Studies in Hard Rubber Reaction.
Part III.   Effect of Metallic Oxides and Metallic Oxide–Accelerator Combinations

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Synopsis

A study of thermal effects accompanying exothermic hard rubber reaction with the help of differential thermal analysis has been extended to 68/32 rubber–sulfur compounds containing different metallic oxides and metallic oxide–accelerator combinations. Metallic oxides do not affect the heat of reaction appreciably; however, they affect the slope value, litharge showing an unusually low value.   In combination with accelerator, metallic oxides exert specific effects on heat of reaction, initiation temperature, and slope value.   Attempts have been made to explain these findings on the basis of the known behavior of the individual oxides and the accelerators.

INTRODUCTION

Metallic oxides such as zinc and magnesium oxides are known to increase the activity of accelerators in vulcanization reactions.   They are, however, reported not to activate the hard rubber reaction, since they usually reduce the acceleration factor.[1]   Moreover, the effect of accelerators in raising the yield temperature is not enhanced by either of the above-mentioned oxides.   Nevertheless, it is found that mixes with metallic oxides do cure rather more quickly than those without, probably due to the fact that the oxides themselves are mild accelerators.   There are indications, also, that they exert specific effects, since the relative efficiency of the accelerators in enhancing the acceleration factor does not fall in the same order in combination with metallic oxides as without.[2]   It is believed that metallic oxides in conjunction with organic accelerators help in "set curing" and that by using suitable accelerator–metallic oxide combinations the critical curing rate can at least be doubled, making it possible roughly to halve curing times without increasing the danger of overheating.[3]

In course of the work on determination of the heat of the hard rubber reaction by a DTA method, the authors investigated the effect of organic accelerators on heat evolution.[4]   It was seen that the beneficial effect of

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the accelerators is due mainly to (*1*) lowering of the initiation temperature for the exothermic reaction and (*2*) decreasing the rate of temperature rise.   It would be of interest to see the effect of the different metallic oxides and metallic oxide–accelerator combinations on heat evolution in order to be able to come to a conclusion regarding the relative suitability of the above additives in hard rubber mixes.

EXPERIMENTAL

The experimental methods for the determination of the heat of the hard rubber reaction is the same as elaborated in Part I[5] of the present series.

The effect of the metallic oxides was studied after incorporating 5 phr each of zinc oxide, magnesium oxide, and litharge in 68/32, rubber–sulfur base stocks, with or without 1% of various organic accelerators: diphenyl-guanidine (DPG), butyraldehydeaniline (BA), cyclohexylbenzthiazyl sulfen-amide (CBS), zinc diethyldithiocarbamate (ZDC), and tetramethylthiur-amdisulfide (TMTD).

The above stocks were press-cured at 153°C. for a suitable period to combine about 4–6% sulfur so as to permit the results to be correlated with the earlier observations.[4,5]

RESULTS

The thermographs of the samples containing the metallic oxides are shown in Figure 1 and the data calculated from the same samples are shown in Table I. Figure 2 shows the disappearance of free sulfur as the samples are heated in the DTA.

In Table II and Figure 3 are shown the effect of magnesium oxide–accelerator combinations, while the corresponding data and thermographs with zinc oxide–accelerator combinations are shown in Table III and Figure 5.   The disappearance of sulfur during DTA of the same samples are shown in Figures 4 and 6, respectively.

TABLE I

Data Calculated from the Thermographs of 68/32 Compounds Containing 5% Metallic Oxides (Fig. 1)

