

Studies in Hard Rubber Reaction. Part II. Effect of Organic Accelerators

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Synopsis

The method of differential thermal analysis has been applied to the study of thermal effects accompanying exothermic vulcanization reaction in hard rubber compounds accelerated with common rubber accelerators. Exothermic reaction was found to start at about 1% sulfur, in the case of CBS-accelerated compound which increases linearly up to 32% and then decreases, probably due to predominance of a dehydrogenation reaction. 68/32 Rubber-sulfur compounds containing increasing amounts of combined sulfur evolve decreasing quantity of heat and a plot of ΔH vs. combined sulfur of the precured compounds shows three stages of reaction. Accelerators were found not to affect the heat of reaction of the compounds to a great extent except in the special cases of those containing MBT and ZDC. The beneficial effect of certain accelerators is to be traced in the lowering of initiation temperatures and a decrease of slope values whereby the reaction becomes more regulated and spread out. Increase of concentration of accelerators (CBS and TMT) was found to have little effect.

INTRODUCTION

In the rubber industry production of high grade hard rubber (ebonite) requires a very long time owing to the inherent slowness of the process at usual curing temperature. Attempts to speed up the vulcanization of ebonite involve the risk of excessive heat development.

The use of organic accelerator suggests itself as a means of shortening the curing time. It is, therefore, important to know how effectively such accelerators speed up the hard rubber reaction and if they have any effect on the heat of exothermic hard rubber reaction. From the published information¹⁻¹⁴ it is found that organic accelerators do not basically alter the nature of the rubber-sulfur reaction that produces ebonite; their effect is essentially to reduce the time of reaction. Information available on the effect of organic accelerators on heat of hard rubber reaction is, however, conflicting.¹⁻¹³

In the earlier communication,¹⁵ the authors reported results of their investigations on the determination of the heat of hard rubber reaction with the help of differential thermal analysis (DTA). The present paper

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describes such determinations with the same instrument and following the same experimental procedure on stocks containing various accelerators. Determination of the thermal parameters of the hard rubber reaction in the presence of accelerators would be an important guide to the industry in selecting the correct accelerator system in the production of ebonite and also in the understanding of the mechanism of the reaction.

EXPERIMENTAL

Six accelerators, e.g., diphenylguanidine (DPG), butyraldehyde aniline (BA), tetramethylthiuram disulfide (TMT), zinc dimethyl-dithiocarbamate (ZDC), mercaptobenzothiazole (MBT), and cyclohexylbenzthiazyl sulfenamide (CBS) were used for this investigation. These comprise the more important accelerators used in the rubber industry and also represent important chemical classes of accelerators, excepting the very "scorchy" xanthate class.

Experiments were conducted with CBS-accelerated compounds of increasing concentration of sulfur (type A compounds) and also with those having a fixed total concentration (32%) but varying in initial sulfur combination (type C compounds). The effect of other accelerators has been studied on a 68/32 rubber-sulfur compound having an initial sulfur combination of 4-6% (type B compounds) in order to be able to correlate the results with the earlier determinations.¹⁵ Free and combined sulfur contents of the samples heated to various chosen temperatures in the DTA were determined in order to obtain relevant information about the hard rubber reaction.

RESULTS AND DISCUSSION

Heat of Reaction

Type A Samples. The differential thermographs of compounds containing increasing amounts of both total and free sulfur are shown in Figure 1. The experimental data and the results calculated therefrom are reported in Table I.

Figure 2 shows the relation between heat evolution and total sulfur of the compounds mentioned above along with those of unaccelerated compounds. The heat of reaction increases linearly in both the cases. In the case of stocks accelerated with CBS, the heat of reaction increases linearly up to 32% of total sulfur and then decreases, the curve showing a maximum at 32%, compared to 30% in the case of unaccelerated stocks.¹⁵ The higher vulcanization coefficient with the accelerated stock agrees with the observations of earlier workers.¹⁶⁻¹⁹ The observed decrease beyond 32% is attributed to the increased endothermic dehydrogenation reaction with high sulfur compounds at high temperature.^{20, 21}

It may be observed (Fig. 2) that the straight lines for the accelerated and unaccelerated stocks intersect at about 16% sulfur (0.5 g.-atom of sulfur per

TABLE I
Data Calculated from the Thermographs of CBS-Accelerated Compounds of Increasing Total Sulfur Content

Compound no.	Rubber/sulfur ratio	Free sulfur, %	Combined sulfur (calc. by difference), %	Sample weight, g.	Thermo-graph no. (Fig. 1)	Heat evolved, cal./g. Rubber		Initiation temp., °C.	Furnace temp. at peak thermo-graph, °C.	Slope value
						Mix	Rubber			
116/B	95.3/4.7	3.2	1.5	0.1695	1a	46	48	150	185	0.18
114/B	89.4/10.6	8.7	1.9	0.1720	1b	76	85	145	184	0.58
116/B	83.4/16.6	12.8	3.8	0.1698	1c	136	164	140	146	1.33
111/B	80/20	16.4	3.6	0.1717	1d	159	199	140	185	1.28
109/B	73/27	23.3	3.7	0.1664	1e	189	259	141	184	2.14
106/B	88/32	28.4	3.3	0.1635	1f	219	322	142	185	2.47
105/B	60/40	36.1	3.9	0.1741	1g	159	265	141	183	2.75

isoprene unit) showing that at this composition equal amounts of heat are evolved or the accelerator has no effect. Whether this is a mere coincidence [16% sulfur corresponds to the formula $(C_5H_8)_2S$] or not is difficult to say.

