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THERMAL ANALYSIS OF PYROTECHNICAL MIXTURES II.
STUDY OF THE MECHANISM OF THE REACTION OF $MnO_2 + Pb_3O_4$

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A two-component pyrotechnical mixture containing MnO_2 and Pb_3O_4 has been investigated by TG, DTG and DTA. It was found that under 48% MnO_2 content the oxygen release exceeds the value calculated on the basis of the reactions $MnO_2 \rightarrow Mn_3O_4$ and $Pb_3O_4 \rightarrow PbO$. Above a MnO_2 content of 7.5% the decomposition is partly delayed and shifted to higher temperatures. With under 60% of MnO_2, at about 700° the components react exothermally with an increase in weight. The combined heats of the reactions $MnO_2 \rightarrow Mn_2O_3$ and $Pb_3O_4 \rightarrow PbO$ give the highest value at 83% ofMnO_2.

The behaviour of the MnO_2 + FeSi 90 mixture was reported previously [1]. The investigation of the oxidant mixture $MnO_2 + Pb_3O_4$ is presented in this paper.

Experimental

Our tests had been carried out by a MOM Derivatograph using a ceramic sample holder. The components were MnO_2 of mineral grade (pyrolusite homogenized by AKZO Amsterdam) and Pb_3O_4 of technical grade 99% purity (made by Metallochemia Budapest). The components were air dried. Grain size: $>60\ \mu m$.

Weight of sample was 2000 ± 5 mg in every case.

The heating rate was 10°C/min. The TG, DTA and DTG sensitivities were constant. The tests were carried out in air. The TG scale was marked by mg as the weight of sample was constant.

Results

The thermal decomposition of the pure Pb_3O_4 is presented in Fig. 1. The thermal behaviour of MnO_2 has been discussed in a previous paper [1].

In the thermal treatment of Pb_3O_4, the following reaction takes place: $Pb_3O_4 \rightarrow$ $\rightarrow PbO$ indicated by the simultaneous change on DTA and DTG curve. The second DTA change indicates the melting of PbO. The temperatures of changes agree with literature data [2, 4]. The weight loss corresponds stoichiometrically to the decomposition $Pb_3O_4 \rightarrow PbO$. The thermal curves of mixture of the two components are presented in Figs 2–6.

In pyrotechnical practice, the use of mixtures of different oxidants results in quicker burning, that is, between given temperature limits more oxygen is released from the mixtures than from the individual oxidants. This assumption may be verified by means of the method published earlier [1], by comparing calculated

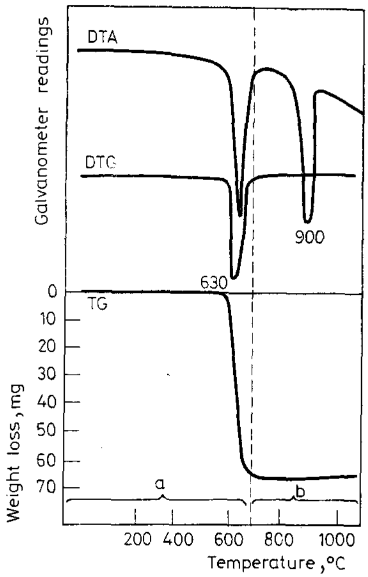

Fig. 1. TG, DTG and DTA curves of Pb_3O_4

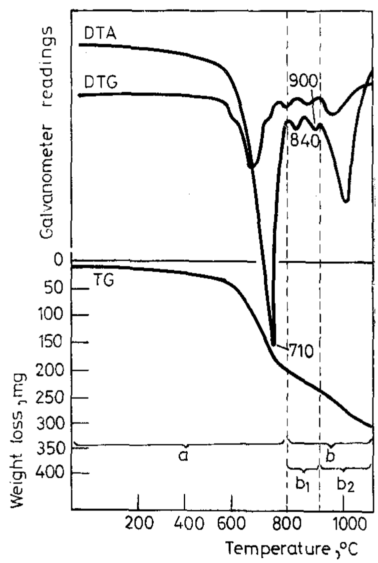

Fig. 2. TG, DTG and DTA curves of the mixture 90% MnO_2 + 10% Pb_3O_4

and measured weight changes. Between 20 and 1050° the weight loss of MnO_2 is 11.7%, and that for Pb_3O_4 is 2.1%. A comparison of the calculated and measured weight losses for mixtures of different ratios leads to the following findings: With over 48% of MnO_2 only a slight difference is experienced, and thus between 20 and 1050° both oxidants decompose but no other reaction takes place. With less than 48% of MnO_2 the measured values exceed the calculated ones, which shows an additional reaction besides the normal decompositions.