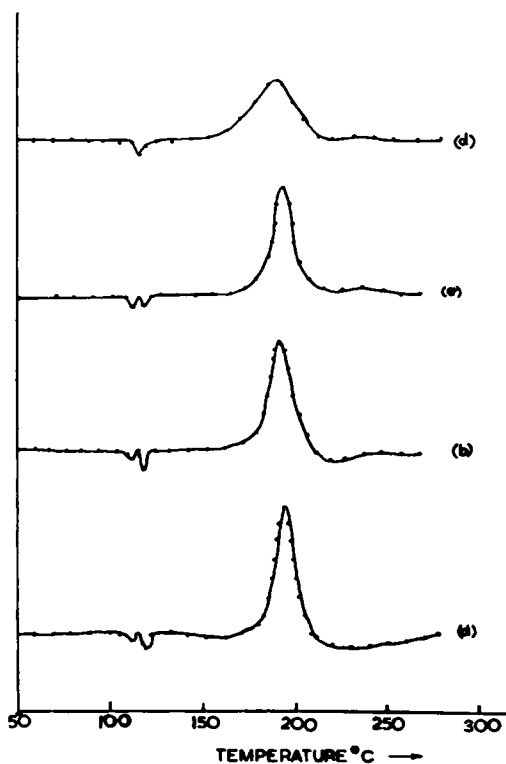| Com-pound	Type of Metallic oxide	Sulfur in the stock, %		Sample weight, g.	Heat evolved, cal./g.		Initia-tion temp., °C.	Furnace temp. at peak point of thermo-graph, °C.	Slope value
		Free	Combined (calc.)		Mix	Rubber			
106	—	27.4	4.6	0.1482	220	323	160	193	9.00
123	Magnesium oxide	25.1	5.4	0.1938	195	301	150	190	5.67
124	Zinc oxide	25.5	5.0	0.1575	210	324	155	193	7.11
126	Litharge	25.0	5.5	0.1481	200	309	150	190	1.24

Fig. 1. Thermographs of 68/32 rubber-sulfur stocks containing metallic oxides: (a) none, sample wt. 0.1482 g.; (b) magnesium oxide, sample wt. 0.1938 g.; (c) zinc oxide, sample wt. 0.1575 g.; (d) litharge, sample wt. 0.1481 g.

Table IV and Figure 7 reports the results of investigation with litharge–accelerator combinations.

TABLE II

Data Calculated from the Thermographs of 68/32 Compounds Containing Magnesium Oxide–Accelerator Combinations (Fig. 3)

Com-pound	Accel-erator	Sulfur in the stock, %		Sample weight, g.	Heat evolved, cal./g.		Initia-tion temp., °C.	Fur-nace temp. at peak point of thermo-graph, °C.	Slope value
		Free	Com-bined		Mix	Rubber			
123/1	CBS	26.9	3.3	0.1830	225	351	134	182	2.14
123/2	DPG	26.2	4.0	0.2007	221	344	140	178	4.70
123/3	BA	26.7	3.6	0.1736	213	332	145	180	4.01
123/5	TMT	26.4	3.8	0.1926	223	347	156	188	5.67
123	None	25.1	5.4	0.1938	195	301	150	190	5.67

TABLE III

Data Calculated from the Thermographs of 68/32 Compounds Containing Zinc Oxide–Accelerator Combinations (Fig. 5)

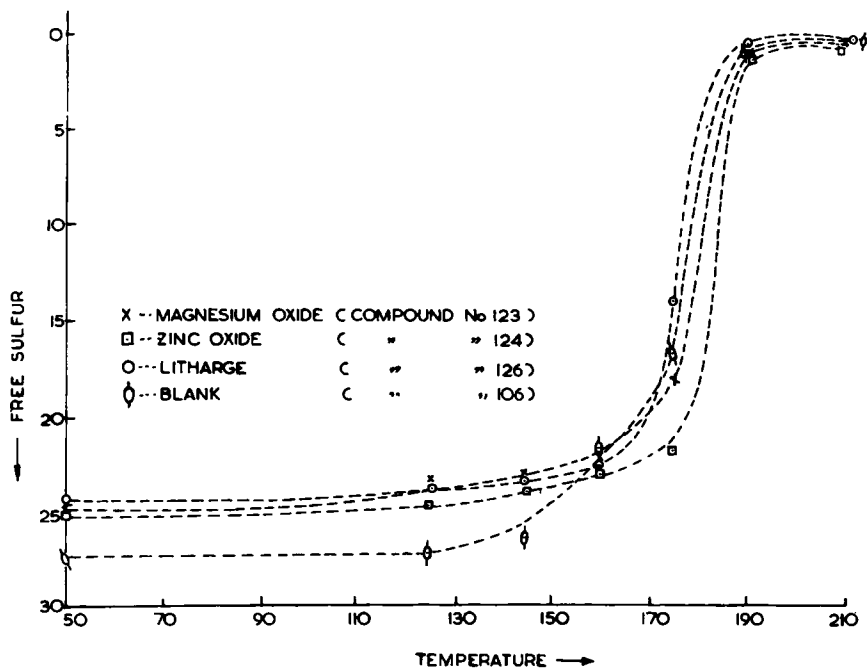| Compound	Accelerator	Sulfur in the stock, %		Sample weight, g.	Heat evolved, cal./g.		Initiation temp., °C.	Furnace temp. at peak point of thermo-graph, °C.	Slope value
		Free	Combined		Mix	Rubber			
124/1	CBS	24.7	5.5	0.1804	194	309	142	186	2.75
124/2	DPG	26.6	3.6	0.1822	204	318	152	183	3.73
124/3	BA	26.5	3.7	0.1811	196	306	152	183	3.27
124/4	ZD C	25.2	5.0	0.1622	234	365 (65 + 300)	118, 152	180	0.25, 1.03
124/5	TMT	26.3	3.9	0.1739	266	415 (70 + 345)	116, 157	175	0.26, 1.11
124	None	25.5	5.0	0.1575	210	324	155	193	7.4

