

## Studies on Sulfur Vulcanization of Natural Rubber Accelerated with Diphenylguanidine both in Presence and Absence of Dicumyl Peroxide

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### Synopsis

Diphenylguanidine acceleration of sulfuration of natural rubber both in the presence and absence of dicumyl peroxide (DCP) has been studied. DPG enhances the rate of decomposition of DCP, and the crosslinking maxima due to DCP are lowered by DPG to some extent, which increases with the concentration up to a limiting value. The rate of sulfur decrease is very high and is dependent on DPG concentration but practically independent of the presence of ZnO and stearic acid. It is observed that with constant level of DCP and sulfur, crosslinking increases with the increase of DPG concentration and finally becomes additive when the molar proportion of DPG:S, approximately equals 1:1. In presence of ZnO and stearic acid, with each increment of DCP concentration crosslinking is retarded for both systems. Mechanisms have been suggested in terms of polar and radical process.

### INTRODUCTION

Organic bases are the compounds first successfully employed as the accelerators of sulfur vulcanization of rubbers. Till recently, the mechanism of their reaction has been studied in the least details. Though a limited number of workers<sup>1,2,3-5</sup> unanimously advocated a polar character of the reaction, they differ especially in regard to the mode of heterolysis of the sulfur octet ring. Moreover, these studies are mostly confined to the systems without activators. In a recent review of the chemistry of vulcanization, British authors<sup>6</sup> have indicated the probability of formation of a zinc-accelerator complex, as in other accelerators of vulcanization, but their discussion is mainly limited to the amines having  $\alpha$ -hydrogen atoms. Moreover, they have not shown any such possibility with DPG which is not having any  $\alpha$ -hydrogen, and with which it seems highly improbable that any such complex will be formed in that fashion.

In view of the above complications, the present investigation using DPG as an accelerator, both in the presence and absence of activators, has been undertaken to throw more light on the subject. DCP has been employed as a chemical tool, as it has been found to furnish distinct information with regard to the polar or radical nature of the vulcanization reactions.<sup>7,8</sup>

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TABLE I  
Compounding Formulations and Chemicals Used<sup>a</sup>

Materials	A	B	C	D	E	F	G	H	I	J	K	L	M
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100
Dicumyl peroxide	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Diphenylguanidine	0.5	0.5	1.0	1.5	2.0	3.0	1.0	2.0	3.0	0.5	1.0	1.5	2.0
Diphenylamine							1.0	2.0	3.0	2.0	2.0	2.0	2.0
Sulfur	N	O	P	Q <sup>b</sup>	R <sup>b</sup>	S	T	U	V	W	X	Y	
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100
Dicumyl peroxide	1.0				1.0			1.0	1.0	2.0	2.5	1.0	
Sulfur	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Diphenylguanidine	3.0	1.0	2.0	2.0	2.0	1.0	2.0	1.0	2.0	1.0	1.0	1.0	
Zinc oxide						5.0	5.0	5.0	5.0	5.0	5.0	5.0	
Stearic acid						3.0	3.0	3.0	3.0	3.0	3.0	3.0	

<sup>a</sup> Letters leading the columns are stock designations.

<sup>b</sup> Sulfur used was free of H<sub>2</sub>S or H<sub>2</sub>SO<sub>3</sub>.

## EXPERIMENTAL

The compound formulations used in the present investigation are given in Table I. Diphenylguanidine was recrystallized in alcohol. Other chemicals were procured from the sources mentioned in our earlier communication<sup>7</sup>

All other experimental details are the same as reported in our earlier communications.<sup>7,9</sup> The method of estimation of DPG was as follows: DPG is extracted from the finely ground vulcanizates using alcohol as a solvent. The extracted DPG is then estimated by conductometric<sup>10</sup> titration with hydrochloric acid.

## RESULTS AND DISCUSSION

### Kinetics of DCP Decomposition

The pertinent data on DCP decrease with cure time are represented graphically in Figure 1 as a plot of log of free DCP versus time. Figure 1 shows that DCP decomposition is a first-order process in all cases, however with different rate constants (values reported in Table II).

