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Thermal decomposition of mixtures containing nitrocellulose and pentaerythritol tetranitrate

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Abstract

A modified manometric vacuum stability test (MVST) apparatus as well as a differential thermal analyzer (DTA) and a thermogravimetric analyzer (TGA) were used to study the decomposition of nitrocellulose (NC) and pentaerythritol tetranitrate (PETN) and their mixtures. Two NC samples with different nitrogen contents (12.6% and 13.4%) were investigated. The MVST apparatus was operated isothermally at three temperatures (100, 110 and 120°C) for 40 h, and the DTA and TGA experiments were performed with a constant heating rate (10°C $\min^{-1}$). The activation energies of the thermal decomposition reactions were determined from both the MVST and DTA test results. It was found that the activation energies for the decomposition of the mixtures fell between those of PETN and NC. The compatibility between NC and PETN was confirmed by the experiments.

INTRODUCTION

Nitrocellulose (NC) and pentaerythritol tetranitrate (PETN) are two commonly used nitrate ester explosives. NC is widely applied in the manufacture of all types of smokeless powder, blasting gelatine and dynamites; and PETN is used extensively in detonators and priming compositions. A number of studies [1, 2] on the thermal decomposition of PETN and NC have been reported. Kimura [3] recently employed a chemiluminescence analyzer to study the decomposition mechanisms of these two nitrate esters below 100°C. Mixtures of NC and PETN, such as Detasheet C (Du Pont de Nemours), have been produced as a flexible explosive which meets the need of reliable propagation in thin sheets. However, the thermal properties and compatibility testing of mixtures of the two explosives are little reported.

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Although several disadvantages have been reported, the vacuum stability test remains the most readily accepted test for predicting the compatibility of materials with energetic components. Huang and his coworkers [4–6] developed a modified manometric vacuum stability test (MVST) apparatus to improve the application of the conventional vacuum stability test. The modified apparatus has some advantages, including convenient operation, wider testing scope, and a continuous recording of the pressure history during the experiment. In addition, thermal analyses, such as differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC), have been used to ascertain compatibility. The compatibility test by a thermal analysis technique was first proposed by Beach and Canfield of the Honeywell Company [7] in the USA. The criterion of the compatibility evaluation is simply based on the comparison of the exothermic peak temperature (T_m) on the DTA thermogram of a mixture system to that of the corresponding explosive. However, T_m alone only partly reflects the reactivity of a system and additional parameters might be necessary to describe the reactivity. Reich [8] suggested that the activation energy and the reaction order of a system should also be compared for compatibility evaluation. Hemmilä et al. [9] evaluated the compatibility of TNT with contact materials, using DTA and TG with seven mathematical methods to calculate the kinetic parameters. Liu et al. [10] recommended that the compatibility of explosives with contacting materials be evaluated from four parameters: the activation energy, reaction order, and two characteristic temperatures of the DTA curve (peak temperature and decomposition starting point). The components of an explosive system are regarded as compatible if the four parameters are the same or slightly different from those of the parent explosive.

The purpose of this study was to elucidate the thermal decomposition of PETN, NC, and their admixtures using thermal analysis techniques (DTA and TGA) as well as a vacuum stability test. The compatibility between PETN and NC was also investigated.

EXPERIMENTAL

The thermal decomposition of NC and PETN and their mixtures was investigated under vacuum using a modified automated apparatus, which comprised a personal computer (Acer 915P) with a data acquisition system, pressure transducers (Sayama Model 10-760 M-V-R), and a metal heating-block thermostat (Julius Peters) with a temperature control device (West 3000). Before testing, all transducers were well calibrated with a standard pressure gauge. The limit difference of the pressure transducer was ±0.49 mmHg. The temperature of the thermostat was controlled within an accuracy of ±0.1°C. Samples (1 g) were placed in a heating tube

TABLE 1

Summary of test sample compositions (wt.%)

Sample no.	PETN	NC (12.6% N)	NC (13.4% N)
PETN	100	0	
A1	75	25	
A2	50	50	
A3	25	75	
A4	0	100	
B1	75		25
B2	50		50
B3	25		75
B4	0		100

which was then evacuated with a mechanical pump for more than 1 h. The heating tubes were then installed in the thermostat at the desired temperature (100, 110, or 120°C). The heating period was 40 h. The heating tubes and samples were then removed from the thermostat and cooled to room temperature. During the experiment, the pressure was measured every 10 s and stored in the computer. Using the ideal gas law, the pressure readings were then simply converted to the volume, under standard conditions, of the gases released.

A Du Pont 910 thermal analysis system, with a type 1600 differential thermal analyzer and a 951 thermogravimetric analyzer, was employed to investigate the thermal decomposition of PETN, NC and their mixtures. A heating rate of 10°C min^{-1} was employed throughout, with a 50 ml min^{-1} flow of nitrogen gas. The amount of sample used in both DTA and TGA measurements was 3–5 mg. For all DTA measurements, the samples were placed in an open aluminum cell. A standard material, pure silver, was used to calibrate temperature measurements.

PETN and two kinds of NC were examined. The nitrogen contents of two NC samples were 12.6 and 13.4%. Six mixtures of PETN and NC were also investigated. Table 1 lists the composition of the tested samples. All test materials were manufactured by a domestic arsenal. The PETN particle size ranged between 40 and 60 μm, and that of NC between 50 and 100 μm. Before testing, all samples were stored in a vacuum oven at 65°C for at least eight hours. Mixtures were prepared by thoroughly mixing specific weights of PETN and NC powders. "Detasheet C" (Du Pont de Nemours) contains 63% PETN, 8% NC, the balance being a plasticizer.

