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New correlations of the thermogravimetric analysis data of some commercial explosives

Svatopluk Zeman [a,*], Štefan Gazda [b], Agnesa Štolcová [b] and Ján Dráb [c]

[a] *Department of Theory and Technology of Explosives, Faculty of Chemical Technology, University of Pardubice, CZ-532 10 Pardubice (Czech Republic)*
[b] *Commercial Explosives Division, Isotrochem, SK-836 05 Bratislava (Slovak Republic)*
[c] *Technical Department, CHEMKO, SK-072 22 Strážske (Slovak Republic)*

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Abstract

Stability of thirteen commercial explosives is specified by means of isothermal and non-isothermal thermogravimetric analysis (TGA). There is a linear dependence between the positions of TGA onsets, or characteristic DTG peaks, and amounts of explosive samples used. Analysis of the dependence for TGA onsets gave results which are correlated with explosion temperatures. A relationship is also found with temperatures of explosive points (i.e. autoignition temperatures) for the explosives studied. In connection with the former correlation, a value of explosion temperature of 3360°C is assessed for Composition B. In the case of isothermally TGA of explosives which contain liquid nitroesters, evaporation of these liquid parts is confirmed as the dominant process in the resulting mass losses.

INTRODUCTION

Sufficient physical and chemical stability is a prerequisite for explosives from the standpoint of their functional properties, their safety in handling and long-term storage capacity. The physical and chemical stability of explosives can be specified using thermoanalytical methods [1, 2], particularly differential thermal analysis (DTA) (see for example refs. 1–4) and differential scanning calorimetry (DSC) (see also refs. 1, 5–7); fewer data from this field are linked with the application of thermogravimetric analysis (TGA) (see, for example, refs. 2, 8, 9).

In order to specify only chemical stability, the most widely used methods are those of applied manometry; from among these, for the kinetics of the initial stage of thermolysis, the best-known is the Soviet manometric method (SMM) [10–12].

It is well known and has also been deduced that the data from the study

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* Corresponding author.

of the initial non-autocatalysed stage of thermal decomposition of explosives, obtained by DTA, DSC and SMM, correlate well with their detonation characteristics (see, for example, refs. 9, 13–18); the relationship to the impact sensitivity of explosives is also obvious [19, 20].

The existing literature, however, lacks similar correlations for TGA data of commercial explosives. In order to fill this gap we present the results of the application of simple TGA to the specification of the stability of commercial explosives and some viable applications of these results are linked with it. The samples of commercial explosives being studied come predominantly from the oldest Czecho-Slovak producer, i.e. from the firm Istrochem, Bratislava, which was established in October 1873 as a branch factory of the Dynamit Nobel Wien and from 1953 up to 1990 was known as CHZJD, Bratislava.

EXPERIMENTAL

Data and materials

Survey and necessary data on the applied commercial explosives are contained in Table 1: here explosives 1–7 are produced by Istrochem, Bratislava, hydrophobised ammonium nitrate (i.e. sample 8) is a product of VCHZ Synthesia, Pardubice, whose commercial explosives division, Explosia, manufactures a PETN based plastic explosive, i.e. Semtex 10 (sample 9). The remaining explosives in Table 1, i.e. Gradetol (demilitarised granulated trinitrotoluene with a content about 99.5 wt.% of own substance) and Composition B (hexolite 60/40) are products of Chemko's Special Production Plant. The origin and purity of PETN (pentaerythritol tetranitrate) are given in refs. 15 and 26.

Apparatus

Thermogravimetric measurements were carried out in a Perkin-Elmer TGA-7 apparatus; using a weighed amount of sample up to 10 mg, thermolysed in nitrogen atmosphere. Within the framework of TGA, a 60 min exposure of Istrochem's explosives to the temperature of 82°C was carried out (prescribed temperature of Abel test at Istrochem's output check) and also to temperatures of 95 and 110°C: for examples of the corresponding TGA records see Figs. 1–3. Table 1 contains mass losses of the 60 min exposure of the Istrochem samples to temperatures of 82 and 110°C. In the second series of measurements using TGA-7, all samples were thermolysed in the regime with a linear rate of temperature increase of 20°C min^{-1}: examples of the corresponding TGA-records for samples 1–7

