Journal of Thermal Analysis, Vol. 5 (1973) 33–42

THERMAL ANALYSIS OF PYROTECHNICAL MIXTURES, I

STUDIES ON THE MECHANISM OF THE REACTION MnO_2 + FeSi90

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(Received January 15, 1971; in revised form March 14, 1972)

The author investigated a two-component pyrotechnical mixture used in the manufacture of delay detonators. Comparing the thermogravimetric, derivative thermogravimetric and differential thermal analysis curves of components with that of mixtures containing the components in different ratios, a relation has been found between the reaction rate and ratio. Initial temperature of reaction can be defined as well. Release of oxygen and oxidation takes place separately at certain temperatures and ratios. Mixture of highest rate of reaction generates the lowest heat of reaction.

In the last twenty years delay detonators have been widely employed in blasting techniques to improve the efficiency of blastings [1, 2]. As delay elements usually pyrotechnical mixtures are used, containing combustible, oxidants, inhibitor and binding material [3, 4]. Their speed of combustion can mostly be controlled empirically, by variation of the composition and grain size. Since the combustion time, delay effect and the reaction mechanism are closely related, it is hoped that the study of the latter during combustion will help in designing and adjusting the timing of delay detonators. The differential thermal analysis of pyrotechnical mixtures has been described [5–7]. If the behaviour of the components with increasing temperature is known, changes in the behaviour of mixtures indicate reactions among the components. When dealing with several components, it is necessary to investigate mixtures of various ratios of two, three, etc., components by means of the Derivatograph [8]. In the present paper it is intended to demonstrate this method on data referring to a mixture containing one oxidant and one combustible.

Experimental

The tests have been carried out with a MOM Derivatograph using a ceramic specimen holder.

Combustible: FeSi90 of technical grade (made by Ötvözetgyár, Zagyvaróna, Hungary).

Oxidant: MnO_2 of mineral grade (pyrolusite homogenized by AKZO, Amsterdam).

The components were air dried. Grain size $<60\,\mu m$. The parameters during the test were as follows: Weight of sample: 1500 ± 5 mg, heating rate: 10 °C/min, TG, DTA and DTG sensitivities were constant. Tests were carried out in air. TG scale was marked by mg as the weight of sample was constant.

1. MnO_2

Peak temperatures of DTA and DTG curves can be read from Fig. 1. The weight of the sample decreases continuously during the test (TG). The peak at 130° indicates the presence of adsorbed humidity. The reactions expected are

$$\mathrm{MnO_2} \rightarrow \overset{\mathrm{Mn_2O_3}}{\overbrace{\mathrm{MnO \cdot MnO_2}}} \rightarrow \mathrm{Mn_3O_4}$$

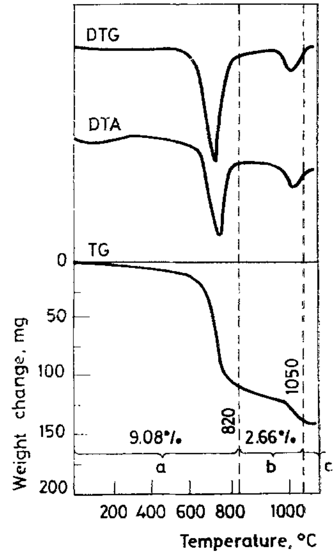

Fig. 1. Thermal curves of MnO_2

The temperature of decomposition corresponds to that given in the literature [9–11]. The calculated loss of weight in the first decomposition is 9.2%, in the second one 3.4%; the observed values are 9.1 and 2.7%, respectively.

2. FeSi90

The constitutional diagram of FeSi [12–14] indicates no change in modification at the Fe : Si ratio of 10 : 90 between 20 and 1050°. The TG curve starts to rise at about 420–460°, that is, the reaction of FeSi90 and the oxygen of ambiency starts at this temperature. In N_2 atmosphere no weight increase takes place and the DTA curve does not rise suddenly. These facts prove that the weight increase is due to oxidation (dashed line in Fig. 2). The DTG curve cannot be evaluated well.

