J. nat. Rubb. Res., 7(2), 85 – 101

Chemistry of the Latex Prevulcanisation Process. Part 1. Migration of Reactants from the Solid Phase into Rubber Particles

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High-ammonia natural rubber latex has been prevulcanised with a zinc diethyldithiocarbamate-accelerated sulphur system in which either the sulphur or the accelerator was incorporated into the latex from a solid deposit on the wall of the containing vessel. The occurrence of prevulcanisation under these conditions is best explained on the thesis that both the accelerator and sulphur dissolve in the aqueous serum of the latex before migrating into the rubber phase. Heating the uncompounded latex in a sulphur-coated flask and subsequently compounding it with accelerator in a separate vessel and then heating it, also causes prevulcanisation, demonstrating that the presence of other ingredients is not necessary for sulphur to dissolve in the latex. However, the degree of prevulcanisation is limited by the quantity of sulphur dissolved. Similarly, latex can be prevulcanised by heating it in a ZDEC-coated flask (in the presence of diethylamine), compounding it with a sulphur dispersion in a separate step, and reheating it. In this case, the degree of prevulcanisation is not limited, presumably because ZDEC is continuously regenerated as crosslinking proceeds.

Aqueous leaching of films deposited from a prevulcanised latex usually causes increases in film modulus and, particularly, strength. In the experiments described, aqueous leaching had very little effect on these or other stress-strain properties.

Prevulcanisation of a rubber latex may be defined as a process in which crosslinking of the rubber takes place inside discrete particles dispersed in the aqueous serum of the latex. Subsequent formation of a coherent film of vulcanised rubber by deposition and drying should not, according to this definition, involve further crosslinking of the rubber. In practice, unless the vulcanising ingredients have been exhausted or removed, this condition is not met. In many cases, manufacturers rely on further crosslinking taking place in the dry, or drying, film (post vulcanisation) to achieve the product properties they require.

The process of prevulcanisation of natural rubber (NR) latex has been known for more than seventy years[1] but many aspects of it are not at all well understood. These include:

- The means by which the vulcanisation chemicals, originally present as dispersed solids, are transported into the rubber particles
- The extent to which the chemistry of crosslinking resembles that which is believed to occur during the vulcanisation of bulk rubber
- The structure of the wet gel deposit and the factors which affect its cohesion
- The structure of the dry film and the factors responsible for its physical properties, especially its strength

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- The physical chemistry of the changes brought about by leaching the wet gel or dry film in water.

This series of papers is concerned only with the first two of these aspects: the organic and physical chemistry of the vulcanisation process *per se*.

Present Understanding

Transport through the aqueous phase. Blackley[2] recently discussed the nature of the chemical processes which must lead from the solid reactants dispersed in the aqueous phase to the sulphur crosslinking of rubber molecules inside colloidal particles. The three types of reactant: sulphur, zinc oxide and (usually) a zinc dialkyldithiocarbamate, are essentially insoluble in water and some commentators on the process have postulated that reaction takes place as a result of direct contact between particles of reactant and rubber[3,4] or have apparently accepted this as the mechanism[5,6]. Others have started from the premise that the reactants must dissolve in the aqueous phase before diffusing into the rubber particles[2, 7-10]. What has always remained unclear is the form in which this dissolution occurs, whether the reactants undergo any prior reaction in the aqueous phase, and the nature of the diffusing species.

It has been known for many years that zinc oxide is soluble in ammoniated latex[11]. Dissolution depends upon the presence in the latex of acidic substances which form ammonium ions from the ammonia and promote the formation of soluble, positively charged, zinc ammine complexes. These complexes are transported at least as far as the surface of the rubber particles[11]. Hence a well-established mechanism for the transport of zinc ions from zinc oxide to the rubber particles exists. However, this appears to be irrelevant so far as the chemistry of prevulcanisation is concerned since the presence of zinc oxide, although beneficial, is not necessary for prevulcanisation to take place, provided the accelerator being used contains zinc[12]. As in the case of bulk rubber vulcanisation, the function of zinc oxide in the vulcanisation process appears to be to act largely as a secondary source of zinc, to regenerate the accelerator as it becomes consumed[2]. Under the chemically most simple conditions then – those in which sulphur and a zinc dialkyldithiocarbamate are used – only two vulcanising reagents have to be considered.

The transfer of sulphur from its solid dispersion into the latex rubber particles is clearly a rapid process: with a very active accelerator, such as zinc dibutyldithiocarbamate (ZDBC), detectable crosslinking[13] of the rubber occurs in less than 12 h at 27°C. Although milling sulphur with a surfactant in water to provide a fine dispersion is a ubiquitous practice, it is known to be unnecessary for vulcanisation to take place[9,14]. More recently, Gorton and Pendle[15] showed that variation of the average particle size of the sulphur dispersion over quite a wide range (number-average particle diameter, 1.5-13 μm) has no effect on the rate or extent of crosslinking. This finding indicated that the sulphur either dissolves in the aqueous serum or, possibly, that it reacts with the accelerator (perhaps in the presence of the natural substances in the serum) to form some sort of colloidal species which is transported to the rubber particle surface. The latter possibility was suggested by the observation[2] that the initial rate of crosslinking of a synthetic polyisoprene latex was proportional to the number of particles present and not to their total surface area, which would have been expected had the reagents been in solution. Transport of sulphur through the serum by one of these routes had already been demonstrated by Van Dalfsen[7], who regarded the process as one of dissolution of sulphur in the serum.