For the sake of simpler explanation, the decompositions of the mixtures are treated separately in two temperature ranges.

Section (a): up to the end of the simultaneous decompositions $MnO_2 \rightarrow Mn_2O_3$ and $Pb_3O_4 \rightarrow PbO$.

The first decomposition of MnO_2 ($MnO_2 \rightarrow Mn_2O_3$) ends at 820°. The decomposition $Pb_3O_4 \rightarrow PbO$ takes place between 560 and 670°. The peak temperatures of both changes can be read off the thermal curves. The peak areas and the quantities of the components are naturally related, and their characteristic temperatures are more or less shifted (Figs 2–4). The presence of 10% of Pb_3O_4 in 90% of MnO_2, and of 5% of MnO_2 in 95% of Pb_3O_4, is already noticeable, causing bends or peaks.

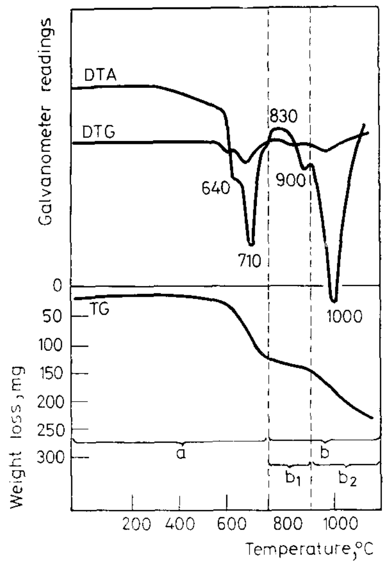

Fig. 3. TG, DTG and DTA curves of the mixture 70% MnO_2 + 30% Pb_3O_4

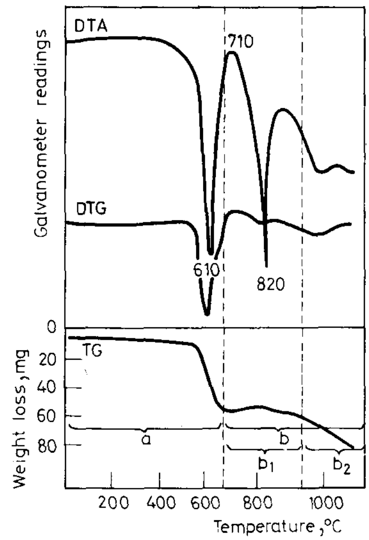

Fig. 4. TG, DTG and DTA curves of the mixture 5% MnO_2 + 95% Pb_3O_4

The oxygen released in section (a) should theoretically be the amount of oxygen released from the pure components calculated from their TG curves. On comparison of the measured and calculated weight-losses in this section, with a MnO_2 content of more than 7.5% the measured value is always less than the calculated one. Hence the components in mixtures are unable to release as much oxygen as in the pure state. With less than 7.5% of MnO_2, the amount of oxygen released exceeds the calculated value.

Accordingly, mixtures containing less than 48% of MnO_2 react somewhere between 20 and 1050° and mixtures containing less than 7.5% of MnO_2 react in section (a). Thus, mixtures containing 7.5–48% of MnO_2 react in section (b).

Heat of reaction

The area below the endothermic peak indicating the double decomposition is considered a measure of the combined heat of reaction. According to the procedure described in [1], the greatest heat of reaction is found for the mixture containing 83% MnO_2, i.e. the decomposition of this mixture needs maximum heat.

Section (b): from the end of the reactions $MnO_2 \rightarrow Mn_2O_3$ and $Pb_3O_4 \rightarrow PbO$ up to 1050° (up to the end of the decomposition $Mn_2O_3 \rightarrow Mn_3O_4$).

