Studies in Hard Rubber Reaction.   Part IV.
Effect of Fillers

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Synopsis

The effects of the different fillers i.e., china clay, light magnesium carbonate, Pliolite S_6E, and ebonite dust, on the exothermic hard rubber reaction has been studied with the help of differential thermal analysis.   The data for heat evolution show some unexpected features in that china clay, a more or less inert filler, lowers heat evolution.   The behavior of magnesium carbonate also can not be fully explained.   Attempts have been made to explain the data for Pliolite S_6E and ebonite dust on the basis of their composition and effects of the individual components on heat of reaction.   The differences in initiation temperature and slope values have been explained.

INTRODUCTION

In the earlier communications the authors reported results of investigations on the determination of the heat of the hard rubber reaction[1] and the effect of the different accelerators[2] and metallic oxides[3] on the heat of reaction and related aspects as determined with the help of differential thermal analysis (DTA).   The present paper describes such determinations on stocks, loaded with ebonite dust, magnesium carbonate, and a commericial high styrene resin (Pliolite).   The fillers used represent those which are of current interest in industrial ebonite compounding.   China clay has also been included in the study in order to have a loading material which is chemically more or less inert and would therefore serve as a basis for comparing the results with other more reactive materials.

EXPERIMENTAL

Methods

The experimental methods and procedure are the same as described earlier,[1] and a heating rate of 5°C./min. was used as before.

Samples

The active materials were prepared after incorporating different proportions of the fillers, under investigation, in a 68/32 rubber–sulfur base stock

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and heating at 153°C. in a platen press for such time as is necessary to combine about 4–6% sulfur, in order to obtain results comparable with those of the earlier investigations.[1–3]

The ebonite dust used had the following characteristics: total sulfur, 29.2%; acetone extract, 4.50%; free sulfur, 3.7%; ash, 0.35%.
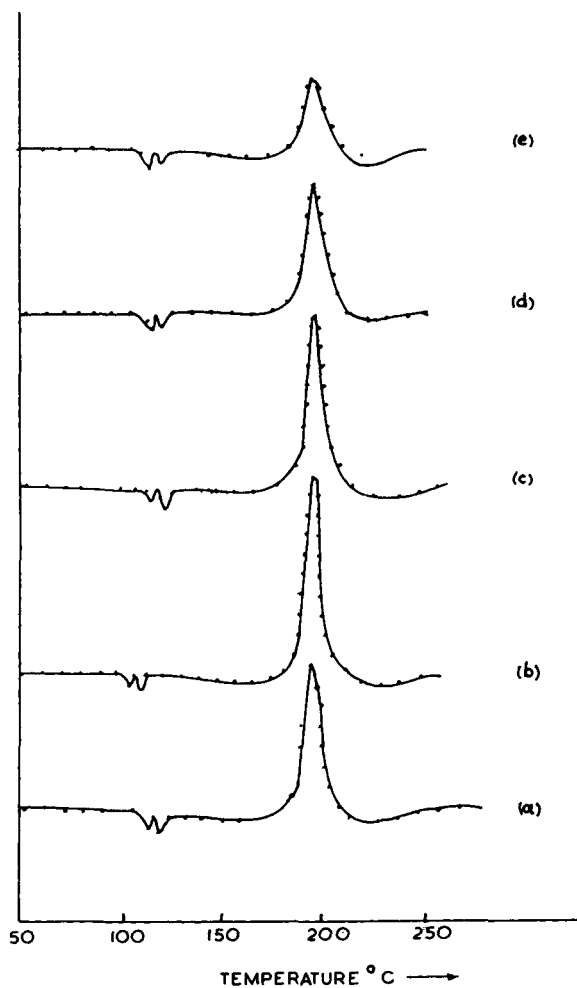

Fig. 1. Thermographs of 68/32 rubber–sulfur stocks containing different concentrations of china clay: (a) 0%, sample weight 0.1476 g.; (b) 10%, 0.1930 g.; (c) 17%, 0.2033 g.; (d) 34%, 0.2048 g.; (e) 68%, 0.2323 g.

