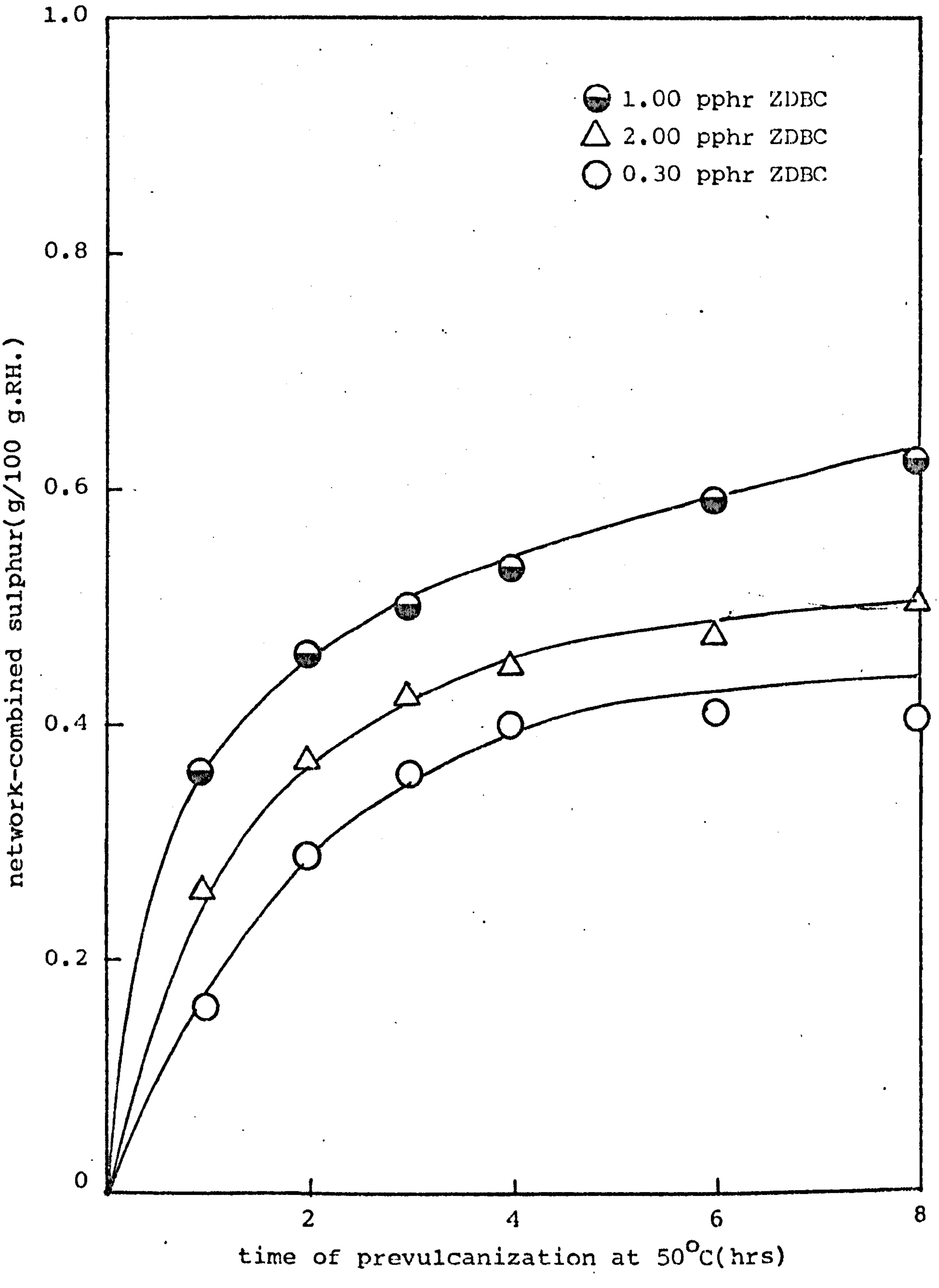


Fig. 7.3 Effect of different levels of ZDBC upon network-combined sulphur as a function of time of pre-vulcanization(sulphur level constant at 1.00 pphr)

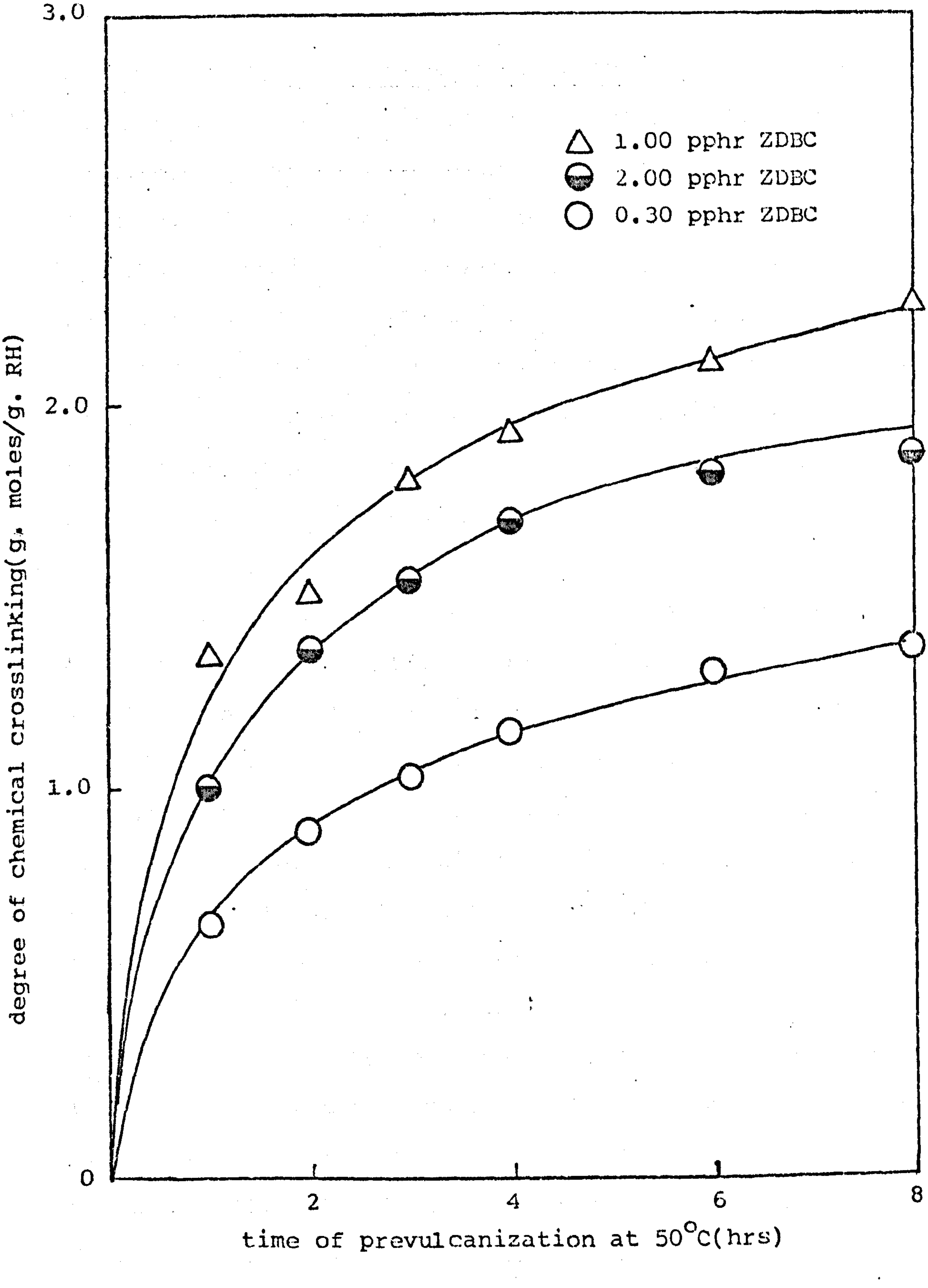


Fig. 7.4 Effect of different levels of ZDBC upon degree of chemical crosslinking as a function of time of prevulcanization (sulphur level constant at 1.00 pphr)

agreement with the results for free and network-combined sulphur: increase in the amount of sulphur combined results in a corresponding increase in degree of chemical crosslinking. The apparent anomaly noted earlier concerning the results for free and network-combined sulphur for the system containing 2.00 pphr ZDBC is also apparent from Fig. 7.4; the results for degree of chemical crosslinking for vulcanizates obtained using 2.00 pphr of ZDBC were lower than those for vulcanizates obtained from the system containing 1.00 pphr of ZDBC at any given prevulcanization time.

Fig. 7.5 shows the results for the variation of free (unreacted) ZDBC with time of prevulcanization at different levels of added ZDBC. In contrast to the results shown in Fig. 7.2-Fig. 7.4 for network-combined sulphur, free sulphur and crosslink densities, the results for free ZDBC as a function of prevulcanization time can all be represented by straight lines. This implies that the rate of disappearance of ZDBC is independent of the concentration of ZDBC in any given reaction system. In terms of reaction kinetics, the rate of ZDBC disappearance is of zero-order with respect to ZDBC concentration. However, the results shown in Fig. 7.5, taken as a whole appear to contradict the conclusion concerning the rate of disappearance of ZDBC being independent of the ZDBC concentration. Thus, suppose a line is drawn across the graph parallel to the time axis at 0.80 pphr ZDBC, as shown in Fig. 7.5. The line cuts the lines for the systems which contained 1.00 pphr ZDBC at just after 2 hours

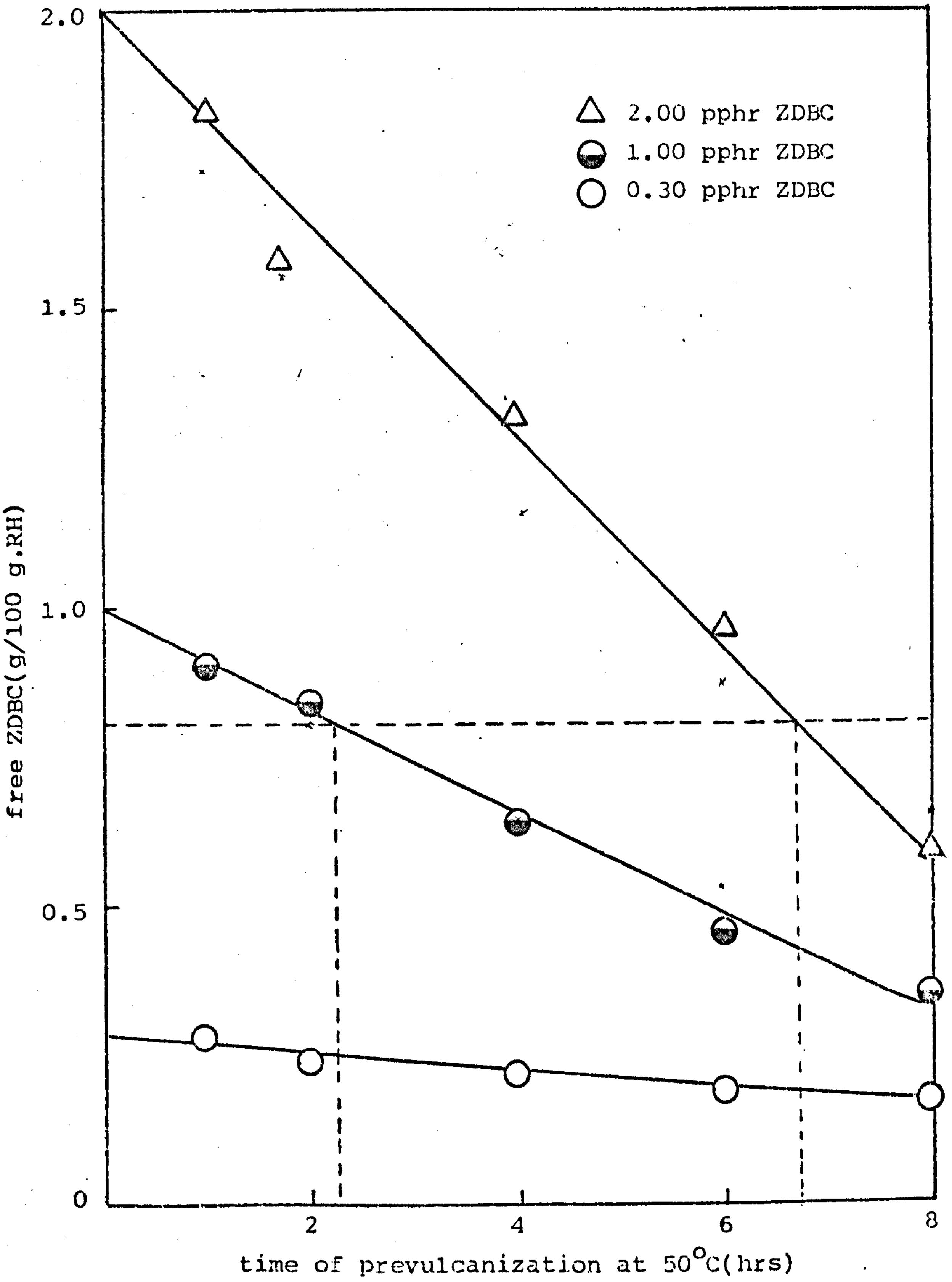


Fig. 7.5 Effect of different levels of ZDBC upon free ZDBC as a function of time of prevulcanization (sulphur level constant at 1.00 pphr)

and about 7 hours of prevulcanization respectively. Hence, after these respective times of prevulcanization, in both the systems there was 0.80 pphr ZDBC. But if we consider the rate of disappearance of ZDBC for these two systems from this concentration of ZDBC onwards, it can be seen from the gradients of the two straight lines, that the two rates of disappearance were very different. In the system which contained 2.00 pphr of ZDBC initially, the remaining 0.80 pphr ZDBC was disappearing at a much faster rate compared to the system which contained initially 1.00 pphr. These considerations lead to the conclusion that whereas the rate of disappearance of ZDBC is independent of ZDBC concentration in any one system, when the results for systems having various levels of ZDBC are considered together, the rate of ZDBC disappearance is dependent upon the initial level of ZDBC. Indeed, further consideration of the results showed that the dependence of rate of ZDBC disappearance upon the initial level is first-order. This is shown in Fig. 7.6 where the zero-order rates of disappearance of ZDBC for the individual system are plotted against the initial level of ZDBC. The data are well represented by a straight line which passes through the origin. Possible reasons for this phenomenon will be discussed in the following sections and in Section 7.1.2.

The results for the degree of chemical crosslinking can be combined with the results for network-combined sulphur to yield estimates of a parameter known as "cross-

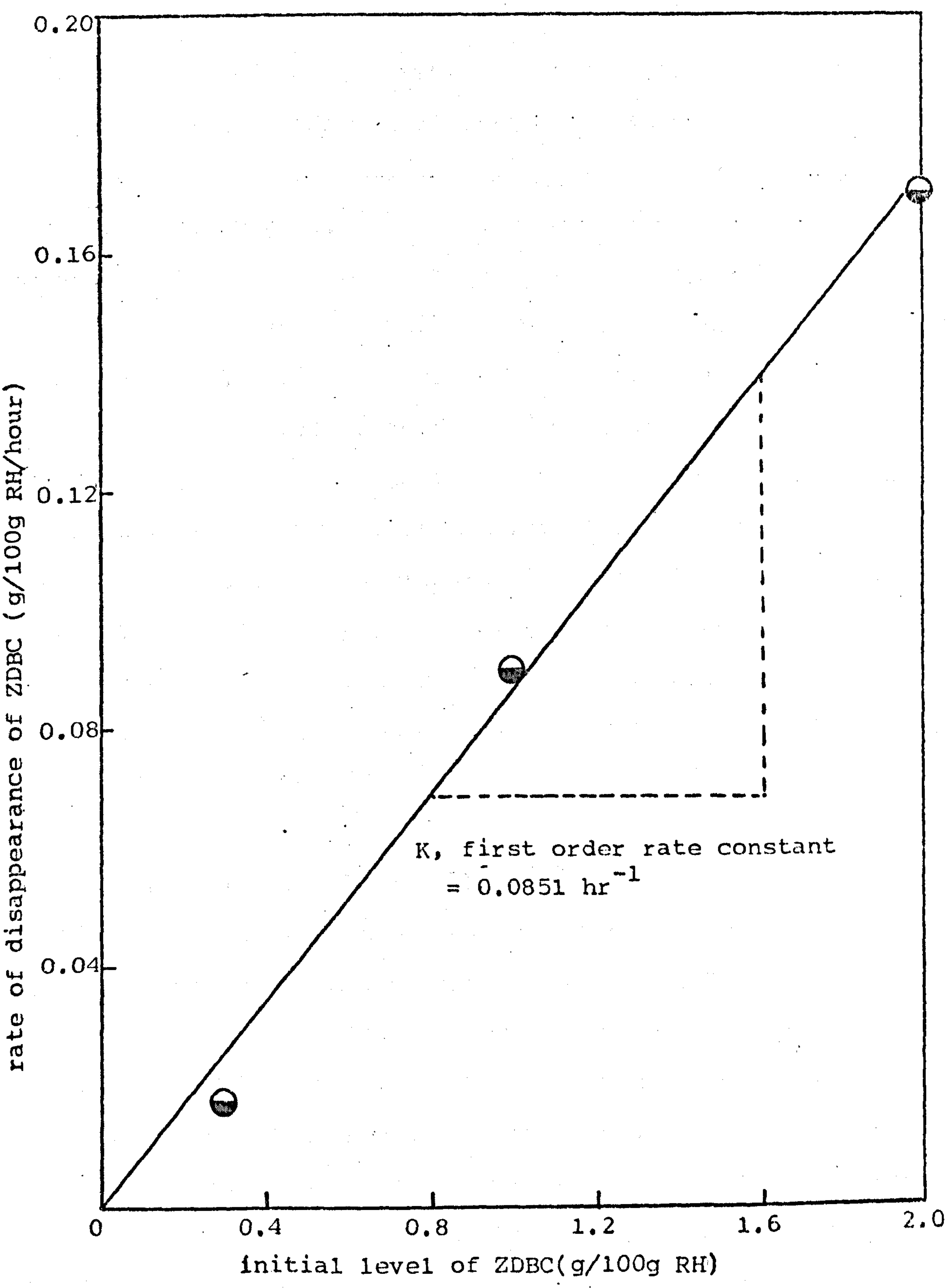


Fig. 7.6 Plot of rate of disappearance of ZDBC against initial added level of ZDBC.

linking efficiency", E (which should really be crosslinking "inefficiency"). As previously defined this is the average number of atoms of combined sulphur per single chemical crosslink. Fig. 7.7 shows the results for the variation of crosslinking efficiency, E, with time of prevulcanization at different levels of ZDBC. The prevulcanization system which contained 0.30 pphr of ZDBC had a crosslinking efficiency of 11 during the early stages of prevulcanization. It gradually reduced to about 9 after some 8 hours of prevulcanization. On the other hand, the system which contained 2.00 pphr ZDBC had, a crosslinking efficiency of approximately 8, and this remained unchanged over the 8 hours of prevulcanization. This result is consistent with theoretical expectation based on chemistry of dry vulcanization of NR.

Results for the tensile strengths of air-dried cast films obtained from the prevulcanized latices as a function of prevulcanization time are shown in Fig. 7.8. The results show that the prevulcanization system which contained only 0.30 pphr ZDBC (and 1.00 pphr of sulphur) gave air-dried cast films having tensile strengths which were some three times higher than the tensile strengths of film from prevulcanized latices made using the recipe which contained no added ZDBC. Increasing the level of ZDBC to 1.00 pphr and 2.00 pphr did not seem to have any significant effect upon the tensile strength of air-dried cast films.

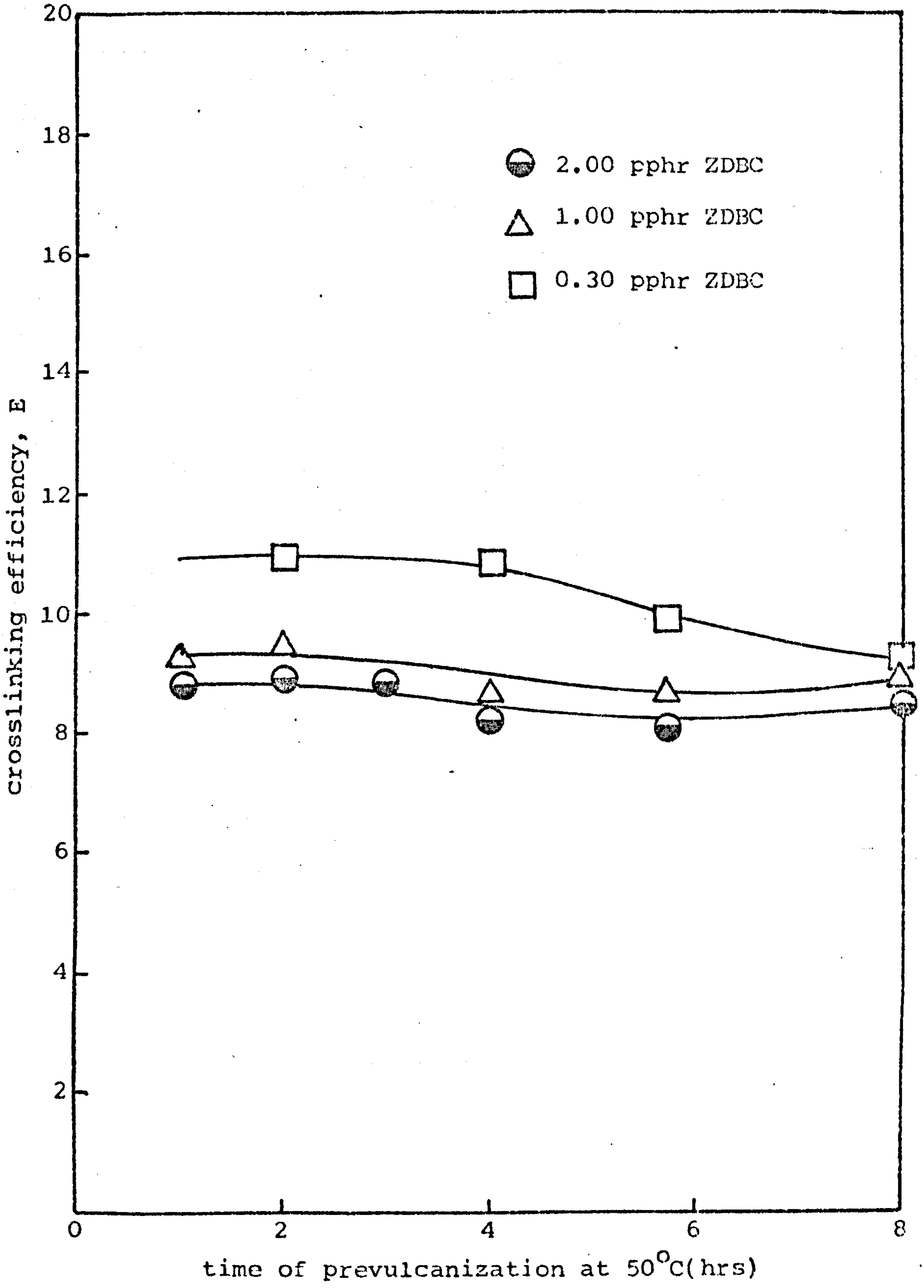


Fig. 7.7 Effect of different levels of ZDBC upon crosslinking efficiency as a function of prevulcanization time (sulphur level constant at 1.00 pphr).