In fact, the presence of the accelerator is known not to be necessary for the sulphur to be transported into the rubber

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particles. Although sulphur is said not to be appreciably soluble in aqueous ammonia[9 16], it is soluble in the serum of ammoniated latex. This was most convincingly shown by Van Gils[9] who also demonstrated that sulphur is soluble in a solution of cysteine (actually the hydrochloride) in water. Cysteine is present in natural latex[17] and it was inferred that other amino acids and/or proteins present in latex might behave likewise. The activity of such substances in prevulcanisation has recently been demonstrated[18] using a deproteinised and purified latex. In a zinc diethyldithiocarbamate(ZDEC)-accelerated system at 60°C, the crosslinking of this latex showed an induction period and was much slower than that of a standard high-ammonia (HA) latex. Addition of ammonia to the purified latex had no effect but addition of the amino acid, 3-aminopropionic acid (1% on the latex) accelerated crosslinking strongly (as did addition of aqueous serum from HA latex). However, it must be pointed out that, while the presence of such substances accelerates the prevulcanisation process, their absence does not actually prevent prevulcanisation from occurring[2]. In these cases, some other species would have to promote the dissolution of sulphur in the aqueous phase.

The behaviour of a zinc dialkyldithiocarbamate is different. The rate of its disappearance during prevulcanisation appears to follow zero-order kinetics[2,10,19]. This indicates either: i) that its concentration in the aqueous serum is constant, the bulk of the solid remaining undissolved[2,19]; or ii) that its disappearance is limited by the rate of diffusion of the accelerator (or a reaction intermediate derived from it) into the rubber[20,21]. The first of these explanations is more likely to be correct since the zero-order rate of disappearance of the accelerator varies with the initial accelerator concentration (or with the accelerator:sulphur ratio)[2 10,19]; a diffusion-controlled process might be expected to be independent of this external factor. Loh[10] found the solubility of ZDBC in water and in ammoniated water (pH 10.2) to be very small (0.003% – 0.005%). In diluted serum from NR latex, it was appreciably higher (0.011%). However, it appears that interaction between sulphur and the zinc dithiocarbamate may take place in the aqueous phase to form a species which is more soluble than the dithiocarbamate in both water and rubber. This was deduced by Blackley[2] on the basis of opacity or clarity of films containing one or both components and is supported by the fact that an increase in initial sulphur concentration raises the rate of disappearance of ZDBC. However, it should be pointed out that any deduction made on the basis of the disappearance of a zinc dithiocarbamate may be vitiated by the fact that a dithiocarbamate can disappear from ammoniated latex by a reaction unrelated to vulcanisation. Thus, Loh[10] observed a significant zero-order loss of ZDBC even in the absence of sulphur, while Loadman[22] noted its reaction with some unextractable component of NR. This did not occur with a synthetic polyisoprene latex. These observations are likely to be connected with the better documented decomposition of zinc dimethyldithiocarbamate (ZDMC) in latex[23].

There is, nevertheless, further evidence that dissolution of the accelerator in the aqueous phase is a rate-limiting feature: the rate and extent of crosslinking were hardly affected by changes in the initial dithiocarbamate concentration at constant sulphur concentration[20,21], or by dithiocarbamate concentrations above 1 p.h.r. when the sulphur concentration was changed *pro rata*[20].

In summary, present evidence favours the concept that both sulphur and zinc dithiocarbamate accelerator dissolve in some form in the aqueous serum of the latex and are thus transported to the surface of the rubber particles from where they diffuse into the rubber and crosslink it. Sulphur appears to undergo this process relatively rapidly, dissolving in the latex serum without the aid of the accelerator. In contrast, the low solubility of the accelerator in the serum appears to be rate-limiting but its solubility seems to be increased by the presence of sulphur, indicating that some degree of interaction may take place in the aqueous phase and before the reactants enter the rubber phase.

Reaction in the rubber particles. The sequence of events following the arrival of the vulcanising reagents at the surface of the rubber particles is also of some importance. The main question, of course, concerns the relative rates of diffusion of the reagents in the rubber and of their reaction with the rubber to form crosslinks. For one extreme (diffusion much faster than reaction), one can visualise homogeneously crosslinked rubber particles, irrespective of size; for the other (reaction much faster than diffusion), one would envisage the production, from large particles at least, of a highly crosslinked shell of rubber surrounding an uncrosslinked core. These two scenarios would be expected to be highly important for film formation from the vulcanised latex. If the particles are preferentially crosslinked near their surfaces, the reduced mobility of the rubber chains there should make it more difficult for the particles to coalesce and a highly coherent film would not be expected. In contrast, a latex composed of homogeneously crosslinked particles might be expected to coalesce well and to form a film with optimal physical properties.

At present, there seems to be no direct evidence which bears on this point. Hu and co-workers[24] claim, without providing evidence, that the rate of crosslinking is much greater than the rate of diffusion. They deduce that crosslinking occurs rapidly as the vulcanising agents enter the surface of the rubber particles and that the crosslinks formed hinder further diffusion of the reagents into the interior of the particles. Support for this conclusion is elicited from the work of Grushetskaya *et al.*[25] but this, and their associated work[26-29], all appear to apply to crosslinking *after* a film has been formed (although it is difficult to be certain in all cases because Russian authors seldom provide complete experimental details of their work). Hu and co-workers[24] also hold the view that the rubber molecules in latex particles are considerably more mobile than those in bulk rubber and that, when crosslinked with 'flexible' polysulphide crosslinks, it is possible for the crosslinks originally formed near the surface to become gradually re-distributed throughout the particle. The proposed time scale for this process is not at all clear. However, the rates of crosslinking exhibited by the various dithiocarbamate accelerators vary over a wide range and if crosslinking were so much faster than diffusion that surface crosslinking was prevalent, one might expect to see evidence of poor film properties from a ZDBC-accelerated prevulcanised latex at 50°C compared, for example, to those from a ZDMC-accelerated prevulcanised latex prepared at 70°C, after extended maturation at room temperature. The question of homogeneity of crosslinking inside the particles in a prevulcanised latex must be regarded as an open one.