The sample of Pliolite S_6E was supplied by the Goodyear Tire and Rubber Co. and had the following properties:[4] polymer composition, 85% styrene/15% butadiene; specific gravity, 1.04; ash (total), 0.08%; softening point, 48°C.; bulk density, 19.2 lb./ft.[3]; solubility, very limited in aromatic hydrocarbons, chlorinated hydrocarbons, ketones; heat stability,
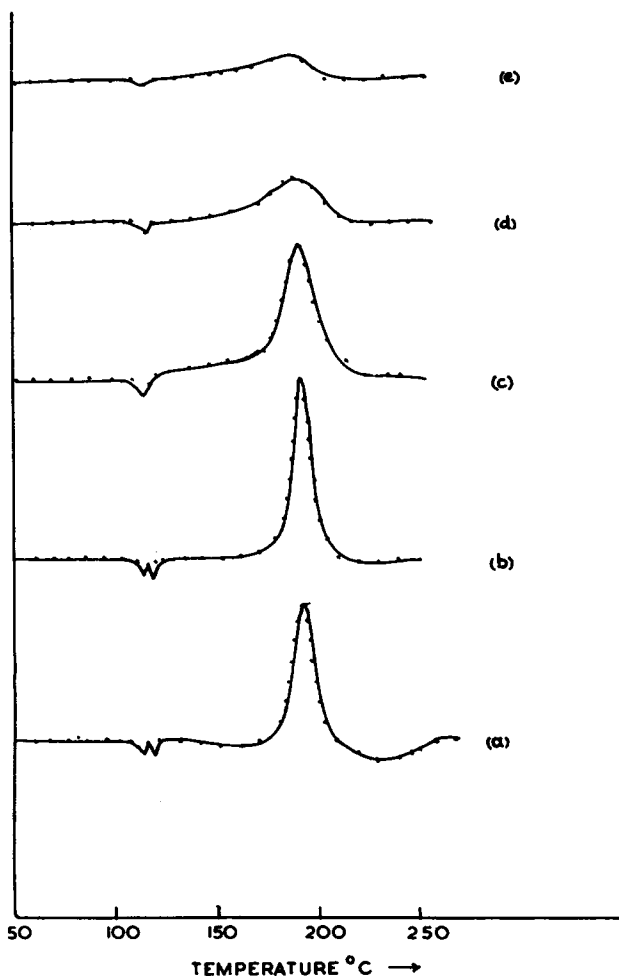
Fig. 2. Thermographs of 68/32 rubber–sulfur stocks containing different concentrations of light magnesium carbonate: (a) 0%, sample weight 0.1482 g.; (b) 10%, 0.1622 g.; (c) 20%, 0.2586 g.; (d) 30%, 0.1498 g.; (e) 40%, 0.1497 g.

no change in properties after several hours heating at 250°F.; typical particle, porous granules; color, white; taste, none; toxicity, none.

China clay and light magnesium carbonate were rubber grade materials corresponding to IS 505-1958 and IS 1420-1959, respectively.

RESULTS

Table I shows the effect of different concentrations of china clay on the heat of reaction, while Tables II, III, and IV give similar data for compounds with magnesium carbonate, Pliolite, and ebonite dust, respectively. The corresponding data are given in Figures 1–4. Figure 5 shows the

TABLE I

Data Calculated from Thermographs of 68/32 Rubber–Sulfur Compounds Containing Different Concentrations of China Clay

Compound no.	China clay, %	Sulfur in the stock, %		Sample weight, g.	Thermograph[a]	Heat of reaction, cal./g.		Initiation temp., °C.	Furnace temp., at peak thermograph, °C.	Slope value
		Free	Combined (by difference)			Mix	Rubber			
106	0	27.5	4.5	0.1476	1a	220	323	160	192	9.0
135	10	25.6	3.5	0.1930	1b	202	327	165	194	9.5
136	17	24.3	3.0	0.2035	1c	178	306	165	194	9.5
137	34	20.6	3.3	0.2043	1d	143	282	166	194	7.1
138	68	17.0	2.0	0.2323	1e	90	222	168	194	4.0

[a] Refers to curves in Fig. 1.