Table II clearly reveals that DPG enhances the rate of DCP decomposition by about 40–45% and that the rate is practically independent of DPG

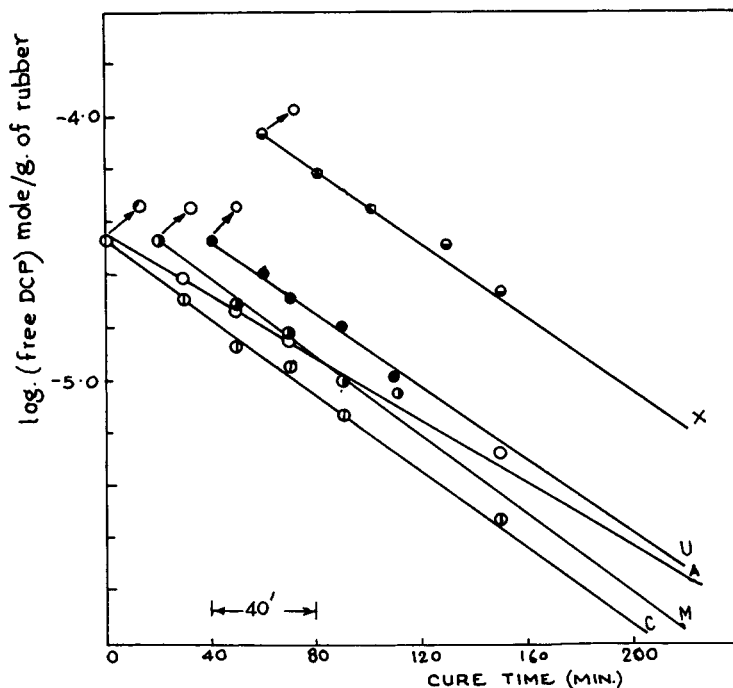
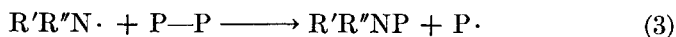
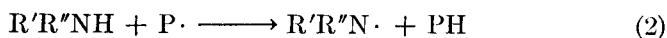


Fig. 1. Decrease of free DCP according to a first-order time law at 140°C. Abscissa, cure time, min; ordinate, logarithm of free DCP, moles/g of rubber.

TABLE II  
 Decomposition Rate Constants

	Stock	A	C	M	U	X
$K$ (140°C), $\text{min}^{-1}$		12.63	16.67	17.35	16.80	16.40

concentration or the presence of sulfur, ZnO, and stearic acid. This process can be represented by the following reactions:



where  $\text{R}' = \text{C}_6\text{H}_5\text{NH}-\text{C}$  and  $\text{R}'' = \text{C}_6\text{H}_6\text{NH}$ .

Reaction (1) represents the dissociation of the peroxide, and reactions (2) and (3) are the representations of the induced decomposition of DPG and peroxide in the presence of each other, leading to higher  $K_d$  values together with retardation of vulcanization due to DCP, to be discussed in connection with crosslink density.

### Decrease of Free Sulfur

The course of free sulfur decrease in various stocks is shown in Figures 2a and 2b. These figures show that free sulfur decrease depends on DPG con-

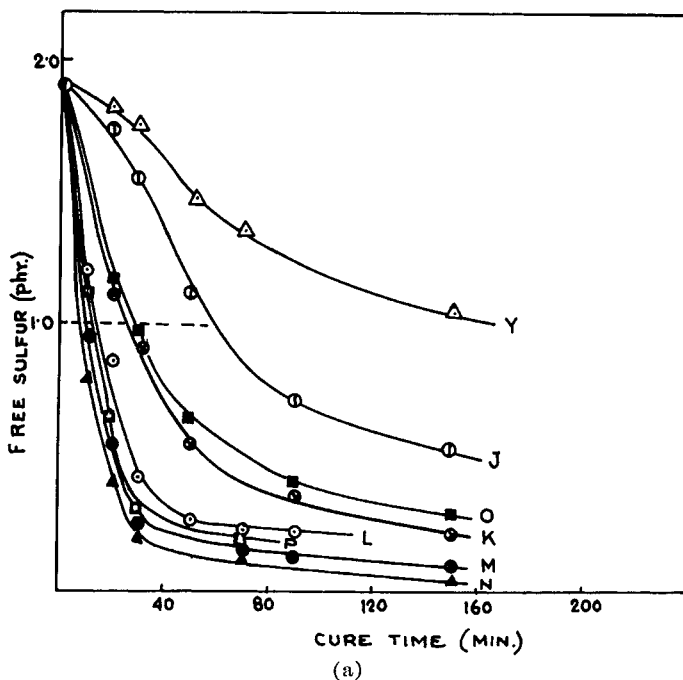


Fig. 2 (continued)