This paper is concerned with the processes by which sulphur and a zinc dithiocarbamate are each able to migrate from a separate crystalline phase to the surface of rubber particles in a HA latex. The starting point for this work was the fundamental experiments of Van Gils[9] who showed *inter alia* that sulphur could transfer from solid lumps in a muslin bag or from a deposit on the wall of a container into the rubber particles of a latex, thus demonstrating the solubility of sulphur in latex serum. This approach has here been applied also to a zinc dithiocarbamate accelerator and has been extended to demonstrating that crosslinking of the rubber can also ensue.

EXPERIMENTAL

Latex Compounding and Vulcanisation

HA latex was a commercial sample, preserved with a 0.7 wt.% ammonia. (Found: N, 0.27%; ash, 0.46%; on evaporated film.) All compounding ingredients were commercial chemicals, used without further purification. Aqueous dispersions of sulphur, zinc oxide and ZDEC were prepared by ball milling under standard conditions[30].

Latex was compounded according to one of the formulations shown in *Table 1*. After compounding, the mixture was stirred slowly for 0.5 h and allowed to stand for 2 h before use. In some cases, longer maturation times were used. Where relevant, these are indicated in the tables and figures.

In experiments where sulphur was incorporated into the latex from a solid deposit on the wall of a flask, sulphur was melted in the lower section of a flanged flask and the flask rotated until the interior surface was coated and then allowed to cool. To coat a flask with ZDEC, it was found to be preferable to melt ZDEC carefully in a separate vessel and pour it into a flanged flask with simultaneous rotation of the flask to distribute the material over the interior surface.

Incubation (heating an uncomponded or incompletely compounded latex in a flask coated with a compounding ingredient) and prevulcanisation experiments were carried out in the covered flask immersed in a water bath maintained at 70°C. The latex was subjected to continuous slow stirring and samples were withdrawn at intervals for chloroform number testing and for preparing evaporated films, *ca.* 0.8 mm thick, by casting on level glass plates. After 24 h, the films were removed from the plates, hung in air and, when translucent, were placed in a vacuum desiccator over silica gel. They were removed from the desiccator and acclimatised in the test laboratory before tensile testing, which was carried out according to *ISO 37*.

Where leaching was carried out, the dried cast film was immersed in a large volume of de-ionised water for 16 h at room temperature (*ca.* 28°C) and then dried and tested as before.

In considering the data in the tables, it should be borne in mind that chloroform number is an instantaneous test which provides a measure of the extent of cross-linking at the time the test was made, whereas the physical measurements were made on films some five to ten days after casting. While ZDEC is a relatively slow accelerator at the ambient temperature of about 28°C, some degree of post-cure may take place between casting and measuring, and this will be reflected in apparently higher physical properties than would be indicated by the chloroform number.

Equilibrium Volume Swelling Measurements

Accurately weighed samples (*ca.* 0.2 g) cut from the vulcanised films (unleached except where indicated otherwise) were immersed in toluene at 35°C or 40°C and allowed to swell for 48 h (with one change

TABLE 1. PREVULCANISATION FORMULATIONS

Ingredient	Quantity (parts by dry weight) of mix				
	A	B	C	D	E
60% HA latex	100.0	100.0	100.0	100.0	100.0
10% Potassium hydroxide	0.3	0.3	0.3	0.3	–
50% Zinc oxide dispersion	0.25	0.25	0.25	0.25	0.25
50% Sulphur dispersion	–	–	1.5	1.5	1.5
50% ZDEC dispersion	1.5	1.5	–	–	–
10% Diethylamine solution	–	2.0	–	2.0	–

TABLE 2 PREVULCANISATION AT 70°C OF HA LATEX, COMPOUNDED ACCORDING TO MIX A, IN A FLASK COATED WITH SOLID SULPHUR

PrVn time (h)	Chloroform number	M300 (MPa) UL	M300 (MPa) L	TS (MPa) UL	TS (MPa) L	EB (%) UL	EB (%) L	V_r at 40°C in toluene UL
0	1	0.52	0.57	1.9	2.7	844	843	0.031
2	1	0.52	0.58	2.7	3.7	863	970	0.0345
5	2	0.53	0.58	5.2	5.2	976	1000	0.047
9	2	0.57	0.63	7.1	7.3	966	989	0.068
14	3	0.69	0.69	13.0	13.9	970	959	0.079
24	4	0.78	0.80	17.8	19.4	970	953	0.113

PrVn = Prevulcanisation
EB = Elongation at break
UL = Unleached; L = Leached

of solvent after 24 h). At the end of this period, surface solvent was removed with filter paper and the sample weighed in a closed weighing bottle. The imbibed toluene was removed by heating at 60°C in an air oven (to constant weight). Values of V_r, the volume fraction of rubber in the swollen gel, were calculated and corrected as previously described[31,32].

RESULTS

Incorporation of Sulphur from a Solid Deposit

The results presented in *Tables 2* and *3* and *Figure 1* show clearly that it is possible to prevulcanise NR latex utilising sulphur from a solid deposit on the wall of the containing vessel. Reaction was slow, the

TABLE 3. PREVULCANISATION AT 70°C OF HA LATEX, COMPOUNDED ACCORDING TO MIX B, IN A FLASK COATED WITH SOLID SULPHUR

PrVn time (h)	Chloroform number	M300 (MPa) UL	M300 (MPa) L	TS (MPa) UL	TS (MPa) L	EB (%) UL	EB (%) L	V_r at 40°C in toluene UL
0	1	0.50	0.55	2.1	3.1	932	892	0.024
2	1	0.50	0.58	4.6	5.0	990	992	–
5	2	0.58	0.64	7.7	9.0	900	967	0.062
9	3	0.70	0.74	13.0	13.3	924	913	0.092
14	3	0.81	0.88	17.3	20.9	811	827	0.113
24	3	0.96	1.15	18.2	28.9	809	737	0.145