TABLE II

Data Calculated from Thermographs of 68/32 Rubber–Sulfur Compounds Containing Different Concentrations of Light Magnesium Carbonate

| Compound no.	Light magnesium carbonate, %	Sulfur in the stock, %		Sample weight, g.	Thermograph[a]	Heat of reaction, Cal./g.		Initiation temp., °C.	Furnace temp. at peak of thermograph, °C.	Slope value
		Free	Combined (by difference)			Mix	Rubber			
106	0	27.5	5.5	0.1482	2a	220	223	160	192	9.00
140	10	14.1	5.0	0.1622	2b	226	366	155	193	9.50
141	20	21.5	5.1	0.2586	2c	223	394	128	191	4.33
142	30	20.0	4.6	0.1498	2d	190	363	125	190	0.73
143	40	18.6	4.2	0.1497	2e	105	216	128	189	0.47

[a] Refers to curves in Fig. 2.
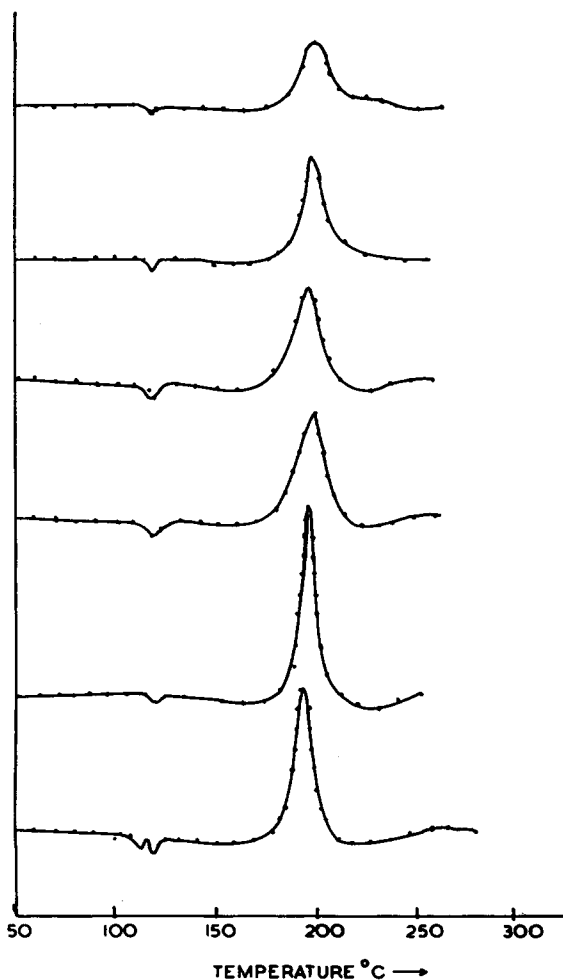
Fig. 3. Thermographs of 68/32 rubber–sulfur stocks containing different concentrations of Pliolite S_6E: (a) 0%, sample weight 0.1484 g.; (b) 10%, 0.1791 g.; (c) 17%, 0.1456 g.; (d) 34%, 0.1482 g.; (e) 55%, 0.1905 g.; (f) 68%, 0.1522 g.

results of a thermogravimetric experiment[5] with light magnesium carbonate, and the results of determination of free sulfur at different points of the thermograph are reported in Figure 6. A thermograph of the Pliolite S_6E–sulfur compound is reported in Figure 7. Figure 8 depicts the change of heat of reaction with increasing proportion of the different fillers.

