New Concepts in Vulcanisation of Natural Rubber

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The present status of vulcanisation is briefly reviewed and the scope for new cross-linking systems outlined. Amine-boranes react rapidly at 140°C with olefins to give trialkylboranes and cross-link natural rubber at similar temperatures under conventional conditions. The vulcanisates obtained are porous but the causes of gas evolution have been determined and remedied by (a) a modification of the amine-borane and (b) the inclusion of a drying agent in the mix. An outline is given of the physical properties of vulcanisates cured with triethylenediamine-bischloroborane.

It is only quite recently that advances in vulcanisation chemistry and knowledge of the network structures thereby formed have enabled rational explanations to be made for empirical methods adopted since the time of Goodyear. Even now, the dependence of the physical properties of the vulcanisate on both the cross-link structure and the nature and amount of any concomitant modification of the rubber is by no means fully understood. The importance of this dependence is illustrated by the fact that structurally simple natural rubber (NR) vulcanisates possessing carbon-carbon or monosulphidic cross-links have, at equivalent degrees of cross-linking, only 50–70% of the strength of more complex networks containing largely polysulphidic cross-links and show similar deficiencies in fatigue and tear properties. It is by no means certain that we have in the present day sulphur cure the optimum in vulcanising systems; for example, it is known (BROWN AND DUKE, 1954) that 'ionic' cross-links obtained by bonding carboxylate groups with metal ions confer great strength on the vulcanisate although, in this case, at the expense of other properties.

Present Status of Sulphur Vulcanisation

Sulphur vulcanisation, in one variant or another, remains overwhelmingly the curing system of choice for NR. One important causative factor is versatility. Thus, sulphur systems are equally applicable to both latex and dry rubber processing, may be used over a range of temperatures from ambient to 200°C, and have good latitude for the control of scorch and rate of cure. It is possible to optimise properties of the vulcanisate for a particular application by varying the composition of the curative recipe. A conventional high sulphur (2.5 parts)–low accelerator (0.5 parts) system, which gives a high percentage of polysulphidic cross-links (MOORE, 1965), produces good strength and fatigue properties at the expense of resistance to oxidative ageing and to modulus and tensile reversion on overcure and during service life (CUNNEEN AND RUSSELL, 1969). At the other extreme, efficient vulcanising (E.V.) systems employing high accelerator and low sulphur levels yield networks containing mainly mono- and di-sulphidic cross-links. These vulcanisates are resistant to reversion and can be better protected against ageing but have inferior strength properties. Further progress will probably rest upon the ability to adjust the level and type of main-chain modification to give stress-crystallising properties to the vulcanisate suited to the particular application required.

Non-Sulphur Vulcanising Systems

In the search for dramatic improvements in vulcanisate properties, the rubber chemist and technologist have constantly looked beyond sulphur to other methods of introducing cross-links into NR. Some of the more important agents which have been used to vulcanise NR are organic peroxides, high energy radiation,
bisazodicarboxylates, polynitro compounds, quinones and their imines and oximes with or without oxidising agent, diazoaminobenzenes, bisthiols, bismaleimides, phenol-formaldehyde resols, and metal ions (for carboxylated NR). None of these have shown to overall advantage over conventional sulphur systems and only peroxides and, to a lesser extent, bismaleimides have found commercial application in NR.

The general disadvantages of such systems have been the inferior physical properties of the vulcanisates and a greater difficulty in processing due to the lack of the well-defined induction period which is such a valuable feature of modern sulphur-accelerator recipes. On the credit side, however, the non-sulphur systems often show much greater resistance to reversion and can generally be more efficiently protected against oxidative ageing.

New Concepts in Rubber Technology

Rubber technology is in a period of rapid change and certain trends are clearly discernible. Perhaps the most important is the desire to approach as closely as possible to the simpler plastics technology in respect of automation and rate of production. Thus, faster curing cycles employing higher temperatures are becoming more common and these place greater demands on the reversion resistance of the curing system, especially in the case of thick articles. Injection moulding of rubbers is also growing in popularity and is another field where improvements in curing systems for NR would be welcomed.

