

## Thiol Group Formation in the Vulcanization of Natural Rubber

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### Synopsis

The determination of thiol groups formed during vulcanization in the complete range of 3-35 parts sulfur per hundred rubber-sulfur stock is reported. The results are explained on the basis of Fisher's mechanism for vulcanization of rubber and the assumption of three stages in the vulcanization process depending on the sulfur concentration.

A number of reports on the structural characterization of natural rubber vulcanizates with the help of chemical probes, which react with specific functional groups, have recently been published.<sup>1-4</sup> One of these is on the reaction of lithium aluminum hydride with di- and polysulfidic groups to form equivalent amounts of mercaptans.<sup>1,2</sup> No work has, however, been reported on the determination of mercaptans, if formed during vulcanization of natural rubber, i.e., before reduction, with any chemical probes, in the complete range of soft to hard rubber, probably because analytical methods for the determination of such small quantities were not available. Such determinations are, however, of particular importance, since the results are useful in confirming some of the assumptions drawn by earlier authors<sup>5,6</sup> in formulating a mechanism of vulcanization. Also some of the physical transformations in the vulcanization of natural rubber with different proportions of sulfur may be correlated with mercaptan formation during vulcanization. The present work reports such determinations by means of a modified amperometric titration method.<sup>7,8</sup>

### EXPERIMENTAL

#### Preparation of the Rubber Sample

Pale crêpe rubber (rubber hydrocarbon 96.7%, acetone extract 2.1%, proteins 2.52%, ash 0.15%) and sulfur (E. Merck, pure) were used without further treatment. The required amounts of these two components in different proportions were mixed in a Berstoff laboratory mixing mill, size 8 × 4 in., necessary precautions being taken to minimize the amount of breakdown and to maintain temperature constant at about  $65 \pm 5^\circ\text{C}$ .

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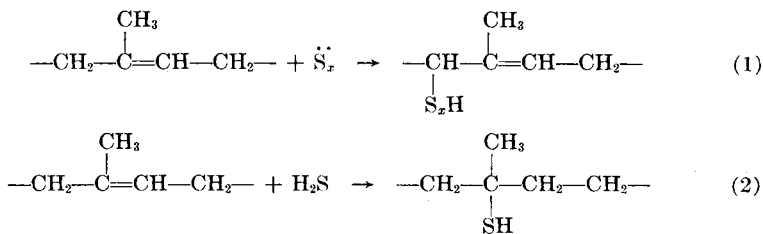
An adequate amount of the mix was vulcanized in a Wabash hydraulic press in a  $10 \times 7$  in. mold with six circular cavity sections of  $1.5 \times 0.1$  in. dimensions for different time and temperatures, the time of vulcanization being counted from the instant the press is closed and full pressure (2000 psi) applied to the mold to the instant it is released. After releasing the pressure the sample was taken out quickly and immediately immersed in cold water in order to stop the reaction.

### Estimation of Thiol Groups

About 0.5 g. of the acetone-extracted and finely powdered sample was allowed to swell in acetic acid. This swollen sample was shaken for 4 hr. with an excess of standard silver nitrate solution in water (25 ml. of 0.005*N* AgNO<sub>3</sub>). The mixture was then titrated amperometrically with a rotating platinum wire indicator electrode and a calomel electrode against standard (0.01*N*) potassium chloride solution in order to determine the excess silver nitrate.<sup>9</sup> The reproducibility of the method was checked and found to vary within 5–7% in three determinations. The average of these titrations was taken. The method was checked with a known amount of 2-mercaptobenzothiazole treated likewise when results varying from 100.8% to 102% were obtained.

## RESULTS AND DISCUSSION

A number of workers<sup>5,6</sup> presumed that thiol groups are formed in the molecular chains of rubber during vulcanization, as the result of reactions between sulfur and  $\alpha$ -methylene groups or of addition of H<sub>2</sub>S or HS<sup>·</sup> at the double bonds.