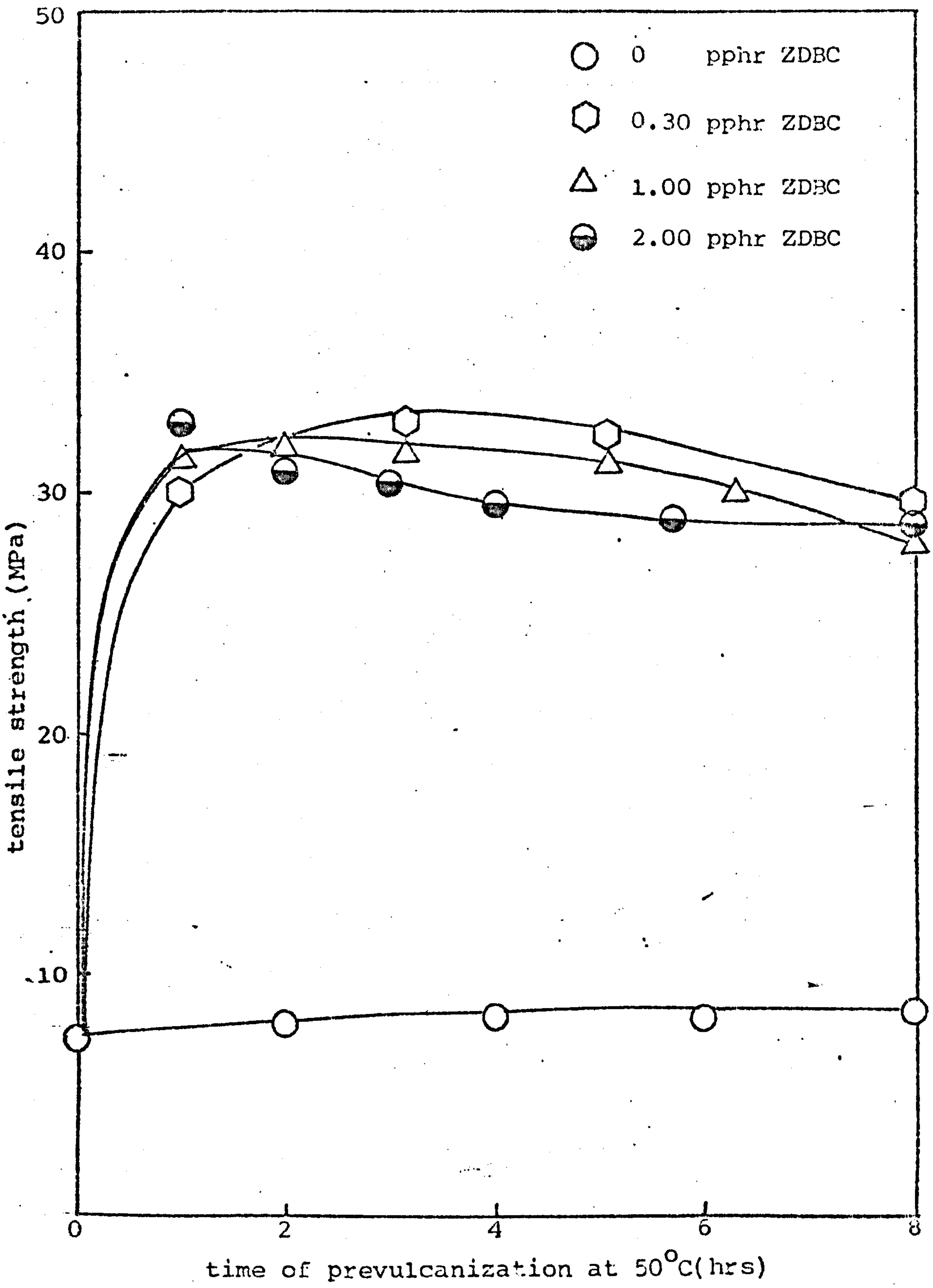


Fig. 7.8 Tensile strength of air-dried cast films obtain from prevulcanized latex containing different levels of ZDBC as a function of prevulcanization time (sulphur level constant at 1.00 pphr).

7.1.1.4. Discussion

In the present discussion, it is proposed to consider to what extent some of the ideas developed in the previous chapter can be used to explain the observations made in the course of the Series A experiments. For this purpose, it is therefore thought useful to recapitulate at this point some of the suggestions which have been made in Chapter 6. It has been shown that ZDBC only dissolves to a limited extent in the aqueous phase of NR latex. It has been suggested that the dissolution of ZDBC is assisted by the coordination to the zinc atom of ZDBC of ammonia or nitrogeneous bases which are present in NR latex. It has also been postulated that, during prevulcanization, a dynamic equilibrium is established in the aqueous phase of the latex between the largely undissolved ZDBC particles and the molecularly dissolved ZDBC. It has also been proposed that, during latex prevulcanization, the dissolved ZDBC or its ammonia/amine complexes react with molecularly dissolved sulphur in the aqueous phase of the latex, thereby forming an active sulphurating agent. This vulcanization-active species is then presumably partitioned into the rubber phase, thereby starting the crosslinking reaction within the rubber particles.

Returning to the present results, consider first the results for free and network-combined sulphur shown in Figs. 7.2 and 7.3. It would be expected that, if the ZDBC was dissolved to only a limited extent in the aqueous phase of the latex, as has been suggested in Chapter 6, the level of added ZDBC should not have any effect upon the course of latex prevulcanization provided that excess ZDBC is present as a solid phase. However, this is not observed to be the case in the present series of investigations. It was observed that the prevulcanization system which contained 0.30 pphr ZDBC had a lower rate and extent of sulphur combination compared to the prevulcanization system which contained 1.00 pphr ZDBC. In order to account for this observation, it is necessary to suppose that the ZDBC used in the present investigation contained some form of active impurity. This supposition is reasonable, as the ZDBC used was an industrial grade, and was used for the preparation of dispersions without any further purification, one of the impurities in the ZDBC could have been dibutylamine, a raw material which is used in the synthesis of ZDBC. If an impurity such as dibutylamine was present in the ZDBC after the synthesis, then a possible explanation for the present results can be given. Higher levels of ZDBC will then imply higher levels of impurity in the latex. It is reasonable to suppose that a nitrogeneous base such as dibutylamine will behave as a complexing ligand for ZDBC as ammonia or other naturally-occurring amines and nitrogeneous bases in NR latex. Hence, comparing the prevulcanization system which contained 1.00 pphr of ZDBC to that which contained 0.30 pphr of ZDBC, the presence of a higher proportion of an impurity such as dibutylamine, presumably soluble in the aqueous phase of the latex, may have resulted in a higher solubility of the ZDBC in the aqueous phase of the latex, because of complex formation of the ZDBC with the impurity. The presence of a higher concentration of dissolved ZDBC complex in turn leads to higher concentration of active sulphurating agent in the aqueous phase from the reaction of the dissolved ZDBC complex with molecularly-dissolved sulphur. This would result in a higher rate and extent of sulphur combination when these active sulphurating agents eventually react with the rubber hydrocarbon.

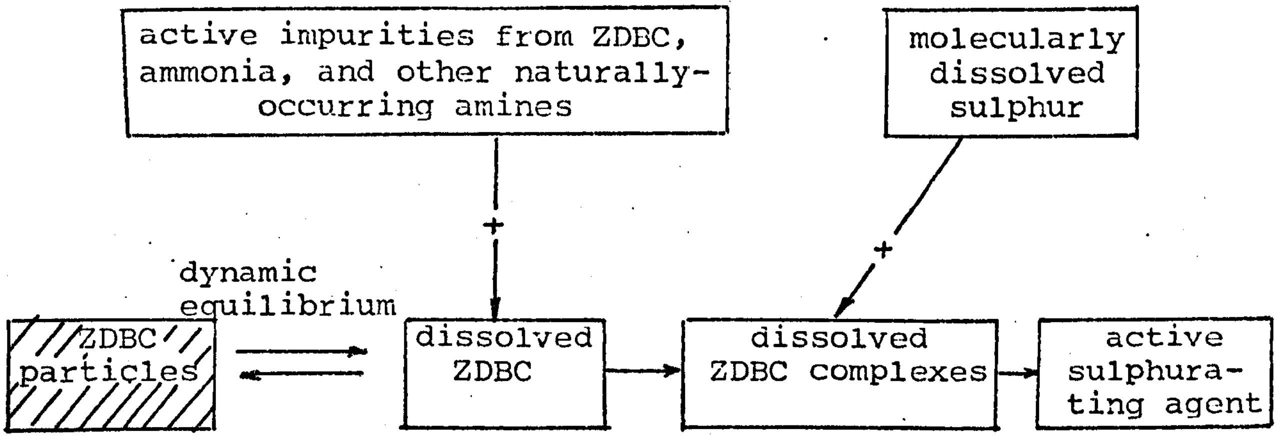
An alternative but related type of impurity which might be present in ZDBC is a ZDBC-dibutylamine complex. A complex of this type could be formed as a secondary product during the synthesis of ZDBC. If this ZDBC-dibutylamine complex impurity is soluble in the aqueous phase of the latex during prevulcanization, then, following the same argument as previously, a higher level of ZDBC will result in a higher level of these impurities in the latex. It thus follows that the results observed in Fig. 7.1 concerning the prevulcanization systems which contained 0.30 pphr ZDBC and 1.00 pphr ZDBC can be explained.

Having discussed possible reasons for the differences in the latex prevulcanization behaviour at the low and medium levels of ZDBC (i.e., 0.30 pphr and 1.00 pphr), the same reasoning should be able to explain the behaviour at the highest level (2.00 pphr) of ZDBC. It can be deduced from Fig. 7.1 and Fig. 7.2 that there exists a level of ZDBC at between 1.00-2.00 pphr at which the rate of combination of sulphur is a maximum. When this optimum level of ZDBC is exceeded (as in the case of the system containing 2.00 pphr), the rate and extent of sulphur combination are reduced. Hence, it is concluded that any excess of ZDBC over the optimum amount required has a deleterious effect upon latex prevulcanization. An explanation that could account for both the retarding effect upon prevulcanization of high levels of ZDBC (such as 2.00 pphr), and at the same time still be consistent with the observations concerning the effect upon prevulcanization of low and medium levels of ZDBC is one which again hypothesises that the effects are associated with impurities in the ZDBC. It is evident from the results for free and network-combined sulphur shown in Figs. 7.2 and 7.3 that the rate and extent of sulphur combination in the prevulcanization system which contained 2.00 pphr of ZDBC is reduced compared to the system which contained 1.00 pphr ZDBC. Yet from Fig. 7.5, which shows the results for the disappearance of ZDBC during prevulcanization, it can be seen that the rate of disappearance of ZDBC is much faster in the system which contained 2.00 pphr of added ZDBC than in the system which contained 1.00 pphr of added ZDBC. Therefore, from the two sets of results, the implication is that, eventhough ZDBC disappeared at a much faster rate in the system which contained 2.00 pphr of ZDBC, yet somehow the reaction with sulphur to form the active sulphurating agent was reduced compared with system which contained 1.00 pphr ZDBC. Therefore, it is possible that in systems which contained high levels of ZDBC, the dissolved ZDBC complexes which are formed during prevulcanization react preferentially with certain impurities of ZDBC to form a secondary product, instead of reacting with sulphur to form an active sulphurating agent. It is then necessary to suppose that the resultant secondary product has a negligible or very much lower affinity for sulphur to form the active sulphurating agent than does the original ZDBC complex.

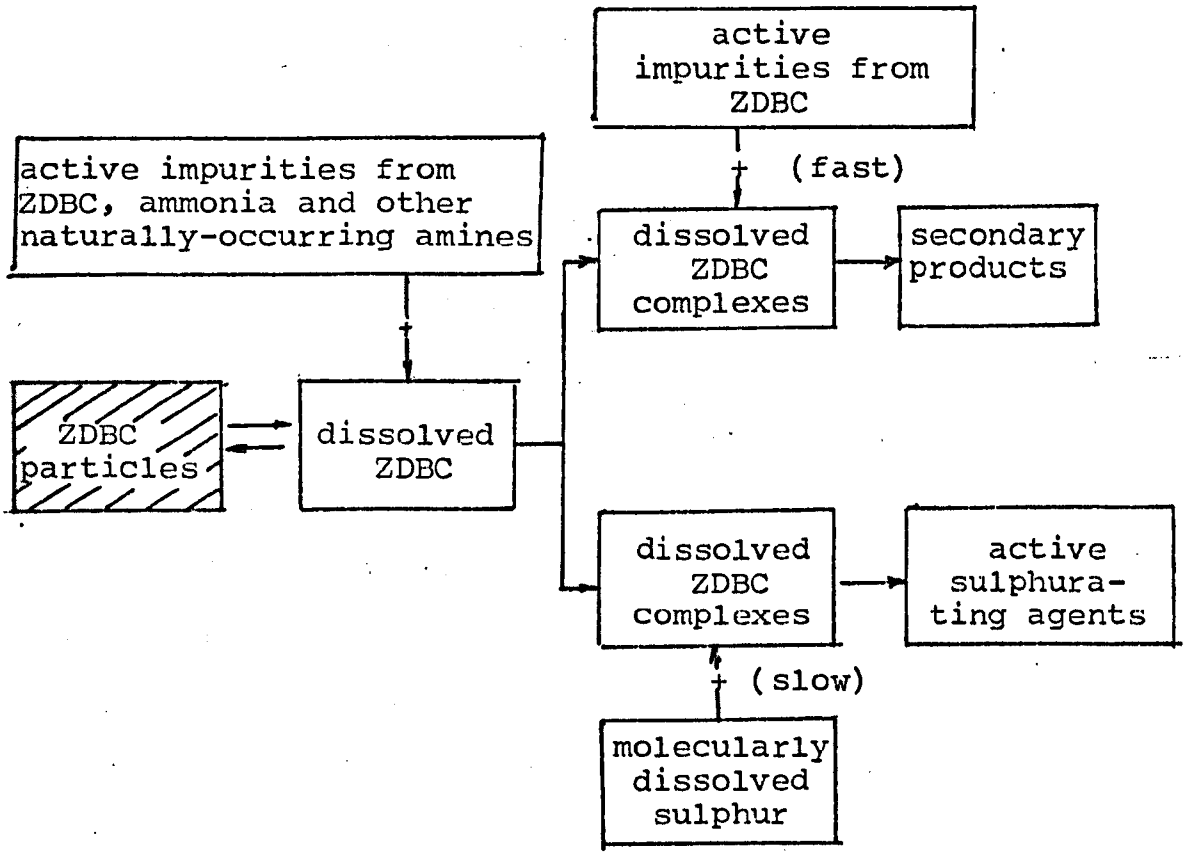
Hence, the reaction scheme shown in Fig. 7.9 may represent the series of reactions which take place between added ZDBC and sulphur during prevulcanization in systems containing respectively low, medium and high levels of ZDBC.

An analysis was carried out on the data of free sulphur in the hope of finding a suitable reaction law or equation to represent them. The exercise was abandoned however, when it was found not possible to represent the set of free sulphur data by any simple order of reaction (integer or fractional).

Results for the variation of degree of chemical crosslinking with time of prevulcanization at different levels of ZDBC (Fig. 7.4) are also consistent with the concept of the existence of an optimal level of ZDBC during prevulcanization. Values for degrees of chemical crosslinking obtained in the present investigation of between 1 and 2×10^{-5}



a) For prevulcanization system which contained low and medium levels of ZDBC



b) For prevulcanization system which contained high levels of ZDBC

Fig. 7.9 Reaction scheme showing series of reactions which may take place between ZDBC and sulphur during NR latex prevulcanization at 50°C gmoles/gRH are somewhat low compared to those for a typical dry rubber vulcanization, which are between 3 and 5x10^{-5}g mole/gRH.(165) But the comparison may not be valid because of differences in vulcanization recipe and reaction conditions. However, it is nevertheless interesting to note that, inspite of the comparatively low degree of chemical crosslinking, there are only about 8-11 combined sulphur atoms for each crosslink present, as revealed by the crosslinking efficiency value (Fig. 7.7). These lower E values, compared to values of 15-20 of dry rubber vulcanization,(165) imply that in latex prevulcanization there is more efficient use of the combined sulphur and a low degree of main-chain modification by cyclic sulphides and other groups. The E-values obtained in the present work are also in agreement with those of Chong(63) who has investigated the post-vulcanization of films obtained from NR latex.

Fig. 7.8 shows that the maximum tensile strength of cast film is attained when the latex from which the films are obtained is prevulcanized for about one hour. Different levels of ZDBC in the prevulcanization recipe do not seem to have any significant effect upon the tensile strength of the films obtained from the prevulcanized latex. Whereas there is a definite relationship observed when the results for network-combined sulphur are plotted against the corresponding results of degree of chemical crosslinking (Fig. 7.10), the same cannot be said of the results for tensile strength and degree of chemical crosslinking (Fig. 7.11).

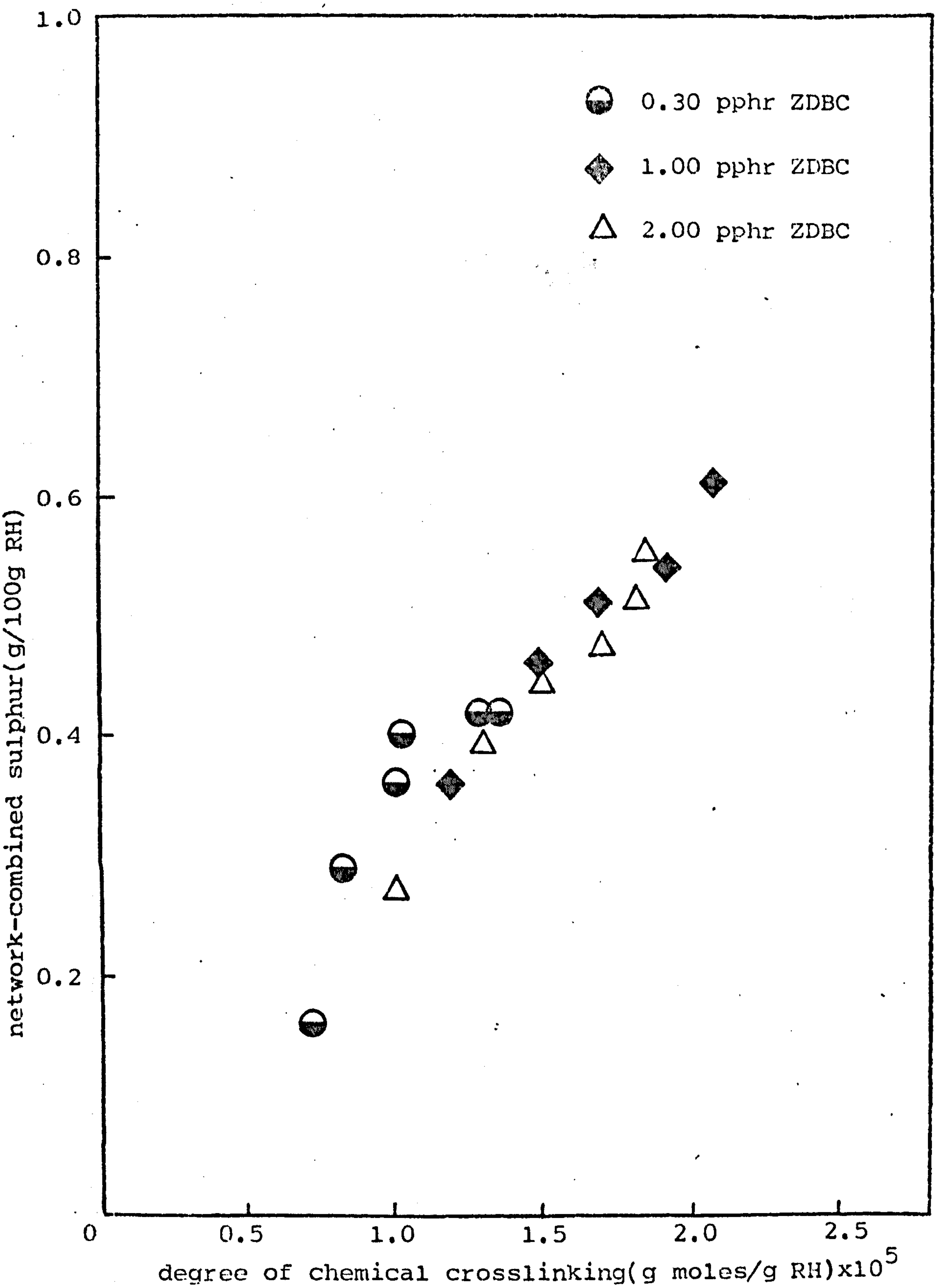


Fig. 7.10 Relationship between network-combined sulphur and degree of chemical crosslinking for NR latex prevulcanization at 50°C (sulphur level at constant 1.00 pphr, ZDBC, varied over range 0.30 to 2.00 pphr).

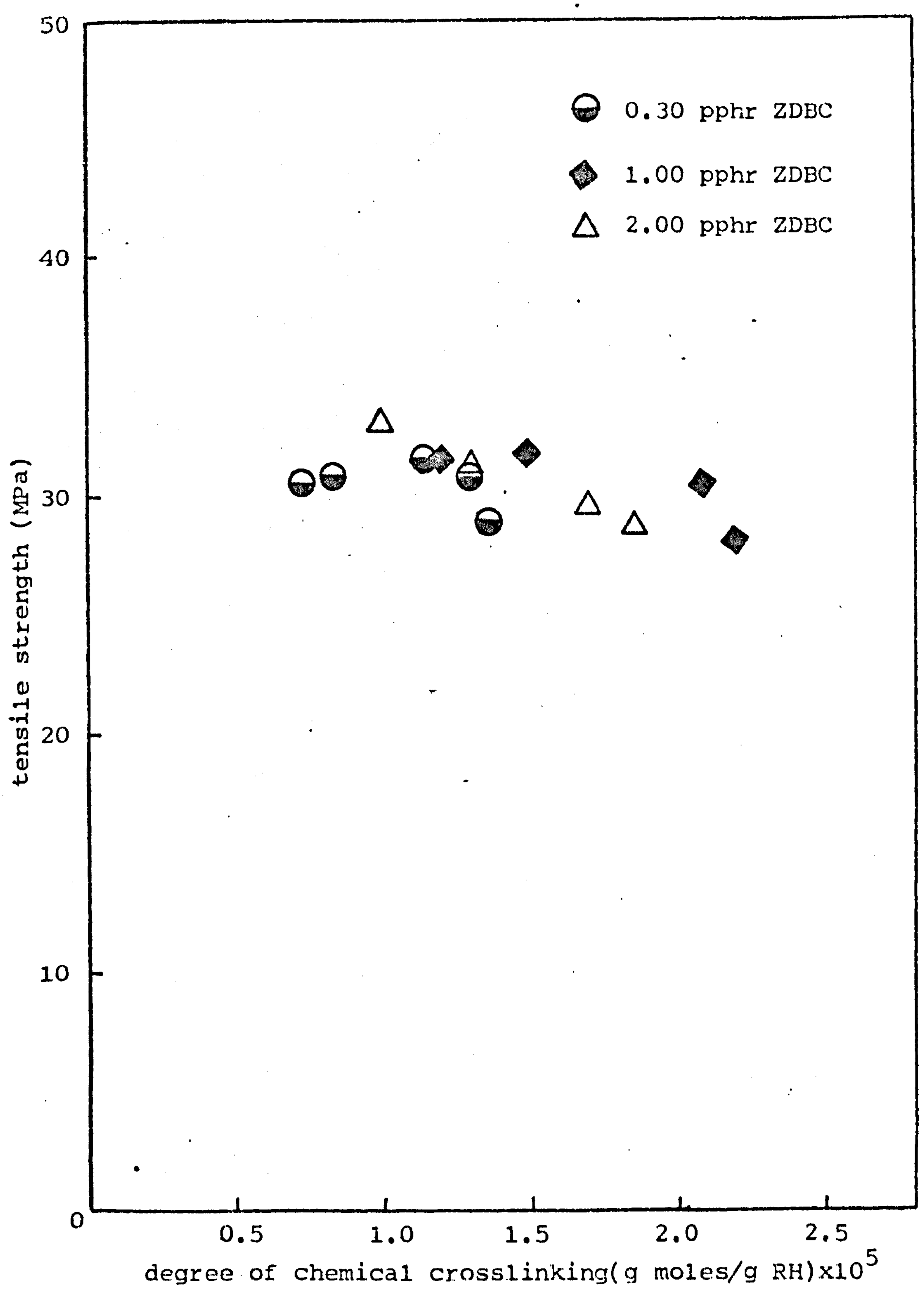


Fig. 7.11 Relationship between tensile strength and degree of chemical crosslinking for NR latex prevulcanization at 50°C (sulphur level at constant 1.00 pphr).