3. Mixtures of MnO_2 and FeSi90

The evaluation of the thermal curves of the mixtures is based on comparing those of pure MnO_2 and pure FeSi90. Depending on the nature of the curves, they can be divided into various sections (denoted in Fig. 3–7); section *a)*: up to the end of the first decomposition of MnO_2; section *b)*: from the end of the first decomposition of MnO_2 up to the end of the second one; section *c)*: from the end of the second decomposition of MnO_2 up to the termination of the test.

The thermal curves can be divided into four groups.

Group I

Mixtures containing 55–80% of MnO_2 are discussed here. Fig. 3 represents the thermal curves of the mixture 72.8% MnO_2 + 27.2% FeSi90, which is the example of the weight change calculations and from which some conclusions can be drawn.

Section a. The weight loss of pure MnO_2 (Fig. 2) is 9.1% up to the end of the first decomposition (820°). In the mixture this decomposition already ends at 780°, therefore the weight increase of FeSi90 should only be calculated up to that temperature. This is 2.3% (Fig. 3). The difference between the calculated

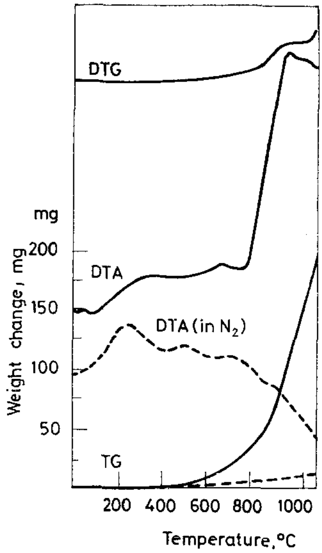

Fig. 2. Thermal curves of FeSi90

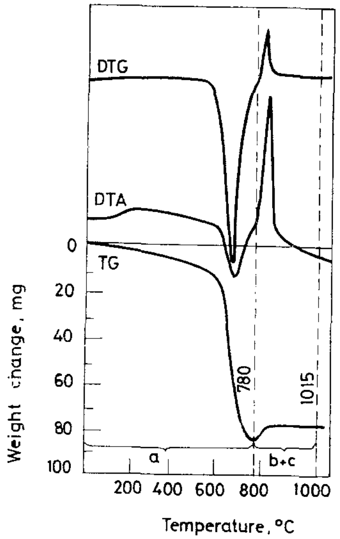

Fig. 3. Thermal curves of the mixture of 72.8% MnO_2 + 27.2% FeSi90

weight loss and weight increase is in good agreement with the measured value within the experimental error. That is, up to 780°, FeSi90 reacts with oxygen released by MnO_2 but there is no further reaction.

Section b + c. In these sections a violent exothermic reaction takes place connected with considerable weight increase and rise in the sample temperature for a short period over that of the oven (see Table 1). The second decomposition of MnO_2 takes place in this interval and the weight of FeSi90 should continuously increase in the whole section. In spite of this the thermal curves only show a weight increase and DTA and DTG changes between 700–810°.

As mentioned above, the sample temperature rises suddenly to 1020°, but afterwards drops to that of the oven. Over 810° neither the weight of the sample nor the DTA and DTG curves indicate further changes. This means that between oven temperatures of 780–810°, in the given circumstances all possible reactions are finished. As the sample temperature rises for a short period to 1020°, even the $Mn_2O_3 \rightarrow Mn_3O_4$ reaction must be completed. The weight increase of pure FeSi90 between 780–810° is 0.6%, but as the temperature is raised temporarily to 1020°, the weight increase should be calculated up to this point. This value would be 16.6% between 780–1020°. Due to the short reaction time and sudden decomposition of MnO_2, the gain of such a considerable weight is impossible. The measured value is 1.7%. Thus the real weight increase is greater than it would be without the exothermic reaction, but less than expected at the temperature of exothermic reaction in air.