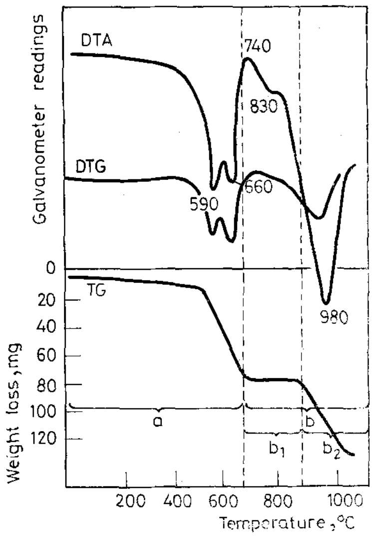

Fig. 5. TG, DTG and DTA curves of the mixture 50% MnO_2 + 50% Pb_3O_4

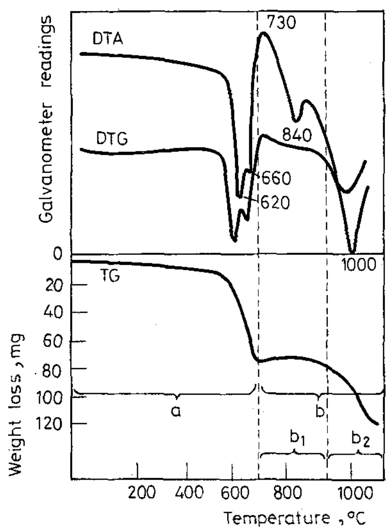

Fig. 6. TG, DTG and DTA curves of the mixture 35% MnO_2 + 65% Pb_3O_4

On raising the temperature further, PbO melts and the second decomposition of MnO_2 takes place in this melt. Both changes can be recognized on the curves; the peak or bend only on the DTA around 900° indicates the melting of PbO, while the peaks on both the DTA and DTG curves below 1000° indicate the decomposition $Mn_2O_3 \rightarrow Mn_3O_4$. The melting of 10% of Pb_3O_4 and the second decomposition of 5% of MnO_2 are still recognisable. With below 60% of MnO_2, besides these two changes, the components react exothermally at around 700°. The shapes of the curves are similar to that of Fig. 6, although the peaks are not so characteristic.

For all the mixtures, around 830–840° an endothermic decomposition takes place.

The measure of this decomposition depends on the source of the MnO_2 mineral but its nature could not be determined from the thermal curves.

By comparing the calculated and measured weight losses in section (b), it was found that the measured values always exceeded the calculated ones, as the oxygen retained in section (a) leaves the system only in this temperature range. Above 48% of MnO_2, the measured values are more or less similar, but below 48% of MnO_2 they decrease continuously.

As the calculated values evidently decrease when the MnO_2 content decreases, the relative amount of oxygen retained in section (a) increases up to 48% of MnO_2.

By dividing section (b) into two parts and comparing the weight change belonging to the decomposition $Mn_2O_3 \rightarrow Mn_3O_4$ with the weight change at 830–840° due to an unknown decomposition, we arrived at the following conclusions: Up to 48% of MnO_2, the weight loss due to the decomposition at 830–840° decreases with the MnO_2 content, and that of the decomposition $Mn_2O_3 \rightarrow Mn_3O_4$ increases to the same extent. At 48% of MnO_2, the weight loss at 830–840° becomes zero, and on further decrease of the MnO_2 content the oxygen released in the second MnO_2 decomposition decreases too. Thus, suppression of oxygen release in section (a) is more effective in the presence of 48% MnO_2, its mass leaving the system only in the decomposition $Mn_2O_3 \rightarrow Mn_3O_4$.

With above 55% of MnO_2, at the beginning of section (b) a weight-loss is observed, while between 55 and 50% of MnO_2 there is no weight change (Fig. 5). Below 48% of MnO_2, the weight increase in the exothermic reaction at 700° (following the end of section (b), but preceding the endothermic reaction at 830–840°) compensates the weight loss of this latter and causes a slight weight increase. In spite of this, as mentioned above, for mixtures between 7.5 and 48% of MnO_2, a weight loss exceeding the calculated value is experienced in section (b).