It thus appears that tensile strength is essentially independent of the degree of chemical crosslinking. This latter finding confirms the theory proposed by Humphreys and Wake.(12) They suggested that the strength of cast films obtained from prevulcanized latex is a manifestation of the secondary-valence forces between the rubber molecules, and therefore is little affected by the extent of sulphur combination of the inner structure of the rubber particles. Hu et al.(21,25) however have reservations concerning the theory proposed by Humphreys and Wake. They believed that, because of the different vulcanizing systems involved (Humphreys and Wake used different levels of sulphur in their experiments), there is the possibility of a different vulcanizing mechanism being operative. In their opinion, it is possible then for vulcanizates which possess different extents of sulphur combination to appear to have the same crosslink density, and hence the same tensile strength. The present results, however, confirm that there is a direct relationship between network-combined sulphur and degree of chemical crosslinking (Fig. 7.10). And since in Fig. 7.11 tensile strength is plotted as a function of degree of chemical crosslinking, whereas Humphreys and Wake plotted tensile strength vs. combined sulphur, the doubt of Hu et al. is therefore unfounded. It nevertheless remains that the present results are then contradictory to those of Hu et al.(21) Working on one prevulcanization recipe, the Chinese workers varied the temperature of prevulcanization from 50°C-90°C, because they believed that the vulcanization mechanism is probably less prone to variation if the degree of vulcanization is varied in this way than if different vulcanization recipes are used. Results for network-combined sulphur, crosslink density and tensile strength were obtained. When these results were plotted against each other (see Fig. 2.12), the conclusion was reached that tensile strength is dependent upon the crosslink density of the rubber molecules in the inner structure of the rubber particles.

In Figs. 7.5 and 7.6 the apparent contradiction between zero-order kinetics for the disappearance of ZDBC in individual prevulcanization reactions, and yet a first-order dependence of the zero-order rate upon the initial ZDBC level, is unusual. It is, however, interesting to note that this phenomenon is consistent with, and can be explained by the hypothesis of active impurities in ZDBC which has already been proposed. According to this hypothesis, the higher is the initial level of ZDBC, the higher will be the concentration of active impurity present in the reaction system; and this higher concentration of active impurity reacting with the molecularly-dissolved ZDBC is responsible for the faster rate of ZDBC disappearance at higher level of initial added ZDBC. More importantly because the concentration of such impurities in the reaction mixture is first-order in initial ZDBC level, therefore, the observation that the zero-order rate of disappearance of ZDBC in individual prevulcanization reaction is first-order with respect to initial ZDBC level is thus fully consistent with this hypothesis.

To test the proposed hypothesis, the series of experiments in Series A was repeated using recrystallized ZDBC. The results of this latter investigation will be reported in Section 7.1.2.1.

Other possible explanations for the results for the kinetics of ZDBC disappearance will also be discussed in the following section, Section 7.1.2.

7.1.2. Experiments carried out to test possible explanations to account for apparent contradiction between zero-order and first-order kinetics for disappearance of ZDBC reported in Section 7.1.1.

It has already been demonstrated that, in the Series A experiments, a curious phenomenon was encountered concerning the kinetics of the disappearance of ZDBC. During any individual prevulcanization, the disappearance of ZDBC followed zero-order kinetics with respect to the ZDBC level. But when the level of added ZDBC was varied, the zero-order rate of disappearance of ZDBC was found to be first-order with respect to ZDBC level. As the ZDBC used in those experiments was an industrial grade, it has been suggested that there might have been present in the ZDBC active impurities which may be responsible for the observed phenomenon. To test this hypothesis, a series of experiments similar to the Series A experiments was carried out using recrystallized ZDBC.

Another possible explanation for the observed phenomenon is that it arises from the presence of increased amounts of dispersing agent in the ZDBC dispersion which is associated with higher levels of added ZDBC. This hypothesis was also tested using prevulcanization systems which contained different concentrations of dispersing agent.

The third possibility which would account for the observed phenomenon is the increase in number of particles when the level of ZDBC is increased. To examine this hypothesis, the number of particles of ZDBC in a prevulcanization system of constant ZDBC level was varied and the rate of prevulcanization followed.

All three possibilities are consistent with zero-order disappearance of ZDBC in any individual prevulcanization reaction, and all three can plausibly explain why the zero-order rate is directly proportional to the initial level of ZDBC.

7.1.2.1. Effects of varying level of recrystallized ZDBC with fixed 1.00 pphr sulphur

a) Recrystallization of industrial-grade ZDBC

Industrial-grade ZDBC was recrystallized once using toluene. The crystals were washed three times with ethanol, and dried in a vacuum oven at 25°C. The recrystallized ZDBC was then used for the preparation of 33.33% ZDBC dispersion by the procedure previously described in Chapter 5. For the purpose of determining residual unreacted ZDBC, a calibration graph was obtained by preparing solutions of known concentration of the recrystallized ZDBC in chloroform, and measuring their optical densities at wavelength of 435 nm using a UV spectrophotometer.

b) Prevulcanization recipe and reaction conditions

Table 7.2 shows the recipes used for present series of experiments.

Table 7.2 Recipes for experiments using recrystallized ZDBC

	parts by weight dry				
Ingredient Experiment No.	1	2	3	4	5
Rubber as 50% latex (previously deammoniated to pH 9.8 as in Series A)	100	100	100	100	100
Potassium Oleate as 10% solution; (added before deammoniation of latex)	0.75	0.75	0.75	0.75	0.75
Sulphur (33.33%)	1.00	1.00	1.00	1.00	1.00
Recrystallized ZDBC (33.33%)	0.50	1.50	2.00	2.50	4.00

The prevulcanization reactions were carried out in a 2-litre reaction vessel at 50±0.5°C. All the experimental procedures were similar to those used in the Series A experiments (Section 7.1.1.1).

c) Results and observations

Fig. 7.12 shows the calibration curves used in the determination of free ZDBC. The calibration curve which was used in the Series A experiments was obtained using industrial-grade ZDBC. In Fig. 7.12 it is compared with the calibration curve which was obtained using recrystallized ZDBC. It can be seen that the two calibration curves are not the same, although both are linear.

Results for the variation of free ZDBC with prevulcanization time at different levels of added recrystallized ZDBC and 1.00 pphr sulphur are shown in Fig. 7.13. For purpose of comparison, some of the results from the Series A experiments are also included in the same graph as broken lines. The rate of disappearance of ZDBC was much faster in the Series A experiments than in the present series of experiments using recrystallized ZDBC. Furthermore, the shape of some of the curves in the present series of experiment was also found to be dependent upon the level of added ZDBC. At the lowest level of ZDBC (i.e., 0.50 pphr), the results can be adequately represented by a straight line, so that for this reaction the rate of disappearance of ZDBC was independent of the concentration of ZDBC, i.e., the reaction followed zero-order kinetics. However, at higher levels of added ZDBC (i.e., from 1.00 pphr onwards), the results are represented by curved lines, indicating that the disappearance of ZDBC is dependent upon ZDBC concentration in the prevulcanization system. Indeed, an analysis of the results

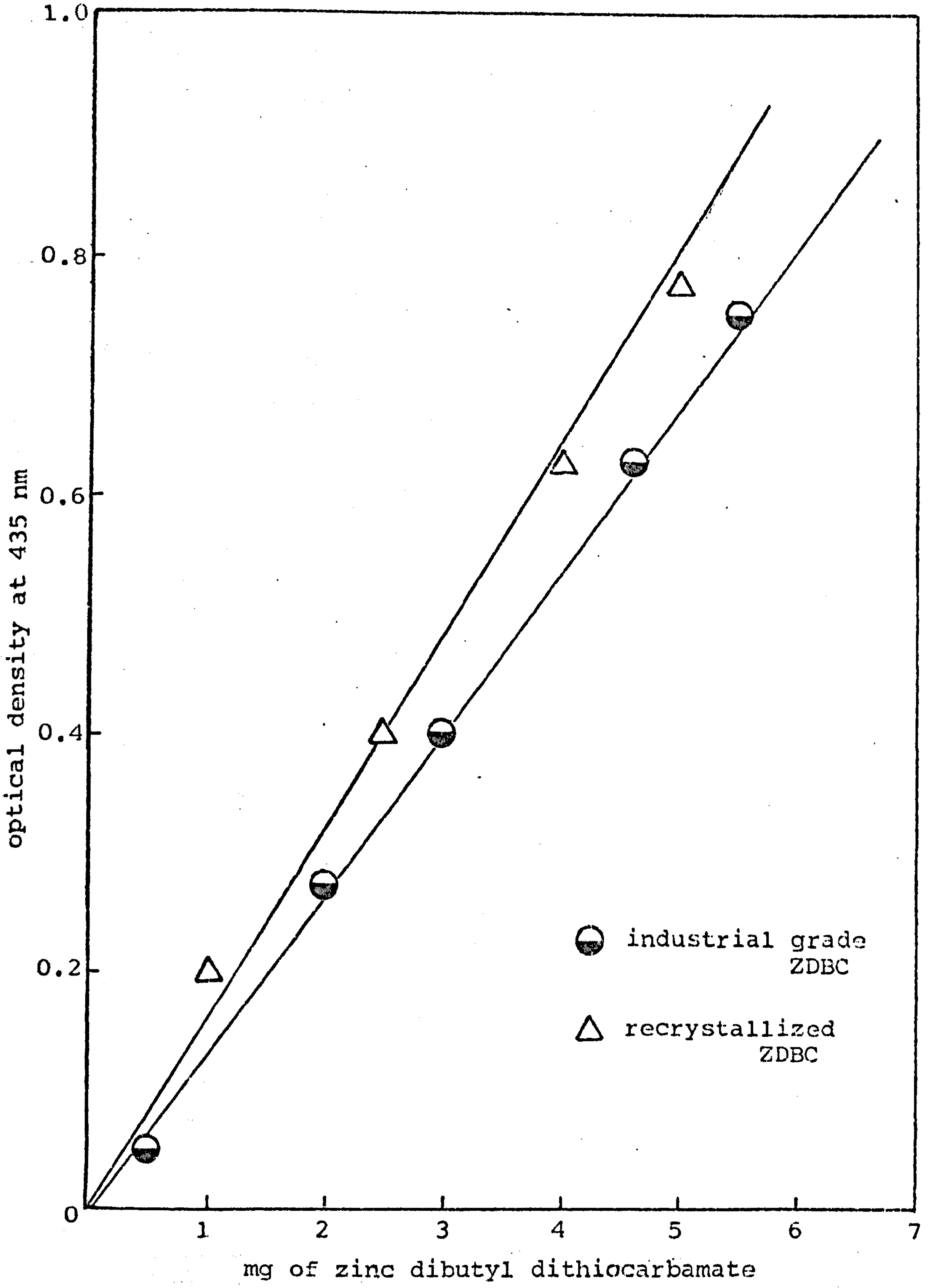


Fig. 7.12 Calibration curve for free ZDBC showing difference between curve for industrial-grade ZDBC and that for recrystallized ZDBC.

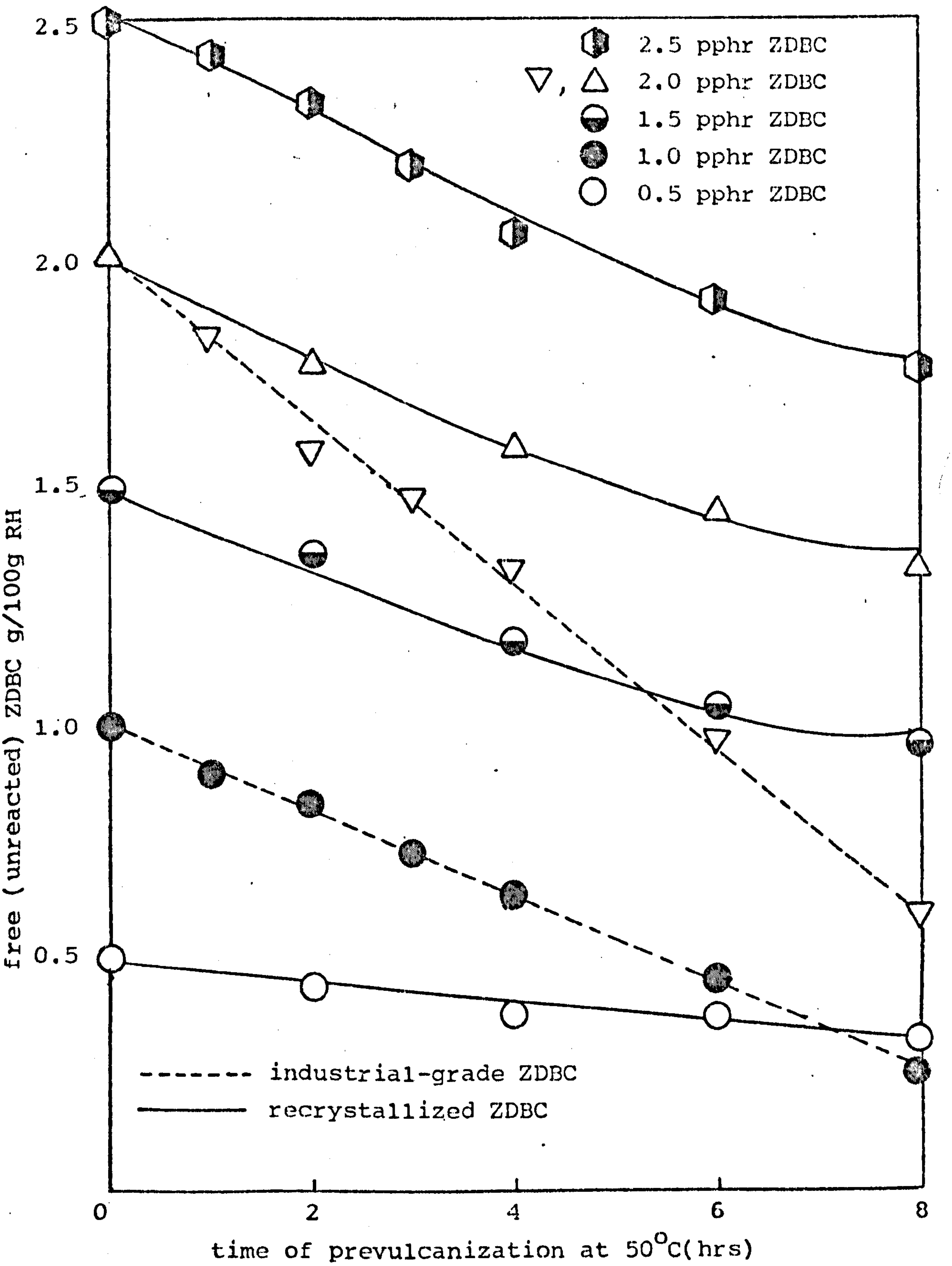


Fig. 7.13 Variation of free ZDBC with prevulcanization time for NR latex systems of different levels of ZDBC (continuous line - recrystallized ZDBC; broken line - industrial-grade ZDBC; sulphur fixed at 1.00 pphr).

revealed that all the rates of disappearance of ZDBC in experiments which contained 1.00 pphr or higher of added ZDBC (recrystallized) follow first-order kinetics. This is demonstrated by the straight line plots shown in Fig. 7.14. It is also seen, that within probable experimental error, the first-order rate coefficient for the disappearance of ZDBC is approximately independent of the initial ZDBC level.

Fig. 7.15 shows the effect of different levels of added recrystallized ZDBC at 1.00 pphr of sulphur upon free sulphur as a function of prevulcanization time. At first sight, apart from the system that contained 0.50 pphr of ZDBC, the free sulphur results of all the other systems, in which the ZDBC level ranged from 1.50 pphr to 4.00 pphr appear to cluster together. On closer examination of Fig. 7.15, it is noticed that there is probably an optimum level of ZDBC between 1.50 and 2.00 pphr which gives a maximum rate of disappearance of free sulphur. The rate of disappearance of free sulphur at any time in a system which contained 4.00 pphr ZDBC was slower than that in a system which contained 2.00 pphr ZDBC. It is also interesting to note in Fig. 7.15 that, at certain times of the prevulcanization, some of the reaction curves intersect other reaction curves. These observations will be further discussed in the following section (Section 7.1.2.1.(d)).

Fig. 7.16 shows the comparison for results of free sulphur as a function of prevulcanization time between

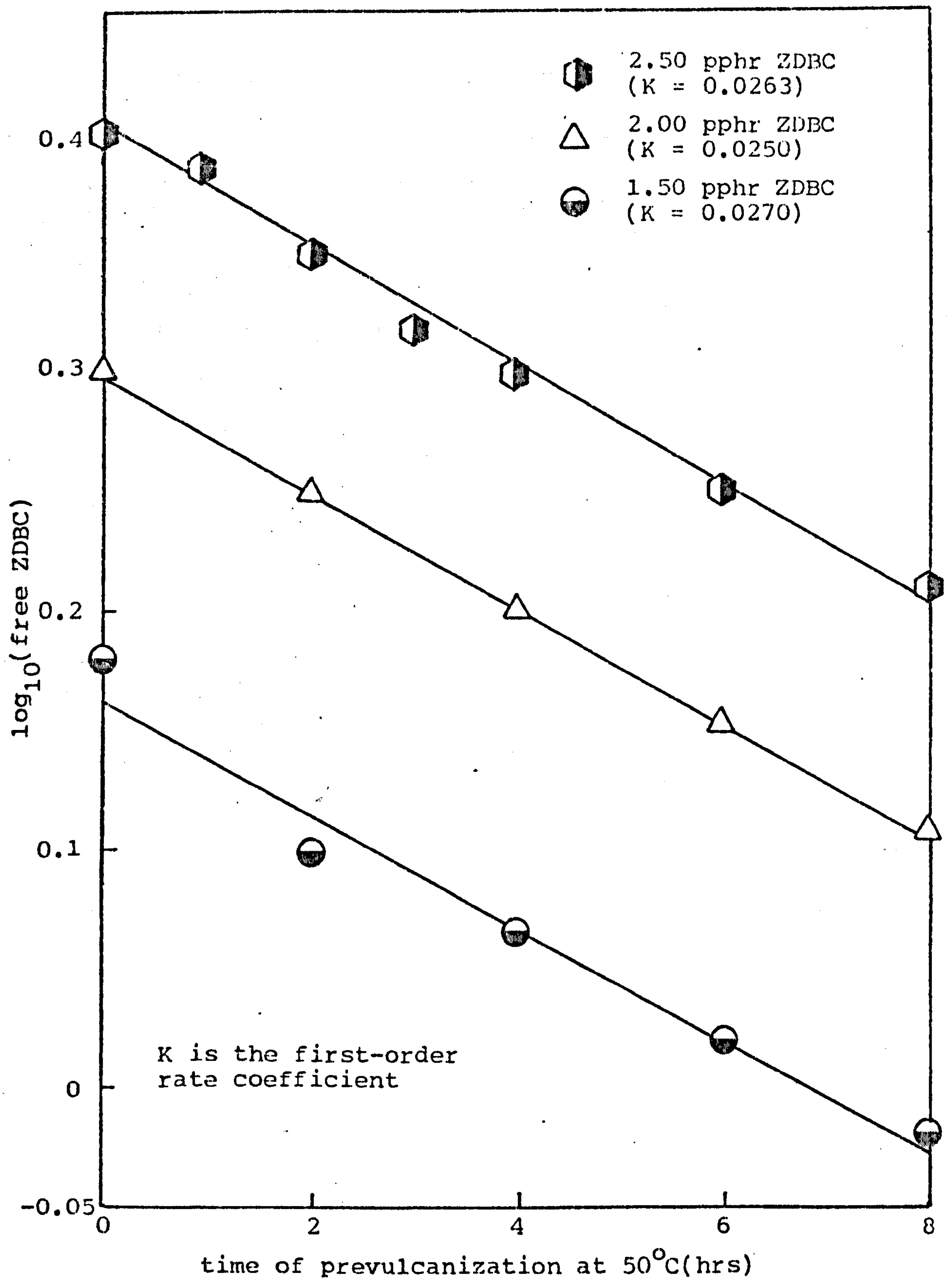


Fig. 7.14 First-order plots for disappearance of recrystallized ZDBC during prevulcanization of NR latex systems containing different levels of recrystallized ZDBC and a constant 1.00 pphr sulphur.

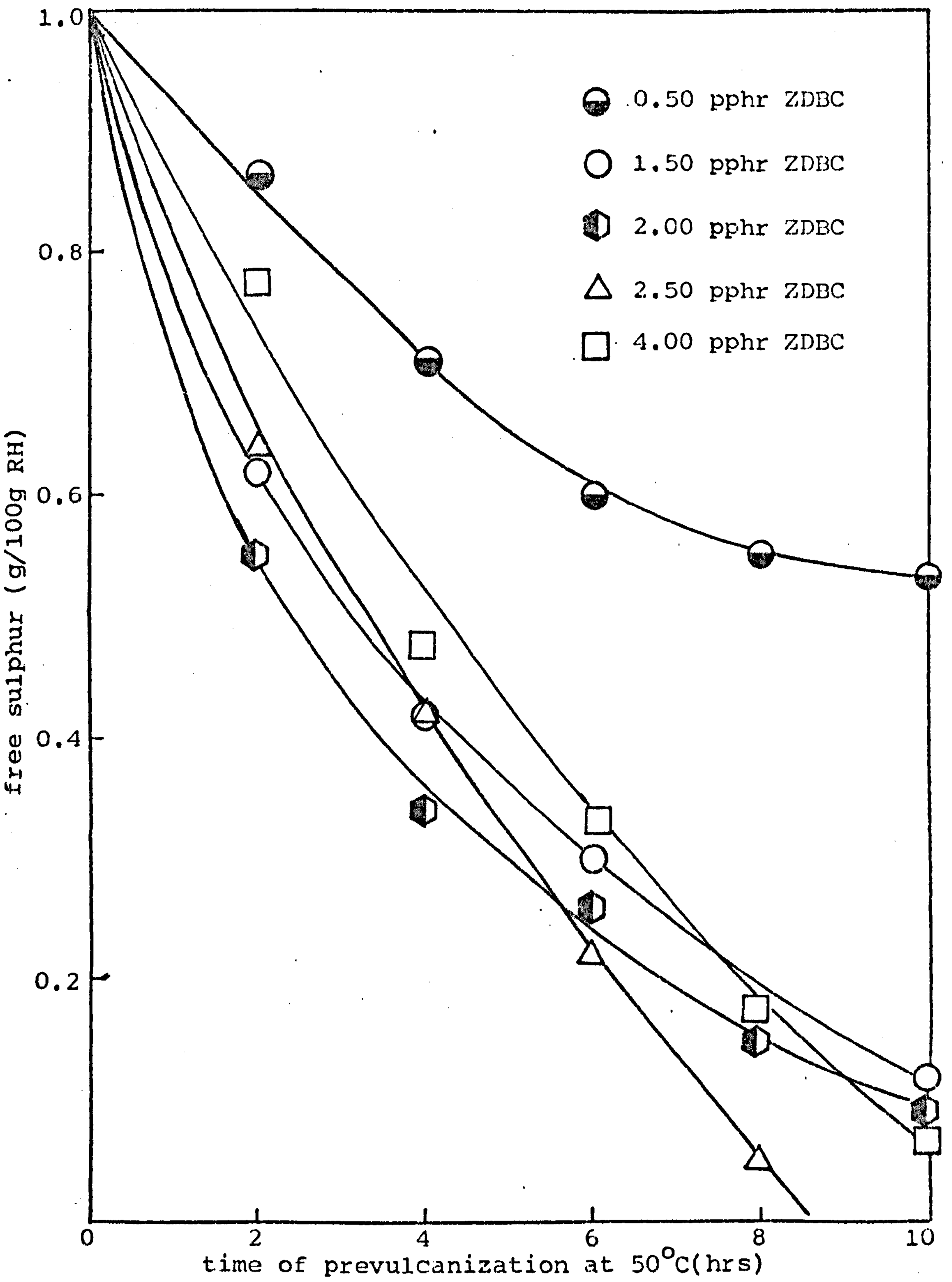


Fig. 7.15 Effect of different levels of recrystallized ZDBC upon free sulphur as a function of time of prevulcanization (sulphur level constant at 1.00 pphr).