Table 1

Thermal properties of powdered MnO_2 + FeSi90 mixtures

MnO_2 content, %	Minimum of the first decomposition of MnO_2, °C	Peak temperature of sample, °C	Duration of exothermic reaction, min	Heat of reaction referred to 1 g mixture, cal
1	2	3	4	5
85	650	850	15	86
83	640	880	16	99
82	655	1040	4	61
80	640	1030	6	86
75	655	1025	4	40
72.8	660	1015	3.5	45
69 7	660	1000	4	52
60	635	980	6	71
55	650	970	6	74
50	640	980	6	70
45	640	955	10	85
41	640	955	12	103
39	640	860	18	141

This behaviour is characteristic of this group of mixtures. It is remarkable that, at a given heating rate, in mixtures containing about 70% of MnO_2, about 3 min are necessary to complete exothermic reactions. At 60% of MnO_2 this time increases to 6 min. The knowledge of this relation between reaction rate and composition is important when designing and adjusting delay mixtures.

Group II

Mixtures containing 83% and more MnO_2 are discussed here. The behaviour of the mixture with 85% MnO_2 and 15% FeSi90 is described below (Fig. 4).

Section a. Similar to that of group I.

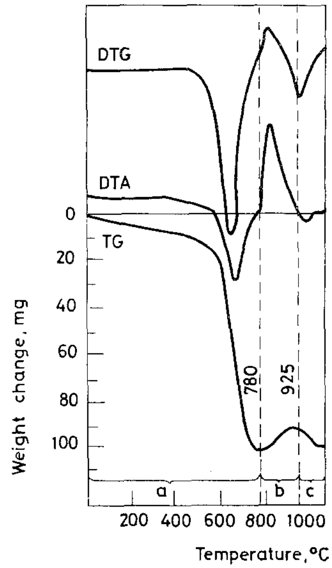

Fig. 4. Thermal curves of the mixture of 85% MnO_2 + 15% FeSi90

Section b. Although the exothermic reaction taking place in this temperature interval is also connected with a weight increase, its rate is much less than that of group I. The time requirement is 15 min. The weight increase is greater than calculated, because as MnO_2 does not provide a sufficient amount of oxygen, the reactive FeSi90 interacts with the oxygen of ambiency too.

Section c. On the DTA and DTG curves, the second decomposition of MnO_2 can be well recognized. This means that the reaction of section *b)* around 800° cannot induce Mn_2O_3 to a quick oxygen release, the excess of oxygen leaves the system slowly. Thus above 925° a weight loss is observed. The calculated and measured values agree within the error of experiment.

Group III

Mixtures containing 31 – 50% of MnO_2 are discussed here. The TG curves of these have a special bend. Fig. 5 shows the curves of a mixture of 50% MnO_2 + 50% FeSi90.

Section a. Weight losses calculated and measured agree well within the experimental error up to 750°. The released oxygen reacts with the FeSi90 present, but no other reaction takes place.

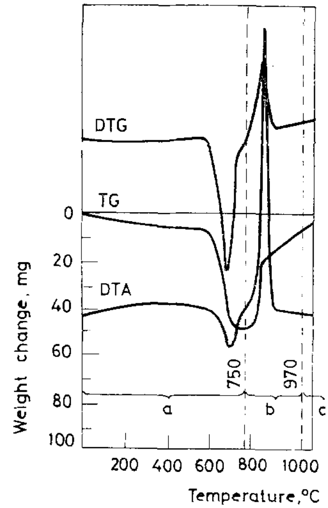

Fig. 5. Thermal curves of the mixture of 50% MnO_2 + 50% FeSi90

Section b. In this interval an exothermic reaction takes place connected with a weight increase which is considerably greater than that of group I, and within 2 min its conversion reaches about 80%. The peak temperature of the sample reaches 980°, so that also the $Mn_2O_3 \rightarrow Mn_3O_4$ reaction should be completed. According to the calculation procedure described for group I, the weight increase of FeSi90 has to be calculated up to this point (12.2%), but the measured value is only 4.4% due to the short reaction time (see also group I, section *b* + *c*). The process is rather complicated. The sudden weight increase coincides with the sudden rise in temperature. Most probably the release of the second oxygen of MnO_2 and its reaction with FeSi90 is instantaneous. This process is not connected with weight change, but as the oxygen released is not sufficient to oxidize the total reactive FeSi90, the balance will be taken from the air.

Section c. Over the exothermic reaction, the TG curve shows a mild weight increase but neither the DTA nor the DTG curve indicates further changes.