The thiol groups are then presumed to be oxidized by sulfur and/or vulcanizing ingredients to form crosslinks.<sup>5,10,11</sup> No direct proof of such reactions was, however, obtained. Hull<sup>12</sup> and also Bloomfield<sup>13</sup> carried out such reactions with model compounds of low molecular weight. Dogadkin and Beniska<sup>14</sup> attempted to follow the kinetics of thiol group formation during vulcanization of sodium-butadiene rubber with and without zinc oxide and observed appreciable variation in the systems mentioned, though their methods of determination were not very accurate.

Figure 1 shows a plot of the thiol fraction of combined sulfur with time over the complete range of 2.9–33.9% sulfur. All the curves show a maximum which shifts to lower vulcanization time as sulfur increases from

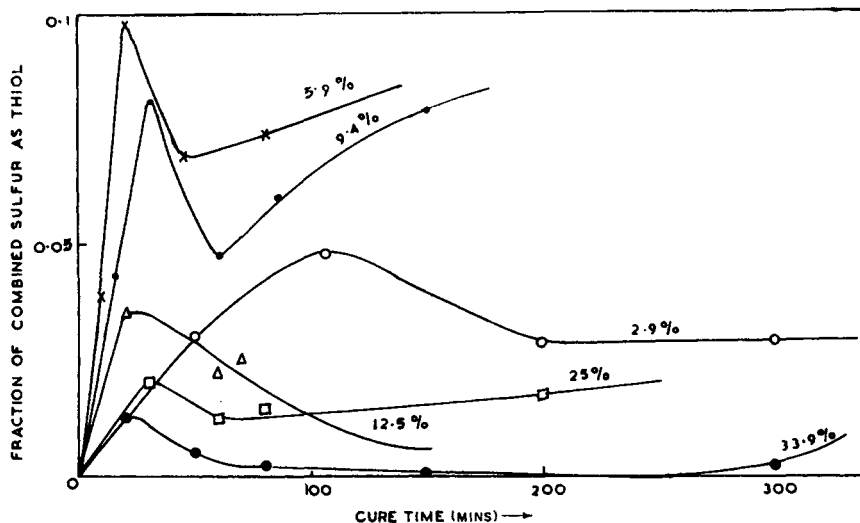


Fig. 1. Variation of thiol fraction with sulfur concentration. Cure temperature 160°C.

2.9–5.9% and then remains more or less constant. It may also be found that the fraction of sulfur combined as thiol continues to increase as one goes from 2.9–5.9% sulfur and then decreases as the proportion of sulfur is further increased. All these facts can, more or less, be explained if we assume three different stages of vulcanization as enunciated by previous workers,<sup>15</sup> a soft rubber stage (up to 6% S), a “rotten rubber” stage (6–12% S) and a hard rubber stage (above 25% S), for which the mechanisms of formation are different. At the lowest sulfur concentration (2.9%), the fraction of thiol goes on increasing up to 100 min., showing that during this time thiols are being generated at a faster rate than they are consumed in crosslinking or other reactions. The reverse holds true after this, and consequently the proportion of thiol goes on decreasing until about 200 min., after which it remains more or less constant at about 0.03 parts of sulfur combined. After this stage it may be assumed that either the fraction of thiols formed and consumed reaches an equilibrium or the distribution of thiol groups becomes so sparse that they have no chance for further reaction.

The next higher combinations of sulfur 5.9%, 9.4%, and 12.5% fall, more or less, in the region of the “rotten rubber” stage which is known to be very much prone to oxidative degradation reactions. The formation of the maximum and the subsequent decrease may be explained as in 2.9% sulfur. The formation of higher proportion of thiol may be explained as due to the relatively inefficient utilization of thiols in crosslink formation which is consistent with the concept of reactions in the rotten rubber stage. Also the ultimate increase of the proportion of thiols after the minimum point (after about 60 min.) may be visualized as due to further generation of thiols due to degradative reactions as shown in eq. (3).