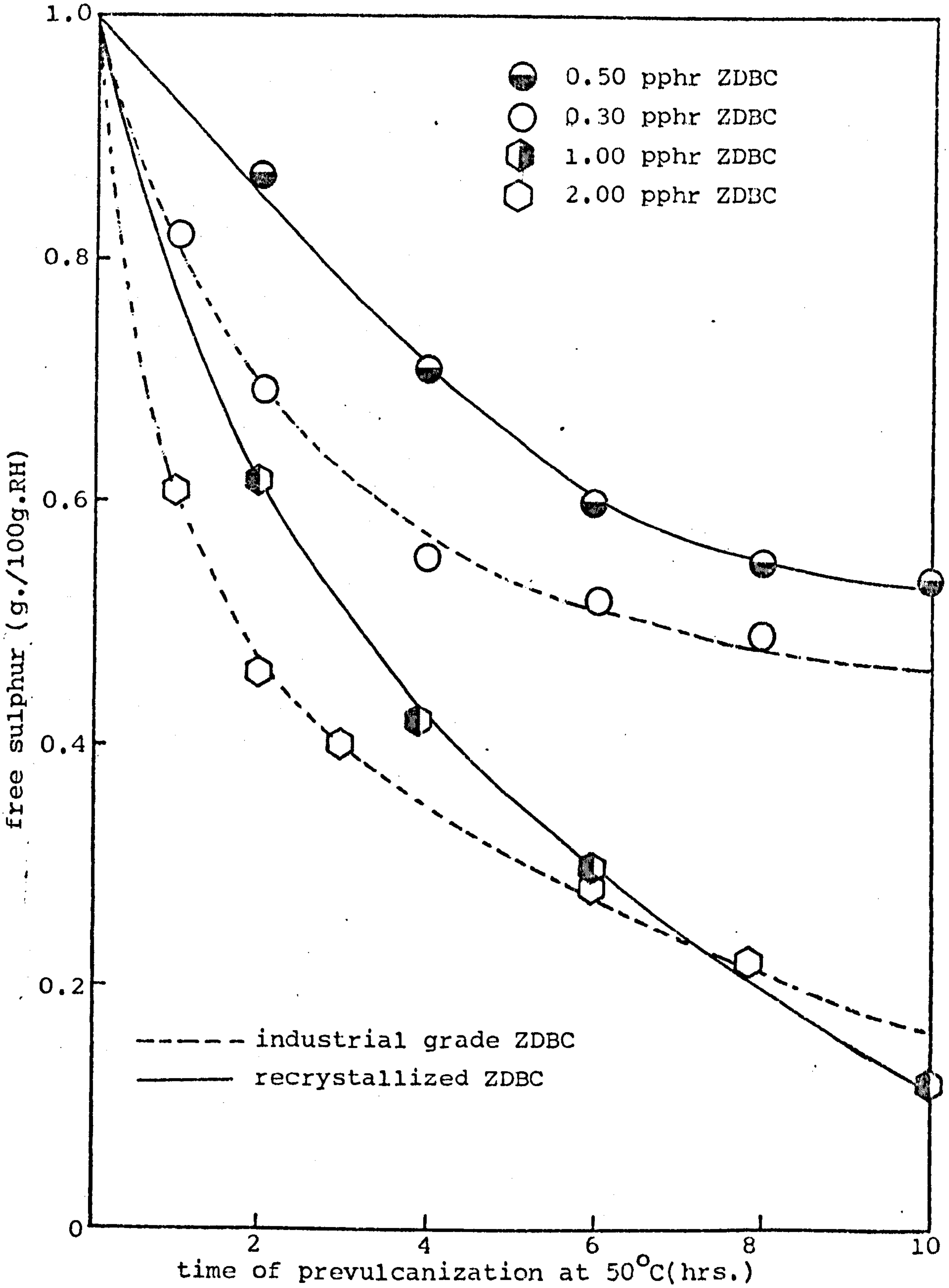


Fig. 7.16 Effect of different levels of recrystallized and industrial-grade ZDBC upon free sulphur as a function of time of prevulcanization (sulphur level constant at 1.00 pphr)

systems that contained industrial-grade ZDBC and those which contained recrystallized ZDBC. The rate of disappearance of free sulphur was found to be lower in reactions where recrystallized ZDBC was used.

The results for the variation of degree of chemical crosslinking as prevulcanization progresses for the systems which contained recrystallized ZDBC are shown in Fig. 7.17. The broken lines are previous results from the Series A experiments; these are included for the purpose of comparison.

d) Discussion

The results using recrystallized ZDBC in NR latex prevulcanization described in the preceding section confirm two suggestions made earlier in this thesis. Firstly, it can be seen from Fig. 7.12 that there probably are significant amounts of impurities in industrial-grade ZDBC. These impurities can be removed by recrystallization. The second, and more important, finding is that the impurities in industrial-grade ZDBC have a significant effect upon latex prevulcanization. When the impurities are removed by recrystallization, the rates of disappearance of free sulphur, disappearance of free ZDBC and the degree of chemical crosslinking are reduced compared to the corresponding results for systems which contained industrial-grade ZDBC (see Fig. 7.13, Fig. 7.16 and Fig. 7.17). These results confirm the suggestion made previously that impurities present in

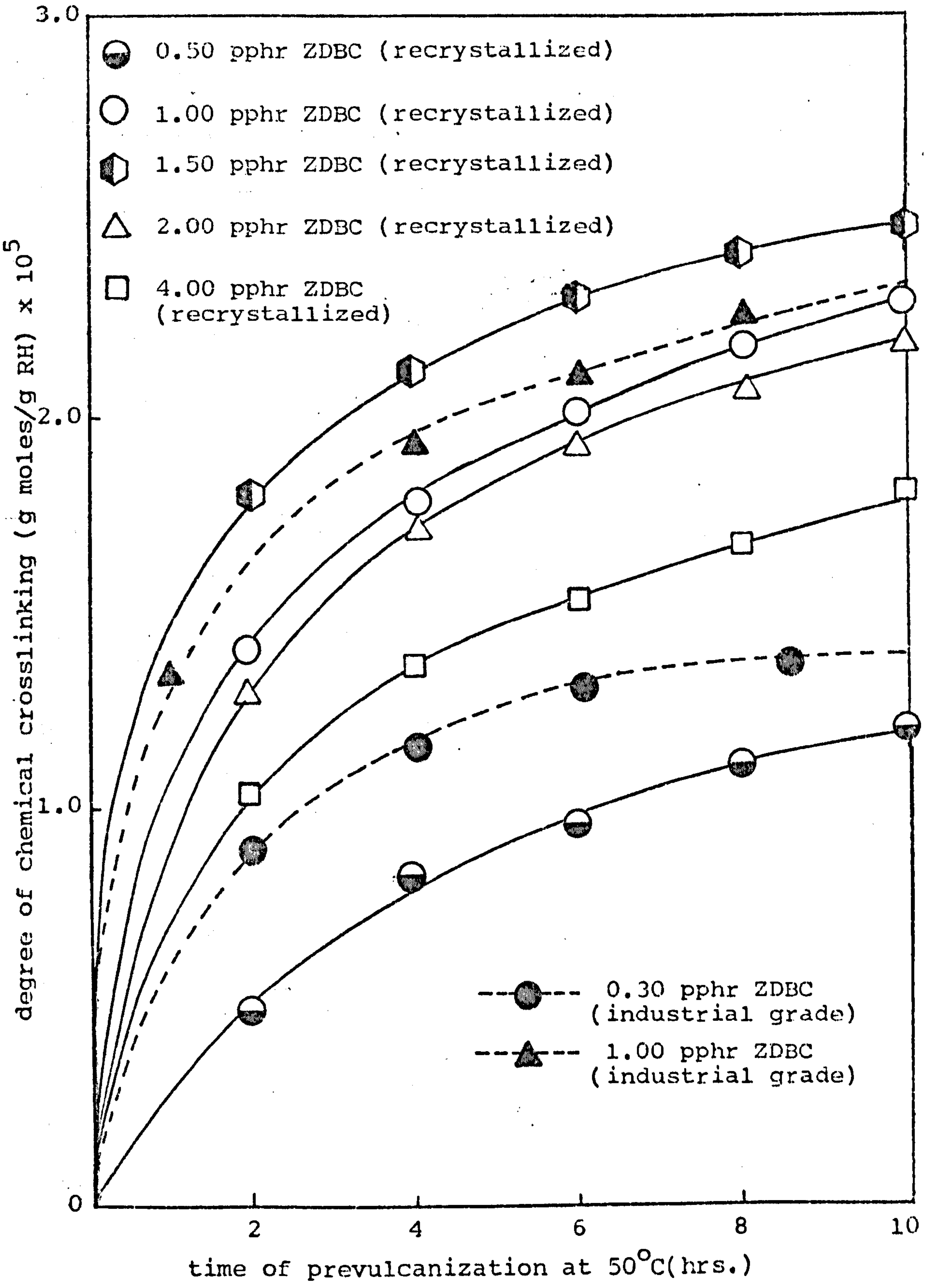


Fig. 7.17 Effect of different levels of recrystallized ZDBC and industrial-grade ZDBC upon degree of chemical crosslinking as a function of time of prevulcanization (sulphur level constant at 1.00 pphr)

industrial-grade ZDBC may play an important part during NR latex prevulcanization, possibly behaving as a ligand for ZDBC.

The results also seem to show that the impurities in industrial-grade ZDBC are at least partly responsible for the phenomenon described in Section 7.1.1, namely, that, whereas the rate of disappearance of ZDBC in any individual prevulcanization reaction is zero-order in ZDBC level, the zero-order rate of disappearance is itself first-order in initial ZDBC level. For prevulcanization systems which contained recrystallized ZDBC, in any one individual system, (except that which contained 0.50 pphr ZDBC) the rate of disappearance of ZDBC was first order with respect to ZDBC level (see Fig. 7.13 and Fig. 7.14).

Removal of impurities from the ZDBC, on the other hand, did not seem to affect the phenomenon of the existence of an optimum level of ZDBC for maximum rate of disappearance of free sulphur during prevulcanization. The optimum level of somewhere between 1.50 and 2.00 pphr which was observed in the Series A experiments has also been observed in the investigation using recrystallized ZDBC (Fig. 7.15).

However, one phenomenon which was not observed in the Series A experiments, but which has been observed in the present experiments, is that some of the free sulphur reaction curves intersect other curves at some particular time during the prevulcanization reaction. For instance, in Fig. 7.15, it can be seen that the disappearance of free sulphur in the prevulcanization system which contained 2.50 pphr ZDBC started off at a comparatively slower rate than did the systems which contained 1.50 pphr and 2.00 pphr ZDBC. After about 4 hours of reaction, the extent of disappearance of sulphur for the system which contained 2.50 pphr ZDBC gradually overtook that of the system which contained 1.50 pphr; and about 2 hours later it further overtook that of the system which contained 2.00 pphr of added ZDBC. This interesting observation is also noted for the system which contained 4.00 pphr of added ZDBC. It is possible to account for this phenomenon if an assumption is made that the active impurities in the industrial-grade of ZDBC are not completely removed during the recrystallization. This is a reasonable assumption, because the recrystallization of the ZDBC was only carried out once. According to the reaction scheme proposed previously in Fig. 7.9(b), it has been suggested that a secondary product may be formed from the reaction between the ZDBC complex and the active impurities. This secondary product has been presumed to have a much lower affinity towards sulphur to form the active sulphurating agent than the original ZDBC complex. Let us suppose that the recrystallization did not remove all the active impurities in the ZDBC. There will then be proportionately more impurities in the reaction system which contained 2.50 pphr of ZDBC than there would be in reaction systems which contained 2.00 pphr or 1.50 pphr ZDBC. It thus follows that, during the early stages of prevulcanization of the system which contained 2.50 pphr ZDBC, the ZDBC complex formed might be mostly reacting with the active impurities to form the secondary reaction product. Because the secondary product has a slower reaction rate towards dissolved sulphur than does the original ZDBC complex, the lower rate of disappearance of free sulphur during the early stages of prevulcanization, compared to the prevulcanization system which contained 2.00 pphr or 1.50 pphr of ZDBC, can thus be understood. However, after a period of reaction, most of the active impurities may have been consumed by the ZDBC complex, and the ZDBC complex is again available primarily for reaction with dissolved sulphur to form the active sulphurating agent. This could account for the now faster rate of disappearance of free sulphur in the later stages for the system which contained 2.50 pphr ZDBC compared to the rates of disappearance in the systems which contained 2.00 pphr and 1.50 pphr ZDBC.

Fig. 7.16 shows clearly the effect of the impurities present in industrial-grade ZDBC upon the rate of disappearance of free sulphur in prevulcanization reaction systems which contain low and medium levels of added ZDBC. These results are consistent with those for rates of chemical crosslink insertion shown in Fig. 7.17. It can be seen from the two sets of results that, from the industrial point of view, there would be no advantage in purifiying industrial-grade ZDBC for use in NR latex prevulcanization. Indeed if carried out, the effect would be detrimental to the prevulcanization in terms of rate of the reaction.

It has been previously proposed (see Section 7.1.1.4) that the active impurity could well be a dibutylamine, one of the raw materials which is used in the synthesis of ZDBC. An experiment was therefore carried out in which the equivalent of 0.10 pphr of dibutylamine was introduced into purified ZDBC. The objective was to find out whether dibutylamine is the type of impurity which is responsible for the results which have been obtained. Unfortunately, the experiment failed because the added dibutylamine seemed to cause difficulties in obtaining a ZDBC dispersion. Further experiments were carried out by introducing the dibutylamine (0.10-1.00 pphr) into the prevulcanization system prior to the reaction. However, no significant difference in results for the rate of disappearance of ZDBC was observed compared to the control which contained no added dibutylamine. It is therefore concluded that a compound such as dibutylamine is probably not the active impurity involved.

7.1.2.2. Investigation of other factors which may have contributed to the apparent contradiction between zero-order and first-order kinetics for ZDBC disappearance observed in Section 7.1.1

It has previously been pointed out that the level of impurities in the prevulcanization system will increase with increasing level of added ZDBC. However, the amount of impurity is not the only variable when a higher level of a given ZDBC dispersion is added to a prevulcanization system. There would also be a larger amount of the dispersing agents and stabilisers which had been used in the preparation of ZDBC dispersion. There would also be present a larger number of ZDBC particles if the particle-size distribution of the ZDBC dispersion remained constant. The effect of these two variables upon NR latex prevulcanization was investigated to find out if they contribute to the phenomenon of the apparent contradiction between zero-order and first-order kinetics for the disappearance of ZDBC reported in Section 7.1.1.

a) <u>Effect of varying amount of dispersing agent upon rate of disappeance of ZDBC during prevulcanization</u>

ZDBC dispersions used throughout the present work were all prepared using 5.0 parts by weight of dispersing agent based upon the ZDBC. The dispersing agent used was a disodium salt of methylene di-napthalene sulphonic acid. In order to investigate the effects of varying the amount of dispersing agent upon NR latex prevulcanization, ZDBC dispersion containing 10.0 parts, 20.0 parts and 30.0 parts of the dispersing agent were prepared. The dispersions were then used for prevulcanization in the usual manner in a prevulcanization recipe which comprised 1.00 pphr of ZDBC and 1.00 pphr sulphur.

The results for free ZDBC as a function of prevulcanization time were found to be the same for the three varied systems and for the control. It is therefore concluded that the dispersing agent has no effect upon the course of the reaction, and was not responsible for the apparent contradiction reported in Section 7.1.1.

b) Effect of varying number of particles of ZDBC upon rate of ZDBC disappearance during prevulcanization

Ideally, ZDBC dispersions which contained in each dispersion ZDBC particles of uniform size but in different dispersions a different size range would have been best suited for this investigation. However, experimental difficulties prevented the preparation of these dispersions. Therefore, as a compromise, a coarse dispersion and a fine dispersion were prepared for the present study. The coarse dispersion was prepared by grinding recrystallized ZDBC crystals in a mortar together with the dispersing agent and water until a coarse slurry was formed. The fine dispersion was prepared by initially ball milling the recrystallized ZDBC crystals alone for 24 hours followed by another 5 days of milling after the dispersing agent and water had been added. The two dispersions were then used for prevulcanization in the usual manner using a formulation which comprised 1.00 pphr ZDBC and 1.00 pphr of sulphur.

The results for the disappearance of free ZDBC as a function of time of prevulcanization for the two systems which contained respectively the coarse and fine ZDBC dispersion were compared with those for a control system in which a conventionally-prepared ZDBC dispersion was used. No significant difference in the results was observed in the three systems. It is therefore concluded that the phenomenon of the apparent contradiction between zero-order and first-order kinetics for the disappearance of ZDBC was not associated with the number of individual ZDBC particles which were initially present in the reaction system.

7.1.3. Series B investigation: Effect of varying level of sulphur with fixed 1.00 pphr ZDBC

The prevulcanization recipes for this series of experiments are given in Table 7.3. The reaction conditions and other experimental procedures were the same as those for the Series A experiments.

Table 7.3. Recipe for experiments in Series B investigation

	parts by weight(dry)			
Ingredients / Experiment No.	1	2	3	4
Rubber as 50% latex	100	100	100	100
Potassium Oleate (added as 10% solution before deammoniation of latex)	0.75	0.75	0.75	0.75
Sulphur (33.33%)	0	0.50	1.00	1.50
ZDBC (33.33%)	1.00	1.00	1.00	1.00

7.1.3.1. Results and observations

The results for the variation of free sulphur with prevulcanization time for experiment 1 in the series (which contained no added sulphur in the reaction system) are omitted because the reaction was very slow and appeared to be non-existence even up to 12 hours of prevulcanization. For experiments 2, 3 and 4, the results are shown in Fig. 7.18. As in the Series A experiments, free sulphur was observed to decrease progressively with increasing prevulcanization time at any sulphur level. The decrease is very rapid for the first two hours of prevulcanization. It is evident from the graph that the absolute initial rate of disappearance of sulphur increases with increasing level of sulphur. However, the relative rate of disappearance of sulphur is essentially independent of initial sulphur level. As a rough measure, it required slightly less than two hours of prevulcanization for the system which contained 1.50 pphr of added sulphur to have 50% of its added sulphur (i.e., 0.75 pphr) reacted. It took almost exactly two hours for the system which contained 1.00 pphr of added sulphur to react 50% of its added sulphur (0.50 pphr). It also required about the same time for the system which contained 0.50 pphr of added sulphur to have 50% of the added sulphur (0.25 pphr) reacted. Therefore based on these half-life results observed, which within experimental error may be considered as virtually independent of the initial sulphur level, the rate of disappearance of free sulphur is probably first-order with respect to level of added sulphur.

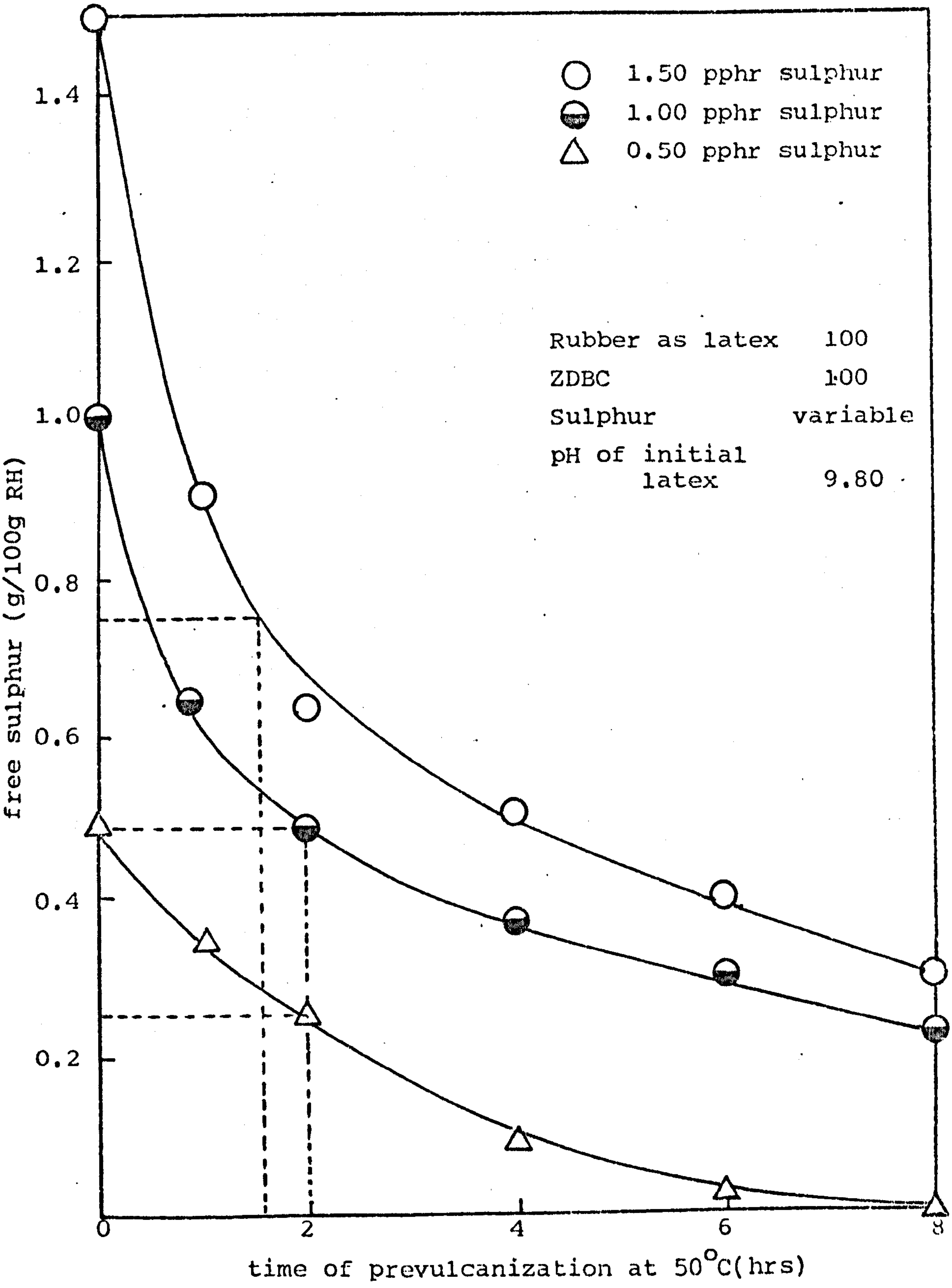


Fig. 7.18 Effect of different levels of sulphur upon free sulphur as a function of time of prevulcanization (ZDBC level constant at 1.00 pphr).

Results for network-combined sulphur as a function of prevulcanization time are given in Fig. 7.19. It can be seen from the graph that the prevulcanization system which contained 0.50 pphr sulphur has a much slower rate of sulphur combination compared to the other two systems which contained 1.50 pphr and 1.00 pphr of added sulphur respectively. It is also observed that at the end of 8 hours of reaction, the proportions of the added sulphur which had become combined in the rubber network by the prevulcanization systems which contained 0.50 pphr, 1.00 pphr and 1.50 pphr were 60%, 65% and 48% respectively. Unlike the Series A experiments, where an optimum level of ZDBC for the rate of disappearance of sulphur existed, no optimum level of sulphur was evident from these results. Higher levels of initial sulphur resulted in progressively higher rates and extends of sulphur combination.

Fig. 7.20 shows the results for the variation of degree of chemical crosslinking with time of prevulcanization. They are consistent with the previous two sets of results; an increase in the amount of sulphur combined results in a corresponding increase in degree of chemical crosslinking.