There is no doubt that a serious challenge for the future lies in the emergence of synthetic rubbers of the thermoplastic type. These have regions built into their molecular structure which 'crystallise' to act as reasonably strong cross-links at ambient temperatures but which 'melt' at elevated temperatures giving a material which can be processed as a plastic without mixing, compounding or curing cycles being required. Reformation of the 'cross-links' on cooling gives a truly elastomeric article. Such materials are as yet in their infancy and are expensive, have inferior physical properties and can be used only at relatively low service temperatures, but their potential challenge is one the NR industry cannot afford to ignore.

Criteria for New Cross-linking Systems

Recent developments in the chemistry of olefins, coupled with a clearer insight into the ideal requirements for a cross-link, suggest that the time is ripe for a new appraisal of potential non-sulphur curing systems. Two principle objectives can be outlined: (a) a network with cross-links of such a nature as to impart optimum strength and dynamic properties to NR vulcanisates without the detrimental attributes in respect of ageing and reversion of polysulphide cross-links; and (b) a thermoplastic vulcanisate which, as we cannot alter the molecular structure of NR, must be achieved by means of cross-links which are strong at normal temperatures, which break or rapidly exchange at moulding temperatures without irreversible chemical change, and which reform on cooling.

Although many organic reactions can be invoked to accomplish one or other of these aims, certain criteria must be applied to ensure ultimate feasibility and acceptance by the manufacturing industry. Thus, mixing and curing with the new reagent must be possible using conventional machinery and conditions; the reagent must not be toxic, explosive, or otherwise hazardous, nor too expensive; cure rate and characteristics should be closely controllable and not too different from conventional systems, and finally, the reagent should not isomerise or otherwise modify the rubber molecule in the course of the curing reaction. This formidable list of restrictions reduces the possible candidates to a very few. It is one of these which is described below.

EXPERIMENTAL

Materials

Trimethylamine- and triethylamine-boranes were prepared by the method of Farbenfabriken Bayer Aktiengesellschaft (1959), and chlorinated with N-chlorosuccinimide (Douglass, 1966) to give the corresponding chloroboranes. Analytical and physical properties of these materials corresponded to those described in the literature.
Triethylenediamine-bisborane (TEDB) was obtained by a method used for phosphite complexes of borane (Monsanto Chemical Company, 1963). Sodium borohydride (56.7 g, 1.5 mole) and triethylenediamine (56 g, 0.5 mole) were added to N,N-dimethylformamide (DMF)(1 l), and carbon dioxide passed in with stirring for about 6 hours while the temperature was maintained at 25-30°C. Sodium formate was filtered off and the solvent removed (40°C/0.2 mm) to yield TEDB as a white powder (65 g, 93%) with infra-red spectrum consistent with that published by GATTI AND WARTIK (1966) (Found: B, 15.6. Calc. for C₆H₁₈B₂N₂: B, 15.5%).

Triethylenediamine-bischloroborane (TEDCB) was prepared from the bisborane complex by a modification of the method of DOUGLASS (1966). TEDB (53 g, 0.38 mole) was dissolved in DMF (700 ml) and a solution of N-chlorosuccinimide (101 g, 0.76 mole) in DMF (450 ml) added dropwise with stirring at 20°C. The DMF was removed (40°C/0.2 mm) to leave a mixture of TEDCB and succinimide. The latter was removed by washing with water (3 X 250 ml) to yield, after drying, TEDCB as a white powder (66.4 g, 84%) (Found: C, 34.3; H, 7.8; B, 10.4; N, 13.4. C₆H₁₈B₂Cl₂N₂ requires C, 34.5; H, 7.7; B, 10.4; N, 13.4%).