TABLE 1

Survey of the studied commercial explosives and of their characteristics

Sample No.	Explosive	Consistency and applicability of the explosive	Liquid nitro-ester content in wt%	Autoig-nition temp-erature [a] in °C	Explo-sion temp-erature [b] in °C	Mass losses from isothermal TGA [d] (in wt.%) for temperature	
						82°C	110°C
1	Danubit 1	Plastic, rock blasting	20.7	280.7	2990	13.38	21.40
2	Danubit 2	Plastic, rock blasting	22.5	min. 172.3 [c]	3139	17.80	29.37
3	Danubit Geofex 2	Plastic, for special use	40.9	192.9	3477	27.00	39.56
4	Carbodanubit	Plastic, permissible (antidust)	25.0	227.0	2485	17.46	26.36
5	Harmonit AD	Semiplastic, permissible second class explosive	10.0	248.4	1535	9.69	9.87
6	Slavit V	Semiplastic, permissible first class explosive	10.0	268.8	1900	9.95	11.83
7	Polonit V	Powdered, surface blasting	0.0	233.3	2977	3.00	
8	Ammonium nitrate [e]	Fine crystals	0.0	418.0	1557 [f]	0.16	0.55
9	Semtex 10	Plastic, for special technologies of blasting and destruction	0.0	233.0 [g]	3870		
10	PETN	Fine crystals, active component of many explosives	0.0	dec. 225 [h]	4050 [i]		
11	Gradetol	Granules, surface blasting, raw material for commercial explosives production	0.0	304.2	2800 [i]		
12	RDX (warmed)	Fine crystals, active component of many explosive mixtures	0.0	dec. 260 [h]	3380 [i]		
13	Composition B	Granules, for boosters and shaped charges production	0.0	dec. 280 [h]			

[a] Averaged values from results of measurements according to standard [22]. [b] Initial temperature of the products of detonation at the moment of their rise which was calculated according to standard [23]. [c] Lowest value from only two results of the measurements. [d] Results of the isothermal TGA during 60 min of sample exposure. [e] Hydrophobised product which is a constituent of the majority of Istrochem's explosives. [f] Maximum value (i.e. 1830 K) from ref. 30. [g] Taken from ref. 21. [h] Taken from ref. 24. [i] Taken from ref. 25.

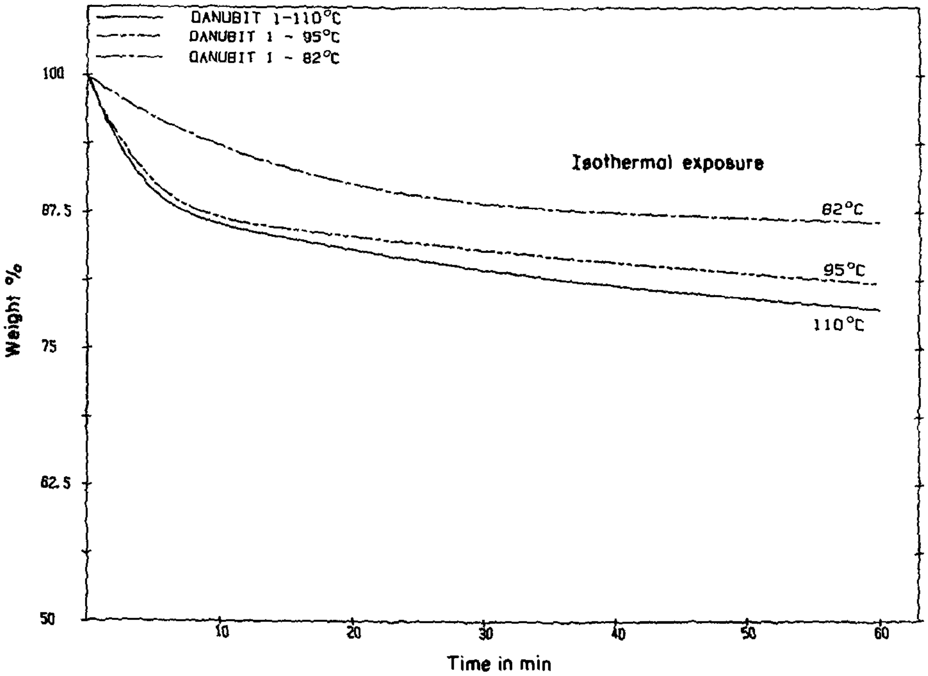

Fig. 1. Isothermal TGA records for Danubit 1 (explosive 1) which also contains nitrocellulose.