DISCUSSION

China Clay

China clay is not used in conventional ebonite mixes but has been included in this study in order to see the effect of a loading material which

TABLE III

Data Calculated from Thermographs of 68/32 Rubber–Sulfur Compounds Containing Different Concentrations of Pliolite S₅E

Compound no.	Pliolite S₅E, %	Sulfur in the stock, %		Sample weight, g.	Thermograph[a]	Heat of reaction, Cal./g.		Initiation temp., °C.	Furnace temp. at peak of thermograph, °C.	Slope value
		Free	Combined (by difference)			Mix	Rubber			
106	0	25.7	4.5	0.1484	3a	220	323	160	192	9.0
150	10	25.8	3.3	0.1791	3b	229	370	168	195	9.0
151	17	24.0	3.3	0.1456	3c	227	390	165	193	3.73
152	34	20.9	3.0	0.1482	3d	180	355	165	195	3.30
153	55	17.6	3.0	0.1905	3e	144	329	170	198	3.50
154	68	16.9	2.1	0.1522	3f	122	301	170	198	2.75

[a] Refers to curves in Fig. 3.

TABLE IV

Data Calculated from Thermographs of 68/32 Rubber–Sulfur Compounds Containing Different Concentrations of Ebonite Dust

Compound no.	Ebonite dust, %	Sulfur in the stock, %		Sample weight, g.	Thermograph[a]	Heat of reaction, cal./g.		Initiation temp., °C.	Furnace temp. at peak of thermograph, °C.	Slope value
		Free	Combined (by difference)			Mix	Rubber			
106	0	27.5	4.5	0.1478	4a	220	323	160	192	9.00
160	17	22.4	4.9	0.1713	4b	206	354	164	196	9.50
161	34	19.2	4.7	0.1712	4c	153	301	163	198	5.60
162	40	18.0	4.5	0.1701	4d	141	290	163	198	1.73
163	50	17.1	4.2	0.1791	4e	118	260	165	200	1.48
164	68	15.5	3.5	0.1758	4f	99	244	168	200	1.33

[a] Refers to curves in Fig. 4.

is chemically virtually inert, with the effect that side reactions are comparatively few. The effect of such a material on the heat evolution should be that simply of dilution of the reactive substance, the heat of reaction decreasing with increasing mass of the latter, while heat of reaction per
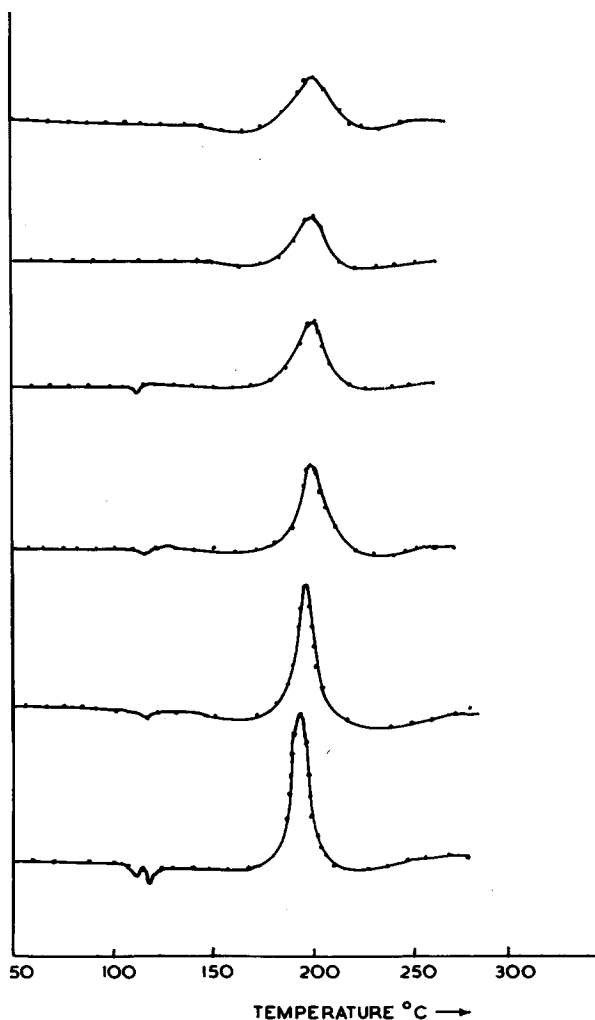