It is apparent from Figure 2 that the slope of the straight line is smaller in the case of CBS-accelerated stocks, which shows that the reaction in this case is a more regulated one. This conclusion has also been drawn from the measurement of slope values which will be discussed later on. Heat evolved per gram of rubber, however, is greater (up to 16% sulfur) than that

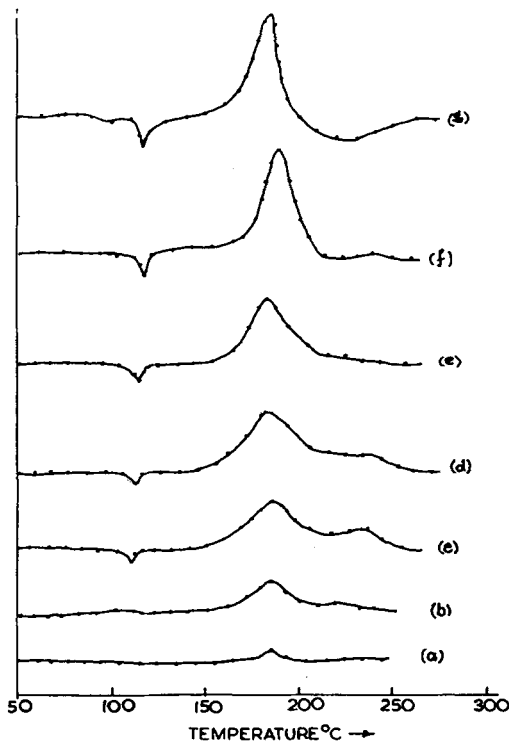


Fig. 1. Differential thermographs of CBS-accelerated rubber-sulfur compounds of increasing total sulfur contents: (a) 4.7% total sulfur, sample weight 0.1695 g.; (b) 10.6%, 0.1720 g.; (c) 16.6%, 0.1698 g.; (d) 20.0%, 0.1719 g.; (e) 27.0%, 0.1664 g.; (f) 32.0%, 0.1635 g.; (g) 40.0%, 0.1741 g.

evolved at equivalent concentration of total sulfur in the case of unaccelerated stocks.¹⁵ This might be attributed to either or both of the following reasons: (1) greater yield of crosslinks (2) suppression of the endothermic scission reactions.

Type C Samples. The ratio of free sulfur to combined sulfur progressively decreased on preheating of the compound (106 D) containing 1% CBS, so as to contain increasing amounts of combined sulfur. The thermographs of these samples are shown in Figure 3. The experimental data and results calculated from the above are reported in Table II.

TABLE II
Data Calculated from Thermographs of CBS-Accelerated 68/32 Compounds of Decreasing Free Sulfur Content

Time of cure at 150°C., min.	Free sulfur, %	Combined sulfur (calc.), %	Sample weight, g.	Thermograph no. (Fig. 3)	Heat evolved, cal./g.	Initiation temp., °C.	Furnace temp. at peak of thermograph, °C.	Slope value
5	28.4	3.3	0.1636	3a	217.0	142	185	2.47
10	25.8	5.9	0.2117	3b	195.0	138	183	2.75
30	24.4	7.3	0.2607	3c	186.0	130	184	2.75
40	18.9	12.8	0.2704	3d	157.0	110	185	2.75
50	15.9	15.8	0.2774	3e	160.0	108	187	1.80
60	14.0	17.7	0.2513	3f	141.0	108	186	1.73
80	11.0	20.7	0.2680	3g	99.0	105	186	1.19
100	6.6	25.1	0.2695	3h	48.0	111	185	0.57
140	1.2	30.5	0.2702	3i	6.0	120	186	0.36
190	0.3	31.4	0.2710	3j	—	—	—	—

Figure 4 shows the graph of combined sulfur versus heat evolution of CBS-accelerated 68/32 rubber-sulfur compound. It is seen that heat evolution decreases with decrease of free sulfur content. This is due to decrease of the available reaction sites in rubber as well as to the decrease of free sulfur. It is also observed that plot of "heat evolution vs. combined sulfur" shows three stages of reaction as noted earlier with the unaccelerated compound.¹⁵ The explanation for the three stages elaborated earlier¹⁵