The results for the variation of free (unreacted) ZDBC with time of prevulcanization at different levels of added sulphur are shown in Fig. 7.21. Zero-order kinetics with respect to ZDBC concentration are observed for all the

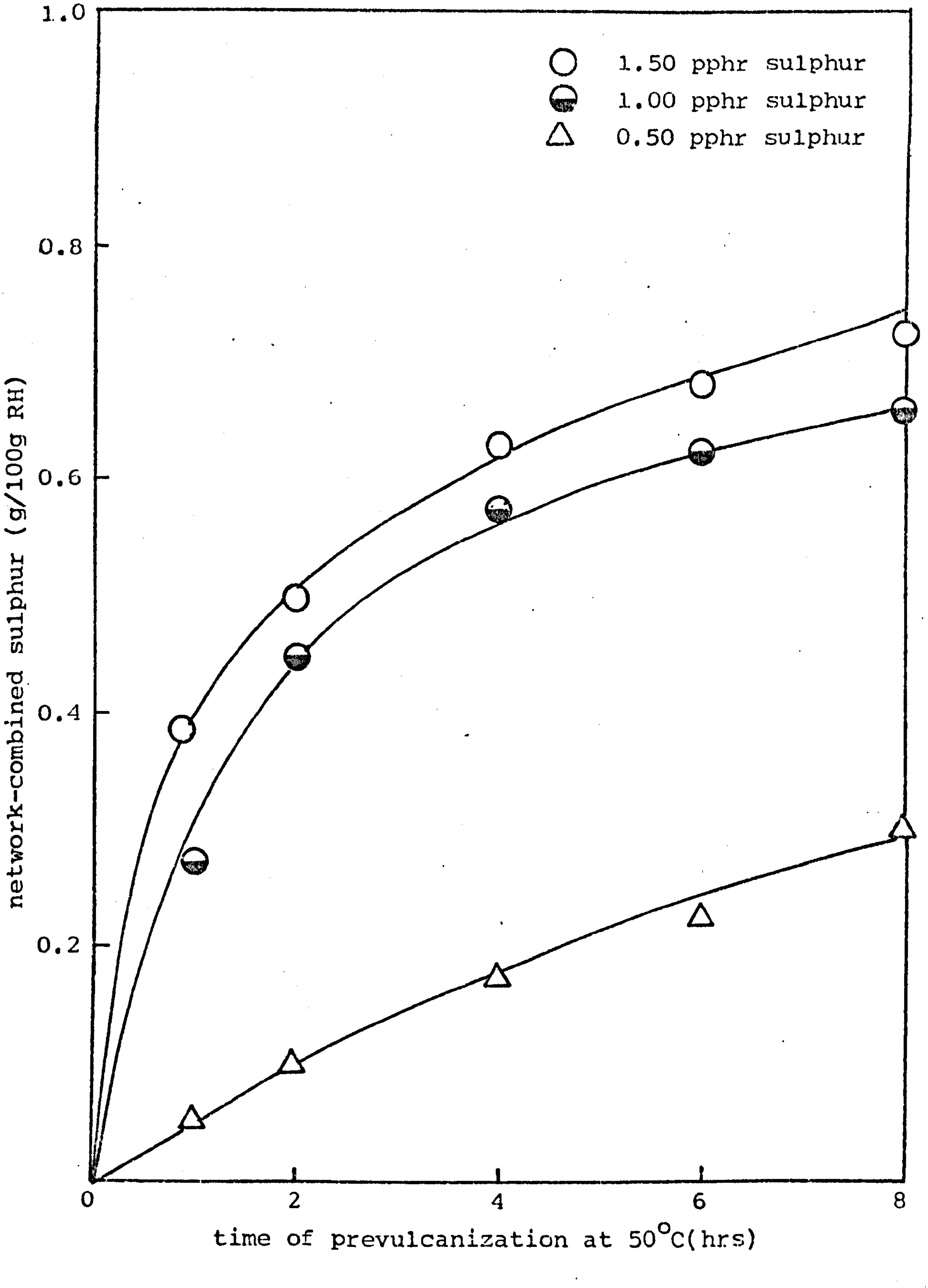


Fig. 7.19 Effect of different levels of sulphur upon network-combined sulphur as a function of time of prevulcanization (ZDBC level constant at 1.00 pphr).

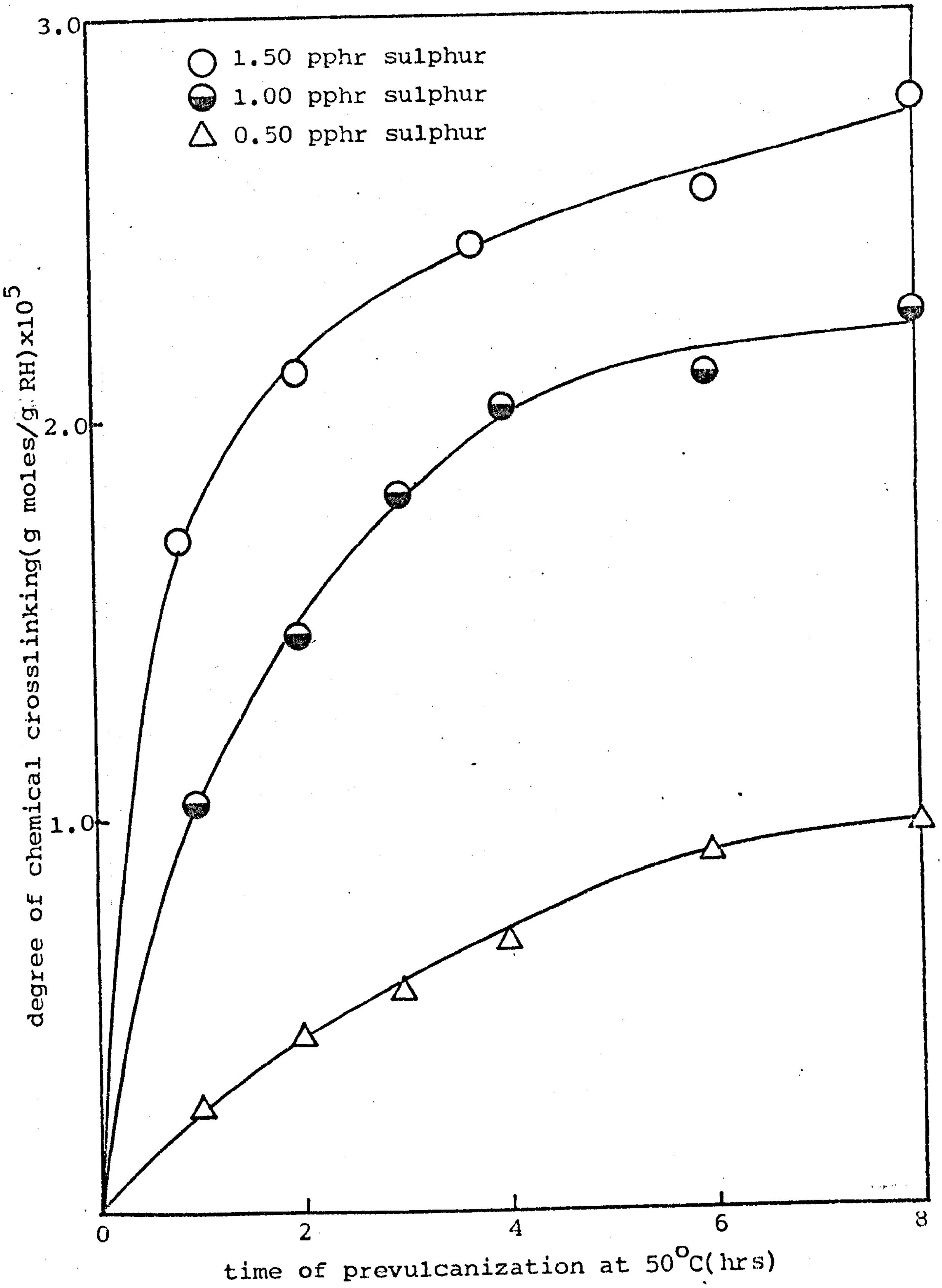


Fig. 7.20 Effect of different levels of sulphur upon degree of chemical crosslinking as a function of time of prevulcanization (ZDBC constant at 1.00 pphr).

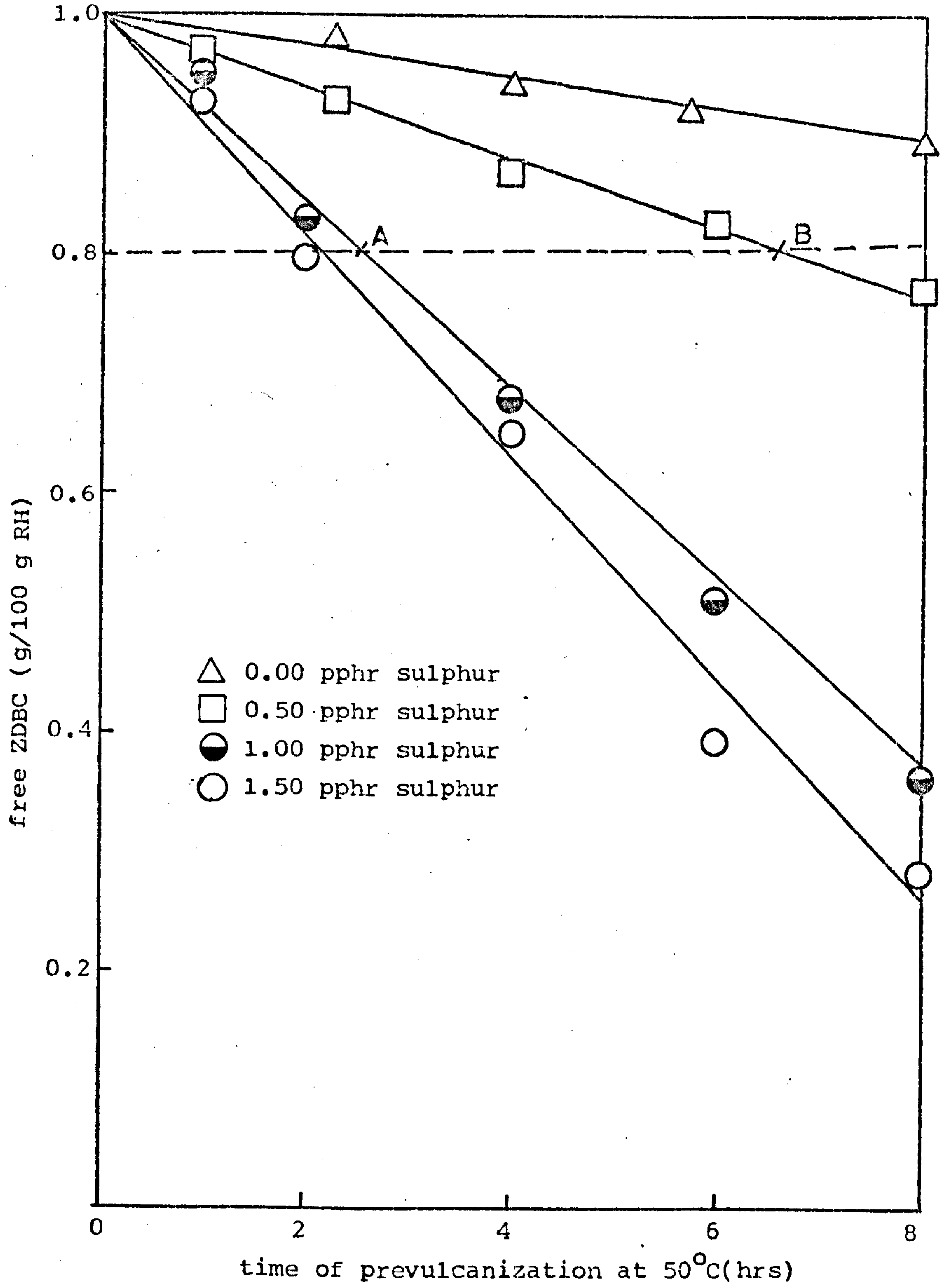


Fig. 7.21 Effect of different levels of sulphur upon free ZDBC as a function of time of prevulcanization (ZDBC level constant at 1.00 pphr).

systems. However, the rate of disappearance is dependent upon the initial level of added sulphur as evident from the slopes of the lines. It is also observed that some free ZDBC disappeared from the reaction system which did not contain any added sulphur during the 8 hours of heating.

Results for the variation of the crosslinking efficiency and the tensile strength of cast films as functions of time of prevulcanization are shown in Fig. 7.22 and Fig. 7.23 respectively.

7.1.3.2. Discussion

Consider first the results for free sulphur shown in Fig. 7.18. Two interesting observations were noted from the graph. Firstly, the absolute rate of disappearance of free sulphur is dependent upon the initial level of added sulphur; the higher the level of added sulphur, higher will be the absolute rate of disappearance of free sulphur and extent of sulphur combination (Fig. 7.19). The second observation is concerned with the kinetics of the disappearance of free sulphur. From the independence of half-life upon the initial level of added sulphur, it can be deduced that the rate of disappearance of free sulphur is probably first-order with respect to sulphur concentration. Indeed, the deduction is confirmed by the first-order plot show in Fig. 7.24. It has been previously proposed in Chapter 6 that sulphur dissolves to an appreciable extent into the aqueous phase during prevulcanization. It thus appears that the effect of initial sulphur level upon absolute rate of disappearance of free

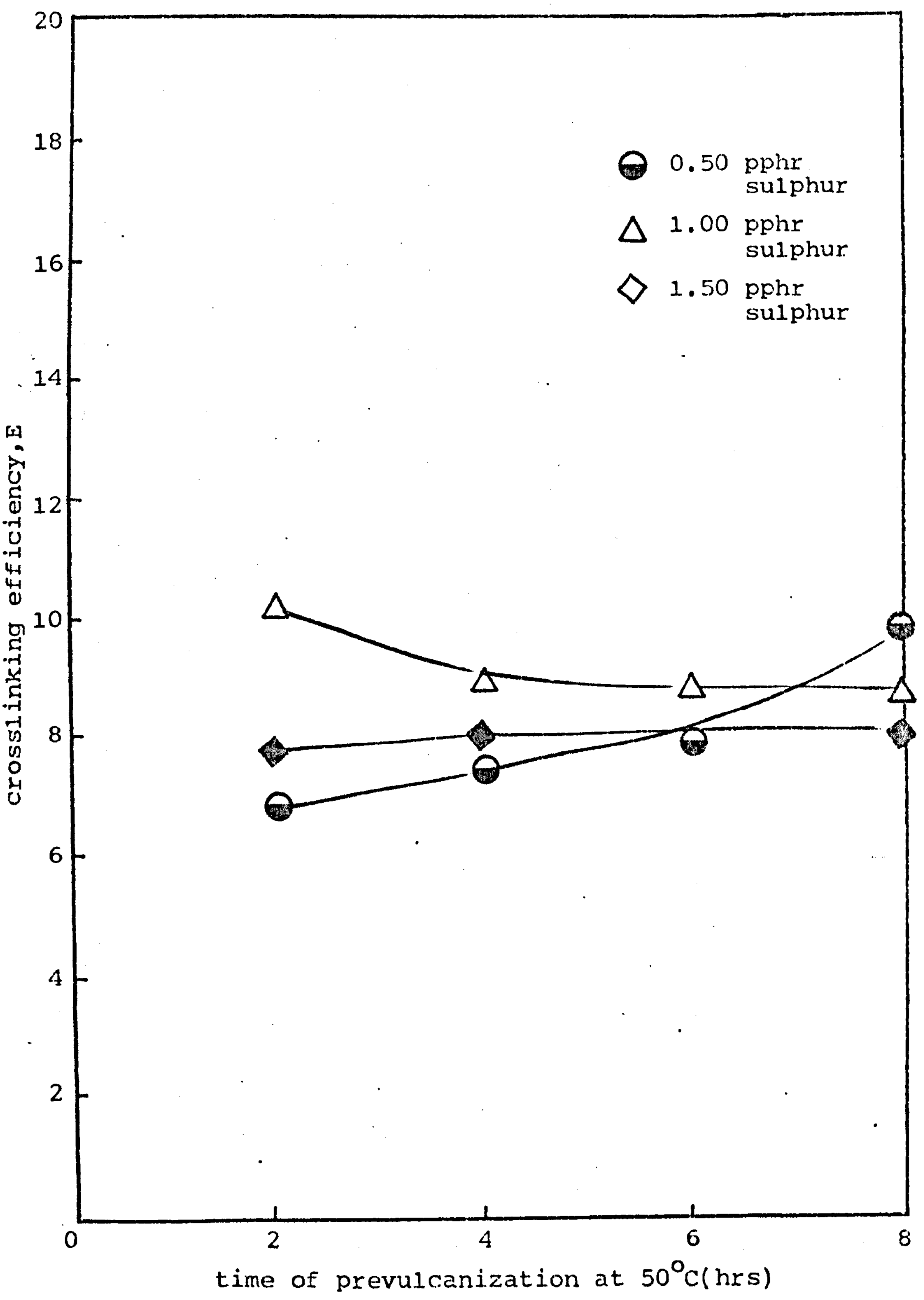


Fig. 7.22 Effect of different levels of sulphur upon variation of crosslinking efficiency with prevulcanization time (ZDBC level constant at 1.00 pphr).

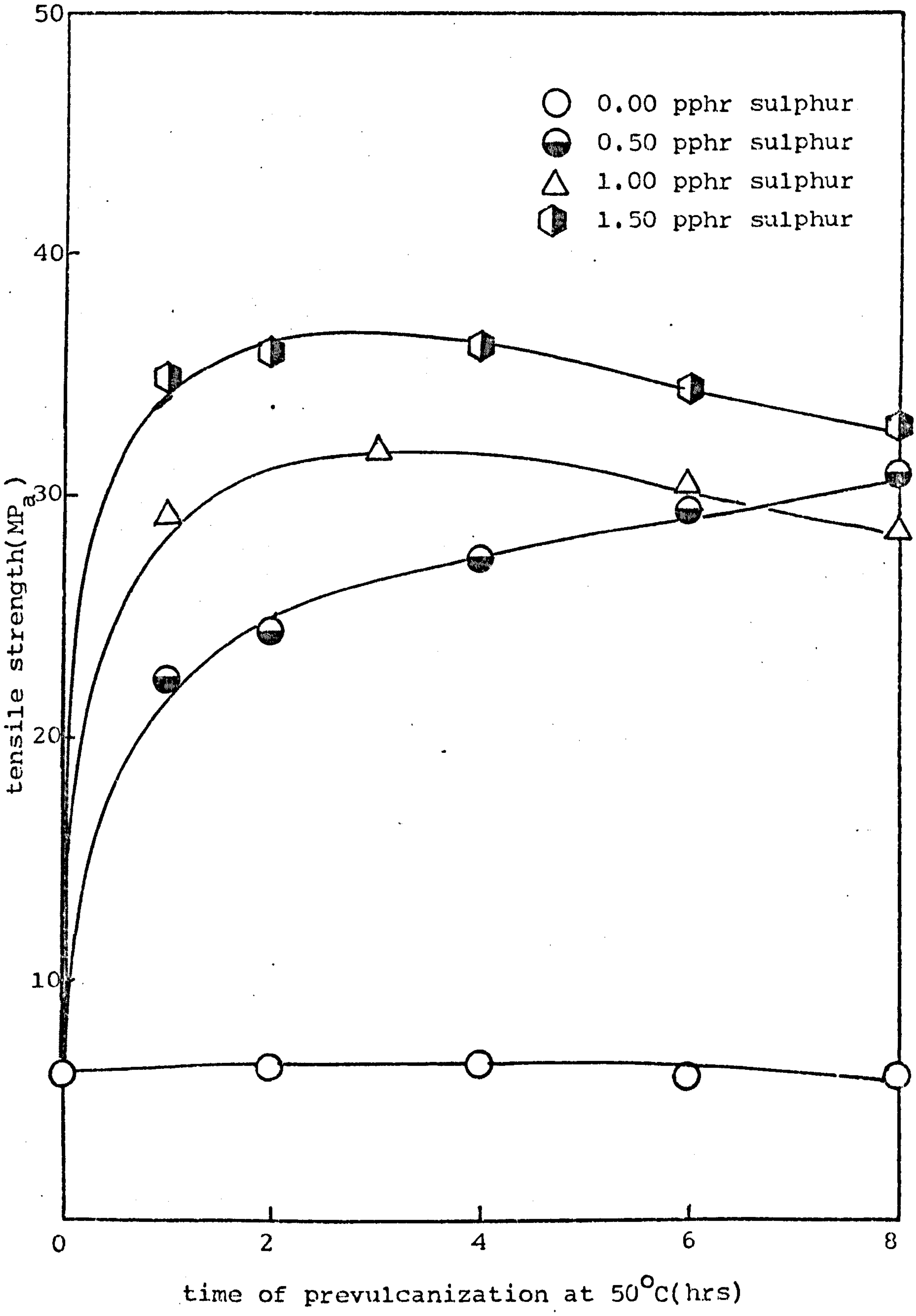


Fig. 7.23 Effect of different levels of sulphur upon tensile strength of airdried cast films as a function of time of prevulcanization (ZDBC level constant at 1.00 pphr).

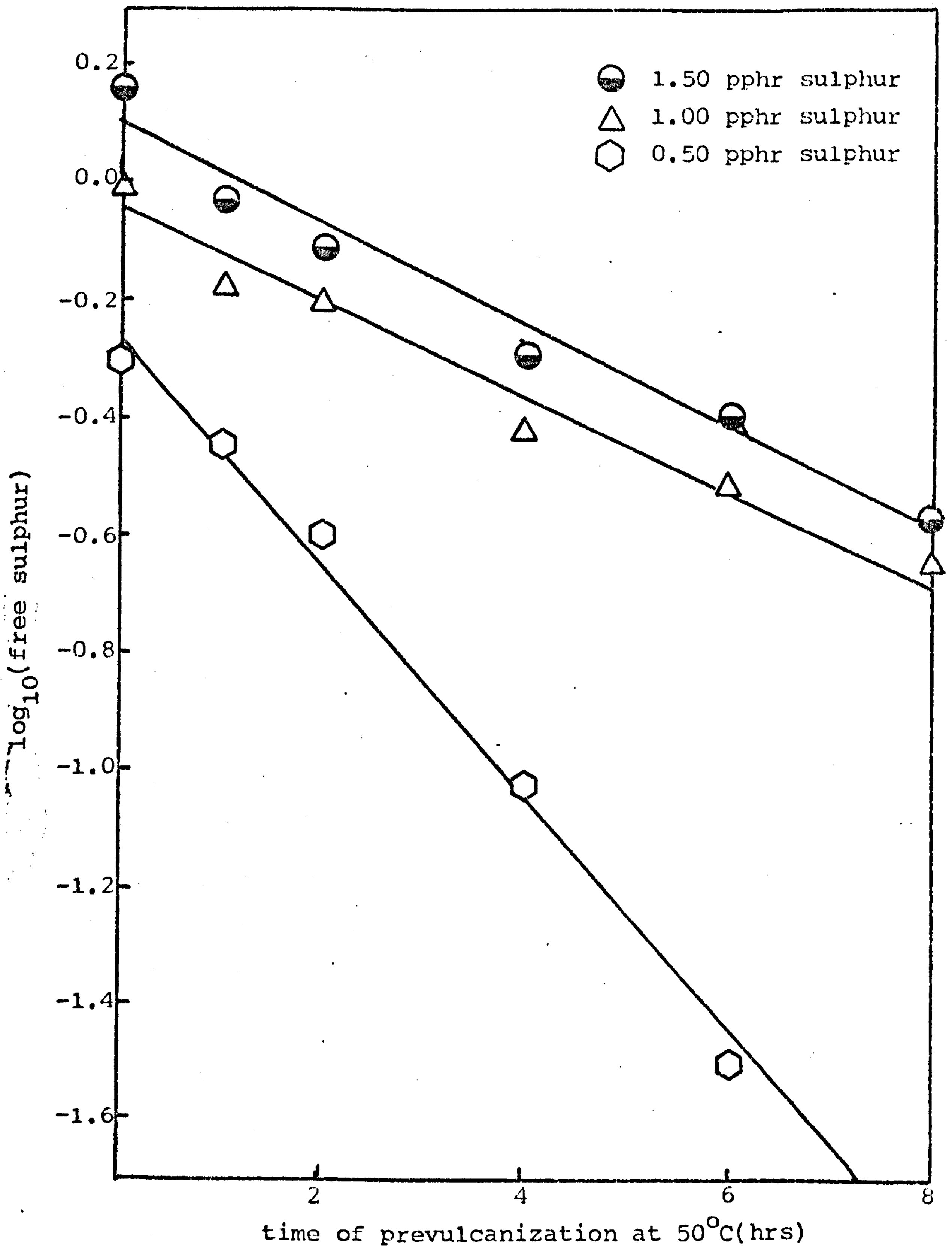


Fig. 7.24 First-order plots for disappearance of free sulphur during prevulcanization of NR latex systems containing different levels of sulphur and a constant 1.00 pphr ZDBC.

sulphur can be reasonably explained by the availability for reaction of different amounts of molecularly-dissolved sulphur in the aqueous phase of NR latex.