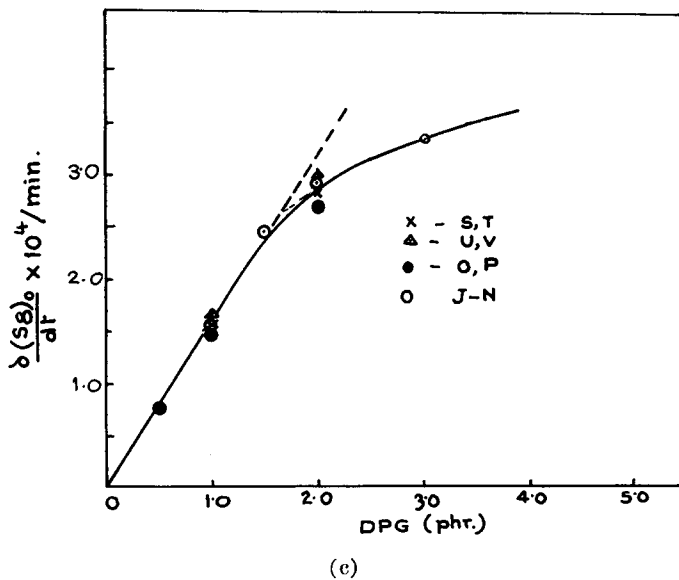
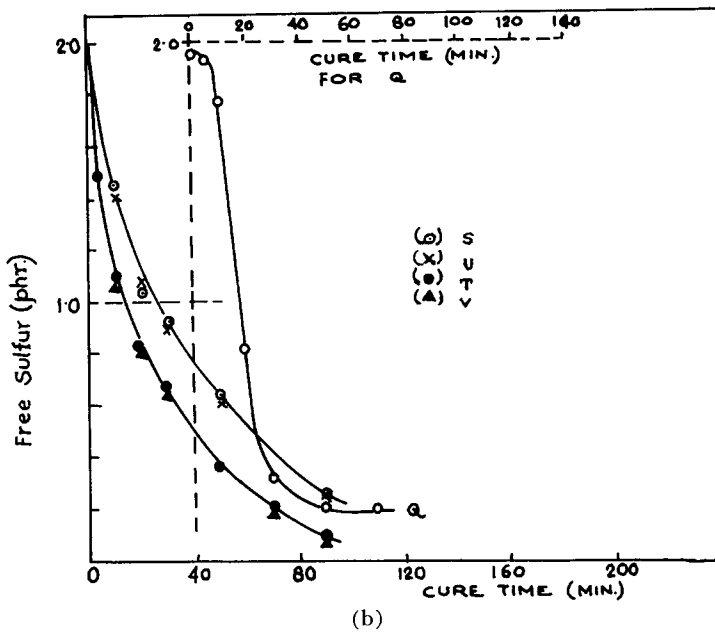


Fig. 2. (a and b) Variation of free sulfur with cure time. (c) Dependence of initial rate of sulfur decrease (calculated from Figs. 2a and 2b) on DPG concentration.

centration both in the absence and presence of DCP. However, in the presence of DCP, sulfur decrease is only slightly higher. It is also evident from the figures that at a particular level of DPG, sulfur decrease is independent

of the presence of ZnO and stearic acid, particularly up to a period of about 50 min. In other words, ZnO and stearic acid for all practical purposes do not show any influence on the sulfur combination, especially in the initial rapid rate period. This is in sharp contrast to what has been observed with other systems. It should be noted, however, that after this rapid rate period, the nature of the curves for sulfur decrease is changed quite markedly, especially with high levels of DPG. In this case, free sulfur decreases steadily, leading to slightly higher consumption than that in the system without ZnO and stearic acid.

Another highly noteworthy fact is the appearance of an S-shaped nature in the sulfur decrease curve (curve Q) when pure sulfur is used along with DPG (pure sulfur in the sense that it was leached in concd.  $\text{H}_2\text{SO}_4$  and recrystallized in pure benzene several times with the aim to free it completely from  $\text{H}_2\text{S}$  or  $\text{H}_2\text{SO}_3$  which are invariably present in traces even in the purest variety of sulfur). That is, sulfur decrease is characterized by a short induction period. But after such induction time, sulfur decrease follows its usual course.

The rates of sulfur decrease in the initial period (values calculated from the portion shown by the horizontal dashed lines on the curves in Figs. 2a and 2b) are plotted against initial concentration of DPG in Figure 2c. It is interesting to note that the rate of sulfur decrease increases linearly with DPG up to a concentration of 1.65 phr. Calculation shows that at this level of DPG, the molar proportion of  $\text{DPG}:\text{S}_8$  is approximately 1:1 or slightly higher. Moreover, the presence of DCP or ZnO and stearic acid or DCP, ZnO, and stearic acid makes little difference, as all the rate values irrespective of the composition of mixes satisfy the same curve.