Fig. 2. Disappearance during DTA of free sulfur in the 68/32 rubber–sulfur stocks containing metallic oxides.

TABLE IV

Data Calculated from the Thermographs of 68/32 Compounds Containing Litharge–Accelerator Combinations (Fig. 7)

| Compound | Accelerator | Sulfur in the stock, % | | Sample weight, g. | Heat evolved, cal./g. | | Initiation temp., °C. | Furnace temp. at peak point of thermograph, °C. | Slope value |
		Free	Combined (calc.)		Mix	Rubber			
126/1	CBS	24.3	5.4	0.1495	192	300	142	187	1.43
126/2	DPG	26.6	3.6	0.1661	180	281	148	184	2.14
126/3	BA	26.9	3.3	0.1620	186	290	148	187	1.73
126/5	TMT	26.3	3.9	0.1622	192	300	150	185	2.14
126	None	25.0	5.5	0.1481	200	309	150	190	1.24

DISCUSSION

Effect of Metallic Oxides without Organic Accelerators

It may be seen in Table I that metallic oxides do not appreciably alter the total amount of exothermic heat. In the absence of any organic accelerator, the metallic oxides are believed to act as mild accelerators,
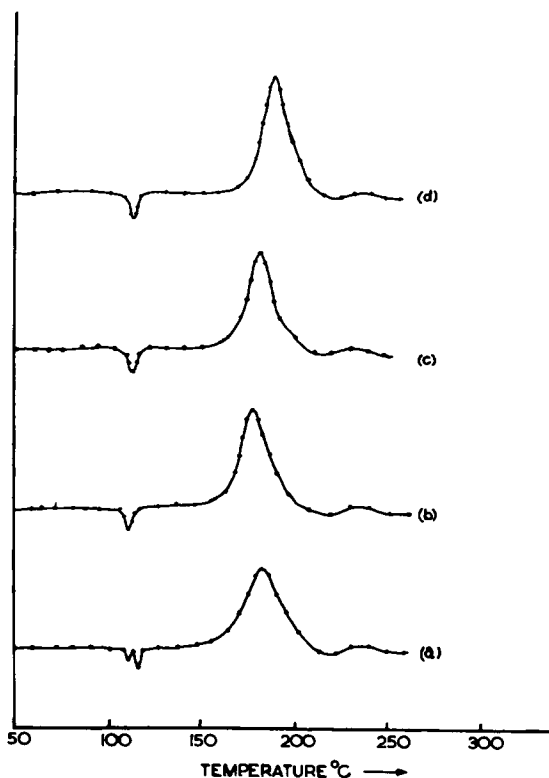
Fig. 3. Effect of magnesium oxide–accelerator combinations (5%/1%) on the thermographs of 68/32 rubber-sulfur stocks: (a) MgO–CBS, sample wt. 0.1830 g.; (b) MgO–DPG, sample wt. 0.2007 g.; (c) MgO–BA, sample wt. 0.1736 g.; (d) MgO–TMT, sample wt. 0.1926 g.

and since organic accelerators themselves do not appreciably alter the exothermic heat,[4] the metallic oxides are not expected to do so.

Like the organic accelerators, the metallic oxides lower the initiation temperature but to a lesser extent (by about 10°C.), as is consistent with their lower acceleration efficiency. Zinc oxide, however, does not show any accelerating effect as is seen by the fact that the initiation temperature of the sample containing ZnO is almost the same as that of the blank (Table I).