It is interesting to note from Fig. 7.19 that, when the sulphur level was increased from 0.50 pphr to 1.00 pphr, there was a substantial increase in the rate and extent of sulphur combination. However, the increase was not as large when the same amount of sulphur was added to further increase sulphur level from 1.00 to 1.50 pphr. This observation suggests that there is probably a limit to the increase in rate and extent of sulphur combination which is possible by increasing the level of added sulphur at constant ZDBC concentration. Firstly, it is possible that the reason is saturation of the latex serum by dissolved sulphur. A very simple experiment was carried out in which samples of NR latex containing between 1.00 and 5.00 pphr sulphur were heated at the temperature at which prevulcanization was carried out in this series of investigation (i.e., 50±1°C). It was found that, after heating for 30 minutes, only the latex which contained 1.00 pphr sulphur gave a clear cast sheet when dried. The latex which contained 2.00 pphr gave a translucent cast sheet, whilst the cast sheets obtained from the latex compounds which contained 3.00 pphr, 4.00 pphr and 5.00 pphr of added sulphur were all opaque when dried. Hence, it is the belief of the present writer that the extent of solubility of sulphur in NR latex serum in the absence of a zinc dialkylthiocarbamate is limited at 50°C to approximately 2.00 pphr.

A second possible reason for the observed effects is the insufficient amount of ZDBC to react with all the sulphur at higher levels of sulphur.

A further, and perhaps more likely, possibility is the existence of an equilibrium in the NR latex serum between dissolved sulphur, dissolved ZDBC complex and their reaction product, the vulcanization-active species. It has previously been hypothesised that the active sulphurating agent, together with the other dissolved vulcanizing ingredients, is partitioned into the rubber phase as prevulcanization progresses. If either the formation of the active sulphurating agent or the partitioning of the sulphurating agent into the rubber phase is a rate-determining step, then as long as there are sufficient sulphur or ZDBC molecules available in the aqueous phase of the latex to form the active sulphurating agent, any excess amount of either of these vulcanizing ingredients will not have a significant effect upon the rate and extent of sulphur combination during latex prevulcanization.

The dependence of the rate of disappearance of ZDBC upon the initial added level of sulphur shown in Fig. 7.21, further suggests the hypothesis that the concentration of dissolved sulphur in the latex serum increases with the level of added sulphur. The results are also in agreement with the results for free and network-combined sulphur, in that the increase in the rate of disappearance of ZDBC brought about by increasing the sulphur level from 1.00 pphr to 1.50 pphr is not as large as that brought about by increasing the sulphur level from 0.50 pphr to 1.00 pphr. The disappearance of ZDBC in the absence of any added sulphur in the prevulcanization system is consistent with the suggestion of complex formation by ZDBC with the naturally-occurring nitrogenous bases and ammonia in NR latex, accompanied perhaps by the partitioning of these water-soluble ZDBC complex into the rubber phase.

Another possibility of this observed effect of disappearance of free ZDBC in the absence of added sulphur is slow hydrolysis of ZDBC to zinc hydroxide, carbon disulphide and dibutylamine during the heating.

The results for crosslinking efficiencies shown in Fig. 7.22 together with those from the Series A experiments, show that the prevulcanization of NR latex with ZDBC and sulphur at $50^{o}C$ occurs relatively efficiently, in that on average approximately 8-9 atoms of sulphur are required per chemical crosslink formed.

7.2. Polymer-solvent Interaction Parameters, χ, for Vulcanizates Obtained from Prevulcanized Latex Swollen in n-Decane

As fas as the present writer is aware, χ-values for vulcanizates obtained from prevulcanized NR latex swollen in n-decane have not been previously reported in any published literature. Merrill(33) in his recent investigation on films obtained from prevulcanized NR latex assumed a χ-value of 0.42 for his calculation of degree of crosslinking using the Flory-Rehner equation.

χ-values for vulcanizates obtained from prevulcanized NR latex swollen in n-decane could be derived in the present work from data for G_{cs} and V_r for vulcanizates from the Series A and Series B experiments. The results for χ as a function of time of prevulcanization are summarised in Fig. 7.25. The calculator programme which was used for the computation of these χ-values from G_{cs} and V_r data is given in Appendix B. It is evident from Fig. 7.25 that the χ-values for vulcanizates obtained from prevulcanized latex swollen in n-decane do vary somewhat with time of prevulcanization. This is particularly true during the early stages of prevulcanization where it varies from 0.39 to 0.46. As prevulcanization progresses, the variation narrows to between 0.41 and 0.42. In view of this variation of χ with degree of crosslinking, it is therefore unwise to determine degree of crosslinking using a single χ-value in the Flory-Rehner equation in the equilibrium volume-swelling method. The ideal method under this circumstance for the determination of degree of crosslinking is the swollen-compression stress-strain method using the reticulometer. The method itself is not tedious, and the reproducibility is

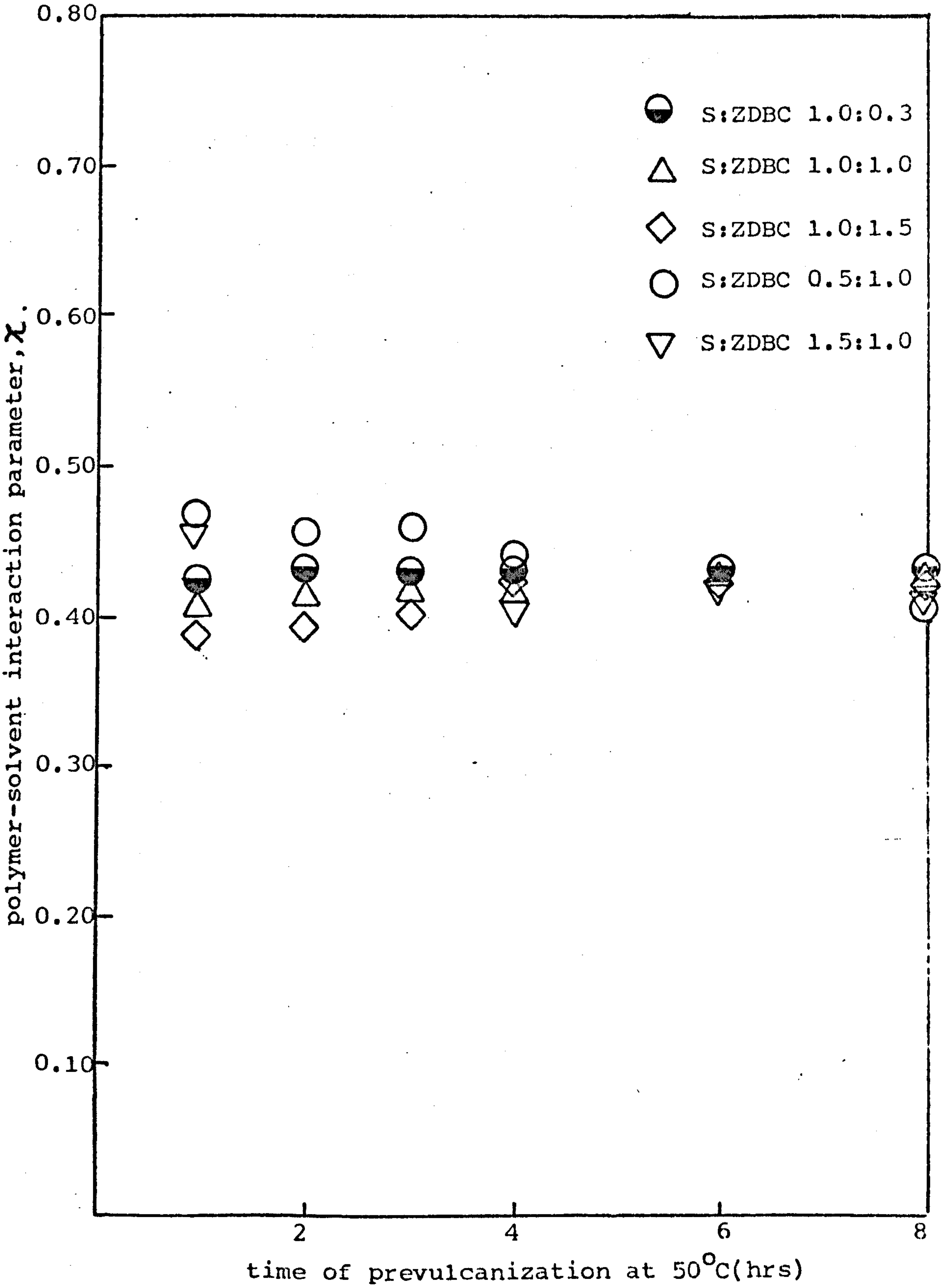


Fig. 7.25 Variation of polymer-solvent interaction parameter χ, with prevulcanization time for prevulcanization systems having various S:ZDBC ratios.

very good compared to C_1 measurements by means of the tensile stress-strain method. Furthermore, the method also eliminates entirely uncertainties concerning the value of χ, as compared to the equilibrium volume swelling method. The advantage of the swollen compression stress-strain method is further apparent when used on vulcanizates which have been treated with chemical probe reagents for the investigation of the various types of sulphidic crosslinks present in the vulcanizate.

7.3. Contribution of Monosulphidic, Disulphidic and Polysulphidic Crosslinks to the Overall Degree of Chemical Crosslinking for Vulcanizates obtained from Prevulcanized Latex

As far as is known, no detailed study of the types of crosslinks present in vulcanizates obtained from prevulcanized latex has been published hitherto. The objective of this part of the investigation was therefore to use the established "chemical probe" technique to study the types and concentration of sulphur crosslinks produced during the prevulcanization of NR latex.

7.3.1. Prevulcanization recipe and reaction conditions

HA latex which had been previously deammoniated to pH 9.8 was used. The prevulcanization recipe contained 1.00 pphr of ZDBC (industrial-grade) and 1.00 pphr sulphur. The prevulcanization was carried out in a 2-litre reaction vessel maintained at 50°C for 8 hours.

7.3.2. Other experimental procedures

To help in presenting the sequence of experiments carried out in the present investigation, a simplified flow diagram is given in Fig. 7.26. All the experimental procedures and underlying principle for these experiments have been described in detail in Chapter 5.

7.3.3. Results and discussion

Fig. 7.27 shows the results of this investigation. As expected, the crosslinks in vulcanizates obtained from prevulcanized latex are mainly polysulphidic in nature. This is probably attributable to the comparatively mild reaction conditions which prevailed during the latex prevulcanization. The concentration of polysulphidic crosslinks was found to increase as prevulcanization proceeded. The concentration of monosulphidic crosslinks was so low that it was difficult to determine experimentally. The concentration of monosulphidic crosslinks is therefore assumed to be negligible.

7.4. Effect of Varying Nature of Dithiocarbamate Accelerator Upon NR Latex Prevulcanization

All the results obtained so far in the preceding sections were obtained using ZDBC as prevulcanization accelerator. In the latex industry, there are various types of dialkyldithiocarbamate available which differ in respect of the chain length of the alkyl group; these compounds include the dimethyl, diethyl, dibutyl and alicylic pentamethylene dithiocarbamates. It is also possible to obtain

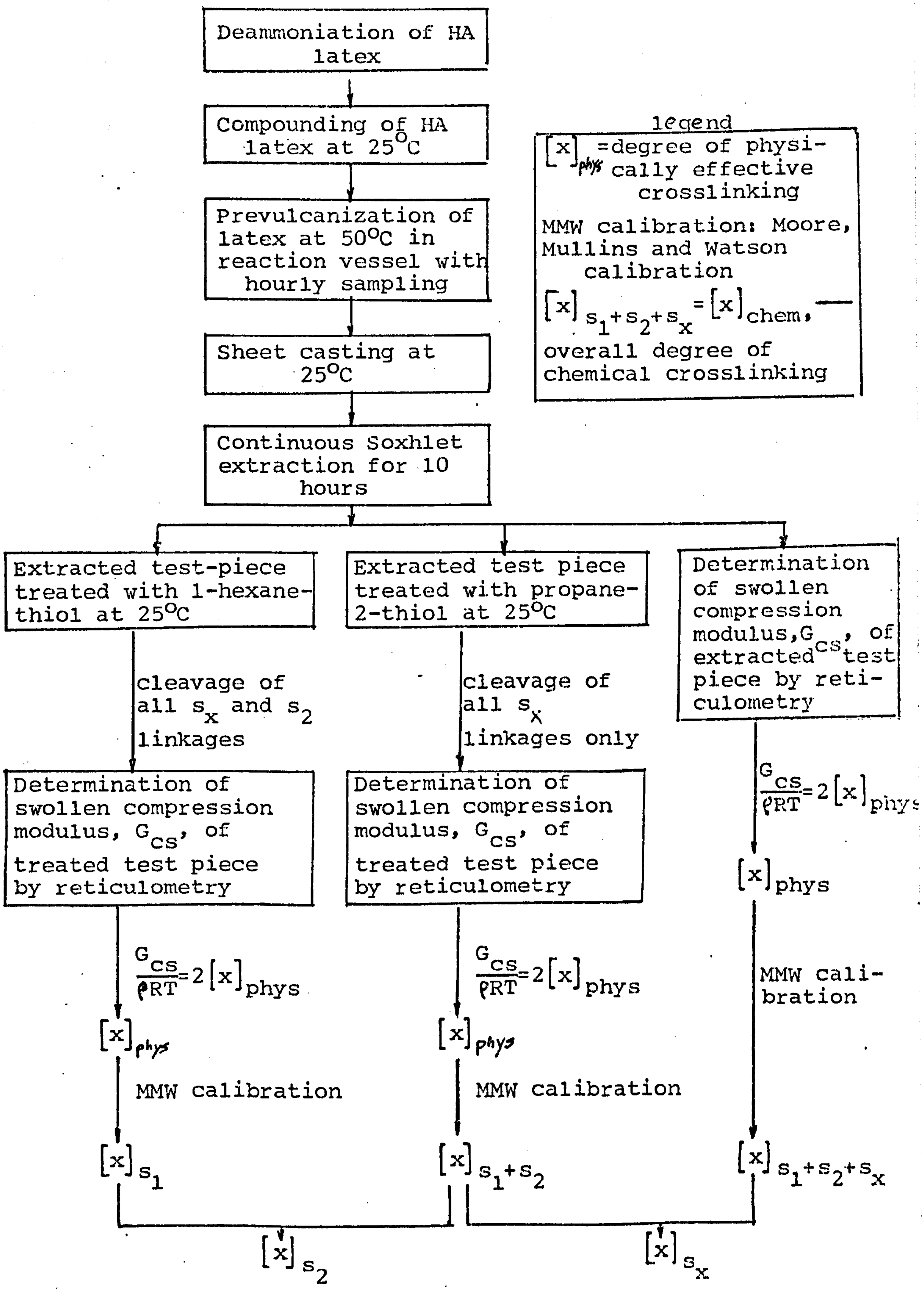


Fig. 7.26 Simplified flow diagram showing experimental procedures used in determination of contribution of monosulphidic, disulphidic and polysulphidic crosslinks to overall degree of chemical crosslinking for vulcanizates obtained from prevulcanized latex.

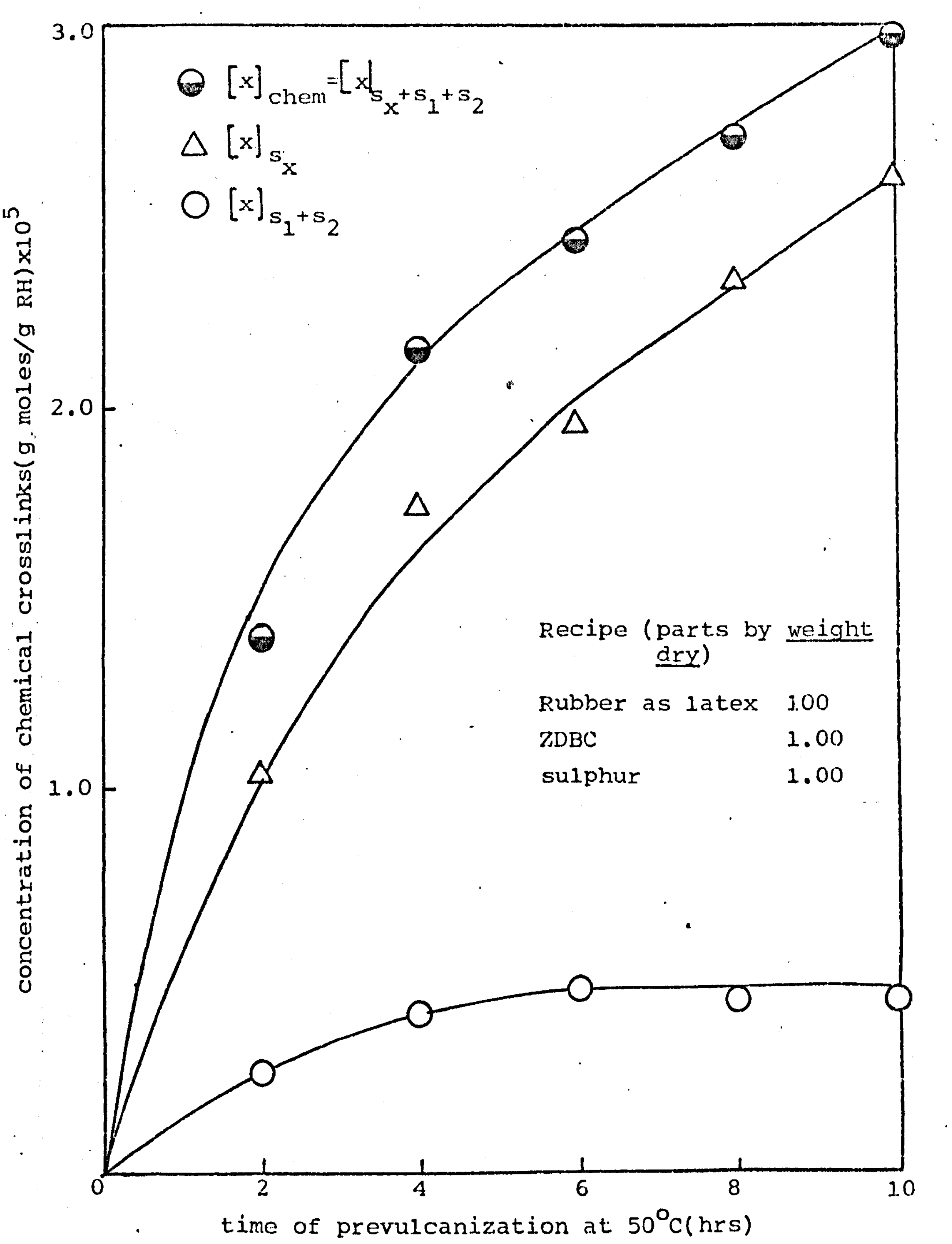


Fig. 7.27 Contribution of monosulphidic, $[x]_{S_1}$, disulphidic, $[x]_{S_2}$ and polysulphidic, $[x]_{S_x}$ to the overall degree of chemical crosslinking, $[x]_{chem}$ as a function of prevulcanization time for vulcanizates obtained from prevulcanized latex.

a variety of dialkyldithiocarbamates which differ in respect of the metal counterion; these compounds include the zinc dialkyldithiocarbamates, the sodium dialkyldithiocarbamates and the lead dialkyldithiocarbamates. It is rather surprising that, although latex prevulcanization was discovered in 1921, there are no published reports of any systematic investigation of the effects on latex prevulcanization of varying the nature of the dithiocarbamate accelerator.

The present section describes an investigation of the effects on latex prevulcanization of:

a) varying the nature of the alkyl chain length of the zinc dialkyldithiocarbamate; and

b) varying the metal counterion of the diethyldithiocarbamates.

The objective of the investigation was two-fold. Firstly, it was hoped that the results of the investigation would provide useful information concerning the different accelerators studied, in particular, in comparison with equimolal quantities of other accelerators in the dithiocarbamate family and under similar reaction conditions. Secondly, it was hoped that the results would provide further understanding of the way in which dithiocarbamate accelerators are transferred <u>via</u> the aqueous phase to the rubber particles during latex prevulcanization.

7.4.1. Effect of variation of alkyl chain length of zinc dithiocarbamate upon NR latex prevulcanization

7.4.1.1. Prevulcanization recipes and reaction conditions

For the purpose of this investigation, it was decided to use amounts of each zinc dialkyldithiocarbamate equivalent on a molal basis to 1.00 pphr of ZDEC. Industrially ZDEC is the most popular zinc dialkyldithiocarbamate accelerator for the sulphur prevulcanization of NR latex. The amounts used were therefore as shown in Table 7.4. The remainder of the recipe in dry weights was 100 parts of rubber as latex (pH 10.20) and 1.00 part of sulphur. The prevulcanization procedures were similar to those used

Table 7.4. Amount of each zinc dithiocarbamate used in prevulcanization recipe

dithiocarbamate	molecular weight	pphr(equivalent on molal basis to 1.00 pphr of ZDEC)
zinc dimethyl dithiocarbamate(ZDMC)	305.68	0.845
zinc diethyl dithiocarbamate(ZDEC)	361.72	1.000
zinc dibutyl dithiocarbamate(ZDBC)	473.80	1.310
zinc dihexyl dithiocarbamate(ZDHC)	587.07	1.623
zinc dioctyl dithiocarbamate(ZDOC)	810.03	2.239
zinc didodecyl dithiocarbamate(ZDDC)	922.12	2.549

previously. The prevulcanizations were carried out in separate sealed bottles. Whilst almost all the reactions previously described were carried out at 50±0.5°C, for reason of convenience, the present series were all carried out at 70±1°C. Again the reaction temperature was maintained constant by immersing the reaction vessels in a thermostatted water bath.

7.4.1.2. Results and discussion

Fig. 7.28 and Fig. 7.29 show the results for free and network-combined sulphur obtained in the present investigation. The first feature which is interesting to note is the very significant effect of varying the alkyl chain-length of straight-chain zinc dialkyldithiocarbamate upon the rate of combination of sulphur during latex prevulcanization. When ZDBC was used as accelerator, after five hours of prevulcanization at 70°C, more than 90% of the added sulphur has been combined with the rubber, compared with 80%, 55%, 30%, 25% and 10% respectively when molal equivalents of ZDEC, ZDHC, ZDOC, ZDMC and ZDDC were used. The free and combined sulphur results in Fig. 7.28 and Fig. 7.29 indicate that the molal effectivenesses of the zinc dialkyldithiocarbamate in accelerating sulphur combination during latex prevulcanization pass through an optimum as the alkyl chain length of the accelerator is increased; thus ZDBC > ZDEC > ZDHC > ZDOC > ZDMC > ZDDC.