### Decrease in DPG

In Figure 3 are shown the changes of DPG concentration with time of cure. Figure 3 shows that DPG concentration falls off rapidly in the presence of sulfur up to a period of about 10 min, and after that, DPG concentration remains practically constant over a wide range of the reaction time. DPG decrease is slightly less when present in higher amounts and more in the presence of DCP. In the absence of sulfur, a very small amount of DPG is lost due to reaction with DCP (represented by curve C). Here again, it is clearly shown that the rate of DPG decrease is practically independent of the presence of ZnO and stearic acid.

### Formation of ZnS

ZnS is formed concurrently with the vulcanization reaction, and the kinetics of its formation in various mixes are shown in Figure 4. Figure 4 obviously indicates that the formation of ZnS continues all through the reaction time covered in this study. The presence of DCP in the system does not alter the kinetics of its formation. However, ZnS formation is higher with higher amounts of DPG.

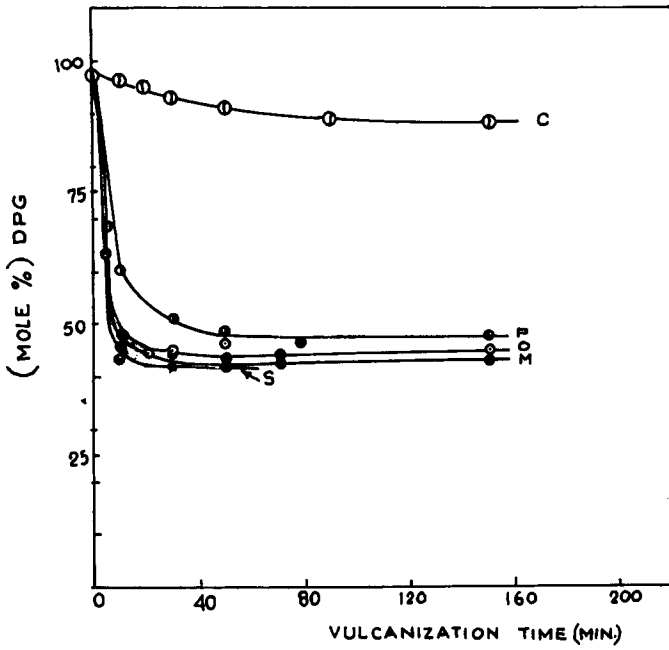


Fig. 3. Change in free DPG with vulcanization time.

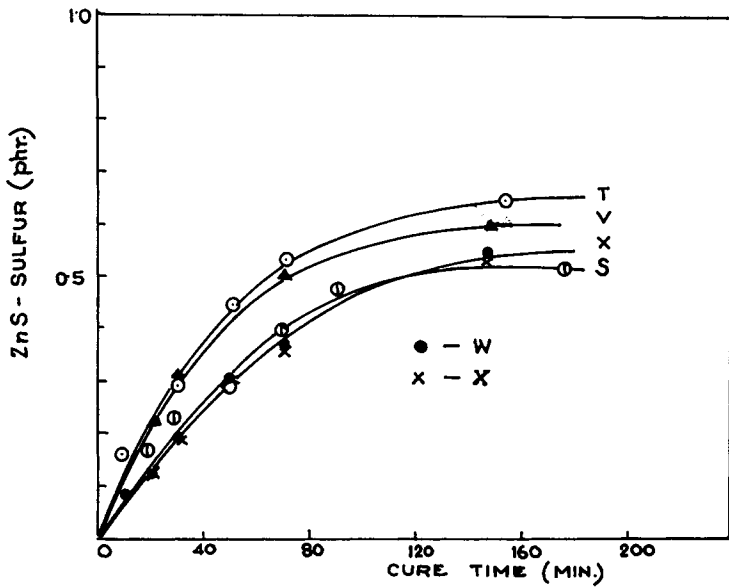
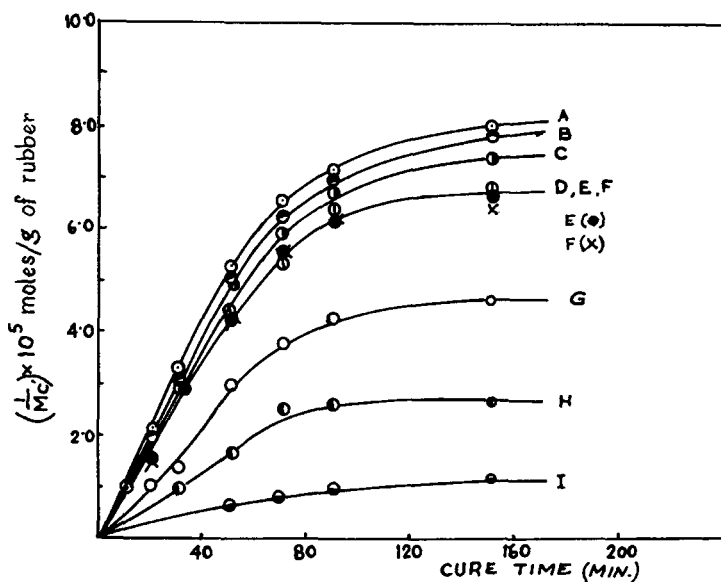
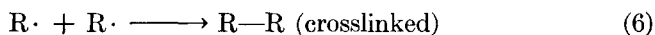
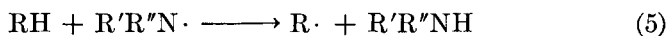
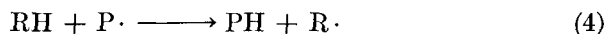
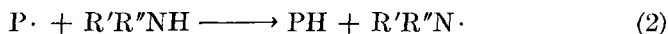