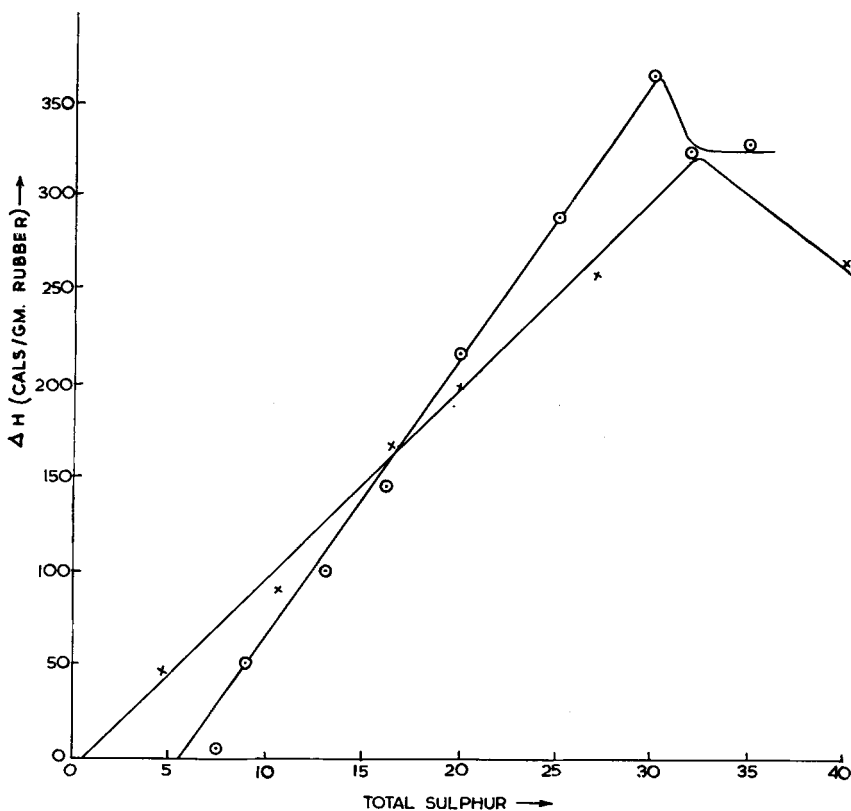


Fig. 2. Relationship between heat evolution and total sulfur in the unaccelerated and CBS-accelerated rubber-sulfur compounds: (⊙) unaccelerated rubber-sulfur compounds of increasing total sulfur contents; (×) CBS-accelerated rubber-sulfur compounds of increasing total sulfur content.

holds good here also. It is, however, observed that the middle portion is smaller in the case of the accelerated compound, because the lowering of heat evolution due to the scission reaction, as presumed earlier,¹⁵ continues up to 12% combined sulfur but the sulfur combination at which the reaction becomes vigorous is smaller (17%). This composition is again very near to 0.5 g.-atom of sulfur per isoprene unit and lends support to the belief that after this composition the reactivity of the mass increases. The overall effect of the accelerator is probably to minimize the scission reac-

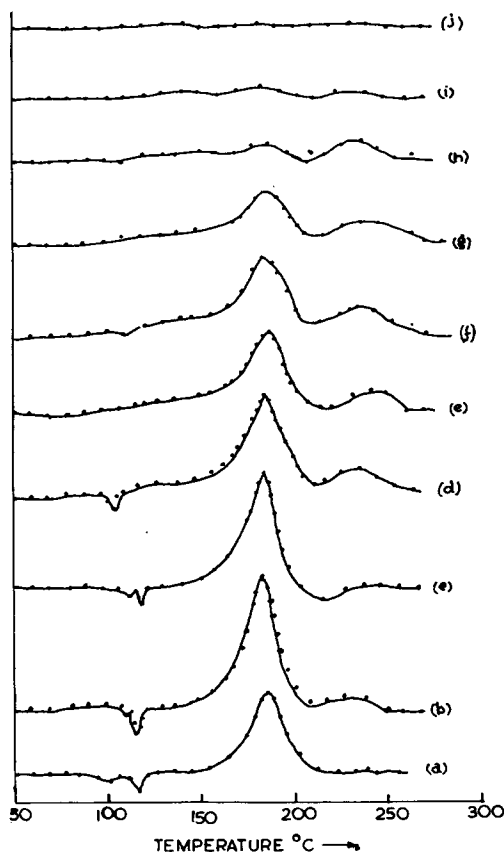


Fig. 3. Differential thermographs of CBS-accelerated 68/32 rubber-sulfur compounds of decreasing free sulfur contents: (a) 28.4% free sulfur, sample weight 0.1636 g.; (b) 25.8%, 0.2117 g.; (c) 24.4%, 0.2607 g.; (d) 18.9%, 0.2709 g.; (e) 15.9%, 0.2774 g.; (f) 14.0%, 0.2513 g.; (g) 11.0%, 0.2680 g.; (h) 6.6%, 0.2695 g.; (i) 1.2%, 0.2702 g.; (j) 0.3%, 0.2710 g.

tions resulting in a contraction of semihard rubber stage and a spreading out of the hard rubber stage.

CBS mixed with alumina (1:1) shows an exothermic curve (Fig. 5) starting at about 110°C. against alumina as the reference material. This is, however, absent in the rubber mix probably because of the low concentration of the accelerator.

Initiation of Exothermic Reaction

It may be noted in Table I and Figure 1 that the temperature at the initiation of exothermic reaction in the case of CBS-accelerated stocks is much lower than that observed with the unaccelerated stocks.¹⁵ In the case of accelerated stocks, the initiation temperature decreases from 150 to 140°C. as the free sulfur content of the compound increases from 4.7 to 16.6%, whereas with the unaccelerated stocks the decrease is from 178 to 154°C. as