Fig. 4. Thermographs of 68/32 rubber–sulfur stocks containing different concentrations of ebonite dust: (a) 0%, sample weight 0.1478 g.; (b) 17%, 0.1713 g.; (c) 34%, 0.1712 g.; (d) 40%, 0.1701 g.; (e) 50%, 0.1791 g.; (f) 68%, 0.1758 g.

gram of rubber remains constant. That this is not true can be seen in Figures 1 and 8. The slight rise of the heat of reaction per gram of rubber, evident at small loadings may be accounted for as due to a change of the thermal characteristics of the stock, the specific heat of china clay being smaller (0.23) than that of the base mix (0.33). The fall at higher load-
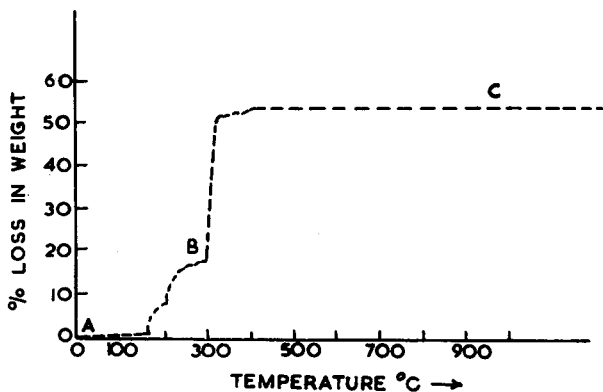
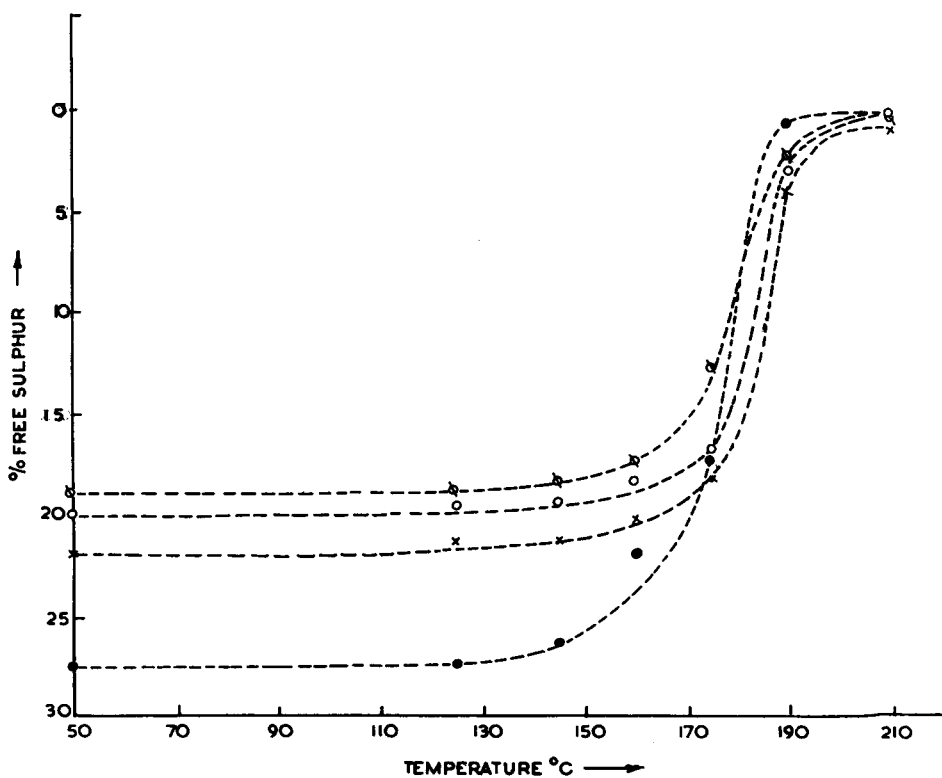Fig. 5. Thermogravimetric diagram of light magnesium carbonate.[5]