Fig. 4. Variation of zinc sulfide sulfur with cure time.

### Crosslink Density

#### DCP, DPG, and NR

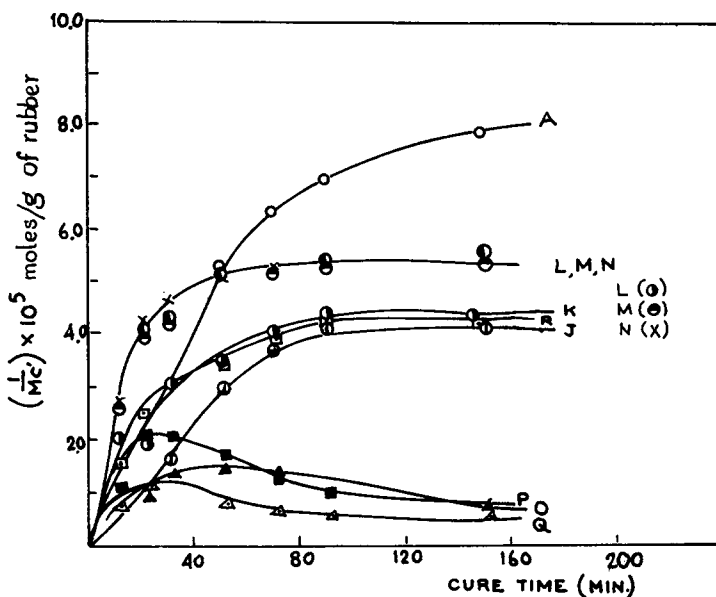
The variation of the density of crosslinks with cure time in the presence of variable amounts of DPG is shown graphically in Figure 5a. It is apparent from the figure that DPG decreases the crosslinking maxima due to DCP in amounts depending on its concentration up to a concentration of 1.4 phr. But the reduction of crosslink density is much less compared to that with other accelerators such as MBT,<sup>7</sup> CBS,<sup>8</sup> etc. The following reactions will probably explain the process:



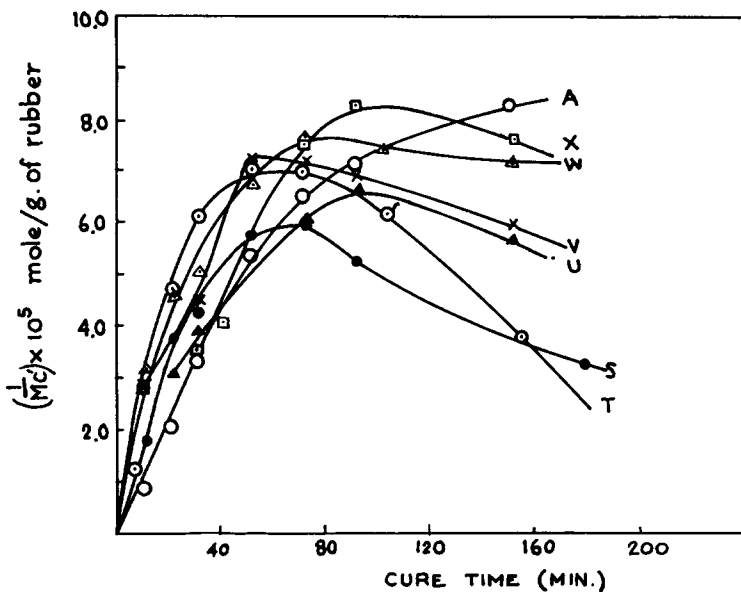
(a)

Fig. 5 (continued)





(b)



(c)

Fig. 5(a). Variation of physical crosslink density ( $1/M'_c$ ) with cure time: curves A to F, different initial concentration of DPG; curve G to I, different initial concentrations of DPA. (b) Variation of physical crosslink density ( $1/M'_c$ ) in systems containing DPG, S, and DCP, with cure time. (c) Variation of physical crosslink density ( $1/M'_c$ ), in systems containing DPG, S, DCP, ZnO and stearic acid, with cure time.