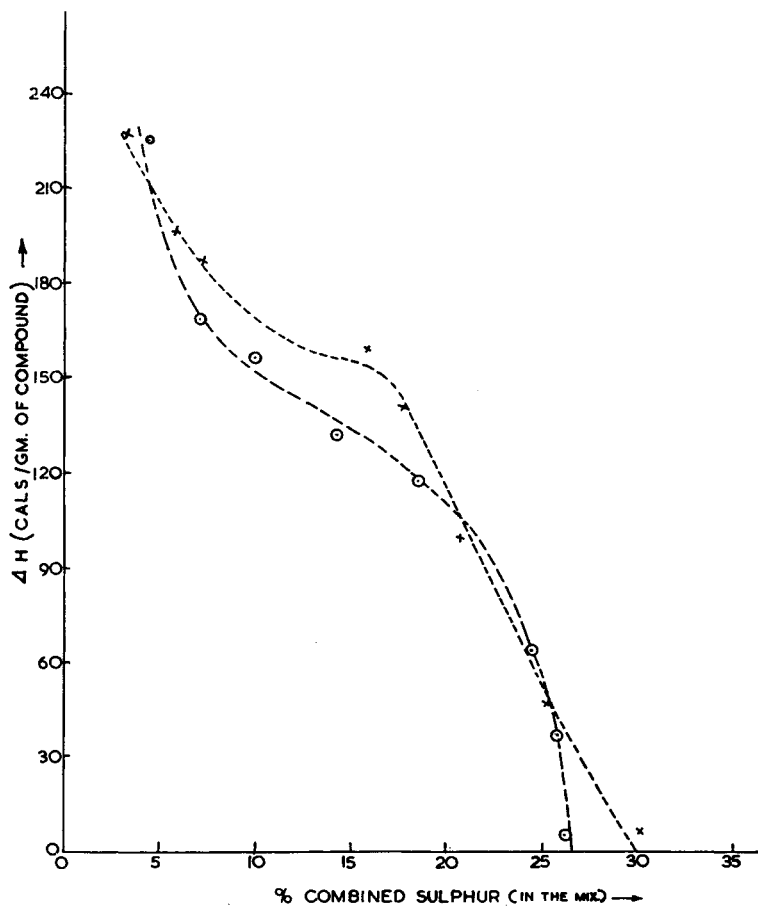


Fig. 4. Effect of combined sulfur of 68/32 compounds on heat of reaction: (○) un-accelerated compounds; (×) compounds accelerated with 1% CBS.

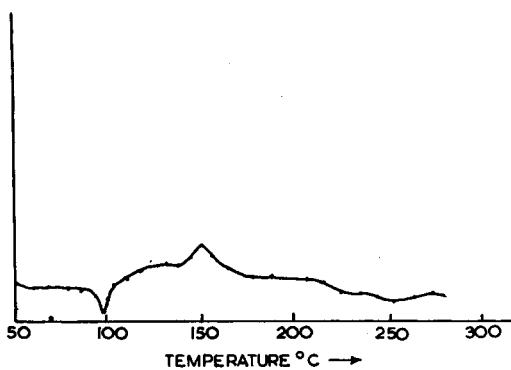


Fig. 5. Differential thermograph of CBS vs. alumina.

the sulfur content increases from about 7.4 to about 20%. The initiation temperatures then remain constant in both the cases. The lower initiation temperature of accelerated stocks may be due to lowering of activation energy and an increase of crosslinking efficiency. The progressive decrease of initiation temperature up to 16.6% sulfur again points to the greater reactivity of the compound as the composition approaches 0.5 g.-atom of sulfur per C_8H_8 unit.

In the case of CBS-accelerated type C samples (Table II), the temperature of initiation at first decreases with increase in combined sulfur, remains almost constant at about $110^\circ C.$ at 13–20% combined sulfur, and then increases again. This again shows that the reactivity of the mass increases with combined sulfur. The increase after 20% combined sulfur is due to decrease of sulfur concentration and nonavailability of reaction sites as the percentage of combined sulfur approaches that required for saturation.

It would be observed (Fig. 2) that the straight line obtained for CBS-accelerated stocks when extended, cuts the abscissa at about 1% total sulfur, showing that the exothermic reaction apparently starts at about this composition. There is no published information on this point with CBS-accelerated stocks. Blake,⁵ however, noted heat evolution with DPG-accelerated stock at about the same sulfur concentration. Initiation at smaller concentration of sulfur (1%) in the case of the accelerated stocks