PrVn = Prevulcanisation
EB = Elongation at break
UL = Unleached; L = Leached

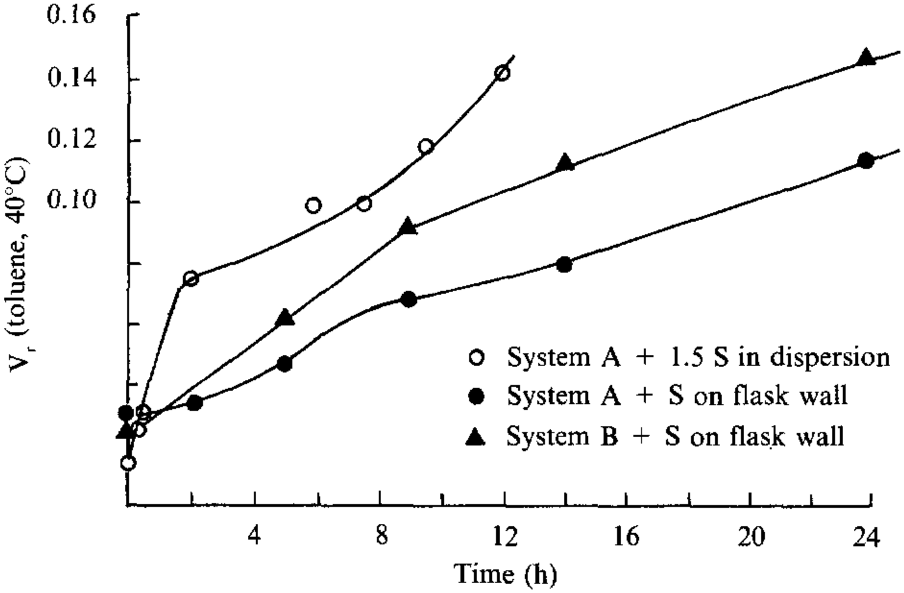

Figure 1. Influence of the form of sulphur on the development of crosslinking (as measured by equilibrium volume swelling) during prevulcanisation with a ZDEC-accelerated system at 70°C.

chloroform number still not having reached 4 in 14 h at 70°C. Nevertheless, M300 values (the stress values at 300% extension) of 0.8 MPa and tensile strength (TS) values of nearly 20 MPa indicate that considerable vulcanisation had occurred after 24 h. This was confirmed by an equilibrium V_r value in toluene of 0.113. For comparison, vulcanisation of *System A* (*Table 1*) containing 1.5 p.h.r. sulphur as a ball-milled dispersion, in addition to the other ingredients, produced, after 2 h at 70°C, the following values (for leached film)[33]: M300, 0.96 MPa; TS, 28.6 MPa. The rate of change of V_r with time is compared with that for the same system[13] in *Figure 1*. (In preparing the deposit, care was taken not to heat the sulphur further above its melting point than was necessary to achieve adequate flow. Nevertheless, allotropic transformation cannot be excluded.)

The inclusion of diethylamine in the latex formulation (*Mix B*) increased the rate of vulcanisation, but only by a factor of about two (*Table 3*) and most of its effect was seen in the early stages of the reaction (*Figure 1*). Primary and secondary amines are known to facilitate the dissolution of sulphur[34,35] and have been recommended[36,37] for activation of sulphur in latex formulations. Whether diethylamine was present or not, prevulcanisation did not show any sign of slowing down in 24 h at 70°C. At the end of this period, the sulphur on the wall of the flask appeared to be heavily coated with coagulum; this evidently did not prevent further reaction.

To determine whether the presence of other compounding ingredients was necessary to effect dissolution of the sulphur, HA latex was heated for a 24-h period at 70°C in a sulphur-coated flask and then transferred to a second flask, where it was compounded with solid dispersions according to *Mix A*, and allowed to stand (mature) for 2 h. As expected, there was little evidence for any crosslinking of the rubber phase having occurred at this point but on further heating at 70°C, a limited amount of crosslinking took place in a 3-h period, after which extensive coagulation occurred (*Table 4*).

However, even after 3 h, there was already evidence that the degree of prevulcanisation was reaching a plateau well short of a level where the best properties would be expected. Thus, the chloroform number did not reach 4 and values of 0.5 MPa for M300 and 10 MPa for TS for cast films were not exceeded. It appeared that prevulcanisation was occurring but to only a limited extent, which was presumably controlled by the amount of sulphur which had dissolved into the latex during the first heating period. It seems that, while sulphur can dissolve in the serum of HA latex, the rate of dissolution is very slow in the absence of ancillary chemicals. This accords with Van Gils's observations, which were made at room temperature[9].

Addition of diethylamine to the latex before incubation in the sulphur-coated flask did not significantly affect the results (*Table 5*). The absence of an effect indicates that the modest acceleration of the earlier prevulcanisation (*Figure 1*) may be due to interaction of the diethylamine with the dithiocarbamate component.

Retaining the 24-h initial heating time but increasing the maturation period at room temperature after subsequent compounding gave a more positive result on prevulcanisation (*Table 6*). A chloroform number of 4 was reached in 3 h at 70°C, after which time the TS of a cast film was 17 MPa. Evidence from TS (*Figure 2*) and equilibrium swelling values (*Figure 3*) indicates that prevulcanisation was rapid for 1–1.5 h and then it became much slower and a plateau was reached, suggesting again that the quantity of sulphur taken up was a limiting feature. However, the results of *Tables 4* and *6*, and *Figures 2* and *3* point to the limiting crosslink density being higher after 17 h maturation than after 2 h maturation. Since the quantity of sulphur in the system is already fixed by the incubation period, this observation implies either that there is a re-distribution of sulphur between the aqueous and polymer phases during the maturation period or that longer maturation allows more accelerator or accelerator complex to enter the rubber phase, producing more efficient crosslinking from the sulphur already present there.