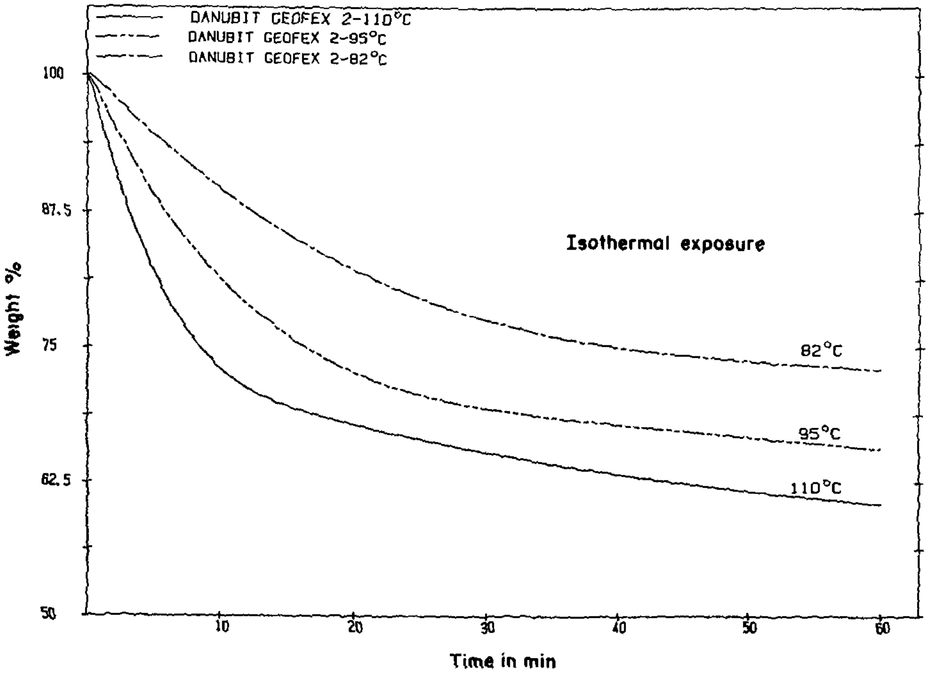

Fig. 2. Isothermal TGA records for Danubit Geofex 2 (explosive 3) which also contains nitrocellulose.

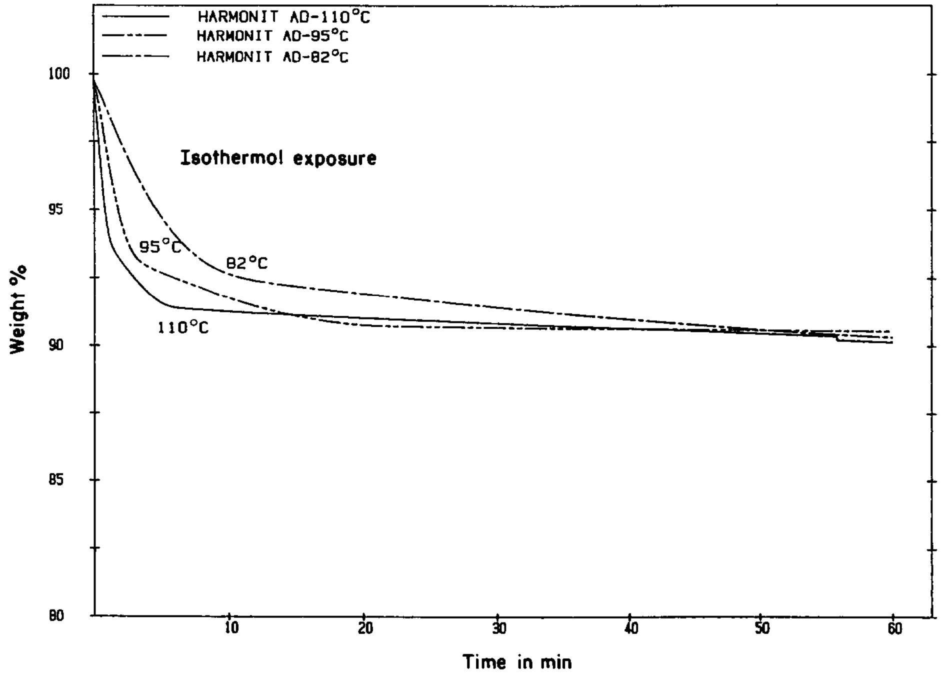

Fig. 3. Isothermal TGA records for high permissible explosive Harmonit AD (explosive 5) which does not contain any nitrocellulose.

are shown in Figs 7–10. Examples of these records of the samples 9, 10 and 13 are presented in ref. 21.

RESULTS AND DISCUSSION

The influence of temperature upon mass losses in explosives 1–8 within isothermal regime of measurements is illustrated by Figs. 1–3: the curves in Figs. 1 and 2 correspond to mixtures also containing nitrocellulose whereas the curves in Fig. 3 belong to the mixture without nitrocellulose (as a matter of fact, they are drying curves). The isothermal TGA results correlate with volatile (liquid) nitroester content in Istrochem explosives as shown by the linear relationships in Fig. 4 for exposure temperatures of 82 and 110°C. From what has been said thus far it follows that the dominant process of isothermally TGA, under the given conditions, is evaporation of nitroesters. In order to the complete idea, Figs. 5 and 6 give the compared mass losses of the samples being followed at 60 min exposure 82°C.