**General Methods**

2-Methylpent-2-ene (2.52 g, 0.03 mole) was added by bulb-to-bulb distillation to triethylamine-borane (0.57 g, 0.005 mole) and the vessel sealed under vacuum. After reaction under the required conditions (see Figures 1 and 2), the mixture was transferred with diglyme (15 ml) into a flask containing 3N sodium hydroxide (2.8 ml) and treated dropwise with a 10% excess of 100-volume hydrogen peroxide. The resulting alcohols, accompanied by diglyme, were extracted with ether and the combined ethereal solution dried (MgSO₄). The ether was carefully removed using a Fenske column, and the yield and ratios of methylpentanols determined by gas-liquid chromatography (g.l.c.) after addition of a known weight of n-pentanol as internal standard. Reactions of 2-methylpent-2-ene (1.68 g, 0.02 mole) with triethylamine-chloroborane (0.75 g, 0.005 mole) and of trans-3-methylpent-2-ene (1.25 g, 0.015 mole) with triethylamine-borane (0.29 g, 0.0025 mole and 0.034 g, 0.0003 mole) were carried out in a similar manner. In the latter series (for investigation of cis-trans-isomerisation), the excess of olefin was removed from the products by bulb-to-bulb distillation and analysed by g.l.c.

**RESULTS AND DISCUSSION**

Free diborane reacts readily with olefins to give organo-boranes (BROWN AND SUBBA RAO, 1959a):

\[
6RCH=CH_2 + B_2H_6 \xrightarrow{\text{diglyme}} 2(RCH_2CH_2)_3B \]

Application of this hydroboration reaction to NR should result in the formation of a vulcanisate cross-linked hexafunctionally by boron and saturated at the points of attachment of the cross-links. Vulcanisation would be expected to be fast and non-reverting although migration of cross-links might be expected at elevated temperatures. Thus, movement of the boron atom to the end of an alkyl chain (reaction 2) and exchange reactions of alkylboranes with olefins (reaction 3) have been observed (HENNION et al., 1957; BROWN AND SUBBA RAO, 1959b; BROWN AND ZWEIFEL, 1966). Such reactions, if sufficiently rapid at high temperatures, could lead to thermoplasticity in boron cross-linked vulcanisates. Alternatively,

\[
RCH=CHCH_3 + 3B \xrightarrow{\text{3N H}_2 \text{O}} 3RCH_2CH_2B \]

if they took place under stress at lower temperatures they might impart a cross-link slippage mechanism to the vulcanisates which would then be expected to exhibit good strength properties. Some oxidation of the carbon-boron-carbon cross-links to carbon-oxygen-boron-oxygen-carbon cross-links might occur in air, although it is known that oxidisability of boranes decreases rapidly with increasing molecular weight. These borate cross-links would be stable to further oxidation.
Boron hydrides have, in fact, been used as vulcanising agents. Hurd and Safford (1951) described the vulcanisation of chloroprene and butadiene-acrylonitrile rubbers by decaborane but addition of calcined clay was necessary to reduce its inflammability and the vulcanising effect was 'not so pronounced' with NR. Obviously the introduction of free diborane (a highly reactive gas) into NR would be technologically impracticable. However, borane (BH₃) forms well-defined, stable, liquid and solid complexes with electron donors such as amines, phosphines, and phosphites. These complexes are readily synthesised and should be capable of being dispersed easily and safely in NR by conventional mixing techniques.

Amine-boranes

Trialkylamine-borane complexes have been shown by Ashby (1959) to react with simple olefins at elevated temperatures in the absence of a solvent to give 77–95% yields of trialkylboranes:

\[ \text{R}_3\text{N.BH}_3 + 3\text{R'}\text{CH} = \text{CH}_2 \rightarrow (\text{R'}\text{CH}_2\text{CH}_2)\text{B} + \text{R}_3\text{N} \]

The suggested mechanism is that, given a sufficiently high temperature, partial dissociation of the boron-nitrogen bond in the amineborane occurs; addition of a boron-hydrogen bond to the olefin can then take place via boron p-orbital interaction with the \( \pi \) electrons of the olefinic double bond. The strength of the amine complex is therefore the factor which controls the rate-temperature profile of the reaction. This aspect was not investigated by Ashby who carried out his reactions at 200°C to ensure completion. Neither did he conduct any experiments with trialkylethylenes which possess the more sterically-hindered olefin structure characteristic of NR.