TABLE 4. PREVULCANISATION AT 70°C OF HA LATEX WHICH HAD BEEN HEATED IN A SULPHUR-COATED FLASK FOR 24 H AT 70°C, COOLED, COMPOUNDED ACCORDING TO MIX A AND MATURED FOR 2 H AT ROOM TEMPERATURE

PrVn time (min)	Chloroform number	M300 (MPa)		TS (MPa)		EB (%)		V_r at 40°C in toluene
		UL	L	UL	L	UL	L	UL
0	1	0.25	0.20	4.3	2.6	879	849	0.031
10	1	0.26	0.24	5.4	3.1	978	970	–
30	2	0.33	0.26	5.7	4.2	998	988	0.048
60	2	0.34	0.36	7.5	5.9	1 006	999	0.062
90	3	0.37	0.37	8.1	7.1	1 010	995	0.062
120	3	0.37	0.48	8.6	7.6	990	995	0.064
180	3	0.39	0.50	9.2	9.8	985	989	0.065

PrVn = Prevulcanisation

EB = Elongation at break

UL = Unleached; L = Leached

TABLE 5. PREVULCANISATION AT 70°C OF HA LATEX WHICH HAD BEEN HEATED WITH DIETHYLAMINE (2 P.H.R.) IN A SULPHUR-COATED FLASK FOR 24 H AT 70°C, COOLED, COMPOUNDED ACCORDING TO MIX A AND MATURED FOR 2 H AT ROOM TEMPERATURE

PrVn time (h)	Chloroform number	M300 (MPa)		TS (MPa)		EB (%)		V_r at 40°C in toluene
		UL	L	UL	L	UL	L	UL
0	1	0.30	0.25	5.3	3.4	999	943	0.023
10	1	0.34	0.30	5.7	4.2	963	980	0.027
30	2	0.36	0.30	7.7	4.7	996	1 000	0.038
60	2	0.36	0.32	9.4	8.7	989	989	0.054
90	3	0.42	0.44	11.0	8.8	1 005	998	0.061
120	3	0.49	0.44	11.5	9.4	1 003	953	0.065
180	3	0.53	0.50	13.4	9.8	986	999	0.069

PrVn = Prevulcanisation
EB = Elongation at break
UL = Unleached; L = Leached

TABLE 6 PREVULCANISATION AT 70°C OF HA LATEX WHICH HAD BEEN HEATED IN A SULPHUR-COATED FLASK FOR 24 H AT 70°C, COOLED, COMPOUNDED ACCORDING TO MIX A AND MATURED FOR 17 H AT ROOM TEMPERATURE

PrVn time (h)	Chloroform number	M300 (MPa)		TS (MPa)		EB (%)		V_r at 40°C in toluene
		UL	L	UL	L	UL	L	UL
0	1	0.30	0.19	5.6	6.2	1 110	987	0.036
0.5	2	0.41	0.31	12.0	9.4	999	990	0.053
1	3	0.48	0.48	14.7	12.3	1 009	992	0.073
1.5	3	0.52	0.49	16.4	13.1	1 102	993	0.084
2	3	0.59	0.51	16.4	14.6	990	989	0.084
3	4	0.60	0.56	16.9	15.2	1 012	1 109	0.086

PrVn = Prevulcanisation
EB = Elongation at break
UL = Unleached; L = Leached

Maintaining the 17-h maturation period but doubling the incubation period increased the initial rate of crosslinking during subsequent prevulcanisation – indeed, there were indications that some crosslinking was now occurring during the maturation period (*Table 7* and *Figures 2* and *3*). However, there was again a fall in rate after 1 – 1.5 h to a low or zero value. In this case, the much higher limiting values of TS and V_r may be ascribed to dissolution of more sulphur in the latex during incubation. Presumably, saturation of the two latex phases with sulphur is not reached in 48 h.

A feature of the results collected in *Tables 4 – 7* which should not pass un-

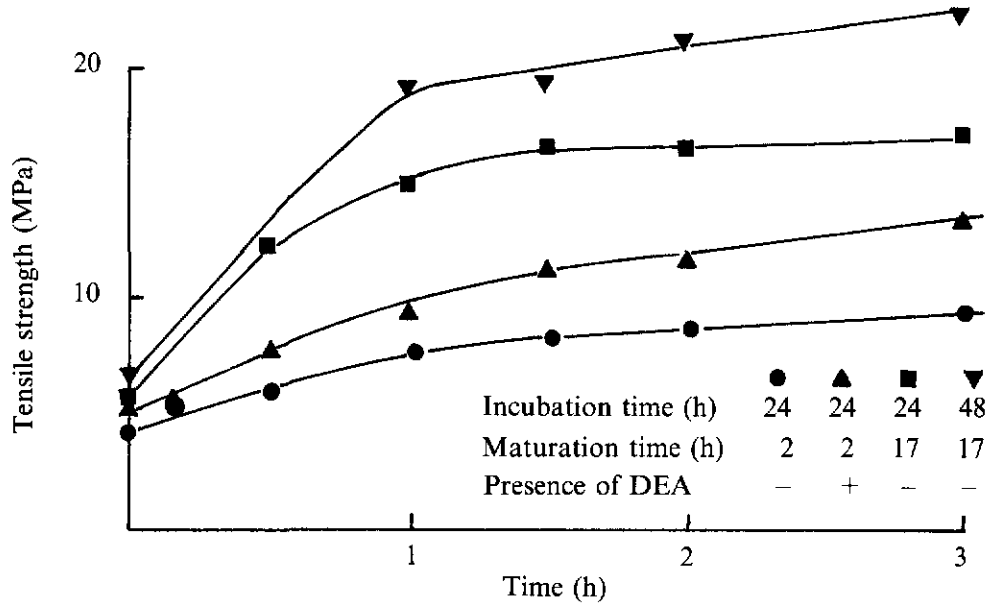

Figure 2. Influence of incubation time and maturation time on the development of tensile strength during prevulcanisation at 70°C of a ZDEC-accelerated system with sulphur present as a solid deposit.