The 39% MnO_2 (see Fig. 6) mixture is the dividing line between mixtures showing predominance of FeSi90 and mixtures exhibiting a more or less violent exothermic reaction. According to the thermal curves of this mixture the end of the exothermic reaction and the beginning of the second decomposition of MnO_2 can only be separated with the help of the above mentioned special TG curve bend, because here the DTA and DTG curves are not suitable for this. A chord is to be plotted over the bend of the curve. The intersection of the height of the circular arc gives the required temperature. During the exothermic reaction of section *b)* the sample temperature does not exceed that of the oven and needs 18 min which is the longest period in our series of measurements.

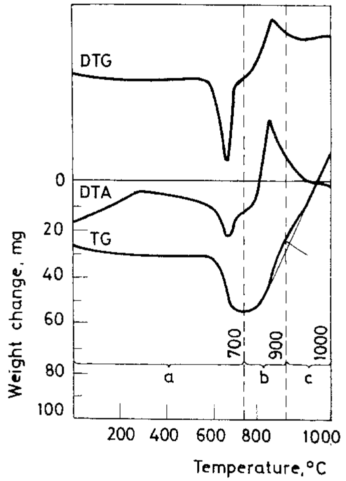

Fig. 6. Thermal curves of the mixture of 39% MnO_2 + 61% FeSi90

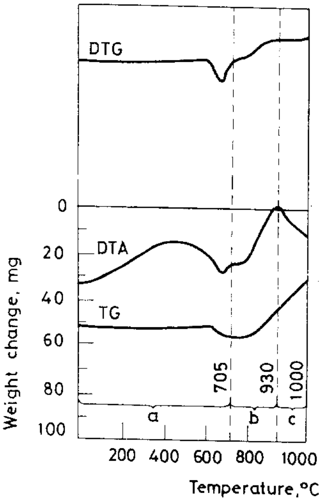

Fig. 7. Thermal curves of the mixture of 25% MnO_2 + 75% FeSi90

Group IV

Mixtures containing 25% and less MnO_2 belong to this group. The curves of the mixture 25% MnO_2 + 75% FeSi90 are presented. By comparing the curves of the pure component with those of mixtures, the predominance of FeSi90 becomes evident.

Section a. Up to 580° there is practically no change on the TG curve. Above this, up to 750°, it shows loss of weight due to the first decomposition of MnO_2 (see also the DTA and DTG curves). The calculated and measured weight losses agree, the oxygen release from MnO_2 reacts with FeSi90 but there is no acceleration of the reaction.

Section b + c. A comparison of the calculated and measured data shows that the reaction is much slower than expected.

The TG curve exhibits a continuous weight increase, i.e. the mixture reacts with ambient oxygen. The characteristic bend of group III can still be recognized

Mixtures below 25% of MnO_2 behave similarly to those referring 25%, but without the characteristic bend. The weight increase measured is less than expected, which indicates that the reaction slows down, thus a small quantity of MnO_2 inhibits the oxidation of FeSi90.

Heat of reaction

The area below the exothermic DTA peaks can be considered as the measure of the heat of reaction [8]. Comparing these areas with those obtained from the NaCl calibration curve (124 cal/g), the reaction heats of different mixtures can be calculated, referring to 1 g of mixture (see Table 1). The minimum value is at 75% MnO_2.

Provided that the $Fe \rightarrow Fe_2O_3$ and $Si \rightarrow SiO_2$ reactions take place and both (first and second) decompositions of MnO_2 can be taken into account, a mixture of 10% FeSi90 and 90% MnO_2 shows zero oxygen balance, and the heat of reaction should be the highest. In spite of this, this mixture hardly burns. During tests, the oxygen of the first decomposition cannot be taken into account, as an exothermic reaction only takes place beyond the temperature of the first decomposition. Without the oxygen of the first decompositions the oxygen balance is zero for mixtures containing 2.4% MnO_2.