Fig. 6. Disappearance of free sulfur in thermographs of 68/32 rubber–sulfur stocks containing different concentrations of light magnesium carbonate: (×) 20% MgCO₃ (compound 141); (O) 30% MgCO₃ (compound 142); (⊘) 40% MgCO₃ (compound 143); (●) blank (compound 106).
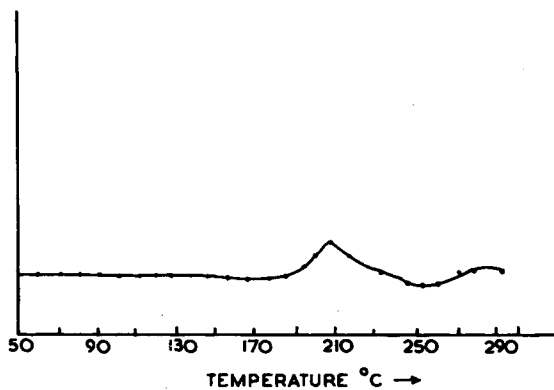
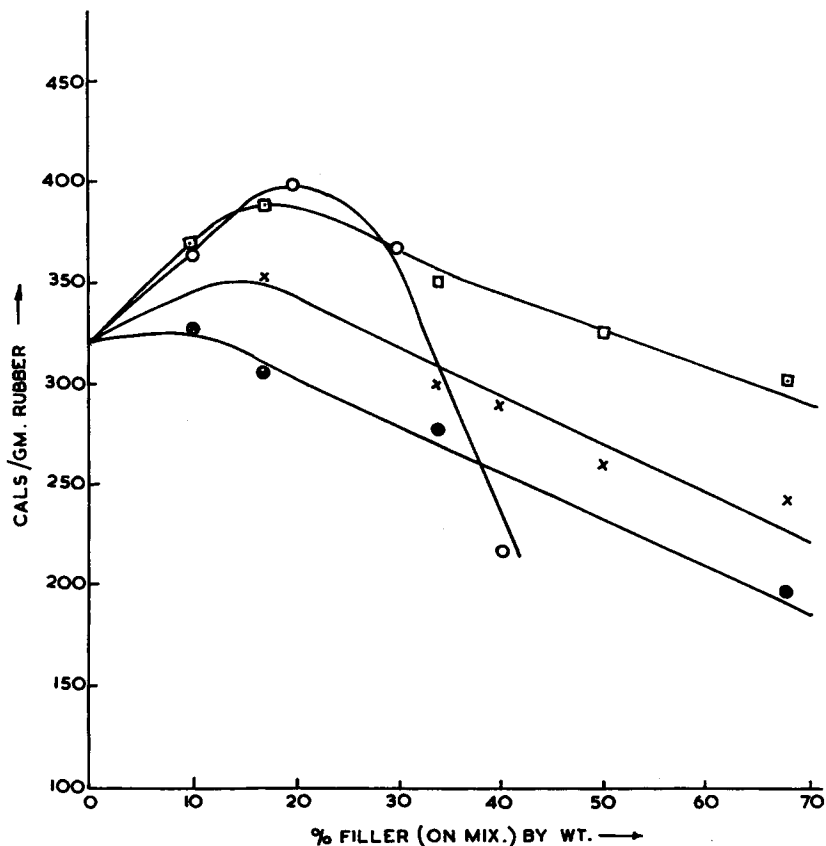Fig. 7. Thermograph of 86/14 Pliolite–sulfur compound.