The results obtained from non-isothermal TGA are illustrated by Figs. 7–10. The first derivative of curves of mass losses (DTG curves) exhibit, under the applied conditions of the experiment, peaks within the temperature range 238–305°C, which are characteristic for the given type of explosive; their position is also influenced by the size of the weighed

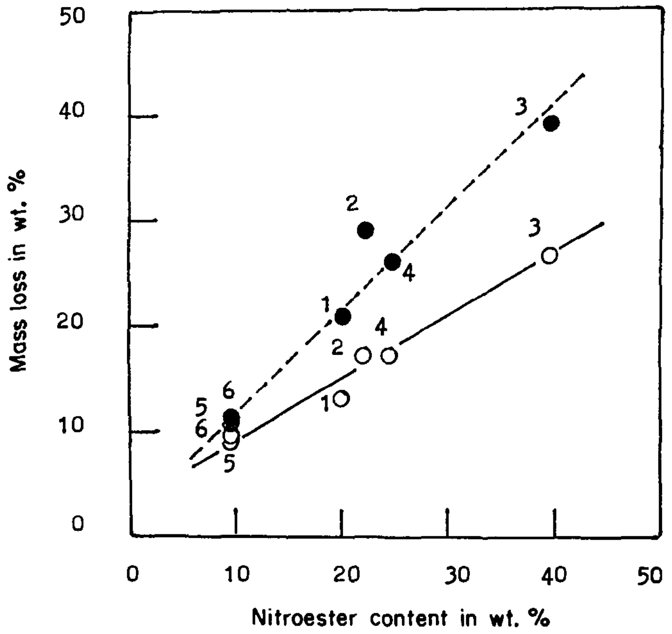

Fig. 4. Relationship between mass losses (in wt.% per 60 min) and content of volatile nitroesters in explosives 1–6: ——○——, TGA isothermal exposure at 82°C ($r = 0.9804$); - - - - ● - - - -, TGA isothermal exposure at 110°C ($r = 0.9713$).

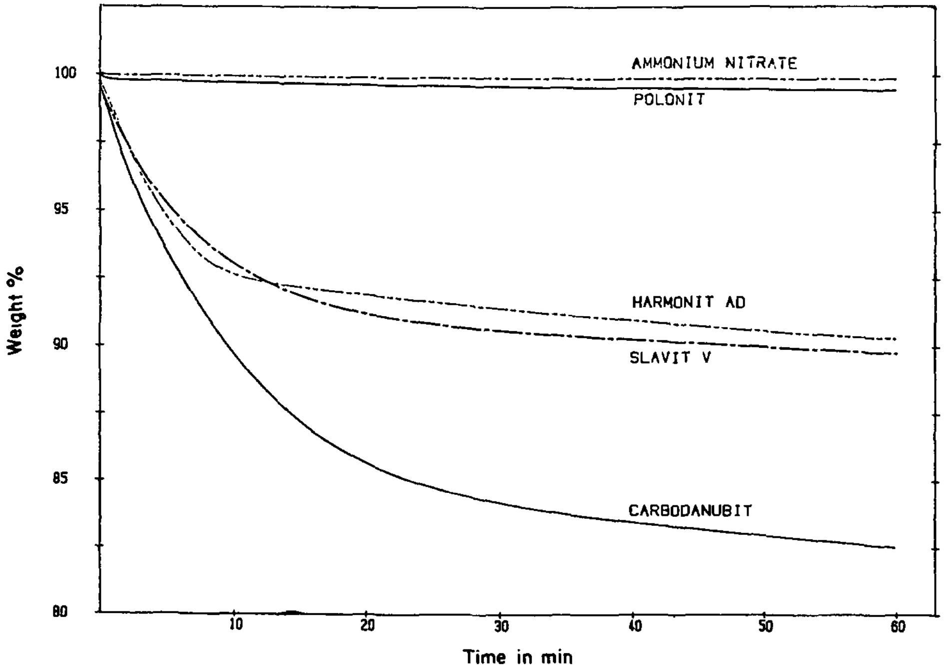

Fig. 5. Isothermal TGA records of ammonium nitrate, powdered and permissible explosives at 82°C.