Amine-boranes are conveniently prepared in 70–80% yield (Farbenfabriken Bayer Aktiengesellschaft, 1959) by the action of carbon dioxide at 0–10°C on potassium borohydride in the presence of the amine:

\[ 2\text{KBH}_4 + \text{CO}_2 + 2\text{R}_3\text{N} + \text{H}_2\text{O} \rightarrow 2\text{R}_3\text{N.BH}_3 + \text{K}_2\text{CO}_3 + 2\text{H}_2 \]

Reactions of Amine-boranes with Trialkylethylenes

Triethylamine-borane (TEB) reacts rapidly at 140°C with the trialkylethylene model, 2-methylpent-2-ene (Figure 1). The extent of reaction (6) is determined by quantitative estimation (g.l.c.) of the alcohols obtained on oxidation of the trialkylborane product with alkaline hydrogen peroxide:

\[ 3\text{Et}_3\text{N.BH}_3 \rightarrow (\text{Et}_3\text{N})_3\text{B} + \text{Et}_3\text{N} \]

One molecule of alcohol is theoretically obtainable per boron-carbon bond in the trialkylborane. The overall yields of trialkylborane, determined in this way, were 80–90% of theory which is considered satisfactory in view of the number of reactions and manipulations involved. In rubber, the yields would be expected to be at least as good, due to the excess of olefinic double bonds being higher than could conveniently be used in the case of 2-methylpent-2-ene.

Migration of the boron atom from its initial point of attachment on the olefin moiety (cf. reaction 2) is also measured by the oxidation procedure since the alcohols obtained are directly dependent on the point of attachment of the boron atom at the time of oxidation. The migration occurs as a direct consequence of the reversibility of the addition reaction; for example, after addition to 2-methylpent-2-ene (boron almost entirely at C-3; reaction 6), any elimination gives either 2-methylpent-2-ene or 2-methylpent-3-ene. The latter, being a dialkylethylene, is the more reactive towards the borane and gives the 3- and 4-substituted products (reaction 8). Subsequent elimination
would give some terminal olefin which is more reactive still and would form the terminal borane. Figure 1 shows that after only 10 minutes at 140°C some 80% migration of boron from C-3 to C-4 has occurred. Subsequent isomerisation to C-5 appears to be much slower however, possibly because B-H groups, which are believed to be catalysts (BROWN AND ZWEIFEL, 1966), are absent at that stage. At 100°C, both the rate of reaction of TEB with 2-methylpent-2-ene and the rate of boron migration are slower (Figure 2).

These results indicate that there is a significant migration (or exchange) of cross-links during the early part of the reaction but little after this. This suggests that rubber mixes prepared with these reagents may have good flow properties in, for example, injection moulding, but are unlikely to yield vulcanisates which are thermoplastic at normal curing temperatures.

The migration of cross-links is not likely to have any significant effect on the physical properties of the vulcanisate provided that positional or cis,trans-isomerisation of residual olefinic double bonds does not occur. To investigate this aspect, TEB was heated for 1.5 h at 140°C with an excess (simulating conditions in NR) of trans-3-methylpent-2-ene and the recovered olefin examined by gas-liquid chromatography. No new olefinic species could be detected (indicating no movement of double bonds) and no more than 1% of the cis isomer...
had been formed. Other experiments showed that extent of isomerisation is dependent on amine-borane concentration and that isomerisation occurs only during the time taken for hydroboration to be completed. Later studies in rubber using infra-red spectroscopy confirmed that, under normal curing conditions (see below), no cis,trans-isomerisation takes place.