It was shown in Part II of the present series[4] that the slope of the prolongation of the exothermic DTA curve is a good indication of the rate of heat liberation and therefore of the relative safety of the different stocks. Results of the values of slope of the DTA curves with metallic oxides given in Table I are consistent with this conclusion. Litharge shows an unusually low value of slope from which it might be concluded that the presence of this metallic oxide in hard rubber mixes would give very safe curing compounds. Unfortunately because of the poor dielectric properties of the product, sufficient data are, at present, not available to
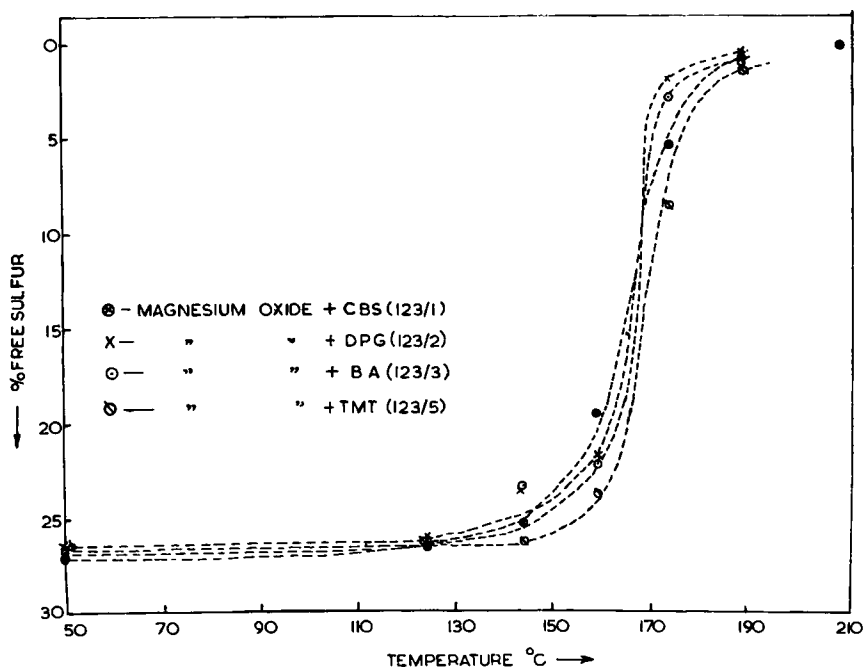
Fig. 4. Disppearance during DTA of free sulfur in the 68/32 rubber–sulfur stocks containing magnesium oxide–accelerator combinations.

support the above finding.   On the other hand, the slopes for zinc oxide are almost equal to those for the blank, which has the highest slope.   This is consistent with the fact that zinc oxide alone has very little accelerating activity.   It may be seen in Figure 2 that combined sulfur at the temperature of initiation (Table I) is about 7–8% in the ZnO sample compared to about 11% with that of the blank.

Magnesium Oxide–Accelerator Combination

Table II shows that the effect of magnesium oxide in combination with accelerators like CBS, DPG, BA, and TMT is to raise the heat of hard rubber reaction.

Initiation temperatures in combination with accelerators are more or less the same as with magnesium oxide alone (150°C., Table I) except in the cases of CBS, in which the temperature is lower (134°C.) and TMT, in which the temperature is higher (160°C.).   Initiation temperatures obtained with the magnesium oxide–accelerator combination are however, very near to those with the corresponding accelerators and slight lowering is observed in all the cases except in the case of CBS combination which shows lowering by about 10°C.

The slope of the exothermic curve is raised by the incorporation of magnesium oxide with the accelerators, except in the case of CBS for which the value is almost the same as with the accelerator alone.[4]   TMT gives a