The above reaction scheme evidently accounts for the higher values of  $K_d$  for DCP decomposition, reaction (3), and the destruction of the more active cumyloxy or methyl radicals by reactions (2), (3), and (8), leading to a retarded vulcanization via reactions (4) and (6). It is expected that reduction in crosslink density will be higher with higher amounts of DPG, but this continues only up to a limiting concentration, which may be associated with the limit to solubility of DPG in rubber or with some other factors.

It is generally known that amines are excellent free-radical traps, and a very small amount of these amines inhibit free-radical polymerization quite markedly, sometimes totally. It would then be expected that the crosslinking reaction due to DCP, which has been established beyond doubt to be entirely a radical process, should largely be inhibited by DPG. This inhibition has actually been observed with diphenylamine which stops the crosslinking reaction almost completely when used in the level of 3.0 phr (results shown in Fig. 5a). The much lower degree of inhibition by DPG may be explained on the basis of the more favorable capture of P radicals by rubber than by DPG or its radical. The observed differences in behavior between DPG and DPA can be considered in terms of the activity of the hydrogen atom. Due to the presence of two delocalized  $\pi$ -systems in the same nitrogen atom, the activity of hydrogen atom is increased in DPA, whereas the activity of hydrogen atom is greatly reduced due to conjugation in the N-C-N system in DPG.

Again, as has been represented by reaction (7), the addition of R'R"N· to rubber radicals seems equally improbable, as this would mean further lowering in the crosslinking efficiency of DCP.

#### *DCP, DPG, S, and NR*

The variation of crosslinking density with time in systems containing S, DPG, and DCP is shown in Figure 5b. It is observed that with a constant level of sulfur and DCP, crosslinking increases with the increase in the amount of DPG, and finally it becomes constant (cf. curves L, M, and N) when the molar proportion of DPG:S<sub>8</sub> approximately equals 1:1 (the rate of sulfur decrease is also highest at this molar proportion). At this limiting or higher concentration of DPG, the total number of crosslinks at any instant, up to 20 min, is approximately equal to the sum of crosslinks due to DCP (curve A) and S with DPG (curve P). Beyond this period, the number of crosslinks remains almost constant. In S-DPG systems, also the crosslinking becomes maximum at the period of about 30 min, but this is followed by a rapid reversion. This initial rapid rate period of crosslinking again coincides with the period for the rapid decrease of both sulfur and DPG. The absence of reversion in the former case is due to the compensation of the destruction of sulfur crosslinks resulting from S-DPG by the continued formation of crosslinks by the undercomposed DCP still remaining in the system.

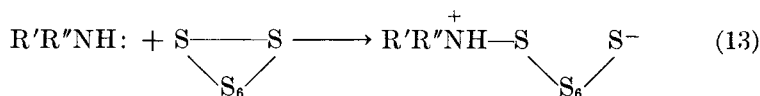
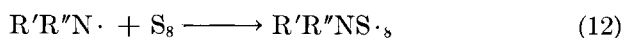
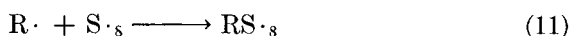
Further support to the above views of additive crosslinking followed by simultaneous crosslinking and reversion at the later stages is obtained by the

study of the reaction of the vulcanizates with methyl iodide (results reported in Table III). The results clearly show that while the number of sulfide links decreases, that of the C-C links continues to rise in a regular manner.