These experiments indicate that TEB reacts with trialkylethylenes rapidly and stoichiometrically at 140°C with negligible isomerisation of any excess of olefin and is therefore a suitable potential vulcanising agent for NR.

Amine-boranes as Vulcanising Agents

Experiments using conventional mixing and curing techniques showed that TEB does indeed vulcanise both gum and black-filled stocks of NR rapidly at 140°C. The vulcanisates obtained had reasonable physical properties—for example, a relaxed modulus at 100% extension (MR 100) of 26 kg/cm² and a tensile strength of 210 kg/cm² from a mix containing RSS 1, 100; HAF black, 50; TEB, 3.2 parts by wt (≈0.3 parts boron).

Porosity of vulcanisates. A difficulty not anticipated from the model work arose from porosity in the rubber vulcanisates due to gas evolution during cure. This could be alleviated by curing test sheets between vegetable paper but diagnosis of the cause of the porosity, and then its prevention, were obviously critical to further progress. The gas evolved was isolated and identified as hydrogen by its mass spectrometer. Two sources of hydrogen can be envisaged. The first, and in the event more substantial, source is the reaction of borane with moisture in the rubber:

\[ B - H + H_2O \rightarrow B - OH + H_2 \]  

This was overcome simply by incorporating a drying agent in the mix. Calcium oxide, either alone or in the form of a 75% dispersion in mineral oil (as sold under the trade name 'Caloxol') was found to be most suitable. Other conventional drying agents such as magnesium sulphate, calcium sulphate hemihydrate, and synthetic zeolites were unsatisfactory, presumably because they hold the moisture only physically or as water of crystallisation. Phthalic anhydride was also unsuitable presumably because it forms phthalic acid, which itself reacts with the borane to eliminate hydrogen.

Although porosity was considerably reduced by use of a drying agent, it was not eliminated completely. The clue to the nature of the second source of hydrogen is to be found in the fact that gas evolution from dry polymers is unique to NR and cis-1,4-polyisoprene; it does not occur with solution-polymerised cis-1,4-polybutadiene, styrene-butadiene, or ethylene-propylene terpolymer rubbers. It is known from the work of Logan and Flautt (1960) and Brown et al. (1966) that a borane hydrogen atom can react with the hydrogen of a configurationally suitable methyl group in the same molecule to give hydrogen gas and a boron heterocycle. The addition of the three hydrogens of a borane molecule to the double bonds of NR will occur in stages, each less easy than the preceding one because of increasing steric hindrance. It is reasonable to conclude that competition would occur for the final hydrogen atom between a now slow addition and a hydrogen elimination with a neighbouring methyl group to give a stable, six-membered boron heterocycle:

If this reasoning is correct, a monosubstituted borane (BH₂X) would cross-link NR without elimination of hydrogen. For use in rubber, the substituted borane would again have to be in the form of a complex.

Amine-chloroboranes

Amine-haloboranes are conveniently prepared by the method of Douglass (1966) (reaction 11) and the amine-chloroboranes were selected for study on steric and reactivity grounds.
Trimethylamine-chloroborane (TMCB) and triethylamine-chloroborane (TECB), prepared by this method, both vulcanised gum or black-filled NR at 140°C in the presence of a drying agent without porosity.

\[
\begin{align*}
\text{CH}_2=\text{CO} & \xrightarrow{\text{NCl + R}_3\text{NH}_2\text{BH}_3} \text{CH}_2=\text{CO} \\
\text{CH}_2=\text{CO} & \xrightarrow{\text{NH+R}_3\text{NH}_2\text{BH}_3\text{Cl}} \text{NH}+R_3\text{NH}_2\text{BH}_3
\end{align*}
\]

TECB reacts slightly less rapidly with 2-methylpent-2-ene at 140°C compared to TEB and gives rise to significantly less migration of the boron atom down the chain (Figure 3). At 100°C the overall rate of reaction and the rate of migration are diminished still further (Figure 4): reaction is still incomplete after 8 h.