The exothermic reaction at 700°, which is actually a reaction between PbO and Mn_2O_3 is most violent at 35% of MnO_2 (Fig. 7). This is proved by the extent of the weight increase and the DTA peak area. The latter, which is a measure of the heat of reaction, is nearly 70 cal/g.

Conclusion

1. In powdered mixtures of MnO_2 and Pb_3O_4 between 20 and 1050° with over 48% of MnO_2, there is no reaction resulting in the release of more oxygen than calculated from the thermal curves of the pure components. With below 48% of MnO_2, the release of oxygen exceeds the value calculated on the basis of the reactions $MnO_2 \rightarrow Mn_3O_4$ and $Pb_3O_4 \rightarrow PbO$.

2. With over 7.5% of MnO_2 the simultaneous decompositions result in the release of less oxygen than corresponds to the pure components.

This retained oxygen leaves the system only at higher temperatures. Its quantity is related to the calculated weight loss, and increases relatively with the decrease of the MnO_2 content up to 48% of MnO_2.

3. With below 60% of MnO_2, around 700° the components react exothermally. The weight increase of this reaction only compensates the weight loss of the endothermic reaction around 830–840° below 48% of MnO_2.

4. The combined heats of the simultaneous decompositions $MnO_2 \rightarrow Mn_2O_3$ and $Pb_3O_4 \rightarrow PbO$ attain the highest value at 83% of MnO_2, about 400 cal/g. The heat of the exothermic reaction around 700° is about 70 cal/g.

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Résumé — On a étudié par TG, TGD et ATD un mélange pyrotechnique de MnO_2 et de Pb_3O_4. Pour une teneur en MnO_2 inférieure à 48 % le départ d'oxygène est supérieur à la valeur prévue d'après les réactions $MnO_2 \rightarrow Mn_3O_4$ et $Pb_3O_4 \rightarrow PbO$. Pour une teneur en MnO_2 supérieure à 7.5 % la décomposition est en partie retardée et déplacée vers des températures plus élevées. Pour une teneur en MnO_2 inférieure à 60 % et à 700° environ, les composants réagissent exothermiquement avec augmentation de poids. La chaleur de réaction globale qui résulte des deux processus $MnO_2 \rightarrow Mn_2O_3$ et $Pb_3O_4 \rightarrow PbO$ atteint sa valeur la plus élevée pour une teneur en MnO_2 de 83 %.

Zusammenfassung — Ein pyrotechnisches Zweikomponentengemisch aus MnO_2 und Pb_3O_4 wurde durch die TG, DTG und DTA Methode geprüft. Der Vergleich der thermischen Kurven der reinen Komponenten und ihrer Gemische ergab, daß unterhalb eines MnO_2-Gehaltes von 48 % die Sauerstoffabgabe den an Hand der Reaktionen $MnO_2 \rightarrow Mn_3O_4$ und $Pb_3O_4 \rightarrow PbO$ berechneten Wert überschreitet. Bei einem Gehalt an MnO_2 über 7.5 % wird die Zersetzung teilweise verzögert und in Richtung höherer Temperaturen verschoben. Unterhalb eines 60 % igen MnO_2-Gehaltes reagieren die Komponenten bei 700° in exothermer Weise unter Gewichtszunahme. Die gesamte Reaktionswärme der Reaktionen $MnO_2 \rightarrow Mn_2O_3$ und $Pb_3O_4 \rightarrow PbO$ erreicht den höchsten Wert bei 83 % MnO_2-Gehalt.

Резюме — Исследована двухкомпонентная пиротехническая смесь. Сравнением термических кривых чистых компонентов с кривыми их смесей обнаружено, что при содермании MnO_2 менее 48% выделение кислорода привышает величину, рассчитанную на основании реакций MnO_2 — Mn_3O_4 и Pb_3O_4—PbO. При содержании MnO_2 выше 7,5%, распад несколько замедлен и сдвинут к более высоким температурам. Ниже 60% MnO_2 около 700° компоненты реагируют экзотермически, причем их вес увеличивается. Теплота реакций $MnO_2 \rightarrow Mn_2O_3$ и $Pb_3O_4 \rightarrow PbO$ достигает наибольшой величины при 83% MnO_2.