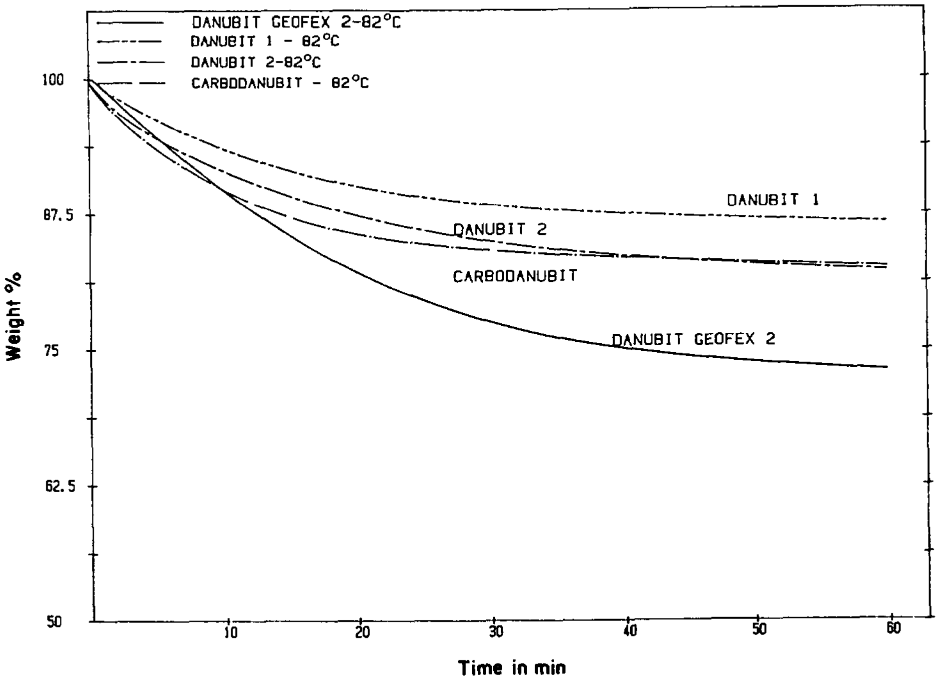

Fig. 6. Isothermal TGA records of Danubit-type explosives at 82°C.

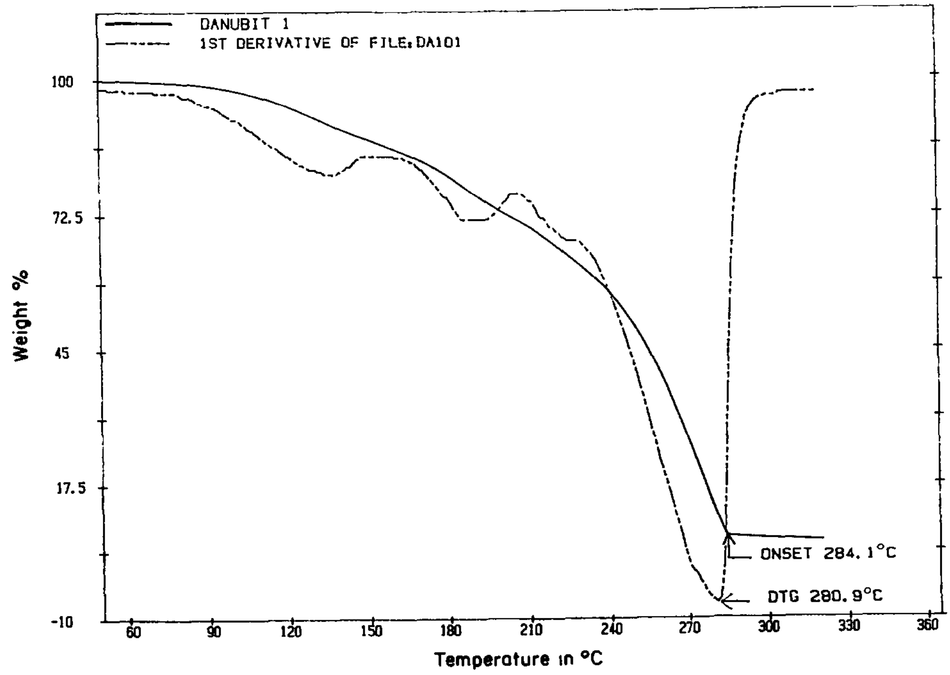

Fig. 7. Nonisothermal TGA record of Danubit 1.