higher slope value even without magnesium oxide. This means that the magnesium oxide in combination with the other two accelerators, i.e., DPG and BA, is likely to cure more quickly than with the accelerators alone but the margin of safety is lowered by incorporation of the oxide. However, the safe-curing characteristics of above mixes, as observed by the slope value, are still better than those of the unaccelerated mix.[5]
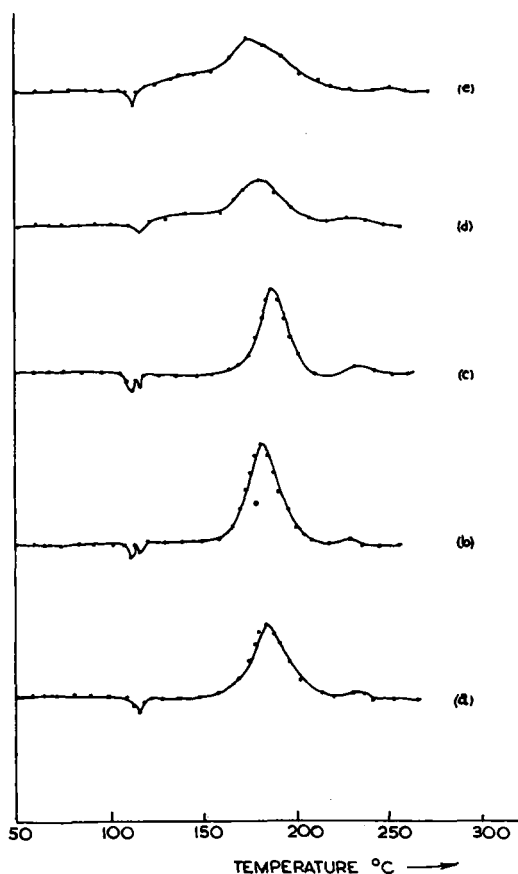

Fig. 5. Effect of zinc oxide–accelerator combinations (5%/1%) on the thermographs of 68/32 rubber–sulfur stocks: (a) ZnO–CBS, sample wt. 0.1804 g.; (b) ZnO–DPG, sample wt. 0.1822 g.; (c) ZnO–BA, sample wt. 0.1811 g.; (d) ZnO–ZDC, sample wt. 0.1622 g.; (e) ZnO–TMT, sample wt. 0.1739 g.

From Figure 5 it is seen that combined sulfur at the temperature of initiation (Table II) lies in the range 4–6%, which is slightly less than was observed with the accelerators[4] or the oxide alone. This means that initiation takes place at a lower combined sulfur level with the magnesium oxide–accelerator combination.
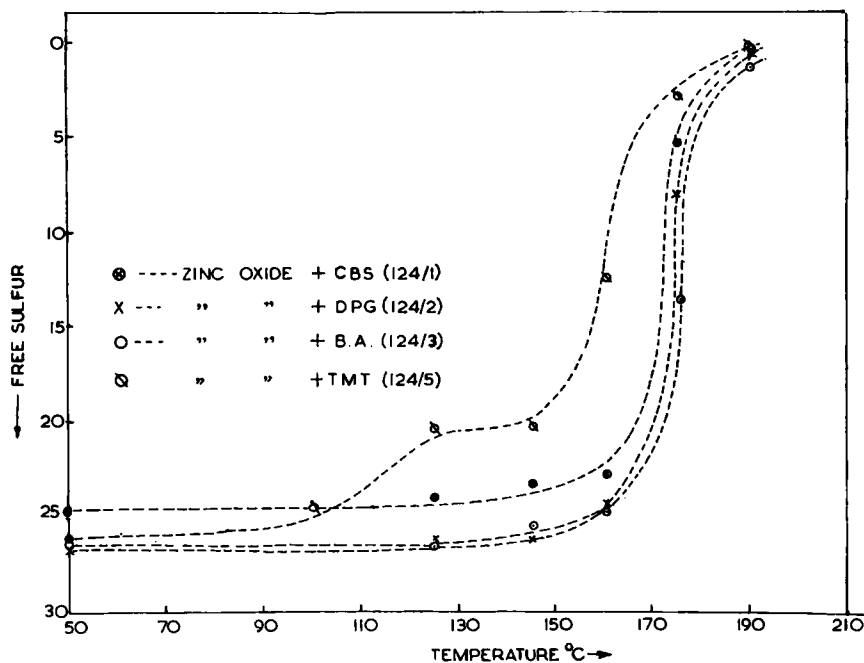
Fig. 6. Disappearance during DTA of free sulfur in the 68/32 rubber–sulfur stocks containing zinc oxide–accelerator combinations.