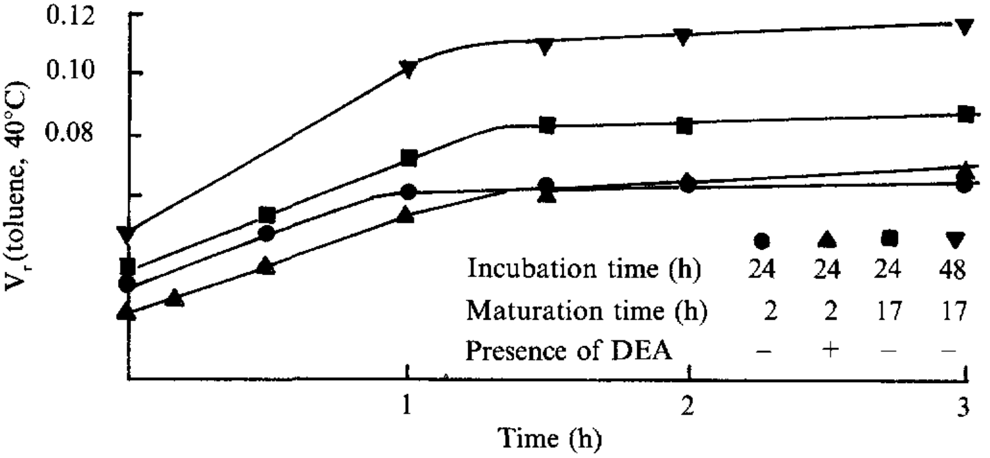

Figure 3. Influence of incubation time and maturation time on the development of crosslinking (as measured by equilibrium volume swelling) during prevulcanisation at 70°C of a ZDEC-accelerated system with sulphur present as a solid deposit.

remarked is the unusual effect of aqueous leaching on the properties of the subsequently dried films. The well-known effects of leaching in increasing strength and, to a lesser extent, stiffness, which have been consistently observed in pre-

TABLE 7 PREVULCANISATION AT 70°C OF HA LATEX WHICH HAD BEEN HEATED IN A SULPHUR-COATED FLASK FOR 48 H AT 70°C, COOLED, COMPOUNDED ACCORDING TO MIX A AND MATURED FOR 17 H AT ROOM TEMPERATURE

PrVn time (h)	Chloroform number	M300 (MPa) UL	M300 (MPa) L	TS (MPa) UL	TS (MPa) L	EB (%) UL	EB (%) L	V_r at 40°C in toluene UL
0	2	0.30	0.28	6.5	6.3	947	843	0.048
1	3	0.42	0.31	19.0	15.1	983	970	0.102
1.5	4	0.42	0.41	19.4	19.7	998	998	0.109
2	4	0.51	0.42	21.1	18.2	997	1 009	0.114
3	4	0.60	0.43	22.2	19.7	999	1 050	0.116

PrVn = Prevulcanisation
EB = Elongation at break
UL = Unleached; L = Leached

vious and concurrent work in these laboratories (see example in Porter and Wong[33]) are absent here. In fact, in many cases, leaching had an adverse effect on tensile strength and modulus. The present lack of understanding of the leaching process prevents any comment being made on the reason for this effect beyond noting that it is presumably related to the unusual procedure used for performing the prevulcanisation.

Incorporation of a Zinc Dithiocarbamate from a Solid Deposit

In spite of the high melting point of ZDEC (175°C), it was possible to spread the liquid material over the wall of a flask without significant decomposition taking place, provided care was taken to avoid overheating. It was found best to pour molten ZDEC from a separate vessel into a cold, rotated flask. Melting ZDEC in the flask to be coated and allowing it to cool did not produce such a robust solid deposit.

When HA latex, compounded as in *Mix C* (*Table 1*), was stirred at 70°C in a ZDEC-coated flask, prevulcanisation took place but only after what appeared to be a long induction period (*Table 8*): the chloroform number was still 1 after 7 h whereas the same mixture containing ZDEC in disper-

TABLE 8. PREVULCANISATION AT 70°C OF HA LATEX, COMPOUNDED ACCORDING TO MIX C, IN A FLASK COATED WITH SOLID ZDEC

PrVn time (h)	Chloroform number	M300 (MPa) UL	M300 (MPa) L	TS (MPa) UL	TS (MPa) L	EB (%) UL	EB (%) L
7.5	1	–	–	–	–	–	–
14.3	4	0.81	1.01	27.1	34.4	911	932
17.7	4	0.83	1.06	25.5	33.3	887	895
24.3	–	0.83	1.16	23.0	31.5	850	895

PrVn = Prevulcanisation
EB = Elongation at break
UL = Unleached; L = Leached

sion attained its maximum tensile strength[33] in 2 h at 70°C. (The TS values in *Table 8* are appreciably higher than those in *Table 9* and in Porter and Wong[33]. This is likely to be because the results in *Table 8* were obtained in a different laboratory and using a cutter and tensile test equipment which were different from those used in obtaining the remaining results in this paper and those in Porter and Wong[33].)

Inclusion of diethylamine in the compounded latex (*Mix D* of *Table 1*) gave the results shown in *Table 9*. After a much shorter induction period (1 – 2 h), prevulcanisation proceeded smoothly for some 4 h, after which M300 of a leached film had reached 0.9 MPa and TS had reached 24 MPa. Thereafter, reaction proceeded more slowly for at least another 12 h, if judged by V_r values (*Figure 4*) (but underwent some reversion if judged by M300).

In view of the results obtained previously, it was anticipated that the presence of sulphur and zinc oxide would not be necessary for the ZDEC to migrate from the solid deposit into the latex. This proved to be the case. Incubation of the latex with ZDEC for 6.5 h in the presence of diethylamine and potassium hydroxide (included to avoid the premature coacervation which had occurred in the experiments with the sulphur deposit) allowed sufficient ZDEC to become incorporated in the latex to obtain rapid and extensive prevulcanisation, after addition of sulphur and zinc oxide (*Table 10*). Indeed, crosslinking appears to be continuing vigorously after 18 h (*Figure 4*). The induction period has disappeared and it is clear that a considerable degree of crosslinking has taken place, if not during the maturation period itself, then during the period before the dried films were tested.