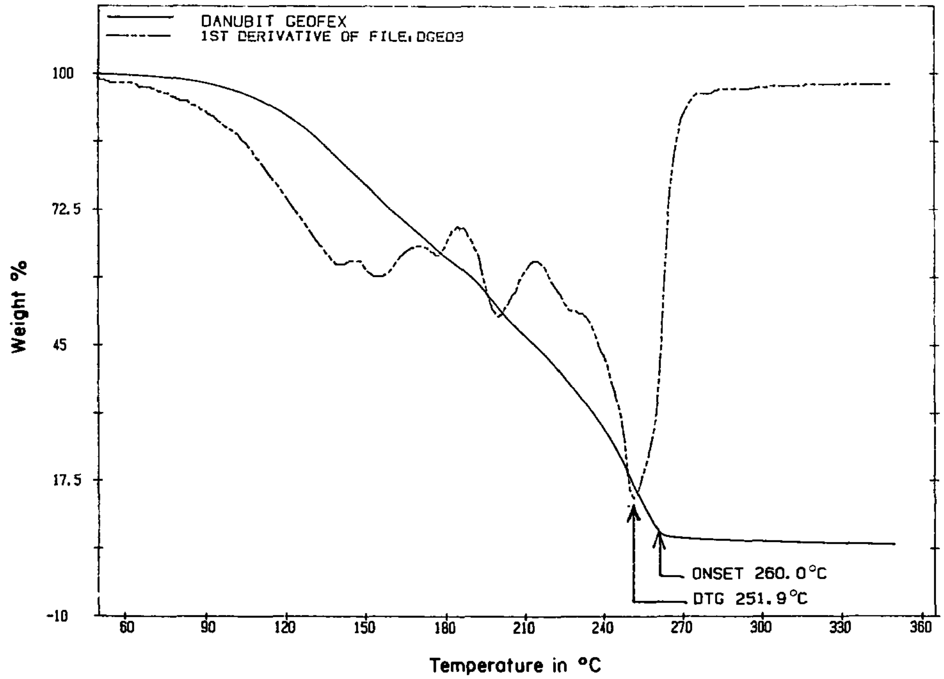

Fig. 8. Nonisothermal TGA record of Danubit geofex 2.

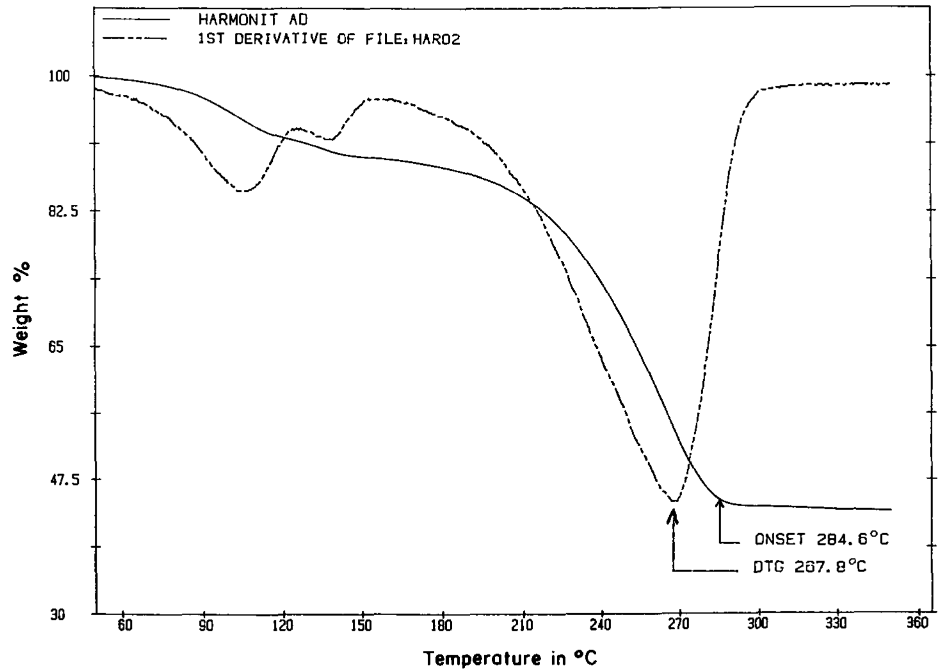

Fig. 9. Nonisothermal TGA record of high permissible explosive Harmonit AD.