Zinc Oxide–Accelerator Combination

Zinc oxide in combination with CBS, DPG, and BA does not appreciably alter the total heat liberation (Table III). The values obtained from these combinations (309, 318, and 306 cal./g. rubber) are lower than those obtained with stocks containing zinc oxide only and are almost the same as or slightly higher than those containing the corresponding accelerators alone. This is consistent with the joint effect of zinc oxide and the respective accelerators as studied.

In the case of the zinc oxide–TMT combination, the heat evolution is increased considerably. The cause of the larger heat evolution is to be found in the very low initiation temperature (116°C.). As shown in Figure 5, the exothermic reaction starts at the melting point of sulfur. This is in accord with the recent findings of Moore, Saville, and Watson,[6] who observed that zinc oxide–TMT combination may accelerate natural rubber vulcanization to such an extent that satisfactory vulcanizate can be obtained at 100°C. The results of estimation of sulfur given in Figure 6, also show that the zinc oxide–TMT system accelerates combination of sulfur at a much lower temperature than the other systems studied.

Another interesting feature of the zinc oxide–TMT system as observed in Figure 5 is that the shape of the thermograph is a little different and the exothermic curve is not a continuous one as in other cases but shows a break at 157°C., after which the rate of heat liberation increases. This
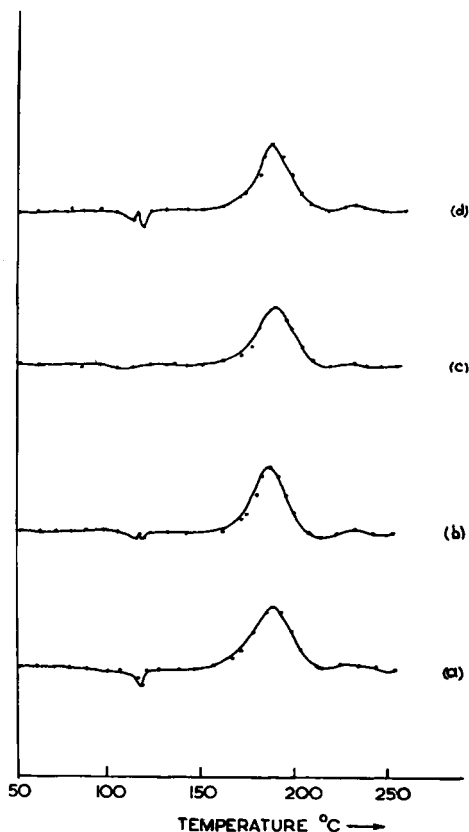
Fig. 7. Effect of litharge–accelerator combinations (5%/1%) on the thermographs of 68/32 rubber–sulfur stocks: (a) litharge–CBS, sample wt. 0.1495 g.; (b) litharge–DPG, sample wt. 0.1661 g.; (c) litharge–BA, sample wt. 0.1620 g.; (d) litharge–TMT, sample wt. 0.1622 g.

means that two rate processes superimposed on one another, are involved. It may be presumed that the first inflection at 116°C. is due to the combination of sulfur to form soft rubber, whereas that at 157°C. is for the formation of hard rubber. The reason for these two stages (not observed in other cases) is probably the lower yield of stable crosslinks and the slowness of the first reaction, which is overshadowed by the much faster second-stage reaction before accumulating sufficient heat. The zinc oxide–ZDC system also shows this two-stage reaction and the same explanation holds good.

Another point in favor of the two-stage reaction is that when the area under two stages (Fig. 5) are separately determined, values of 70 cal./g. rubber for the first stage and 345 cal./g. rubber for the second stage are obtained, making a total of 415 cal./g. The value of 345 cal./g. is comparable with values for the other combinations showing only a one-stage reaction. It may be assumed[7,8] that in the formation of hard rubber

polysulfide bridges are first formed which later on are regrouped, resulting in an increase in network density and redistribution of inter- and intramolecular links. In the above cases, where accelerators with high crosslinking efficiency are involved, stable crosslinks are formed in large numbers from the beginning. This may account for the heat evolution at lower temperature and increase in total heat evolution. The value of 415 cal./g. compares favorably with the average value of 395 cal./g. for the 68/32 compound containing ZDC alone which again presumably is the total for two-stage reaction, the first one not being prominent due to the absence of zinc oxide in the mix. The same explanation holds good for the ZDC–zinc oxide combination.