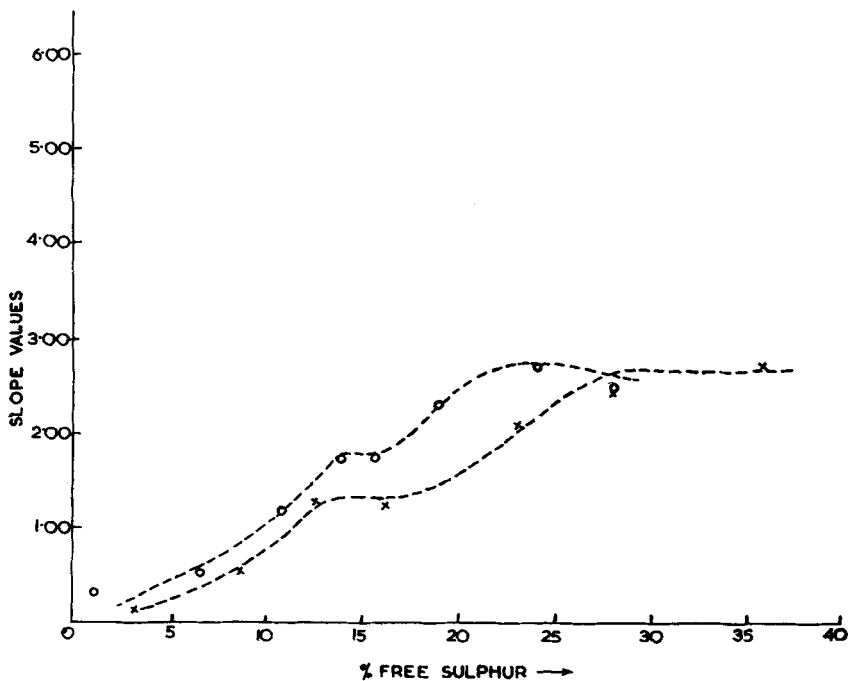


Fig. 6. Plot of slope values vs. free sulfur in the CBS-accelerated compounds: (O) CBS-accelerated compound with increasing sulfur; (X) CBS-accelerated 68/32 compound (106).

may be due to the lowering of activation energy and an increase of cross-linking efficiency for the soft rubber reaction.

Slope Values

The slope value as defined in this work²² is the tangent of the angle formed by the ascending DTA curve (usually linear over a large range) with the temperature axis. The slope value is a measure of the rate of heat evolution in the DTA experiment at a particular rate of heating, since with the same area covered by two thermographs, one having a lower slope value evidently liberates heat more slowly. Since the rate of heating in the present investigation was kept constant at 5°C./min., the slope values of the thermographs would give a fair indication of the rate of heat liberation and thereby of the relative reactivity of the different stocks.

The slope values of different compounds (Table I) have been plotted against free sulfur in Figure 6, along with those obtained from CBS-accelerated 68/32 rubber-sulfur compounds vulcanized to different extents. It would be seen that the slope values are not uniform over the whole range. In fact, three stages, similar to the case of unaccelerated compounds, are also observed here at almost the same ranges of free sulfur. This again lends further support to the conclusion that heat evolution occurs in two well-defined steps indicating two types of sulfur combination.

It is seen from Figure 6, that slope values of accelerated stocks are much smaller than those observed with the unaccelerated stocks,¹⁵ indicating that in presence of the accelerator, the reaction is very much regulated. With the accelerated stocks, the slope value increases from 0.18 to 1.3, whereas in the unaccelerated stocks the increase is from 0.5 to 1.8 if sulfur concentration is kept below 20%. After this concentration (up to 32%) the corresponding increases are from 1.3 to 2.5 and 1.8 to 9.0 for accelerated and unaccelerated stocks, respectively. In this latter stock intramolecular combination is the main reaction, but due to the presence of accelerators in the stocks reported here, the yield of intermolecular linkages increases, which would interfere with the main intramolecular combination. Thus the overall reaction is likely to show a decreased rate. Boström²³ conceives that some of the active sites of polymer molecules are blocked by accelerator fragments, resulting in a hindered reactivity towards ring formation.

Effect of Different Organic Accelerators on the Thermal Parameters

Differential thermographs of 68/32 compounds containing 1.0% each of organic accelerators are shown in Figure 7. The experimental data and the results calculated from these thermographs are reported in Table III.

From Table III it is seen that in all but the compounds with ZDC and MBT accelerators, the heat of reaction values lie between 299 and 322 cal./g. rubber, being either slightly less or equal to that of the unaccelerated compound. The heats of reaction in the compounds containing ZDC and MBT are 356 and 395 cal./g., respectively. It may be assumed that in the

TABLE III
 Data Calculated from the Thermographs of 68/32 Compounds Containing 1.0% Each of Various Organic Accelerators

Compound no.	Accelerator	Free sulfur, %	Combined sulfur (calc. by difference), %	Sample weight, g.	Thermo-graph no. (Fig. 7)	Heat evolved, cal./g. Rubber		Initiation temp., °C.	Furnace temp., at peak of thermo-graph, °C.	Slope value
						Mix	Rubber			
106	None	27.4	4.6	0.1475	7a	220	323	160	191	9.0
106 A	DPG	27.8	3.9	0.1634	7b	202	300	142	185	2.75
106 B	BA	28.4	3.3	0.1530	7c	201	299	150	185	3.73
106 C	TMT	27.5	4.2	0.1670	7d	215	319	154	192	5.67
106 D	CBS	27.4	4.3	0.1635	7e	217	322	144	185	2.47
106 E	ZDC	25.4	6.3	0.1508	7f	266	395	145	191	4.33
106 F	MBT	26.7	5.0	0.1999	7g	239	356	140	188	4.33