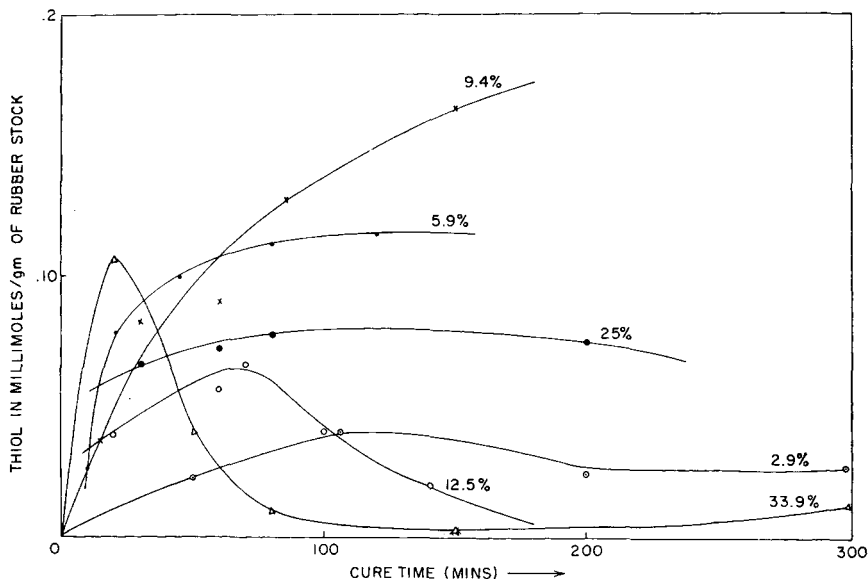


Fig. 2. Variation of thiol with time of cure at 160°C.

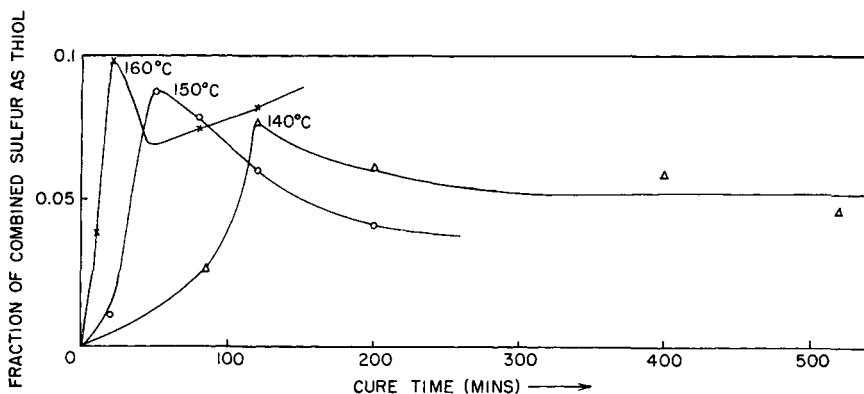


Fig. 3. Variation of thiol fraction with temperature. Composition of stock: rubber 100 parts, sulfur 5.9 parts.

precede the intramolecular hard rubber reaction.<sup>17</sup> The above ideas get some support from the fact that though the relative proportion of thiols is small in the hard rubber stage, their overall number is not very small as is seen in Figure 2, which shows the plot of thiols (in millimoles) with time.

Figure 3 shows the relationship between thiol formation and time as the temperature is varied. It will be seen that thiols are initially formed at a faster rate as the temperature is increased, but the reactions for disappearance of thiols (crosslink formation or others) overtake this reaction sooner as the temperature is increased. Also the subsequent increase of thiols