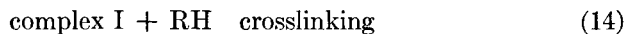
TABLE III  
Characterization of Vulcanizate. Degree of Crosslinking Before and After Treatment with Methyl Iodide

Stock	Vulcanizate corresponding to cure time, min	Reaction temperature and time	Methyl iodide, g/g of vulcanizates	(1/M'c) × 10 <sup>5</sup> before treatment	(1/M'c) × 10 <sup>5</sup> after treatment (C-C crosslinks)	Sulfide crosslinks × 10 <sup>5</sup> (by diff.)
M	20		1.50	4.391	1.897	2.494
	30	80°C,	1.50	4.598	2.623	1.975
	90	96 hr	1.50	5.509	4.216	1.293
	150		1.50	5.738	4.680	1.058
P	20	80°C, 96 hr	1.50	2.342	not measurable	

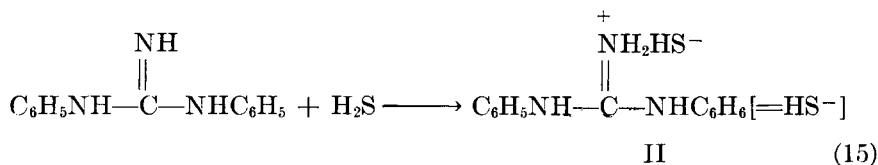
All these observations strongly indicate that DPG-catalyzed initial sulfuration of rubber is a polar process, which can possibly be represented as follows, in addition to reactions (1) to (9):

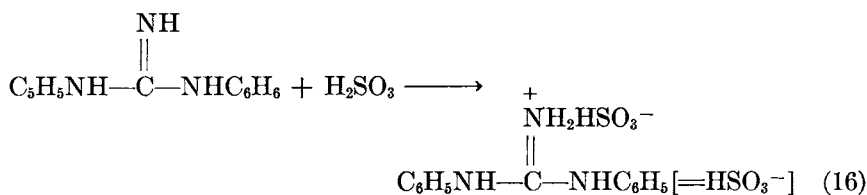


I



However, the transfer of a lone pair of electrons to S as shown in reaction (13) has been doubted by recent workers.<sup>5,11</sup> In their view, the heterolysis is easily effected by the much more nucleophilic hydrosulfide or sulfite ions derived from the interaction of amine with traces of hydrogen sulfide or sulfurous acid present in sulfur. Accordingly, reactions can be written as follows:





III



In view of this, vulcanization was carried out with sulfur carefully freed from  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{SO}_3$ , etc., promoted by DPG both in the presence and absence of DCP (results shown in Figs. 5b and 2b). Figure 2b shows that sulfur decreases with a characteristic induction period. The same effect is also noted in crosslinking reactions (Fig. 5b). But after such induction period, both sulfur consumption and crosslink formation proceed with the usual rapid rate. The additional  $\text{H}_2\text{S}$  required for the rapid rate period certainly results from the interaction of sulfur with rubber or amine. Thus, it is sufficient to conclude that the amine-sulfur reaction is greatly facilitated by the intermediate formation of hydrosulfide or hydrosulfite ion (structures II and III).

It has been mentioned earlier<sup>7</sup> that reaction (10) is the major step by which sulfur lowers the efficiency of vulcanization by DCP. Reaction (13), suggested by Krebbs and co-workers,<sup>2,3</sup> or reactions (15) to (17), lead to the formation of a sulfur-bound accelerator complex, I, or II and III, which are the true sulfurating intermediates. These reactions demand that 1 mole of DPG will split open 1 mole of sulfur ( $\text{S}_8$ ) ring. It is also most probable that in a mixture of DPG and sulfur, sulfur is the main radical scavenger.

Consequently, as long as the proportion of sulfur remains higher than this value, the excess sulfur will inhibit the crosslinking due to DCP, and no additive crosslinking is expected; this is evident in curve K. In mixes L, M, and N, where the ratio  $\text{S}_8:\text{DPG} < 1$ , inhibition due to sulfur will be practically absent, and the crosslinking by both systems will proceed simultaneously and uninterruptedly, leading to an additive relation. Another interesting feature is that the crosslink densities in these three mixes are represented by the same curve, clearly pointing out that a distinct stoichiometry persists in the process.

Now as regards the second part of the vulcanization reaction, which is characterized by a sharp reversion and also attended by marked inhibition of the DCP cure, it seems appropriate to discuss it later in connection with similar systems in the presence of  $\text{ZnO}$  and stearic acid.

#### *DCP, S, DPG, ZnO, Stearic Acid and NR*

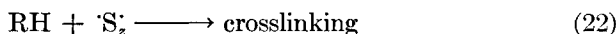
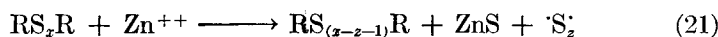
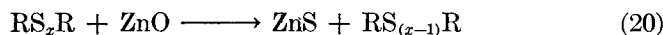
The kinetics of crosslinking reaction with different mixes of this type are shown graphically in Figure 5c. Figure 5c shows that  $\text{ZnO}$ -stearic acid increases the rate of crosslinking as well as the crosslinking maxima compared

to those in stocks without these ingredients. But the effect of ZnO–stearic acid is not so much pronounced as that observed with other systems of accelerators such as MBT, CBS, etc. In the absence of DCP, the crosslinking curves show a sharp reversion.