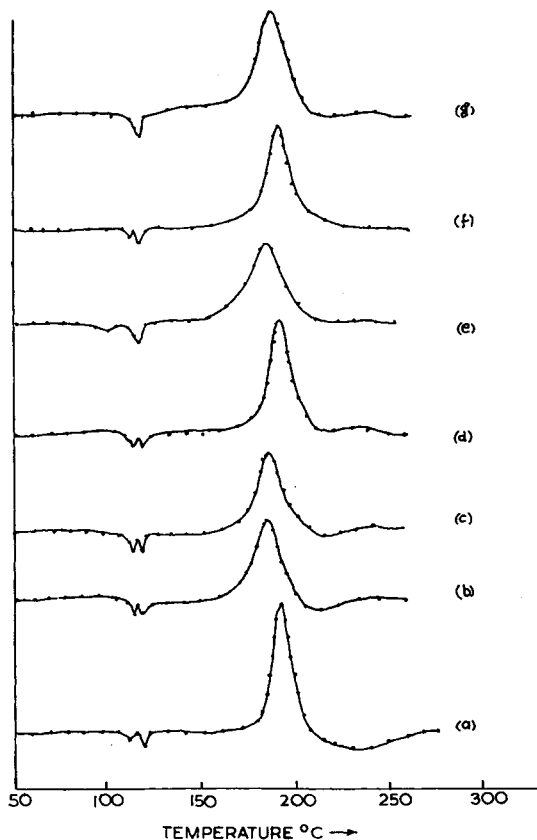


Fig. 7. Differential thermographs of 68/32 compounds containing 1% of various accelerators: (a) no accelerator, sample weight 0.1475 g.; (b) DPG, 0.1634 g.; (c) BA, 0.1530 g.; (d) TMT, 0.1670 g.; (e) CBS, 0.1635 g.; (f) ZDC, 0.1508 g.; (g) MBT, 0.1999 g.

formation of hard rubber from unaccelerated rubber-sulfur compound, polysulfide bridges are first formed, which later on are regrouped, resulting in an increase in network density and redistribution of inter- and intramolecular links.²⁴ Vulcanization accelerators facilitate the transformation to elemental sulfur and thereby decrease the content of sulfur atoms in the bonds. In this respect, different accelerators behave differently. Some accelerators, like TMT,²⁵ may break down into free radicals and initiate vulcanization processes with the formation of $-C-C-$ or $-C-S-C-$ bonds. Nitrogenous accelerators of the diphenylguanidine type,²⁶ on the other hand, promote yield of polysulfide bonds in presence of sulfur. In the vulcanization of hard rubber, formation and decomposition of intermolecular sulfur bonds occur simultaneously.²⁴ The decomposition of intermolecular polysulfide links may lead to the formation of either intramolecular links or a greater number of intermolecular links or both. Some of the sulfur biradicals resulting from the decomposition of intermolecular

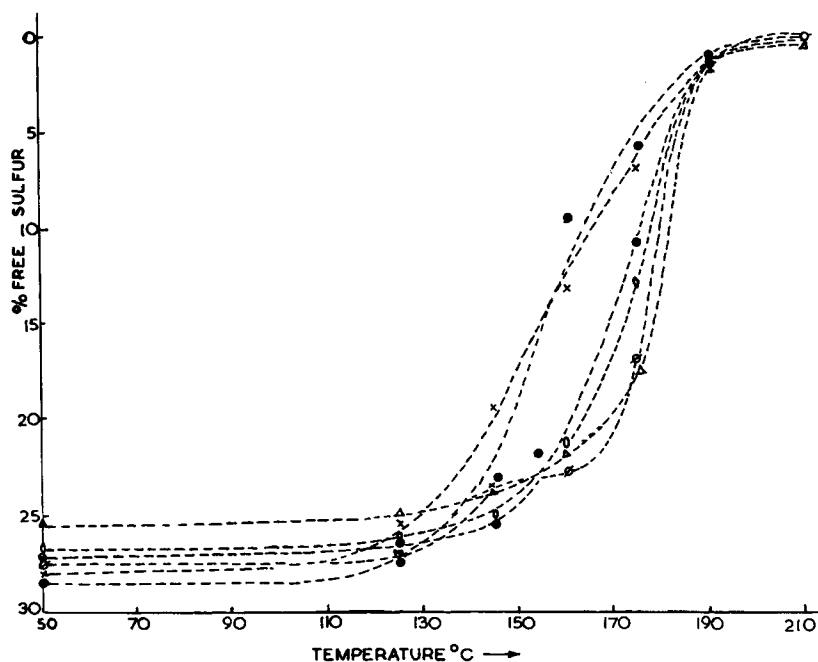


Fig. 8. Disappearance of free sulfur in the thermographs of 68/32 compounds containing 1% of various accelerators: (x) DPG (106A); (●) BA (106B); (φ) TMT (106C); (⊗) CBS (106D); (Δ) ZDC (106E); (○) MBT (106F).

links may form hydrogen sulfide²⁷ by scission of hydrogen atoms from molecular chains of rubber. Polysulfide links, characterized by an energy of 27 Kcal./mole, break at 130°C. The more stable mono- and disulfides having a bond energy of 5 kcal./mole are broken at 150–170°C. Hydrogen sulfide formed during the formation of hard rubber can, however, influence the breaking of both polysulfide²⁸ and disulfide links.^{29,30} The overall heat effect of the hard rubber reaction will, therefore, be influenced by the types of intermolecular links formed and its subsequent redistribution into inter- and intramolecular links. Obviously, accelerators like TMT or ZDC which are known to possess high crosslinking efficiency and thus form stable crosslinks at lower temperature are likely to cause a higher heat evolution.