Fig. 7.30 shows the results for the solubility of the

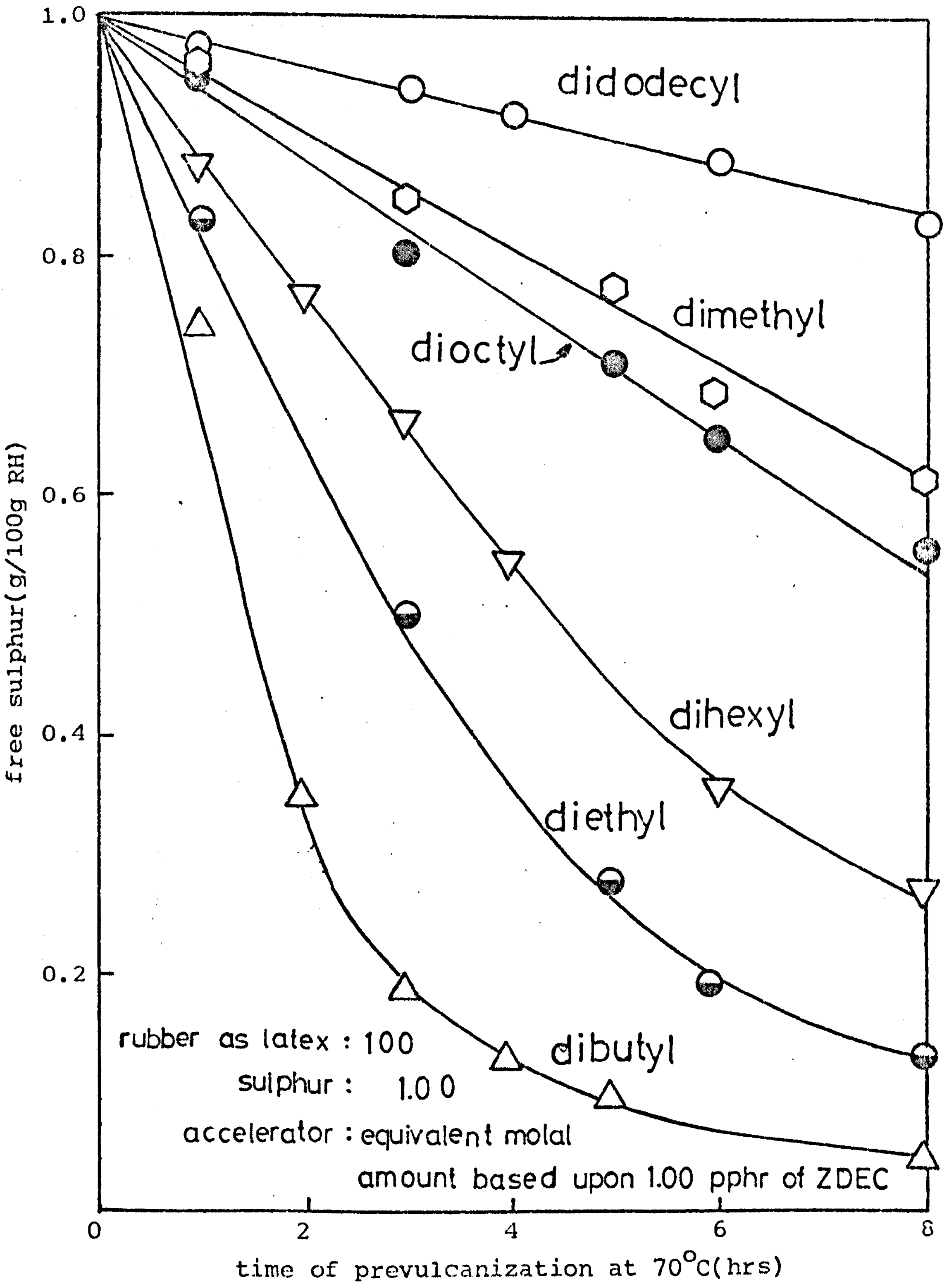


Fig. 7.28 Effect of variation of alkyl chain length of zinc dialkyldithiocarbamate upon free sulphur content as a function of prevulcanization.

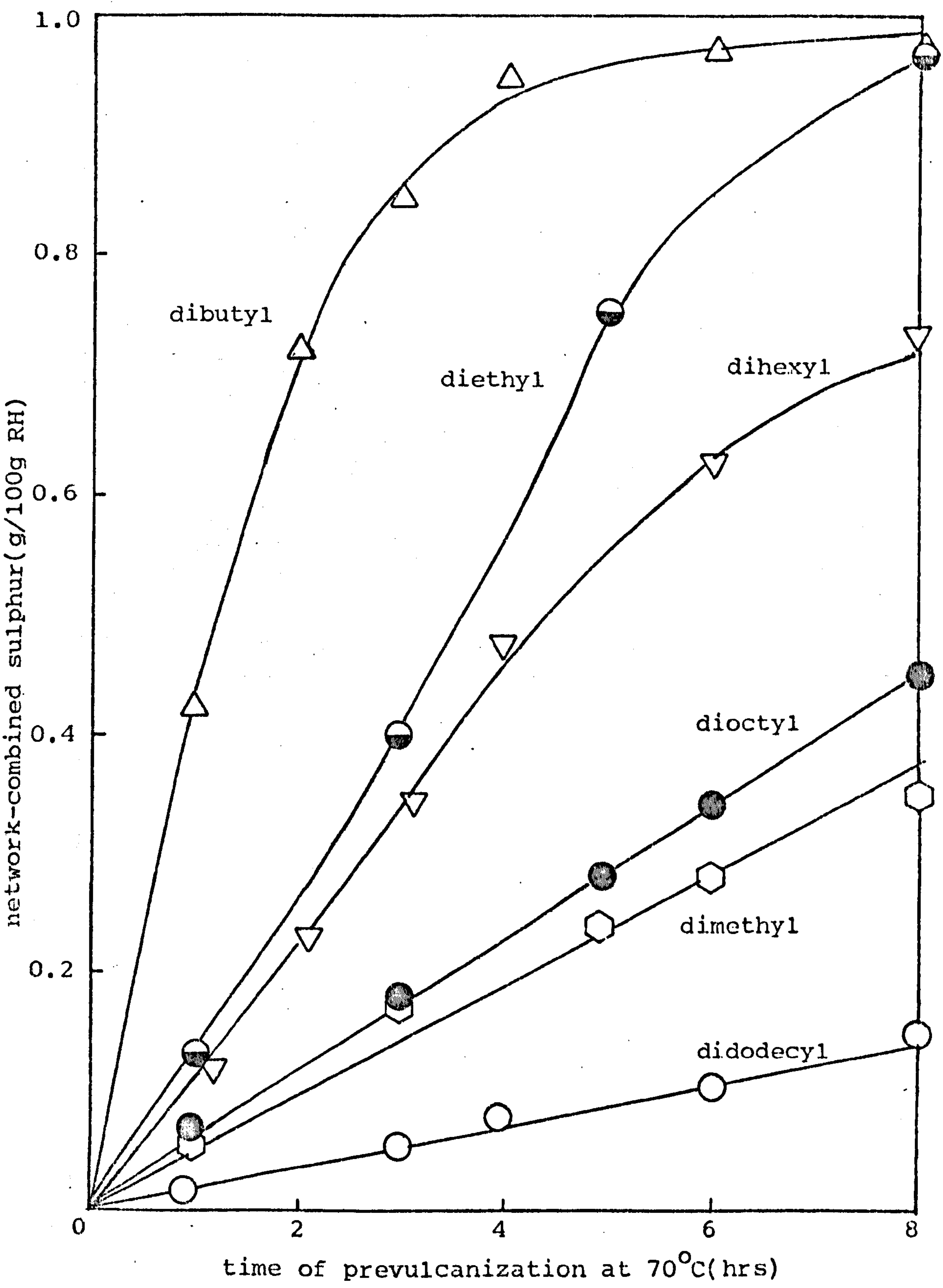


Fig. 7.29 Effect of variation of alkyl chain length of zinc dialkyldithiocarbamate upon network-combined sulphur as a function of prevulcanization time.

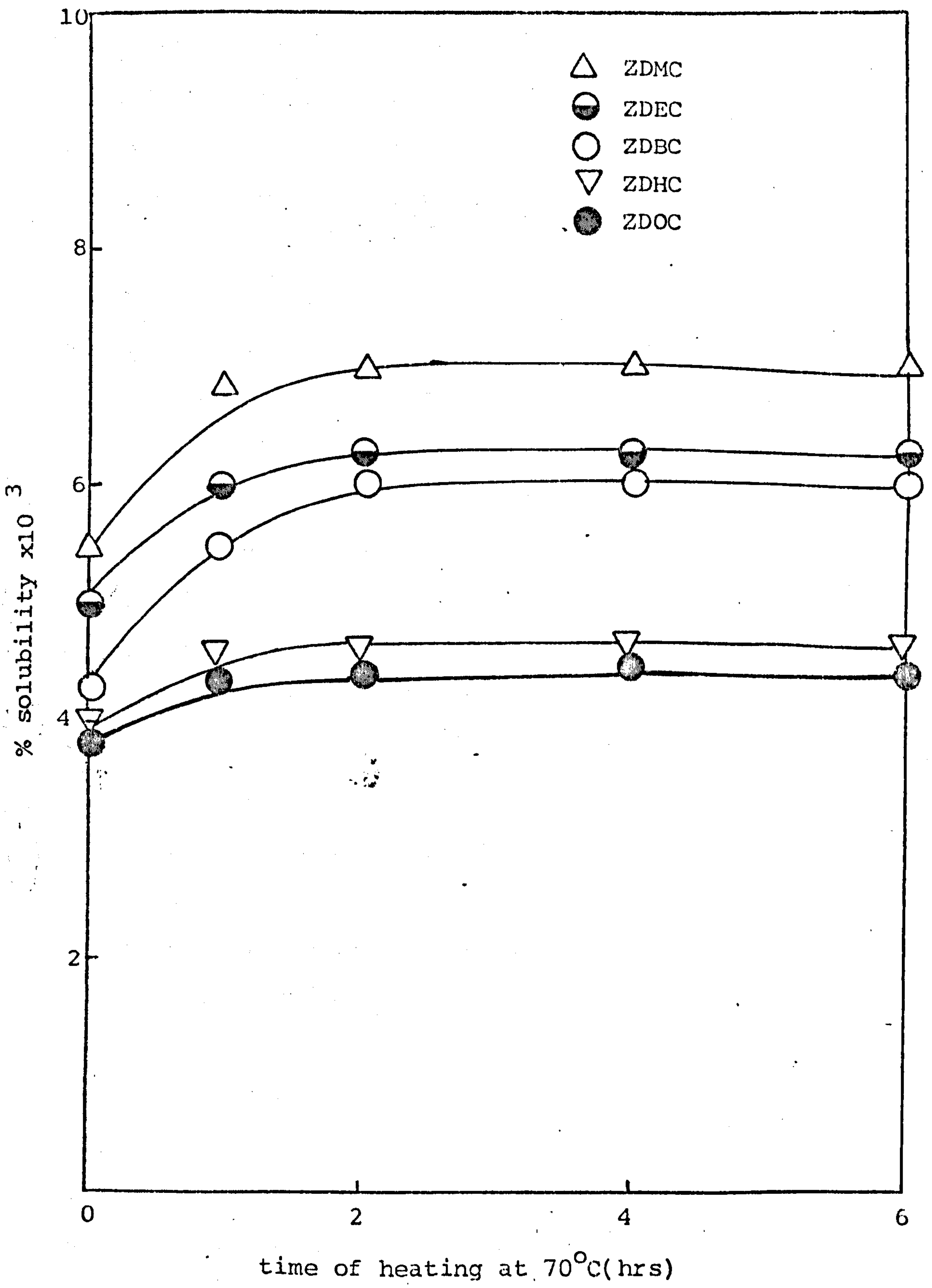


Fig. 7.30 Effect of variation of alkyl chain-length of zinc dialkyldithiocarbamate upon solubility in ammoniated water (pH 10.20) as a function of time of heating.

zinc dialkyldithiocarbamates in ammoniated water (pH 10.20), using an atomic absorption spectrometer. The detailed experimental procedures were similar to those described in Section 6.3. The results were as expected, in that the solubility in ammoniated water is decreased with increasing alkyl chain length of the dithiocarbamate. Combining the results for the solubilities of the zinc dialkyldithiocarbamates with those for their molal effectivenesses in accelerating sulphur combination, assuming that the effectiveness of a zinc dialkyldithiocarbamate as an accelerator of prevulcanization depends jointly on the solubility in the aqueous phase and ability of the active sulphurating agent to become adsorbed on the rubber particles, it seems reasonable then to suppose that the existence of an optimum alkyl chain length for acceleration of sulphur combination arises from the balance of the effects of two opposing tendencies as the alkyl chain length of the dithiocarbamate is increased. On the one hand, the tendency of the hydrocarbon moiety of the active sulphurating agent to become adsorbed on to the rubber particles would be expected to increase. But, on the other hand, the solubility of the dithiocarbamate accelerator in the aqueous phase of the latex decreases, and so too presumably does the concentration of active sulphurating agent. This explanation is illustrated diagrammatically in Fig. 7.31.

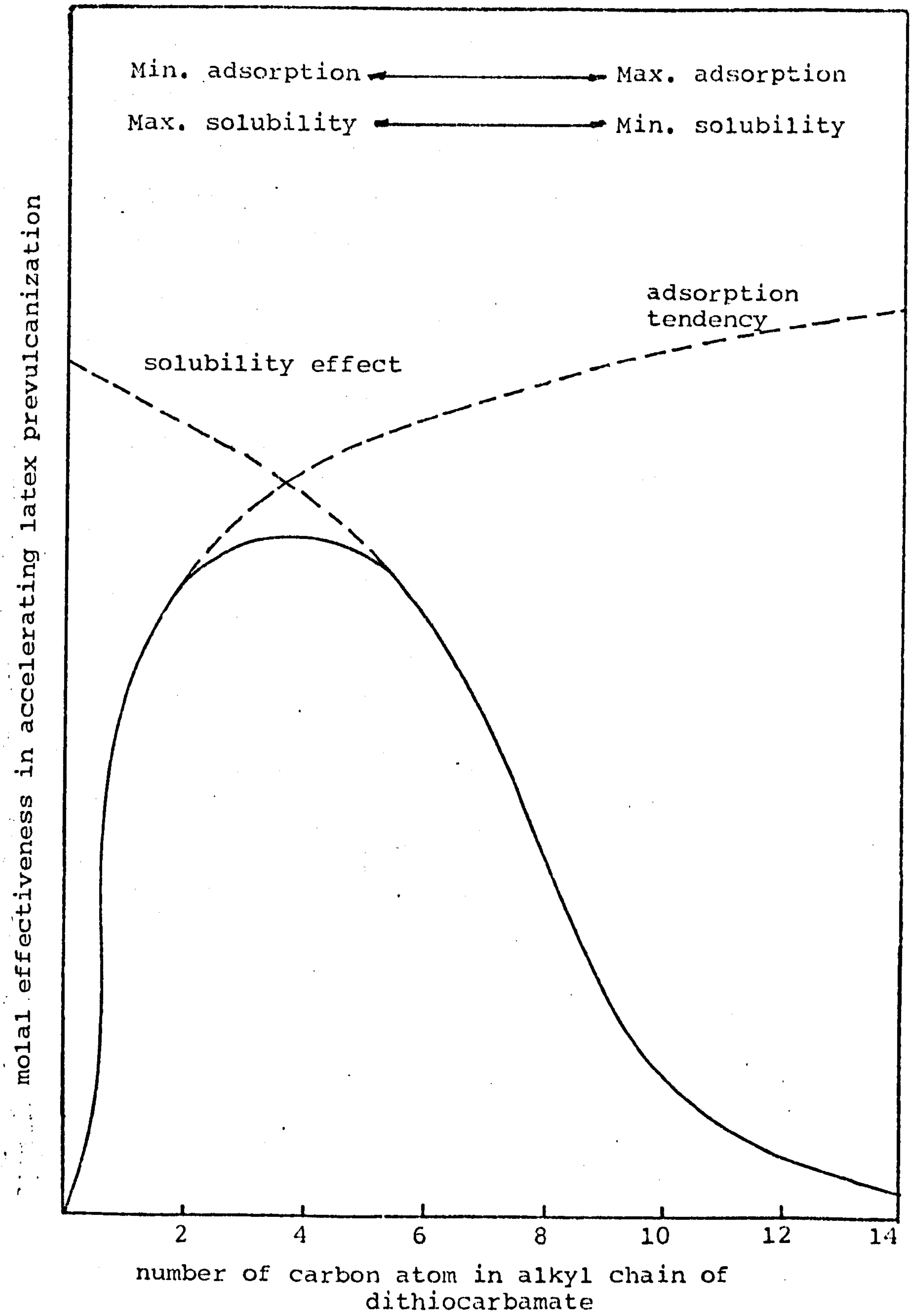


Fig. 7.31 Illustrating explanation for existence of an optimum alkyl chain for molal effectiveness of zinc dialkyldithiocarbamates as accelerators of sulphur combination in NR latex prevulcanization.

7.4.2. Effect of varying metal counterion of diethyldithiocarbamate upon NR latex prevulcanization

7.4.2.1. Prevulcanization recipes and reaction conditions

As in the previous investigation of the effect of varying the alkyl chain-length of the zinc dialkyldithiocarbamates, the present recipes were designed so that the various diethyl dithiocarbamates were present in amounts equimolal to 1.00 pphr of ZDEC. The amounts used were therefore as shown in Table 7.5. The amount of sulphur in the recipes was 1.00 pphr. All the experimental procedures and reaction conditions were similar to those used for the previous experiments, (see Section 7.4.1.1.), i.e., the prevulcanizations were carried out in sealed bottles at 70° ±1°C for 8 hours.

Table 7.5. Amount of each diethyl dithiocarbamate used in prevulcanization recipe

dithiocarbamate	molecular weight	pphr(equivalent on molal basis to 1.00 pphr of ZDEC)
Zinc diethyl dithiocarbamate(ZDEC)	361.72	1.000
Sodium diethyl dithiocarbamate(SDEC)	227.20	0.628
Lead diethyl dithiocarbamate (PbDEC)	503.54	1.392
Selenium diethyl dithiocarbamate (SeDEC)	671.64	1.857
Tellurium diethyl dithiocarbamate (TeDEC)	720.28	1.991

7.4.2.2. Results and discussion

Figs. 7.32 and 7.33 show the results for free and network-combined sulphur as functions of prevulcanization time for reaction systems containing diethyl dithiocarbamates having various counterions. It is interesting to note that the metal counterion of the diethyl dithiocarbamate has a significant effect upon the rate of combination of sulphur during prevulcanization. First, let us compare the results for three of the diethyl dithiocarbamate accelerators, namely, ZDEC, SDEC and PbDEC. ZDEC and PbDEC are both very sparingly soluble in the aqueous phase of the latex, although it is now known that the zinc compound certainly dissolves to a very limited extent at least(see Fig. 7.30). However, ZDEC is known for its ability to form complexes and to react fairly easily with sulphur to form an active sulphurating agent. But PbDEC is thought to be fairly inert. SDEC, on the other hand, is an accelerator which is soluble in the aqueous phase of the latex. Nevertheless, like PbDEC, it is thought to be fairly inert because of its inability to complex with ligands to form reactive intermediates in the way that ZDEC does. Therefore, it is proposed that, whilst the study of the effects of variation of the alkyl chain length in the zinc dialkyldithiocarbamates has led to consideration of the balance of the effects of solubility in the aqueous phase and adsorption of the resultant active sulphurating agent on to the rubber particles, the results obtained for the effects of varying the metal counterion of the diethyl dithiocarbamate suggest

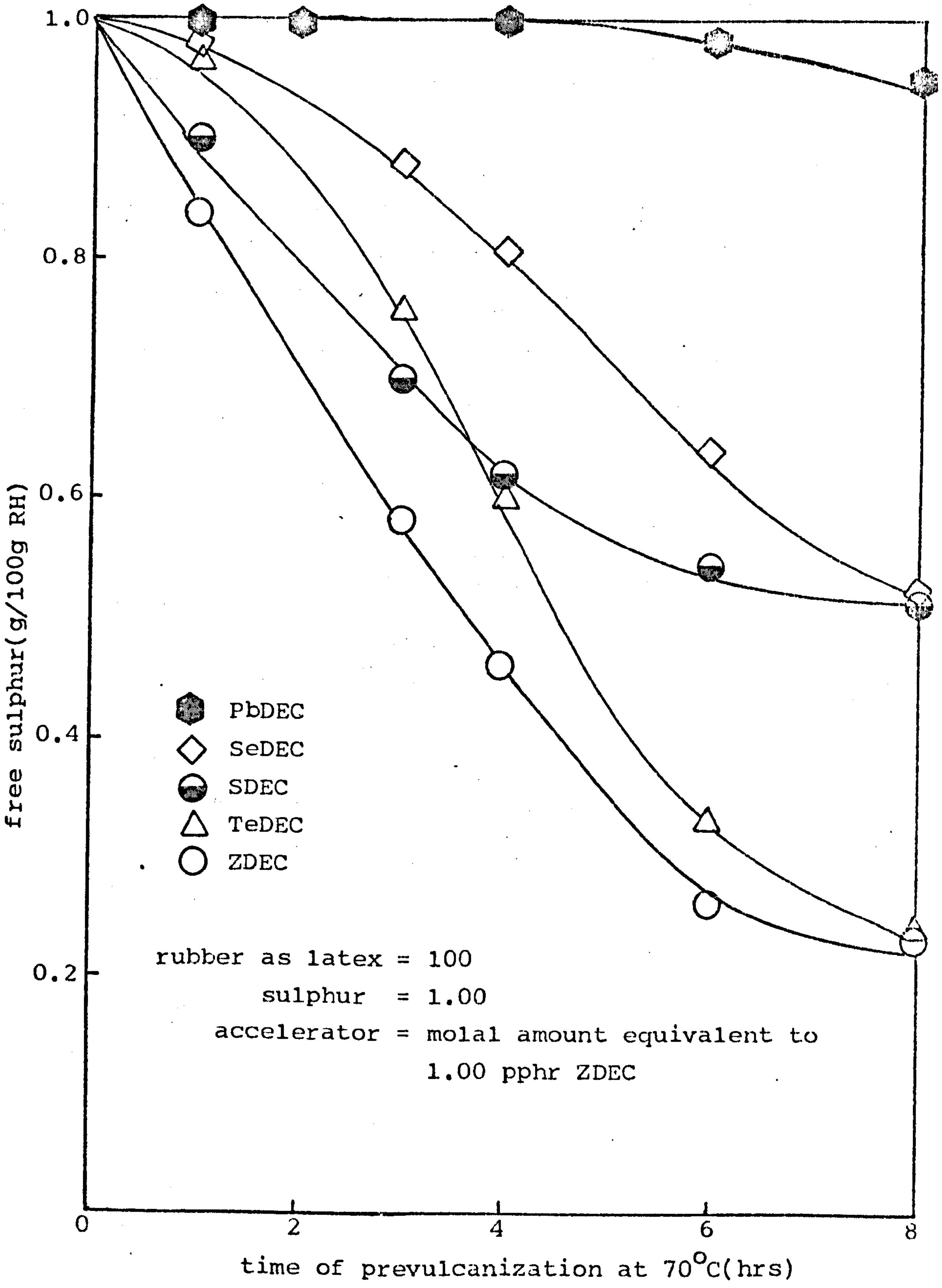


Fig. 7.32 Effect of variation of metal counterion of diethyl dithiocarbamate upon free sulphur as a function of prevulcanization time.