![Figure 3. Course of reaction of triethylamine-chloroborane with 2-methylpent-2-ene (100% excess) at 140°C as determined by alkaline hydrogen peroxide oxidation.](image)

![Figure 4. Course of reaction of triethylamine-chloroborane with 2-methylpent-2-ene (100% excess) at 100°C as determined by alkaline hydrogen peroxide oxidation.](image)

(cf. 3 h for TEB, Figure 2) and even then over 90% of the boron is still attached to C-3 (cf. 27% for TEB after 3 h). As the B-H group is known to catalyse boron migration (Brown and Zweifel, 1966) this effect is probably due to the lower availability of uncomplexed B-H in the chloroborane reaction. The above results suggest that amine-chloroborane complexes may possibly have advantages over amine-boranes other than in preventing hydrogen elimination; their lower reactivity could give rise to a greater freedom from scorch, and the lower propensity for migration of the boron atom would imply even less cis,trans-isomerisation of the rubber.
For the technological use of chloroborane as a vulcanising agent, complexes with the lower amines are not ideal since the amine liberated during cure imparts an unpleasant odour to the vulcanisate. Higher straight-chain amines, such as tri-n-butylamine, apart from giving weaker complexes and therefore scorch problems, also require, for a given boron level, the introduction of a large weight of amine which, on liberation after cure, blooms to the surface. Triethylenediamine, however, forms a strong complex with a high boron content and is itself a solid at cure temperature. Triethylenediamine-bischloroborane (TEDCB) is the curing agent that has been used to obtain many of the physical properties given below, although it is by no means certain that this necessarily represents the optimum choice of complex. For example, hexamethylenetetramine would be a more satisfactory complexing agent from an economic viewpoint although its polyfunctionality presents certain difficulties in the synthesis of the chloroborane complex.

\[ \text{CH}_2\text{——CH}_2\text{——N.BH}_2\text{Cl TEDCB} \]

Properties of Vulcanisates Prepared with Triethylenediamine-bischloroborane.

Technological evaluation of the new vulcanising agents is still in progress and hence the results described below can be regarded as giving only a preliminary assessment of their curing characteristics and of the vulcanisate properties obtainable. Table 1 lists some properties of RSS 1 loaded with 50 p.p.h.r. of HAF black and vulcanised with sufficient TEDCB to give a 100% relaxed modulus (MR 100) of nearly 20 kg/cm\(^2\) and a hardness of 65 degrees.

The chloroborane complex and drying agent were introduced into the rubber-carbon black masterbatch on a two-roll laboratory mill in the usual way. Appropriate test pieces were moulded at 120°C and the press temperature was then raised rapidly to 150°C to effect cure. This procedure was adopted to prevent scorch-

<table>
<thead>
<tr>
<th>Compounding ingredients</th>
<th>RSS 1</th>
<th>100</th>
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<tbody>
<tr>
<td>HAF black</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Caloxol C31</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>TEDCB</td>
<td>2.9 (≈0.3 p. boron)</td>
<td></td>
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| Compound viscosity, Mooney ML-4 at 120°C | 77 |
| Scorch time, Mooney t + 5 at 120°C (min) | 8  |
| Cure time, at 150°C (min)               | 30 |

Initial vulcanisate properties (measured at 21°C)

- Hardness (°B.S.) | 65 |
- Relaxed modulus, MR 100 (kg/cm\(^2\)) | 19.1 |
- M 100 (kg/cm\(^2\)) | 39 |
- Tensile strength (kg/cm\(^2\)) | 146 |
- Elongation at break (%) | 235 |
- Tear strength, maximum (kg/mm) | 1.24 |
- Lüpke resilience (%) | 71 |
- Akron abrasion loss, average (cc/500 rev) | 0.085 |
- De Mattia flex life (kc to Grade B) | 1000* |
- Compression set (25%; 3 days at 21°C) (%) | 54 |

Aged vulcanisate properties (% retention of initial after ageing 10 days at 70°C)

- Tensile strength | 92.5 |
- Elongation at break | 112 |

*Evidence of thermal degradation on reverse side of test piece
ing since there is no induction period before vulcanisation begins, as indicated by the short Mooney scorch time (Table 1) and by data obtained using the Shawbury Curometer (Figure 5).