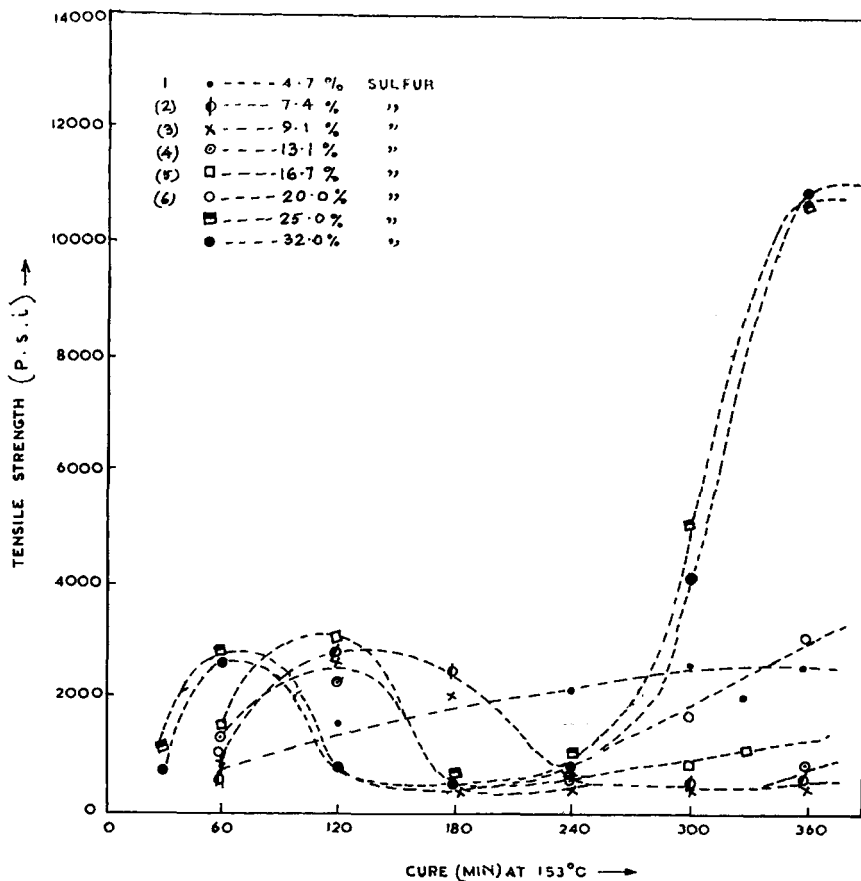


Fig. 4. Tensile strength-cure relationship of rubber-sulfur compounds of increasing sulfur content. Data of Bhaumik, Banerjee, and Sircar.<sup>18</sup>

which has been explained above as due to reversion is more prominent at the highest temperature (160°C.).

The assumption of the occurrence of three stages in the vulcanization of rubber (soft rubber, rotten rubber, and hard rubber) is supported by the tensile-time of cure data obtained by Bhaumik, Banerjee, and Sircar,<sup>18</sup> which are reproduced in Figure 4. It may be noted that all compounds above 4.7% sulfur pass through a stage at which tensile strength is very much reduced (rotten rubber stage), and a perceptible regain in tensile strength occurs only when sulfur concentration is increased to 20%. Also tensile strength consistent with hard rubber is achieved only at sulfur compositions higher than 25%. The results indicate that formation of predominantly intramolecular links in hard rubber is preceded by formation and subsequent degradation of intermolecular bonds. This fits in with the idea of vulnerability of rubber in the rotten rubber stage to degradative reactions. Unfortunately, curing of these compositions was carried out at

a different temperature (153°C.) than reported here (160°C.) and at slightly different sulfur contents, so that exact correlations between the work mentioned and those reported in the present work are not possible.

### CONCLUSION

It is not presumed that the analytical method employed for the determination of thiol groups is flawless. It cannot be proved that extraction of the thiol groups is complete and it is not known how it is influenced by the coefficient of vulcanization. However, from the limited data at present available it was found that reproducibility is within the range reported and the data show enough variation with composition and conditions of vulcanization to enable us to make relative assessment and to correlate them with current concepts of the mechanism of vulcanization reactions.

One of the authors (S.N.C.) wishes to thank the Council of Scientific and Industrial Research, India, for financial assistance.

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### Résumé

La détermination de groupes thiols, formés durant la vulcanisation dans le domaine complet de 3 à 35% de soufre par rapport au caoutchouc, a été étudiée. On a expliqué les résultats sur la base du mécanisme de Fisher et en admettant une vulcanisation du caoutchouc résultant de trois phases dans le processus de vulcanisation suivant la concentration de soufre utilisé.

### **Zusammenfassung**

Über die Bestimmung von Thiolgruppen, die bei der Vulkanisation im vollständigen Bereich von 3 bis 35% Schwefel bezogen auf Kautschuk-Schwefelrohmaterial entstehen, wird berichtet. Die Ergebnisse werden auf Grundlage des Kautschukvulkanisationsmechanismus von Fisher und der Annahme von drei Stufen im Vulkanisationsprozess in Abhängigkeit von der Schwefelkonzentration erklärt.

Received October 29, 1963