It is seen from Figure 7 that the temperature of initiation is lowered by about 10–20°C. Initiation of the exothermic reaction at a lower temperature without significant change of furnace temperature at the thermograph peaks means that heat evolution is distributed over a wider range of temperatures. This is evident on comparing Figure 6b–6g with the thermograph of the unaccelerated stock (Fig. 6a). It is also seen from Figure 7 and Table III that initiation of the hard rubber reaction takes place between 130 and 154°C. in all the accelerated compounds as against 160°C. in the case of the unaccelerated compound. Once the reaction is started it is quicker with the unaccelerated stock, giving rise to a steeper thermograph

TABLE IV
Data Calculated from Thermographs of 68/32 Compounds Containing Different Concentrations of CBS and TMT

Compound no.	Accelerator	Concentration of accelerator, %	Free sulfur, %	Combined sulfur, %	Sample weight, g.	Thermograph no. (Figs. 9 and 10)	Heat evolved, cal./g. Rubber		Furnace temperature at peak of initiation thermograph, °C.	Slope value
							Mix	temp., °C.		
106	None	0	27.4	4.6	0.1478	9a	220	160	191	9.0
106 D	CBS	1.0	25.8	5.9	0.1477	9b	217	142	187	2.47
106 D ₁	"	2.0	26.0	5.4	0.1479	9c	218	130	183	1.54
106 D ₂	"	4.0	25.5	5.1	0.1490	9d	213	125	178.5	1.43
106 D ₃	"	5.0	25.2	5.1	0.1466	9e	213	130	178	1.19
106	None	0	27.4	4.6	0.1480	10a	220	160	191	9.0
106 C	TMT	1.0	27.5	4.2	0.2661	10b	215	155	192	5.67
106 C ₁	"	2.0	26.5	4.9	0.2672	10c	187	122	183	3.73
106 C ₂	"	3.0	25.7	5.3	0.2678	10d	186	122	185	2.14
106 C ₃	"	5.0	25.3	5.0	0.2702	10e	195	125	183	1.73

than with the accelerated stocks. The fact that the reaction starts at a lower temperature in the accelerated stocks, coupled with the slower rate of the exothermic reaction probably explains the well-known greater "safe curing rate" of the accelerated stocks as observed by earlier workers.⁸ The disappearance of free sulfur at various points of thermographs of accelerated stocks lends support to the concept of the safe curing rate of these stocks. The results of this determination are plotted in Figure 8.

It is seen from Figure 8 that combined sulfur at the point of initiation varies from 6 to 12% for different accelerators compared to 11% in the unaccelerated compound. Two accelerators, DPG and BA, known to be the best for accelerating hard rubber reaction, show more gradual disappearance of free sulfur and more combined sulfur (10.7 and 12.7%) at the point of initiation (Fig. 8) compared to the others. TMT shows two breaks in the curve. CBS and MBT initiate reaction at the lowest combined sulfur (6.2 and 6.5%, respectively).

When the slope values are calculated from the thermographs of accelerated stocks (Table III) it is found that the slope is lowest with DPG and CBS stocks. Of these DPG is customarily known to be the safest accelerator for the hard rubber reaction; no published information is available on the use of CBS in hard rubber. The accelerator falling in the next category (BA) is also known to be a safe accelerator, whereas those showing high

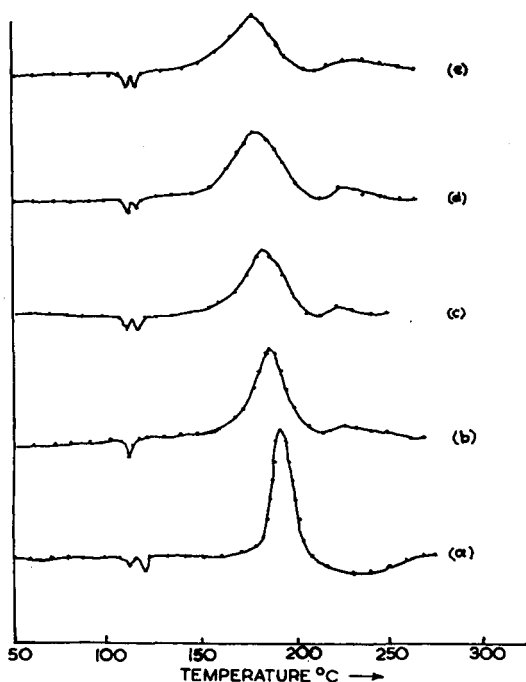


Fig. 9. Differential thermographs of 68/32 compounds containing different concentrations of CBS: (a) 0%, sample weight 0.1478 g.; (b) 1%, 0.1477 g.; (c) 2%, 0.1497 g.; (d) 4%, 0.1490 g.; (e) 5%, 0.1466 g.

slope values, viz., ZDC, MBT, and TMT, give compounds likely to cause overheating.

From the above discussion it is seen that once the initiation point is reached, the rate of heat evolution is lower in presence of accelerators. This is in contradiction with the earlier belief that the hard rubber reaction is accelerated by organic accelerators, though to a smaller degree than the soft rubber reaction, causing quicker generation of heat. The reason for this belief probably lies in the fact that it has not been possible in the earlier work to isolate fully the exothermic stage from the other stages, so that the conclusion as regards acceleration has been drawn from the overall rate. The determination of "acceleration factor," proposed by Fisher, Newton, and Scott,⁷ expressed as the number of hours (at 155°C.) required for the unaccelerated mix to reach the same degree of cure (judged by the free sulfur and yield temperature) as is reached by the accelerated mix after 1 hr. seems to be arbitrary and has no significance on the actual exothermic hard rubber reaction.