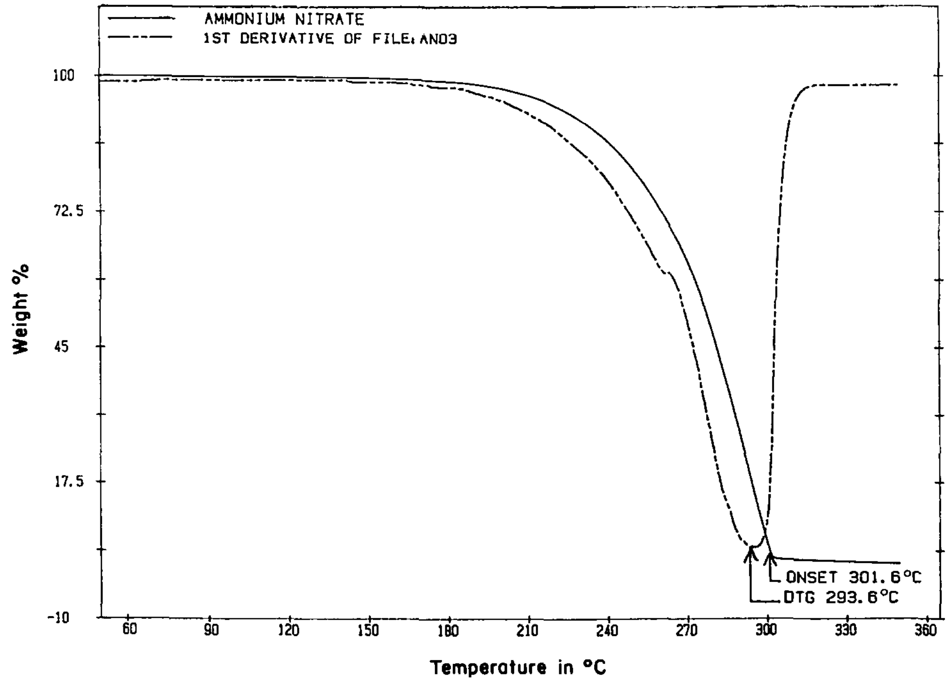

Fig. 10. Nonisothermal TGA record of hydrophobised ammonium nitrate.

amount of sample. Similarly, the positions of TGA onsets depend upon the type of explosive and the quantity used. For a given sample of commercial explosive, the position of the DTG peak or the TGA onset is related to the quantity used by the general equation [21,27–29]

$$P_t = A_t n + B_t \qquad (1)$$

where P_t is the position of the DTG peak (P_{peak}) or the TGA onset (P_{onset}) in °C and n is the amount used in mg. Figure 11 is the graphic representation of eqn. (1) for DTG peaks of Istrochem explosives. Table 2 contains coefficients of eqn. (1) for TGA onsets.

In the case of DTG peaks, an analogous relationship was found in the TGA of urea–formaldehyde polycondensates [27]: in this case it was proved that the A_{peak} gradient of the equation was linked to the reactivity of the given polycondensates, and the section B_{peak} was linked to their nitrogen content. To seek analogous dependence in the explosives studied, a specified relationship of the A_t coefficient of eqn. (1) is relevant for the TGA onsets towards the explosion temperature T_E as given by

$$\ln T_E = aA_{\text{onset}} + b \qquad (2)$$

Use of eqn. (2) enables the studied explosives to be divided into two groups, the first of which includes explosives 1–4, 7, 10, 11 and 12: coefficients of eqn. (2) for this group are, $a = -0.03178$, $b = 8.1691$ and

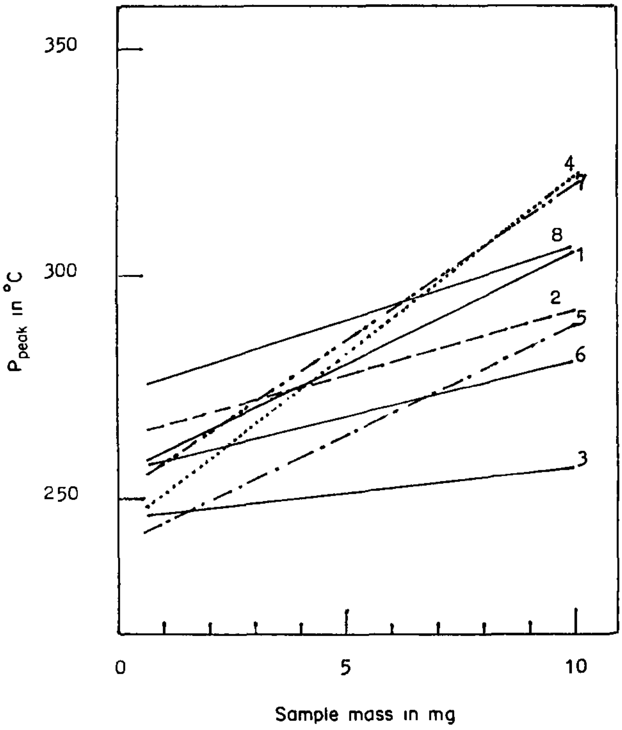

Fig. 11. Graphic representation of eqn. (1) for DTG peaks (P_{peak}) of Istrochem explosives 1–7 and hydrophobised ammonium nitrate (sample 8) having the following correlation coefficients: 1, $r = 0.9571$; 2, $r = 0.9447$; 3, $r = 0.8113$; 4, $r = 0.9659$; 5, $r = 0.9191$; 6, $r = 0.8446$; 7, $r = 0.9730$; 8, $r = 0.9811$.

TABLE 2

Coefficients of eqn. (1) for TGA onsets

No.	Explosive	$A_{onset}/(°C\,mg^{-1})$	$B_{onset}/(°C)$	r
1	Danubit 1	4.50	263.65	0.9375
2	Danubit 2	2.55	280.09	0.9207
3	Danubit Geofex 2	2.85	254.38	0.9228
4	Carbodanubit	10.76	240.40	0.9577
5	Harmonit AD	4.87	261.72	0.9528
6	Slavit V	2.68	265.94	0.9712
7	Polonit V	7.06	254.22	0.9774
8	Ammonium nitrate	3.61	279.38	0.9659
9	Semtex 10 [a]	−4.36	237.04	−0.9869
10	PETN [a]	−2.20	231.97	−0.9386
11	Gradetol	5.97	237.40	0.9974
12	$RDX_{(warmed)}$	−1.20	260.28	−0.9982
13	Composition B [a]	−3.06	268.44	−0.9355

[a] Values taken from ref. 21.