However, this discussion is purely theoretical, as practically in detonators, due to the closed space and quick temperature rise, oxygen can be reckoned with in both steps. The most violently burning mixture is of negative oxygen balance which is a well known fact in pyrotechniques. Its heat of reaction referred to 1 g is less than that of the zero oxygen balance mixture. The explanation is that, being a powdered mixture, the greater the quantity of combustible material present, the larger is the surface area where burning starts and the larger is the substance to be heated. On further increasing the amount of combustible material, however, the ratio of oxidant decreases, the reaction time becomes longer, and the reactive material reacts with the oxygen of air too, thus the released heat of reaction increases. The error is rather high. Testing the 50 : 50% mixture in nitrogen results in an exothermic reaction of higher starting point (480°), lower peak temperature (860°) and considerably less heat of reaction (46.3) than those in air and it is not followed by an increase in weight. These facts support our conclusions. The actual situation may be much more complicated. Simultaneous reactions in various layers and the mechanism of oxidation may be different. However, we have drawn the following conclusions.

Conclusions

1. At the beginning of heating partial release of oxygen from MnO_2 precedes the temperature where FeSi90 becomes reactive, thus a part of oxygen leaves the system. The knowledge of this phenomenon is important when designing a delay

mixture containing these substances. The situation may be entirely different in mixtures where the combustible becomes reactive before the oxidant releases oxygen.

2. Maximum velocity of the first decomposition of MnO_2 ($MnO_2 \rightarrow Mn_2O_3$) is practically independent of the component ratio.

3. FeSi90 becomes reactive around 800°. In mixtures containing 41 – 82% of MnO_2, the components react exothermic around this temperature. The reaction is the most violent in mixtures containing 72.8% of MnO_2, its duration being 3.5 min. The temperature and duration of reaction are sufficient for the completion of all reactions possible in the given circumstances. Thus the release of oxygen and oxidation take place simultaneously.

4. The most violently burning mixture is of negative oxygen balance and its heat of reaction is the lowest.

5. In mixtures containing 31 – 50% MnO_2, the oxidation of FeSi90 takes place in two stages, rapidly between 780 – 850°, and slowly above 850°.

6. Below 41% and above 82% MnO_2 content, the two stages, namely the decomposition of MnO_2 and the oxidation of FeSi90, are independent processes and no reaction takes place.

7. If the changes on the DTA and DTG curves cannot be distinguished with the required certainty, the procedure described in the case of 39% MnO_2 mixture may be useful.

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The author wishes to acknowledge the helpful suggestions and comments of Dr F. Paulik, Dr J. Paulik and Dr T. Kompolthy.

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RÉSUMÉ — L'auteur a étudié un mélange pyrotechnique à 2 constituants utilisé dans la production des détonateurs à retardement. En comparant les courbes d'analyse thermogravimétrique, de thermogravimétrie dérivée et d'analyse thermique différentielle de chacun des constituants à celles de leurs mélanges en proportions différentes, on a trouvé une corrélation entre la vitesse de réaction et la composition. La température initiale de la réaction peut également être étudiée. Le dégagement de l'oxygène et l'oxydation s'effectuent séparément à températures données dépendant du rapport des constituants. Les chaleurs de réaction les plus faibles correspondent aux mélanges possédant les vitesses de réaction les plus élevées.

ZUSAMMENFASSUNG — Verfasser untersuchte ein bei der Herstellung von Verzögerungszündern verwendetes pyrotechnisches Zweikomponentengemisch. Der Vergleich der thermogravimetrischen, derivativ-thermogravimetrischen und differentialthermoanalytischen Kurven der Komponenten mit jenen von Gemischen, welche die Komponenten in verschiedenen Verhältnissen enthielten, führte zu der Auffindung eines Zusammenhanges zwischen Reaktionsgeschwindigkeit und Verhältnis. Die Anfangstemperatur der Reaktion kann ebenfalls ermittelt werden. Sauerstoffabgabe und Oxydation erfolgen gesondert bei bestimmten Temperaturen und unter bestimmten Verhältnissen. Gemische von höchster Reaktionsgeschwindigkeit entwickeln die geringste Reaktionswärme.

Резюме. — Исследована пиротехническая смесь состоящая из 2 компонентов, используемая в производстве замедляющих детонаторов. Дериватограммы компонентов сравнены с дериватограммами смесей, содержащих компоненты в различных пропорциях и найдено соотношение между скоростью реакции и долей компонентов. Отмечено четкое определение начальной температуры реакции. При различных температурах и содержании компонентов исследован эффект удаления. Смесь, обладающая наибольшей скоростью, реакции, дает наименьшую теплоту реакции.