Fig. 8. Effect of different fillers on heat of reaction of 68/32 rubber–sulfur compound:
(⊗) china clay; (O) magnesium carbonate; (□) Pliolite S_6E; (×) ebonite dust.

ings, however, points to a decrease in reactivity of the rubber–sulfur compound due to intervention of the inert filler.

The data (columns 9 and 11) in Table I which correspond to initiation temperature and slope value[2] also give the impression that characteristics of the stocks containing china clay are not fundamentally different from those of the blank (compound 106), except that at high dilution of the loading material, the initiation temperature rises slightly showing decreased reactivity and slope values fall showing the safe curing characteristics expected at high dilutions.

Light Magnesium Carbonate

Light magnesium carbonate is used to some extent in ebonite mixes due to its stiffening effects, anisotropic character, and decreased swelling in solvents.[6] The effect of magnesium carbonate on heat of reaction and other related aspects is a little more complicated than that with china clay, as is evident from Table II and Figures 2 and 8. It is seen in Figure 8 that heat evolved, in calories per gram of rubber, increases up to about 20% loadings and then decreases sharply as the loading is increased further. There is no apparent reason for the sharp rise at the earlier point shown in Figure 8. It cannot be ascribed wholly to change in thermal characteristics or acceleration effect, as china clay having almost the same specific heat (magnesium carbonate 0.227, china clay 0.230) shows much less rise, and organic accelerators which are much better accelerators than magnesium carbonate do not show an increase in the heat of reaction to the extent shown in Figure 8. The sharp fall in the values at higher loading may, however, be ascribed to the endothermic reactions of magnesium carbonate with evolution of water and carbon dioxide. The results of a thermogravimetric experiment[5] (Fig. 5) lend support to this conclusion where, it may be seen, that there is gradual loss in weight. Table II and Figure 2 also show that the initiation temperature is lowered to a great extent; the reason for this is not apparent.

Determination of free sulfur at selected points of the thermograph (Fig. 6) shows that magnesium carbonate behaves in the same way as organic accelerators, i.e., it lowers both the initiation temperature and combined sulfur at the point of initiation.

Pliolite

Pliolite is basically a 85/15 styrene–butadiene polymer.[4] It is, therefore, likely to react with sulfur to some extent. This expectation is borne out in Figure 7, which shows that heat evolution to the extent of 104 cal./g. of the polymer occurs when a 86/14 polymer–sulfur mix is heated. This means that a proportion of sulfur will be consumed by Pliolite when it is mixed with the 68/32 stock, which will alter the ratio of rubber to sulfur available for reaction to a slightly higher ratio. It was seen earlier[1] that a 70/30 rubber–sulfur has a higher value of heat of reaction (364) than that of 68/32 stock (324) as a result of less absorption of heat in the

endothermic dehydrogenation reaction. This may explain the increased heat of reaction per gram of rubber at smaller loadings of Pliolite. At higher loadings it is possible that, due to the reaction with Pliolite, not enough sulfur is available to react with the rubber. As a result of incomplete reaction, the heat of reaction diminishes, and the reaction with Pliolite, evolving less heat per gram, is not sufficient to make up the deficit. The result will be a progressive decrease in the heat of reaction value per gram of rubber with increase in the proportion of Pliolite, as is seen in Figure 8. Decrease of heat evolution with increasing Pliolite concentration agrees with the observation of Sell and McCutcheon,[7] who studied the effect of mixing Pliolite with SBR and concluded that it provides means of controlling the exothermic curing reaction, so troublesome in hard rubber manufacture, without sacrifice in physical properties. Conversely, it affords a means of curing thicker sections or using faster cures without the danger of charring. The initiation temperature (Table III) remains almost constant, which is as expected, as both the constituents (68/32 stock and Pliolite) have almost the same initiation temperature (Figs. 3 and 4), but the slope values (Table III) decrease with the introduction of a higher proportion of Pliolite, as may be expected from the safe curing characteristic referred to above.