The initial physical properties of the vulcanisate show a number of unusual features. The most striking of these is the extremely high set after subjection to a 25% compression for 3 days at 21°C which, in conjunction with the normal values of MR 100 and hardness, is indicative of a large proportion of the cross-links being exchangeable at room temperature. Consistent with this, vulcanisates prepared with TEDCB exhibit very high rates of creep at room temperature. Figure 6 shows that the creep rate of such a vulcanisate containing 50 p.p.h.r. HAF black (curve A) approaches that of a thermoplastic rubber (Shell TR-226) (curve B), the ‘cross-links’ of which are not covalent but consist of glassy domains which might be expected to ‘slip’ easily (CHILDERS AND KRAUS, 1967). The creep rates of gum vulcanisates produced with TEDCB, whether cured for moderate or long times (curves C and D), are much larger still—to such an extent as to suggest that carbon black influences the nature of the cross-links in this curing system.

As a consequence of the high rate of creep and of the associated high rate of stress-relaxation, the observed values of MR 100 and hardness (which are both measured after a period of stress-relaxation) do not accurately reflect the total concentration of cross-links in the material. Thus, the modulus at 100% extension
(M 100), as measured on an automatic photo-electric extensometer (Farlie, 1965), is higher by a factor of two than the same modulus (MR 100) measured after one minute’s relaxation (British Standards Institution, 1953) (Table 1). This implies that the sample is effectively cross-linked to a much greater extent than was originally estimated, a conclusion which is supported by the high resilience and very low elongation at break. Evidently, the cross-link density is also too high for the best strength properties to be obtained (cf. tensile strength, tear strength, and abrasion loss in Table 1; also a and b in Figure 7). Tensile

Figure 6. Creep characteristics of NR vulcanised with triethylenediamine-bischloroborane (2.9 p.p.h.r.).
Figure 7. (a) and (b): Modulus at 100% extension ($M_{100}$) and tensile strength as a function of cure time at 150°C for NR vulcanisates containing HAF black (50 p.p.h.r.) and triethylenediamine-bis-chloroborane (TEDCB) to give parts boron per hundred rubber as indicated.

(c) and (d): Variation of tensile strength with $M_{100}$, and with boron concentration, for NR vulcanisates containing HAF black (50 p.p.h.r.) cured under the conditions indicated with different borane complexes.
strengths approaching 250 kg/cm² have, in fact, been attained using TMCB or TED (c and d in Figure 7), even though hydrogen elimination resulted in some porosity of the vulcanisate in the latter case. No sustained attempt has yet been made to optimise the mechanical properties of these vulcanisates since the high rates of creep and stress-relaxation preclude their use for most applications and also render the results of some tests of doubtful value (cf. the apparently excellent flex life in Table 1). Nevertheless, they are likely to show good resistance to thermal and oxidative ageing, as indicated by the data of Table 1 (which refers to a vulcanisate without added anti-oxidant).

**Nature of cross-links.** The formation of a high proportion of cross-links which are exchangeable or 'slipping' at room temperature is unexpected. Present efforts are being directed towards understanding the nature of these cross-links and towards determining the total number of effective cross-links produced by a given amount of curative. The vulcanising process, as originally envisaged, would give rise to a network with carbon-boron-carbon cross-links which, while they might undergo reversible elimination and addition (and hence exchange) at elevated temperatures, would be expected to be stable at ambient temperatures. In the event, the properties of the vulcanisate are more consistent with networks containing a relatively small proportion of stable cross-links together with a much higher proportion of cross-links which are labile under stress at room temperature.