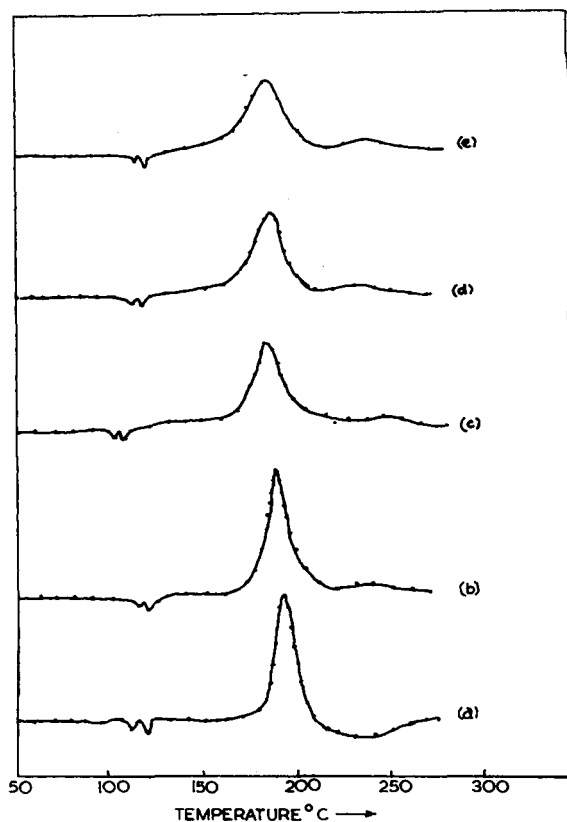


Fig. 10. Differential thermographs of 68/32 compounds containing different concentrations of TMT: (a) 0%, 0.1480 g.; (b) 1%, 0.2661 g.; (c) 2%, 0.2672 g.; (d) 3%—0.2678 g.; (e) 5%, 0.2702 g.

Effect of Concentration of Accelerators

It is seen from the results reported in Table IV and Figures 9 and 10 that the heat of reaction does not change appreciably with accelerator concentration. The initiation of exothermic reaction takes place at a lower temperature with 2.0% accelerator (125–130°C.) after which there is no further lowering with further increase of accelerator concentration. Slope values, however, show a gradual decrease with accelerator concentration, indicating increased intervention of accelerator in the hard rubber reaction as indicated before.

From the present study it may be considered that organic accelerators of the type commonly used in soft rubber are effective in the vulcanization of ebonite in the sense that they speed up the soft rubber reaction and thus make it possible to reach the point of initiation of exothermic hard rubber reaction more quickly and at a lower temperature. Once the initiation point is reached, the reaction is slower in presence of accelerators, thereby decreasing the rate of evolution of heat which is again a welcome feature.

The authors are thankful to Prof. S. R. Palit for his helpful criticism and encouragement during the course of this investigation.

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Résumé

On a appliqué la méthode d'analyse thermique différentielle à l'étude des effets thermiques qui accompagnent la réaction exothermique de vulcanisation des composés du caoutchouc dur, accélérée avec les accélérateurs habituels du caoutchouc. On a trouvé que la réaction exothermique débute à environ 1% en soufre dans le cas du composé accéléré par CBS, augmente linéairement jusque 32% et puis diminue, ce qui est probablement dû à la prédominance d'une réaction de déshydrogénation. Les composés 68/32 contenant des quantités croissantes de soufre combiné dégagent une quantité décroissante de chaleur et un graphique représentant ΔH en fonction du soufre combiné pour les composés prétraités présentent trois étapes de réaction. Les accélérations n'affectent pas d'une façon marquée la chaleur de réaction des composés, excepté dans le cas spécial de ceux contenant du MBT et du ZDC. L'avantage de certains accélérateurs est d'abaisser les températures d'initiation et de diminuer les valeurs tangentes; la réaction devient ainsi plus régulière et s'étend plus facilement. On a trouvé que l'augmentation de la concentration en accélérateurs (CBS et TMT) avait une légère influence.

Zusammenfassung

Die Methode der thermischen Differentialanalyse wurde zur Untersuchung der die exotherme Vulkanisationsreaktion in mit üblichen Kautschukbeschleunigern beschleunigten Hartgummimischungen begleitenden thermischen Effekte angewendet. Eine exotherme Reaktion beginnt im Fall von HBS-beschleunigten Mischungen bei etwa 1% Schwefel, nimmt bis zu 32% linear zu und fällt dann, wahrscheinlich wegen des Überwiegens einer Dehydrierungsreaktion wieder ab. 68/32-Mischungen, welche steigende Mengen an gebundenem Schwefel enthalten, entwickeln eine geringer werdende Wärmemenge, und die Auftragung von ΔH gegen gebundenen Schwefel der drei vorvulkanisierten Mischungen zeigt drei Reaktionsstadien. Die Beschleuniger haben keinen grossen Einfluss auf die Reaktionswärme der Mischungen, ausgenommen im speziellen Fall derjenigen Mischungen, die MBT und ZDC enthalten. Der günstige Einfluss gewisser Beschleuniger kann auf die Erniedrigung der Starttemperatur und auf eine Abnahme der Neigungswerte zurückgeführt werden, wodurch die Reaktion gleichförmiger und besser verteilt wird. Es wurde gefunden, dass eine Zunahme der Beschleunigerkonzentration (CBS & TMT) nur einen geringen Einfluss besitzt.

Received June 8, 1964