Ebonite Dust

Of all the fillers, ebonite dust is most commonly used in the preparation of hard rubber, as it is considered to improve processing of the hard rubber mix and to reduce the undesirable temperature rise[9] and volume shrinkage during vulcanization. The effect of using ebonite dust in reducing the exothermic temperature rise has been studied,[8,10] and the results show that incorporation of ebonite dust makes possible higher curing temperature and hence shorter cure times.

The effect of ebonite dust as found in the present investigation is an increase of heat of reaction per gram of rubber, as may be seen in Table IV and Figures 7 and 8. Ebonite dust contains both residual unsaturation[11] and free sulfur and so is likely to react at a higher temperature, evolving a quantity of heat. This is in effect equivalent to an increase of both rubber and sulfur which is not taken into account while calculating the heat of reaction per gram of rubber in Table IV. The result will be an increase of the heat of reaction both per gram of mix or per gram of rubber. The results of Church and Daynes,[12] showing an exothermic character of 100 parts ebonite dust when heated at constant temperature (157°C.), may be cited in support of this explanation. This interpretation has, however, a drawback, in that when a mixture of ebonite dust and sulfur is used as the active material, an endothermic dehydrogenation reaction instead of the exothermic reaction is observed.[1] An alternative explanation would be an absorption of sulfur by ebonite dust, as evidenced by Scott,[13] so as to alter the rubber–sulfur ratio to an optimum higher value corresponding to higher heat generation.[1] At very high proportions of ebonite dust, this

increase is probably neutralized partially due to a small increase of the dehydrogenation reaction, resulting in a tendency of the heat of reaction values to decrease. However, no conclusive explanation can be put forward until the reactions of ebonite dust in hard rubber stock have been clarified. The initiation temperature is virtually unaltered, and the slope value decreases with increase of ebonite dust, a fact which corroborates the current views that ebonite dust lessens the chance of overheating of a hard rubber compound in proportion to its volume.

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Résumé

On a étudié, au moyen de l'analyse thermique différentielle, l'influence sur la réaction exothermique de durcissement du caoutchouc de différentes charges par ex. terre à porcelaine, carbonate de magnésium, Pliolite S₆E et poudre d'ébonite. Les résultats concernant le dégagement de chaleur présentent certains caractères inattendus en ce sens que la terre à porcelaine, qui est une charge plus ou moins inerte, abaisse le dégagement de chaleur. On ne peut pas non plus expliquer complètement le comportement du carbonate de magnésium. Des essais ont été effectués en vue d'expliquer les résultats pour la Pliolite S₆E et la poudre d'ébonite sur la base de leur composition et des effets des composants individuels sur la chaleur de réaction. On a expliqué les différences entre la température d'initiation et les valeurs des pentes.

Zusammenfassung

Der Einfluss verschiedener Füllstoffe, z.B. Kaolin, leichtes Magnesiumcarbonat, Pliolit S₆E und Ebonitstaub auf die exotherme Hartgummireaktion wurde differential thermoanalytisch untersucht. Die Wärmeentwicklungsdaten zeigen insofern ein unerwartetes Verhalten, als Kaolin, ein mehr oder weniger inerter Füllstoff, die Warmeentwicklung herabsetzt. Auch das Verhalten von Magnesiumcarbonat lässt sich nicht völlig erklären. Eine Erklärung der Daten für Pliolit S₆E und Ebonitstaub wurde auf Grundlage ihrer Zusammensetzung und der Einflüsse der individuellen Komponenten auf die Reaktionswärme versucht. Unterschiede in der Starttemperatur und in den Neigungswerten konnten erklärt werden.