In both experiments with solid deposits of ZDEC, it is noteworthy that tensile strength reaches a maximum after 6 h, at a rather lower modulus than usual[38]. As with the sulphur deposit experiments, aqueous leaching of the vulcanised films had only minor effects on modulus and strength.

DISCUSSION

Sulphur can migrate from a continuous solid deposit where it is present as cyclo-octasulphur, S_8, into the rubber particles of HA latex[9]. It has now been demonstrated

TABLE 9. PREVULCANISATION AT 70°C OF HA LATEX, COMPOUNDED ACCORDING TO MIX D, IN A FLASK COATED WITH SOLID ZDEC

PrVn time (h)	Chloroform number	M300 (MPa)		TS (MPa)		EB (%)		V_r at 35°C in toluene	
		UL	L	UL	L	UL	L	UL	L
0	1	0.29	0.37	1.7	4.0	1 050	700	–	–
1	1	0.28	0.37	3.9	3.2	1 050	1 250	–	–
2	1	0.31	0.43	5.5	8.2	1 025	1 100	0.048	0.050
4	2	0.57	0.66	17.2	18.3	1 017	1 050	0.121	0.071
6	3	0.66	0.86	19.8	24.0	1 000	1 050	0.147	0.154
8	3	0.86	0.93	23.2	22.3	1 000	950	0.154	0.151
12	4	0.83	0.89	21.7	20.8	900	950	0.156	0.157
18	4	0.60	0.76	19.0	17.4	850	800	0.166	0.167

PrVn = Prevulcanisation
EB = Elongation at break
UL = Unleached; L = Leached

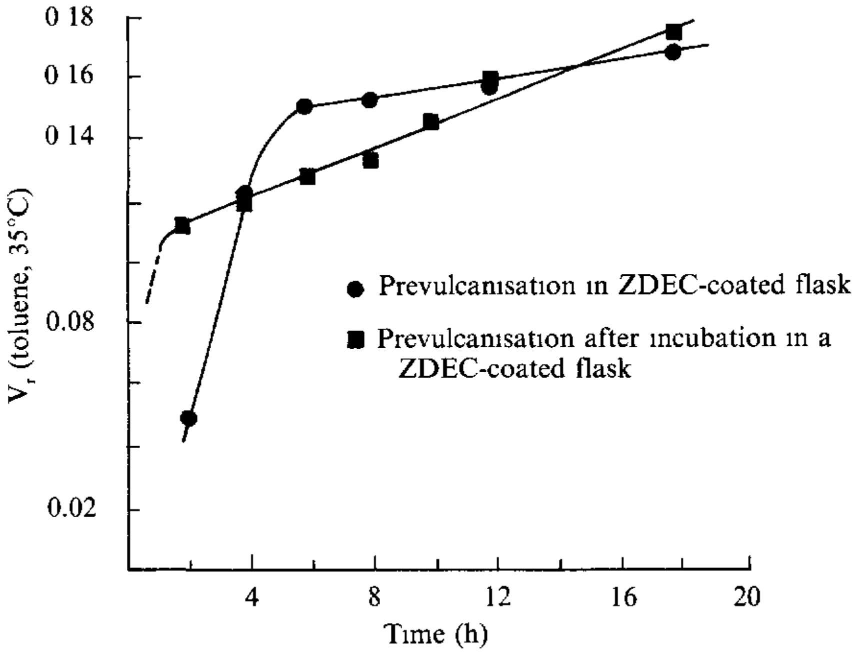

Figure 4 Development of crosslinking (as measured by equilibrium volume swelling) during prevulcanisation at 70°C with ZDEC present as a solid deposit.

TABLE 10 PREVULCANISATION AT 70°C OF HA LATEX WHICH HAD BEEN HEATED WITH DIETHYLAMINE (2 p.h.r.) AND POTASSIUM HYDROXIDE (0.3 p.h.r.) IN A ZDEC-COATED FLASK FOR 6.5 H AT 70°C, COOLED, COMPOUNDED ACCORDING TO MIX E AND MATURED FOR 17 H AT ROOM TEMPERATURE

PrVn time (h)	Chloroform number	M300 (MPa) UL	M300 (MPa) L	TS (MPa) UL	TS (MPa) L	EB (%) UL	EB (%) L	V_r at 35°C in toluene UL	V_r at 35°C in toluene L
0	1	0.51	0.51	12.9	15.2	1 100	1 150	–	–
2	2	0.63	0.69	21.4	21.7	1 100	1 000	0.119	0.105
4	2	0.75	0.82	22.3	22.9	1 100	1 050	0.121	0.116
6	3	0.74	0.83	21.8	23.4	1 050	1 000	0.128	0.126
8	4	0.75	0.81	20.2	20.3	1 025	950	0.136	0.127
10	4	0.85	0.92	21.8	22.5	950	950	0.146	0.142
12	4	0.85	0.94	21.6	21.5	900	900	0.160	0.158
18	4	0.77	0.94	19.3	20.0	850	875	0.174	0.170

PrVn = Prevulcanisation
EB = Elongation at break
UL = Unleached, L = Leached

that if the latex contains, or is subsequently compounded with, dispersions of a zinc dithiocarbamate accelerator and zinc oxide and heated, the rubber becomes crosslinked. Van Gils[9] finding that the presence of an accelerator or any other compounding ingredient is not necessary for the migration to occur is confirmed; neither is any additional surfactant required. In view of the form of sulphur used in these experiments (a hard deposit), it is difficult to imagine any other transport mechanism for the migration than dissolution in the aqueous serum followed by diffusion into the rubber particles.