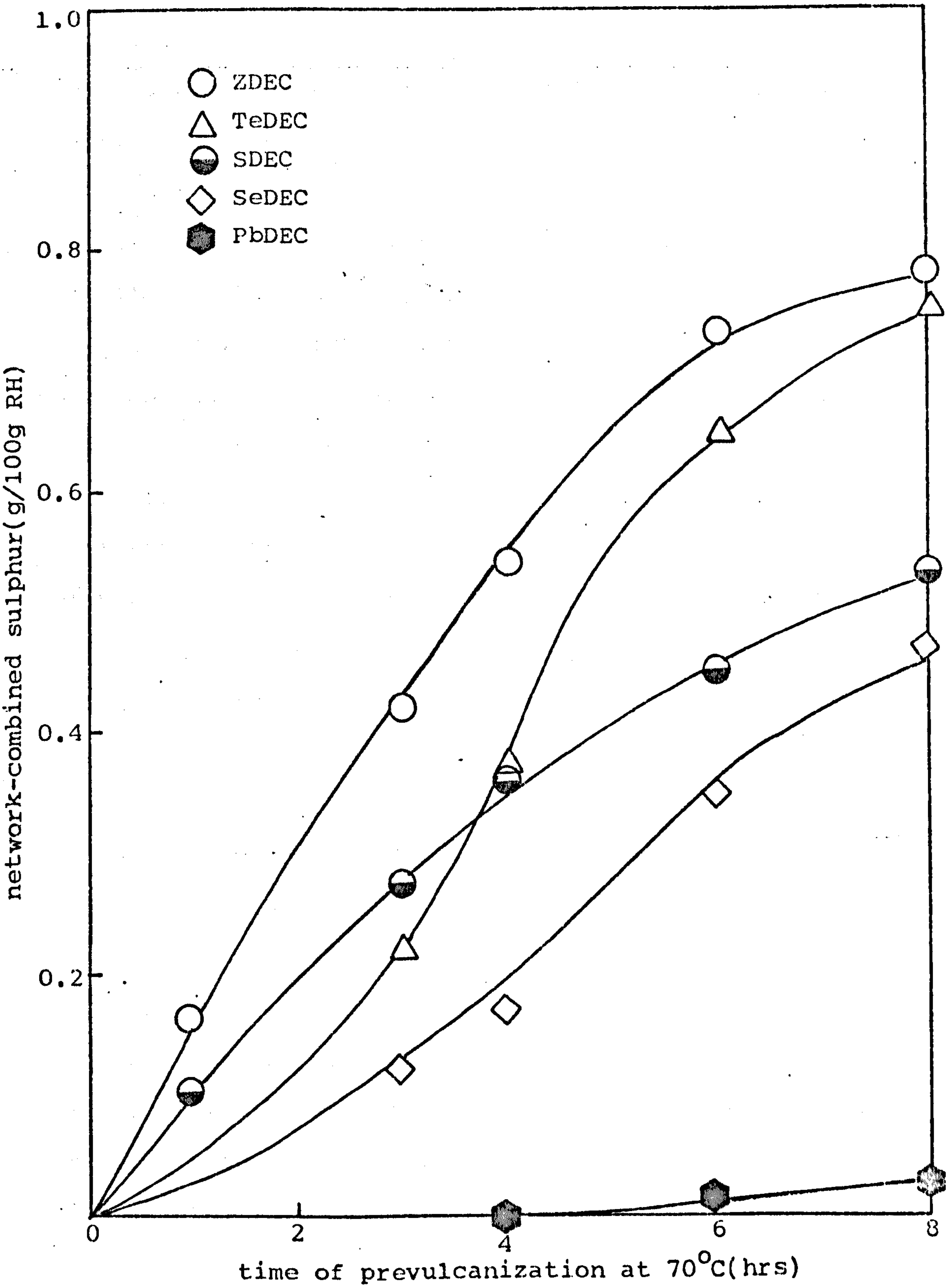


Fig. 7.33 Effect of variation of metal counterion of diethyl dithiocarbamate upon network-combined sulphur as a function of prevulcanization time.

the importance of the solubility and particularly the reactivity of the metal counterion of the dithiocarbamate towards sulphur. Despite complete solubility in the aqueous phase, SDEC prevulcanizes NR latex more slowly than does the equivalent molal quantity of ZDEC. It is suggested that, in the SDEC prevulcanization, the rate-determining step is reaction between the dissolved accelerator in the aqueous phase and sulphur to form the active sulphurating agent. By contrast, in the case of prevulcanization using ZDEC as accelerator, the reaction between the accelerator and sulphur in the aqueous phase (as hypothesised previously) is very rapid because of the reactivity of zinc towards sulphur. The rate-determining step is then adsorption on to the rubber particles. PbDEC, having neither the solubility of SDEC nor the ability to complex and react with sulphur in the aqueous phase of ZDEC, is expected to be relatively inert, as indeed it is.

The results obtained using SeDEC and TeDEC as accelerator shown in Figs. 7.32 and 7.33 give inverted 'S'-shaped curves. Selenium and tellurium are both in group six of the Periodic Table, and are similar in many respects to sulphur, which is also in group six. Therefore, the two accelerators can actually be regarded as a type of thiuram analogue. The inverted 'S'-shaped curves suggests an autocatalytic reaction. These curves are quite different in shape from most other curves for the combination of sulphur obtained in this work.

In summary, this investigation of the variation of the metal counterion of the diethyl dithiocarbamate has yielded very interesting results. However, the lack of sufficient information has prevented the development of a satisfactory theory to account for their effect upon the prevulcanization of NR latex. Suggestions for further work have been proposed in the next chapter, particularly in connection with the effect of variation of the metal counterion of a dialkyldithiocarbamate accelerator upon its behaviour as an accelerator for the prevulcanization of NR latex.

CHAPTER 8

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

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8.1. Comparison Between NR Latex Prevulcanization and Dry Vulcanization of NR

8.2. Comparisons Between Latex Prevulcanization and Dry Vulcanization of Synthetic Cis-polyisoprene, and Between NR Latex and Synthetic Cis-polyisoprene Latex Prevulcanization

8.3. Conclusions Concerning Solubility of Sulphur in Aqueous Phase of Latex During Prevulcanization from Clarity of Sheets Dried Down from Latex Compounds

8.4. Solubilities of ZDBC in Various Aqueous Media

8.5. Effect of Ammonia upon NR Latex Prevulcanization

8.6. Effect of Varying Levels of Sulphur and ZDBC upon NR Latex Prevulcanization

8.7. Contribution of Monosulphidic, Disulphidic and Polysulphidic Crosslinks to Overall Degree of Chemical Crosslinking

8.8. Effect of Variations in Nature of Dithiocarbamate Accelerators upon NR Latex Prevulcanization

CHAPTER 8

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

In this concluding chapter, an attempt is made to summarize the main findings of Chapters 6 and 7. Where appropriate, suggestions for further work have also been made.

8.1. Comparison Between NR Latex Prevulcanization and Dry Vulcanization of NR

At 50°C, and using a formulation comprising 1.31 pphr of ZDBC and 1.00 pphr sulphur, natural rubber in the form of latex vulcanizes at a very much faster rate than when it is in the dry form. After 8 hours of reaction, about 90% of the added sulphur was combined with the rubber when prevulcanized as latex compared with less than 10% in the case of the corresponding dry vulcanization of NR. To account for this phenomenon, it is suggested that some chemical reactions between the sulphur and the ZDBC may have occurred in the aqueous phase during latex prevulcanization. This may have resulted in the formation of an active sulphurating agent. It is also thought that the polar environment presented by the aqueous phase of the latex may have promoted this reaction, which is believed to have a polar mechanism.

It would be of interest to find out if the difference in vulcanization behaviour between dry NR and NR in latex form is reduced if, instead of the original compounding procedure in which sulphur and ZDBC dispersion are added directly to the latex as dispersions, the sulphur and ZDBC are first heated with NR latex serum under prevulcanization conditions. If the proposed hypothesis is correct, the subsequent vulcanization of the rubber in dry form should occur at a rate more nearly approaching that of prevulcanization in latex form.

8.2. Comparisons Between Latex Prevulcanization and Dry Vulcanization of Synthetic Cis-polyisoprene, and Between NR Latex and Synthetic Cis-polyisoprene Latex Prevulcanization

In the present work, synthetic *cis*-polyisoprene latex was obtained from a Japanese source and used for prevulcanization and dry vulcanization. It is believed that this is the first time that an investigation of latex prevulcanization has been carried out using this comparatively unusual type of synthetic latex. The results revealed that synthetic *cis*-polyisoprene latex can also be prevulcanized by reaction with sulphur and ZDBC. When compared with dry vulcanization of synthetic *cis*-polyisoprene, the results also confirm the effect which the presence of the aqueous phase of the latex seems to have upon the prevulcanization process. When the prevulcanization of synthetic *cis*-polyisoprene latex was compared with that of NR latex, using the same formulation and the same reaction conditions, it was found that sulphur combination and crosslink insertion occur somewhat more rapidly in NR latex prevulcanization. These differences are attributed to the presence of indigenous vulcanization accelerators and activators in NR latex, which are not present in synthetic cis-polyisoprene latex. These substances act as additional accelerator and activator during NR latex prevulcanization.

It is suggested that further work be carried out by adding different amounts of NR latex serum to synthetic cis-polyisoprene latex and investigating its prevulcanization behaviour. The results should then reveal the extent of the contribution to prevulcanization made by the naturally-occurring vulcanization accelerators and activators in NR latex.

8.3. Conclusions Concerning Solubility of Sulphur in Aqueous Phase of Latex During Prevulcanization from Clarity of Sheets Dried Down from Latex Compounds

It was realized in the course of the present work that by visual observation of the clarity of dried sheets, it was possible to draw conclusion concerning the solubility of sulphur in the aqueous phase of the latex during prevulcanization. Cast sheets obtained from NR latex with no added sulphur were clear. When 1.00 pphr sulphur was added, without any further treatment, the sheets prepared from the compound were opaque when dried at 25°C. However, when the opaque sheets were heated in an air oven at 50°C over a period of 30 minutes, they gradually turned clear. It is suggested that the presence of particles of sulphur uniformly embedded in the rubber matrix was responsible for the opacity of cast sheets, and that the sheets became clear on heating because the sulphur particles were dissolved molecularly in the rubber and no longer interfered with light transmission through the rubber matrix.

It was also found that, when NR latex containing 1.00 pphr sulphur added to it was heated for 30 minutes @ 50°C, the cast sheets obtained from this compound were clear. Therefore, based on the earlier reasoning, it was proposed that heating the compounded latex for a short while at the prevulcanization temperature (i.e., 50°C) was sufficient to enable the sulphur to become molecularly dissolved in the rubber. This dissolution was presumably achieved initially by an appreciable increase in the solubility of the sulphur in the aqueous phase when the latex compound was heated. This was then followed by gradual partitioning of the dissolved sulphur into the rubber particles. However, it was not certain whether all the sulphur in the latex was gradually partitioned into the rubber phase or a dynamic equilibrium was established between dissolved sulphur in the aqueous phase and sulphur dissolved in the rubber phase of the latex. In either case, cast sheets from the compound would be clear because the sulphur has become molecularly dissolved during the heating.

The dissolution of sulphur in NR latex during heating was found to be dependent upon the time and temperature of heating. In order to obtain clear cast sheets from the latex compound, the compound had to be heated for at least 30 minutes at 50°C or for 5 minutes at 70°C.

Sulphur was found not to dissolve in synthetic cis-polyisoprene latex even on prolonged heating at 70°C. The cast sheet obtained from the treated compound was opaque when dried. When this result was compared with those for NR latex, it appeared that the naturally-occurring non-rubber substances present in NR latex are responsible in some way for bringing the sulphur molecules from the sulphur particles into the aqueous phase of the NR latex during heating. This observation confirms the findings of van Gils,(18) who has indicated similar conclusions from his investigaions.

When NR latex and 1.00 pphr sulphur were heated at 50°C in the presence of 1.31 pphr ZDBC, only latex compounds which had been heated for 5 hours or longer gave clear cast sheets when dried. It is suggested that the opacity of the cast sheets obtained from latex compounds which had been heated for less than 5 hours was caused by the presence of ZDBC in the form of dispersed particles in the continuous rubber phase. To account for the clarity of sheets obtained from latex compounds heated for 5 hours or longer, it is suggested that the size and number of ZDBC particles were reduced perhaps through reaction with dissolved sulphur during prevulcanization, thereby forming a rubber-soluble active sulphurating agent, to such an extent that they could no longer scatter light when the latex compound was cast into sheets. The same observations were noted when the experiment was repeated using synthetic cis-polyisoprene latex. The only difference between the two series of experiments was that clear cast sheets were obtained from latex compounds which had been heated for 7 hours or longer instead of 5 hours or longer in the case of the experiment using synthetic cis-polyisoprene latex. This finding was considered interesting because the results indicate that, even though the solubility of sulphur in the aqueous phase of synthetic cis-polyisoprene latex was insufficient for clear cast sheets to be obtained from latex + 1.00 pphr sulphur alone (even with heating), it is sufficiently soluble to permit prevulcanization to occur when ZDBC is present. The finding is also consistent with, and lends credibility to, the proposal that sulphur and ZDBC react together in the aqueous phase to form an active sulphurating agent.

Based on these results on the clarity of cast sheets, an outline reaction scheme has been proposed to account for the disappearance of particles of vulcanizing ingredients during latex prevulcanization (see Fig. 6.14).

The present series of investigations suggests the importance of the naturally-occurring non-rubber substances in NR latex serum in bringing the sulphur molecules from the sulphur particles into the aqueous phase of NR latex during heating. Since these substances are not present in synthetic cis-polyisoprene latex, it would be of considerable interest to find out if there is any difference in the clarity of cast sheets when NR latex serum is added to the synthetic latex prior to heating the latex with sulphur.

8.4. Solubilities of ZDBC in Various Aqueous Media

It is concluded from the study of the clarity of cast sheets that the solubility of ZDBC in NR latex during prevulcanization is very low. Using atomic adsorption spectroscopy, the solubilities of ZDBC at 50°C in ordinary deionised water, deionised water which had been previously ammoniated to pH 10.20, and 28% NR latex serum were found to be 0.003%, 0.005% and 0.011% respectively. From these results, it is suggested that the solubility of ZDBC in normal NR latex is at least 0.011%, possibly somewhat higher. Although a solubility of 0.011% is very small by conventional standard, it is nevertheless in the same order as that of styrene monomer in the aqueous phase of a styrene emulsion polymerisation system. An analogy was discussed in which the disappearance of ZDBC during latex prevulcanization was likened to the disappearance of styrene monomer during emulsion polymerisation. It is proposed that the 0.011% of ZDBC dissolved in the serum reacts with dissolved sulphur to form an active sulphurating agent. The active sulphurating agent then presumably becomes partitioned into the rubber phase, thereby bringing about the crosslinking reaction. In the same way as the styrene monomer in a styrene emulsion polymerisation reaction system replenishes the styrene which has polymerised in the reaction loci, it is suggested that more ZDBC is then dissolved into the aqueous phase of the latex to re-establish the equilibrium.

To account for higher solubility of ZDBC in dilute NR latex serum and in ammoniated water compared to that in unammoniated deionised water, it is suggested that the naturally-occurring amines present in the dilute NR latex and the ammonia present in the ammoniated water assist the dissolution of ZDBC by complex formation. These ZDBC-ammonia and ZDBC-amine complexes are suggested to be more soluble in aqueous media than is the uncomplexed ZDBC.

A revised outline reaction scheme for latex prevulcanization (Fig. 6.17) which takes into account the present results for the dissolution and complex formation of ZDBC in the aqueous phase of NR latex is proposed.

It is hoped that further work will be done to extend the present investigation of the solubility of ZDBC in aqueous media. In particular, the following investigations would be especially interesting: Firstly, the solubility of ZDBC in normal NR serum should be determined. This would give a more accurate figure for the solubility of ZDBC during the prevulcanization reaction than the estimate which has been obtained for the solubility in dilute NR serum in the present work. Secondly, it would be of interest to extend the study on the effect of varying the ammonia concentration upon the solubility of ZDBC in ammoniated water. In conjunction with this, study of the solubility of ZDBC in an alkaline medium not containing ammonia or amines would provide information concerning the effect of pH, as distinct from ligand co-ordination, upon the solubility of ZDBC in aqueous media. All the present work was carried out by adding ZDBC alone to the various media. It would be of considerable interest to find out the influence of the presence of sulphur upon the solubility of ZDBC in aqueous media. Therefore, in this context, it would be very useful if the chemistry of the interaction between sulphur and a zinc dialkyldithiocarbamate in aqueous medium be investigated.

8.5. Effect of Ammonia upon NR Latex Prevulcanization

Though no information on the effects of ammonia upon NR latex prevulcanization has been reported in the literature, the present work showed that ammonia does have a significant effect upon the rate of disappearance of free sulphur during latex prevulcanization. At high ammonia concentrations (> 0.652%), the rate of disappearance of sulphur was found to be independent of the ammonia concentration. However, the rate of prevulcanization, as indicated by the disappearance of free sulphur, became progressively slower with decrease in ammonia concentration. It is suggested that these results are consistent with ammonia behaving as a complexing ligand for ZDBC during NR latex prevulcanization. The phenomenon of a delay in the onset of prevulcanization was observed for NR latex containing a very low concentration of ammonia (0.043%). It is proposed that the reappearance of free fatty acids when the ammonia is removed from the NR latex was responsible for the phenomenon. It is proposed that the free fatty acid acted as an inhibitor by reacting with the dissolved ZDBC. The proposal of free fatty acid acting as an inhibitor is supported by the observation that, when the alkalinity of the deammoniated latex was readjusted to the original pH using sodium hydroxide, the prevulcanization of this latex showed no delay of the onset of prevulcanization.

An alternative explanation to that of inhibitor causing the delay of onset of prevulcanization in latex containing very low ammonia content is also suggested. It is possible that, under conditions of low ammonia content, the latex may not initially contain sufficient of suitable ligands to complex with ZDBC. But heating for ca. 3 hours at 50°C may create sufficient ligands by hydrolysis of some of the non-rubber substances in NR latex. In view of this alternate explanation, it is suggested that further work be carried out to test it. If the explanation is correct, heating the latex which contained a very low ammonia concentration alone for 3 hours prior to the prevulcanization should then show no delay in prevulcanization when the prevulcanization is carried out. Further work on prevulcanization using synthetic cis-polyisoprene latex in the study of effect of ammonia is also recommended.

8.6. Effect of Varying Levels of Sulphur and ZDBC upon NR Latex Prevulcanization

Two series of studies were undertaken: In Series A, the effect of varying the level of ZDBC over the range 0.30-2.00 pphr with 1.00 pphr sulphur upon NR latex prevulcanization was investigated. In Series B, the effect of varying the levels of sulphur over the range 0.50-1.50 pphr with 1.00 pphr ZDBC upon NR latex prevulcanization was investigated. The following results were obtained from these experiments:

a) rate of disappearance of free sulphur and ZDBC as a function of time of prevulcanization;

b) rate of sulphur combination and crosslink insertion as a function of time of prevulcanization;

c) tensile strength of cast sheets as a function of time of prevulcanization; and
d) variation of χ, the polymer-solvent interaction parameter for the cast films swollen in n-decane, as prevulcanization progressed.

The rate of disappearance of ZDBC in the Series A investigation was found to be zero-order with respect to ZDBC concentration at any one level of ZDBC, but, surprisingly, first-order with respect to ZDBC concentration when the ZDBC concentration was varied. Some light was thrown upon this contradiction when the Series A experiments were repeated with using a purer form of ZDBC. A hypothesis was proposed that while disappearance by zero-order kinetics may be attributed to the limited solubility of ZDBC in the aqueous phase, disappearance by first-order kinetics may be attributable to the presence of active impurities in ZDBC which form complexes with the dithiocarbamates. These complexes are assumed to be more soluble in the aqueous phase than are the simple ZDBC-ammonia complexes.

It is suggested that further work be carried out to study the rate of uptake of sulphur and zinc dialkyldithiocarbamate into a model compound of NR latex, a simple oil-in-water emulsion for example. It would be of considerable interest to investigate the effect upon the reaction by using first a reactive oil phase and then comparing the results with those using a non-reactive oil phase.

8.7. Contribution of Monosulphidic, Disulphidic and Polysulphidic Crosslinks to Overall Degree of Chemical Crosslinking

Experiments have been carried out to determine the types of sulphidic crosslinks found in vulcanizate obtained from prevulcanized latex. The chemical probe technique indicated that the majority of the crosslinks were polysulphidic in nature. These polysulphidic crosslinks were also found to increase in concentration with the progress of prevulcanization. The concentration of monosulphidic crosslinks was too low to be detected.

It is suggested that further work be carried out to establish the fate of the polysulphidic crosslinks in vulcanizate obtained from prevulcanized latex by postvulcanization and comparing the results with that for a postvulcanization of latex deposited from an unvulcanized latex compound.

8.8. Effect of Variations in Nature of Dithiocarbamate Accelerators upon NR Latex Prevulcanization

The effects of varying the alkyl chain-length of the zinc dialkyl dithiocarbamates and the metal counterion of the diethyl dithiocarbamates upon NR latex prevulcanization were investigated.

Results from the study of the variation of alkyl chain-length of the zinc dialkyldithiocarbamate in NR latex prevulcanization indicate significant differences in ability to accelerate prevulcanization. Of those investigated, ZDBC was found to be the fastest latex accelerator under the conditions of the investigation. The following ascending order of accelerating power of the accelerators investigated was observed: ZDDC < ZDMC < ZDOC < ZDHC < ZDEC < ZDBC. Thus, the molal effectiveness of these accelerators appears to pass through an optimum as the alkyl chain-length of the accelerator is increased. It is postulated that the existence of this optimum alkyl chain-length arises from the balance of the effects of two opposing tendencies as the alkyl chain-length is increased. The first is the solubility in the aqueous phase of the dithiocarbamate. The second is the ability of the hydrocarbon moiety of the active vulcanizing species to be adsorbed on to the surface of the rubber particles.

Investigation of the effect of variation of the metal counterion of the diethyl dithiocarbamates in NR latex prevulcanization has revealed the comparative inertness of PbDEC and the poor accelerating behaviour of the water-soluble SDEC. It is suggested that the solubility of the accelerator and, in particular, the ability of the metal-counterion to form complexes during prevulcanization determine the effectiveness of the accelerator during latex prevulcanization. SeDEC and TeDEC behaved quite differently from ZDEC, SDEC and PbDEC, in that S-shaped free sulphur-prevulcanization time curves were obtained. It is suggested that they may behave as a thiuram analogue during prevulcanization because of the close similarity of telurium and selenium to sulphur.

Only initial exploratory work has been carried out in the present study concerning the effects of variation of alkyl chain-length and metal-counterion of dithiocarbamate upon the behaviour in NR latex prevulcanization. It is therefore suggested that a more systematic investigation to be carried out. Such study should include the rate of disappearance of accelerator as a function of prevulcanization time, the solubility of the accelerators in NR latex serum, investigation into the capability of complex formation of these accelerators during prevulcanization, etc.

APPENDIX A

(11)	3
(12)	y^x
(13)	3
(14)	F
(15)	1/x
(16)	)
(17)	÷
(18)	(
(19)	MR
(20)	4
(21)	x
(22)	MR
(23)	5
(24)	)
(25)	=
(26)	R/S
(27)	GOTO
(28)	0
(29)	0

The following data are entered into the memories prior to the execution of the programme.

W the load, in kg into memory 1,

g, 9.81 m/sec^2 into memory 2,

V_r, the volume fraction of rubber of test piece into memory 3, and the dimensions of the test piece which made up the area into memory 4 and 5.

For the right hand side of the equation (i.e., $\left(1 - \frac{h_s}{h_o V_r^{-\frac{1}{3}}}\right)^{-2} - \left(1 - \frac{h_s}{h_o V_r^{\frac{1}{3}}}\right)$), the programme reads as follows:

(1) (
(2) MR
(3) 1
(4) x
(5) MR
(6) 2
(7))
(8) x
(9) (
(10) MR
(11) 3
(12) y^x
(13) 3
(14) F
(15) 1/x
(16))
(17) ÷
(18) MR
(19) 4
(20) =
(21) +/-
(22) +

```
(23)          1
(24)          =
(25)          M
(26)          5
(27)          (
(28)          (
(29)          MR
(30)          5
(31)          y^x
(32)          2
(33)          +/-
(34)          )
(35)          -
(36)          MR
(37)          5
(38)          )
(39)          =
(40)          R/S
(41)          GOTO
(42)          0
(43)          0
```

The following are the data in the memories:

Mercer-dial reading in memory 1,

$4.23\text{x}10^{-7}$, factor which converts dial reading to distance moved vertically, in memory 2,

V_r, the volume fraction of rubber of test piece in memory 3, and the height (or thickness) of test piece, in m, into memory 4.

APPENDIX B

APPENDIX B

Values of χ with time of prevulcanization reported in the present thesis were computed using the following equation:

$$\chi = \frac{\left[-\ln(1-V_r)-V_r\right] - \left[(v_o)(G_{cs}/RT)(V_r^{1/3})\right]}{V_r^2}$$

The programme for the evaluation of the above relationship using the Commodore PR100 reads as follows:

```
 (1)          1
 (2)          -
 (3)          MR
 (4)          1
 (5)          =
 (6)          ln
 (7)          +/-
 (8)          -
 (9)          MR
(10)          /
(11)          =
(12)          M
(13)          2
(14)          MR
(15)          1
(16)          y^x
```

(17)	3
(18)	F
(19)	1/x
(20)	=
(21)	x
(22)	MR
(23)	3
(24)	x
(25)	MR
(26)	4
(27)	÷
(28)	(
(29)	MR
(30)	5
(31)	x
(32)	MR
(33)	6
(34)	)
(35)	=
(36)	M
(37)	7
(38)	MR
(39)	2
(40)	-
(41)	MR
(42)	7
(43)	÷
(44)	(

```
(45)          MR
(46)          1
(47)          x
(48)          MR
(49)          1
(50)          )
(51)          =
(52)          R/S
(53)          GOTO
(54)          0
(55)          0
```

The memories for this programme are:

Memory 1, V_r, the volume fraction of rubber of test piece, memory 2 is zero, memory 3 is G_{cs}, the swollen compression stress-strain modulus, memory 4 is the molar-volume of n-decane, the swelling solvent, memory 5 is the gas constant and memory 6 is the absolute temperature for the swollen test piece.

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