The presence of such labile cross-links makes the determination of the effective cross-link density difficult. Conventional stress-strain methods (cf. Mullins, 1959) are affected by the stress-relaxation arising from cross-link interchange but they give results which are consistent with the relaxed modulus data, while equilibrium swelling of the vulcanisates in liquids such as decane and benzene is such as to suggest the presence of only a small concentration of covalent cross-links. (Paradoxically, quantitative curemeter data suggest the presence at curing temperatures of only stable cross-links in an amount consistent with MR 100 values, and therefore greatly in excess of that indicated by swelling).

**Present Status of Vulcanisation with Chloroborane Complexes**

The vulcanisation of NR by means of chloroborane complexes is now on a routine basis using techniques similar to those employed for peroxide cures. The features of the system which may be of potential use are already emerging. Thus, while most of the initial vulcanisate properties are unlikely to be of special technical interest in themselves, the retention of these properties on ageing promises to be excellent and good resistance towards modulus reversion at curing temperatures up to 200°C, together with the control over rate of cure afforded by variations in the complexing agent, suggest application in injection moulding of NR. The major disadvantage at the present state of development lies in the large proportion of cross-links which are apparently labile at ambient temperatures. This results in a high degree of creep and set in the vulcanisate without the advantages in strength properties which might have been theoretically expected. Attempts are being made to understand the cause and limit the extent of this feature and to improve overall physical properties. Nevertheless, the unusual properties of the existing vulcanisates may prove useful in certain fields. For example, if initial strains are not too high, the ozone resistance is very good, presumably because the high creep rate rapidly brings the surface strain to below the critical level at which cracking occurs. Utilisation in ozone-protective skins, for example, in weather stripping, can therefore be envisaged.

This work forms the subject of British Patent Applications Nos. 21894/67 and 21895/67.

**ACKNOWLEDGEMENT**

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REFERENCES


DISCUSSION

Chairman: Mr. H. M. Collier
(Paper presented by Dr. B. Saville)

Mr. S.T. Semegen asked what occurred when a sulphur vulcanisation system was used with a borane cross-linking system and if the boron cross-links reacted with anti-oxidants to produce vulcanisates with greater resistance to ageing. Dr. Saville agreed that these would be worth investigating, but had not been studied yet. To a further question by Mr. Semegen, Dr. Saville replied that when natural rubber was cross-linked by the borane or chloroborane derivatives there was no substantial degree of cis-to-trans isomerism of the isoprene units to produce an anti-crystallising vulcanisate with resistance to changes at low temperature.

Dr. E.B. McCall enquired how the absence of reversion at 200°C was reconciled with the supposed nature of the cross-link as being ionic or due to an association of two boron atoms. Dr. Saville replied that the cross-links introduced into NR by these novel methods were labile, as indicated by behaviour in creep and set: the final concentration or density of labile cross-links at ambient temperature was not adversely affected by extended cure or cure at high temperatures because as many new cross-links were formed as were broken down.

Dr. P. Thirion asked if stress-relaxation at room temperature had been precisely examined because the relaxation kinetics were indicative of the nature of the cross-links, permanent or labile. Mr. A.G. Thomas said that a few observations had been made, but the stress-relaxation was so great that the stress decayed asymptotically to a very low value producing a curve concave upward; little could therefore be deduced...
about the nature of the cross-links from such experiments. There was a substantial degree of permanent set which recovered with time, suggesting reforming and breaking of the cross-links.

Dr. C.H. Tan referred to the suggested boron-hydrochloride structure after cross-linking and asked if water affected the physical properties. Dr. Saville said numerous tests had shown remarkably little effect on the relaxation of these rubbers due to exposure to water, oxygen, amines, reduced pressure and other environmental factors.