There is no evidence that molecular sulphur can dissolve as such in an aqueous system. Sulphur will dissolve in aqueous alkali[39] and is also solubilised by water-soluble and other organic amines such as methylamine[40], dimethylamine[41], morpholine[42], and ethylenediamine[40,42] but in all cases the sulphur is present in solution in the form of open-chain anions: hydrosulphide, HS^-, hydropolysulphide, HS_n^-, and thiosulphate, $S_2O_3^{2-}$, but mainly as polysulphides, S_n^{2-}, polysulphide anions are likely to be the important species in the present context and it may be recalled that the first successful attempts at vulcanising latex were made with alkaline polysulphide solutions[14].

The present experiments shed no light on the nature of the species in which the sulphur enters the rubber particles, nor whether prior reaction with the zinc dithiocarbamate is involved: no evidence has yet been obtained as to whether, in the absence of the dithiocarbamate, the dissolved sulphur remains exclusively in the aqueous phase or whether it becomes distributed between the aqueous and rubber phases in an equilibrium. Van Gils[9] found sulphur present in both phases of his inoculated latices but since he apparently did not re-centrifuge his fractions, his results can be regarded only as indicative.

It does appear from the present incubation experiments (*Figure 3*) that subsequent crosslinking in the rubber phase is limited by the quantity of sulphur taken up by the latex as a whole during incubation. Doubling the time of incubation from 24 h to 48 h increased the equilibrium V_r in toluene from 0.086 to 0.116. While there is strictly no justification for interpreting v_r values obtained on prevulcanised latex films in terms of concentrations of chemical crosslinks (for a variety of reasons), interpretation in this way would indicate an *approximate* doubling of the crosslink density, indicative of a doubling in total sulphur concentration. Presumably, longer incubation times would eventually lead to a limiting sulphur concentration, corresponding to the solubility of sulphur in the whole latex. Clearly, when a zinc dithiocarbamate is present and active during the dissolution of sulphur, the latter becomes combined with the rubber and more dissolves from the solid phase. The degree of crosslinking ultimately reached will then be controlled by other factors.

It has also been shown that a zinc dithiocarbamate can migrate from a continuous solid deposit into dispersed rubber particles and cause crosslinking of the rubber by sulphur. Neither sulphur nor zinc oxide needs to be present for this migration to occur. It is again difficult to envisage any mechanism other than aqueous dissolution for transport of the ZDEC to the rubber particle surface. The enhanced solubility of the dithiocarbamate in latex serum, observed by Loh[10], is presumably sufficient to allow this to occur. Loh's suggestion that the increased solubility is due to complexing of the zinc compound by ammonia or other nitrogenous bases in the serum is supported by the observed effect of diethylamine in considerably shortening the induction period before crosslinking. Diethylamine has been shown to form a 1:1 complex with ZDEC[43] but no information is yet available on the solubility of such complexes in water, nor on their stability towards water.

The principal effect of added diethylamine (a representative secondary amine) in these prevulcanisations appears to be on the dithiocarbamate accelerator rather than on the sulphur. As has been noted, the amine mildly accelerated prevulcanisation of a compounded latex in the presence of a solid sulphur deposit but it had little effect on the uptake of sulphur into HA latex alone (*Table 5*, *cf. Table 4*). In contrast, it had a dramatic effect on the induction period in prevulcanisation with a solid deposit of ZDEC (*Table 9*, *cf. Table 8*).

The present work does not give any information on the extent the dithiocarbamate alone can penetrate into the rubber particles and whether or not it becomes partitioned between the aqueous and polymer phases. If prior reaction with sulphur is necessary to form a rubber-soluble species, ZDEC incorporated into the latex by incubation will remain in the aqueous phase until the second reactant is added. While this situation is thought to be unlikely, it cannot be excluded on present evidence.

In the sulphur incubation experiments, the final extent of crosslinking attained on subsequent compounding and prevulcanisation appeared to reach a limit controlled by the quantity of sulphur which had entered the latex *(Figure 3)*. For incubation with ZDEC, there was no evidence for such a limit being reached *(Figure 4)*. This is presumably because the ZDEC is largely regenerated during the vulcanisation process so long as zinc oxide is present[2] and remains capable of forming new crosslinks from the sulphur continually entering from the reservoir of the dispersed solid material introduced by the compounding operating.

CONCLUSIONS

The following conclusions are drawn:

- Prevulcanisation of high-ammonia natural rubber latex occurs by prior dissolution of sulphur and zinc dithiocarbamate accelerator in the aqueous serum of the latex.
- Sulphur and accelerator can dissolve independently in the aqueous phase. It is not certain whether they react with one another before penetrating into the rubber particles.
- Latex may be incubated with sulphur and subsequently vulcanised after addition of the accelerator. The degree of prevulcanisation is limited by the amount of dissolved sulphur since no reserve of solid sulphur is present.
- Latex may be incubated with a zinc dithiocarbamate and subsequently vulcanised after addition of a sulphur dispersion. In this case, the degree of prevulcanisation is not limited since the accelerator present is continuously regenerated and remains capable of generating new crosslinks while free sulphur remains.
- Diethylamine, which can catalyse ring-opening (activation) of cyclo-octasulphur and act as a complexing and solubilising agent for zinc dithiocarbamate, appears to exert its main influence on the dithiocarbamate, by drastically shortening the induction period before crosslinking starts.
- The extent of crosslinking attained during prevulcanisation of latex previously incubated with sulphur is sensitive to elapsed time after compounding (maturation time) even though the quantity of available sulphur is fixed.
- Aqueous leaching of rubber films cast from prevulcanised latices in which one ingredient has been incorporated from a solid deposit does not have any significant effect on the stress-strain properties of the films. This behaviour diverges from the enhancement of properties usually observed with films prepared from conventionally prevulcanised latices. The reason for it is not understood.

ACKNOWLEDGEMENT

We appreciate the contribution made to this work by a number of productive discussions with Dr M. D. Morris at the Rubber Research Institute of Malaysia.

Date of receipt: November 1991
Date of acceptance: April 1992

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