The slope values given in Table III indicate that zinc oxide–accelerator combinations are more regulated than the other systems studied, the extreme case being zinc oxide–TMT, and zinc oxide–ZDC systems, where the slope values for the two stages are as low as 0.25 and 1.03, respectively. This is surprising, in view of the fact that zinc oxide, TMT, and ZDC used separately give slope values of 7.11, 5.67, and 4.33, respectively. This means that the danger of overheating is the least in these combinations of zinc oxide in hard rubber vulcanization. This, coupled with the very high overall cure rate, leads us to predict that these systems, which seem not to have been tried earlier for fear of the danger of overheating, will give satisfactory vulcanization of ebonite at a very high cure rate. This is supported by the fact that when a 68/32 compound containing 5% zinc oxide and 1% TMT (both on mix) is heated in a $^3/_{64}$-in. thick former at 153°C., almost half of the sulfur is combined after 10 min. and the curing is virtually complete in a period as low as 70 min. For thick specimens, however, the advantage is largely offset by the accumulation of larger amounts of heat, and the suitability of such a highly accelerated mix is determined by how quickly the heat is generated and how fast it can be conducted away, i.e., by the temperature of vulcanization and the thickness of the specimen.

Litharge–Accelerator Combination

As discussed earlier, the presence of litharge in the mix gives a small slope value (1.2, Table I). It may be seen (Table IV, Fig. 1) that this beneficial effect is maintained even in presence of the accelerator which by itself gives large slope value. Also slope values for litharge in combination with the different accelerators lie in a narrower range (1.4–2.1) than observed with other metallic oxides. Initiation temperature and the heat of reaction also are almost the same as with litharge alone (Table I). All these seem to show that incorporation of the different accelerators does not have much influence, and that the reaction seems to be regulated by the metallic oxide (litharge) alone. This is surprising in view of the diverse nature of the accelerators used and their varied effect on the vulcanization of soft rubber.

CONCLUSION

From the present study it is apparent that metallic oxides in absence of any organic accelerators exert an effect on exothermic reaction similar to that of the organic accelerators but varying in degree, consistent with their weak accelerating activity.   In combination with accelerators, the effects are specific and vary according to the type of the metallic oxide and the accelerator used.   The effect is most specific in the cases of combination of accelerators with zinc oxide, TMT–ZnO having the most significant behavior.   It is least specific in the case of litharge–accelerator combinations, which have almost the same characteristics as litharge alone.   The characteristic effect of litharge is to make the reaction go slow, which is a welcome feature of "safe-curing."

References

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Résumé

L'étude des effets thermiques, qui accompagnent la réaction exothermique de durcissement du caoutchouc, étude effectuée au moyen de l'analyse thermique différentielle, a été étendue aux composés 68/32 caoutchouc–soufre, contenant différents oxydes métalliques et des combinaisons oxyde métallique–accélérateur.   Il a été démontré que les oxydes métalliques n'affectent pas appréciablement la chaleur de la réaction.   Ils affectent cependant la valeur de la pente, la litharge montrant une valeur inhabituellement basse.   En combinaison avec un accélérateur, les oxydes métalliques exercent des effets spécifiques sur la chaleur de réaction, sur la température d'initiation, et la valeur de la pente.   Des essais ont été faits afin d'expliquer ces résultats sur la base du comportement connu des oxydes individuels et des accélérateurs.

Zusammenfassung

Die Untersuchung der thermischen Effekte bei der exothermen Hartgummireaktion mit Hilfe der Differentialthermoanalyse wurde auf 68/32-Kautschuk–Schwefelmischungen mit verschiedenen Metalloxyden und Metalloxydbeschleunigerkombinationen ausgedehnt.   Es wurde gefunden, dass Metalloxyde keinen wesentlichen Einfluss auf die Reaktionswärme besitzen.   Sie beeinflussen aber den Neigungswert, wobei Bleiglätte einen ungewöhnlich niederen Wert zeigt.   In Kombination mit einem Beschleuniger üben Metalloxyde spezifische Einflüsse auf Reaktionswärme, Starttemperatur und Neigungswert aus.   Ein Versuch zur Erklärung dieser Befunde auf Grundlage des bekannten Verhaltens der individuellen Oxyde und der Beschleuniger wurde unternommen.