$r = 0.9224$. The second group involves explosives 5, 6, 8 and 9, which either contain a "cooling component", (i.e. inhibitors of flame spread in explosives 5 and 6, a plastic binder in mixture 9) or which exhibit a "cooling effect", such as the creation of free oxygen and/or nitrogen oxides during detonation of substance 8. Coefficients of eqn. (2) for the latter group are $a = -0.1045$, $b = 7.8019$ and $r = 0.9928$. Trinitrotoluene (substance 11) may be, through its negative oxygen balance, considered as a "cooling component" of sample 13 (Composition B), i.e. of a mixture of trinitrotoluene with RDX. Therefore, the explosion temperature of the mixture could be calculated by means of the second shape of eqn. (2) which gives, in this case, a value of 3360°C.

For B_{peak} and B_{onset} values in eqn. (1) a specified relationship was only found between the reciprocal values of temperatures of the explosive point (i.e. autoignition temperatures) T_{expo} and B_{onset} values; the results are shown in Fig. 12, which also presents the dependence for nitramines and

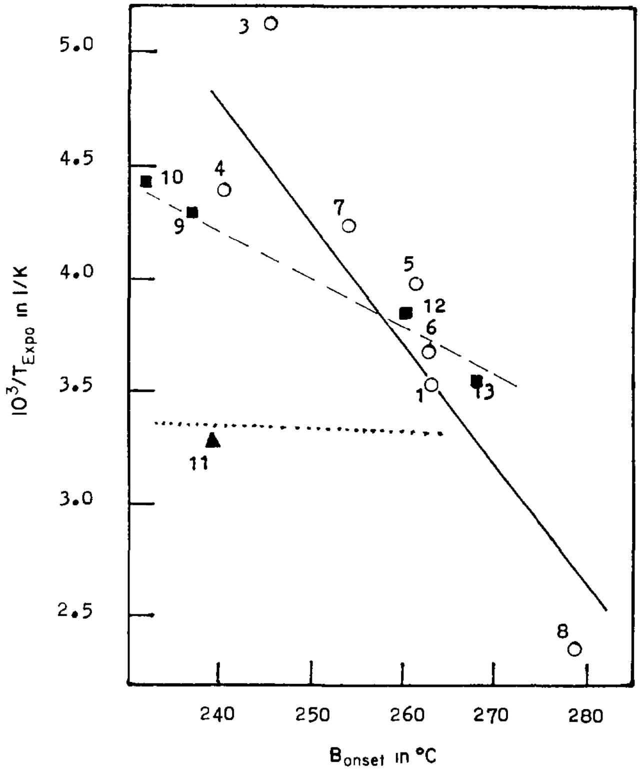

Fig. 12. Relationship between reciprocal values of the temperatures of explosives point T_{expo} (autoignition temperatures) and the values of coefficients B_{onset} from eqn. (1): —— O ——, for Istrochem explosives and hydrophobised ammonium nitrate ($r = -0.9036$); – – – – ■ – – – –, for nitramines and nitroesters (line taken from ref. 21); · · · · ▲ · · · ·, for polynitroarenes (line taken from ref. 29).

nitroesters (taken from ref. 21) and the lack of dependence for polynitroarenes (taken from ref. 29). In the case of the B_{peak} values (i.e. for DTG peaks), no satisfactory correlation was found for any of the characteristics of the explosives being studied.

For comparison purposes it is essential to add that the data, obtained from the initial non-autocatalysed stage of explosive thermolysis by means of SMM, DTA or DSC, are related to the heat of explosion [13, 15, 17], or to detonation characteristics [9, 13] derived from it, i.e. to detonation pressure or detonation velocity.

CONCLUSIONS

As in the case of non-isothermal TGA of urea–formaldehyde polycondensates [27] and polynitro and polynitroso compounds [21, 28, 29], there is a linear dependence of the positions of TGA onsets or DTG peaks upon the amounts of sample used; also this is evident in non-isothermal TGA of commercial explosives. On the basis of the dependence analysis for TGA onsets, relationships can be specified between the slope values of the dependence and explosion temperatures of explosives being studied. The section values of the dependence, however, correlate with temperatures of explosive points (autoignition temperatures). Analogous dependences for DTG peaks of the explosive mixtures are not suitable for making the last type of correlation.

In the case of explosive mixtures containing liquid esters of nitric acid it was confirmed that evaporation of these nitroesters is the dominant process of isothermal TGA.

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