Again the rates of crosslinking and the crosslinking maxima are higher with higher amounts of DPG. The nature of the change in crosslink density with DPG in the presence of ZnO and stearic acid (curves S and T) is comparable with that for the systems without these (ZnO and stearic acid) (curves O and P), and in fact the ratio of  $Mc^{-1}$  for P and O is almost equal to that for curves T and S, at least up to 40 min of vulcanization. This, in conjunction with the fact that both the rate of sulfur decrease and DPG consumption are almost independent of the presence of ZnO and stearic acid, indicates that it is most likely that ZnO and stearic acid do not participate in the reaction leading to the formation of Zn–accelerator complex.

Comparison of curves S and T with curves U and V (which differ from the former pair only in having 1 phr of DCP) reveals that the number of crosslinks, instead of being increased, is reduced by DCP and the extent of reduction is higher in curve U.

These observations can be adequately explained if we assume a mixed mechanism involving both free radicals and charged species for the sulfuration of rubber in the presence of DPG, ZnO, and stearic acid. The polar mechanism has already been discussed; ZnO and stearic acid may induce the following (already published<sup>12</sup>) reactions:



ZnO and zinc salt react with the initially formed polysulfide (reactions (20) and (21)) to form ZnS, with the result that the number of sulfur atoms are now fewer and the crosslinks are more stable. An increase in the number of crosslinks will result from reactions (18), (19), (21), and (22). Free radicals from DCP can react with the thiols as well as with the sulfur biradicals and thereby retard the vulcanization process due to DPG, without themselves contributing anything to the formation of crosslinks. In the case of removal of thiols by P· radicals, the formation of ZnS will be reduced, but it has been observed that ZnS continues to increase uninterrupted by DCP. Hence we are led to the conclusion that additional crosslinks result primarily from reactions (19), (21), and (22). The higher inhibition in U may be reconciled to what has been stated earlier, viz., in this case the ratio of  $S_8$ :DPG >1, and incidentally, this is a pointer to the assumption that ZnO and stearic acid do not affect the mechanism of sulfur vulcanization accelerated by DPG.

With regard to reversion at later stages of the vulcanization, the present study leads to the following observations, other things being identical: (1) The reversion increases with the concentration of DPG (cf. S, T, and U, V); (2) DCP reduces the degree of apparent reversion (cf. S, U, and T, V); (3) reversion increases with the amount of DCP (cf. U, W, X).

In the phenomenon of reversion, much significance is attached to the thermal dissociation and redistribution of polysulfide bonds.<sup>13,14</sup> The dissociation of polysulfide bonds can proceed with or without release of active sulfur radicals as follows:



Sulfur radicals released (reaction (23)) are able to interact with molecules of rubber with the formation of new crosslinks. But this is contradictory to the observed data of the present study. Further, the resulting polymeric radicals can react in two ways: first, these can recombine at the same point or with other radicals, keeping the number of crosslinks unchanged, and second, these can be destroyed by free-radical acceptors present in the system like DPG or DCP. The effect of the concentration of DPG or DCP on the observed degree of reversion strongly points out that reaction (24) is mainly responsible for the reversion. The lower apparent reversion with DCP is due to a balance between the formation of new crosslinks by DCP and the simultaneous destruction of polysulfide links.

It is also frequently advocated that reversion may occur due to excessive main-chain scission. This is again greatly facilitated by the presence of some amines which act as oxygen carrier for such a scission process. But in a recent study<sup>15</sup> of stress relaxation of DPG vulcanizates, it has been proved that scission occurs only to the extent of 3% or less. Evidently, therefore, reversion is due to thermal breakdown of the polysulfide linkages. The present study with DCP, too (though there is no direct evidences so as to reject the above ideas of chain scission), indicates the occurrence of a thermal dissociation process.

In conclusion, it may be said that DPG-accelerated sulfur vulcanization of NR is mainly an ionic process, not very much influenced by ZnO and stearic acid. The high degree of reversion arises from the thermal degradation of polysulfide crosslinks. The presence of ZnO/zinc salt effects further vulcanization by entering into reaction with thiols and polysulfides, probably through a free-radical mechanism which results in a higher degree of crosslinking.

## CONCLUSION

From the present study, it appears most probable that DPG-accelerated sulfuration reaction is a polar process; in the presence of ZnO and stearic acid, the reaction follows a polar mechanism along with a radical mechanism.

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