RESULTS AND DISCUSSION

Typical decomposition curves of PETN and NC (12.6% and 13.4% nitrogen) obtained by the modified manometric vacuum stability test at

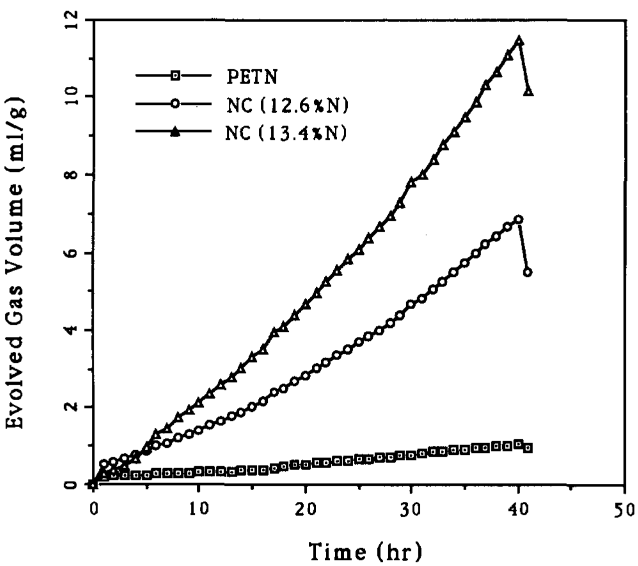

Fig. 1. Vacuum stability test results of PETN and NC (12.6% and 13.4% N) at 120°C.

120°C are shown in Fig. 1. As the decomposition curves show, the decomposition apparently follows an autocatalytic type of reaction. The measurement at the 41st hour was the volume of gas evolved after cooling to room temperature. Owing to the condensation of a portion of the gas products and to the decrease of the system temperature, the pressure readings, as well as the calculated gas volumes, decreased slightly. It was found that the decreasing volume released from the decomposition of NC is much larger than that from PETN. In other words, much more condensable gas products are evolved by NC decomposed at 120°C. Also from Fig. 1, it can be seen that the gas volume evolved by NC is much larger than that evolved by PETN. As expected, the gas product volume of the NC with the higher nitrogen content (13.4%) is much larger than that of the NC with 12.6% N.

Figure 2 shows a comparison of the decomposition curves of NC (13.4% N) at various heating temperatures; the higher the temperature employed, the faster the decomposition. Although there was only slight decomposition of NC at 100°C, there is a significant gas produced when the heating temperature increases to 110 or 120°C. Figures 3 and 4 illustrate the decomposition curves of PETN, NC, and their mixtures, heated at 110 and 120°C, respectively. As shown in Figs. 3 and 4, the observed volume of gas evolved from the decomposition of pure NC is the largest, and that from the decomposition of pure PETN is the smallest. The gas evolved from the mixtures is seen to be proportional to the weight fraction of NC in the mixtures which suggests that PETN and NC are compatible.

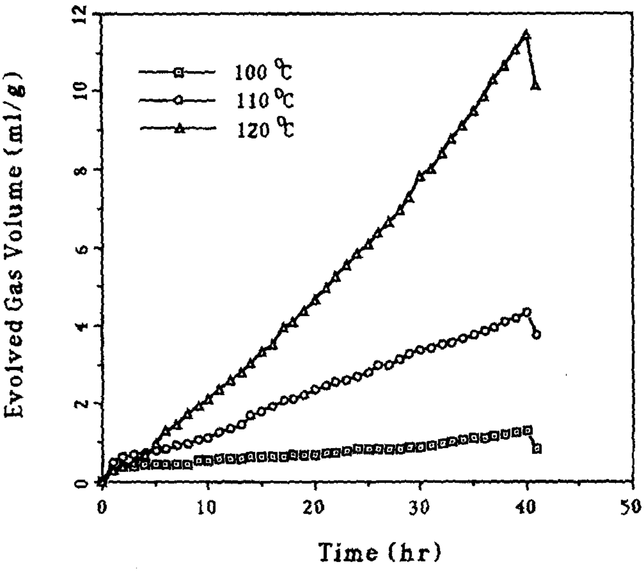

Fig. 2. Comparison of decomposition curves of NC (13.4% N) at various temperatures.

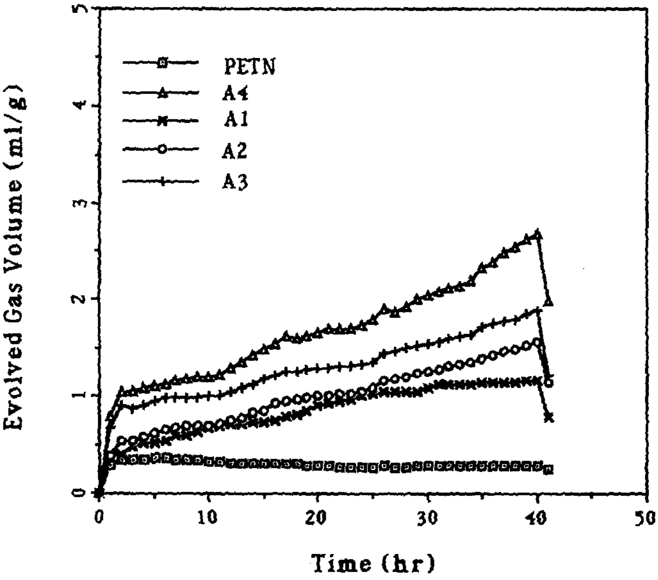

Fig. 3. Comparison of decomposition curves of PETN, NC (12.6% N) and their mixtures at 110°C, testing started in vacuo.

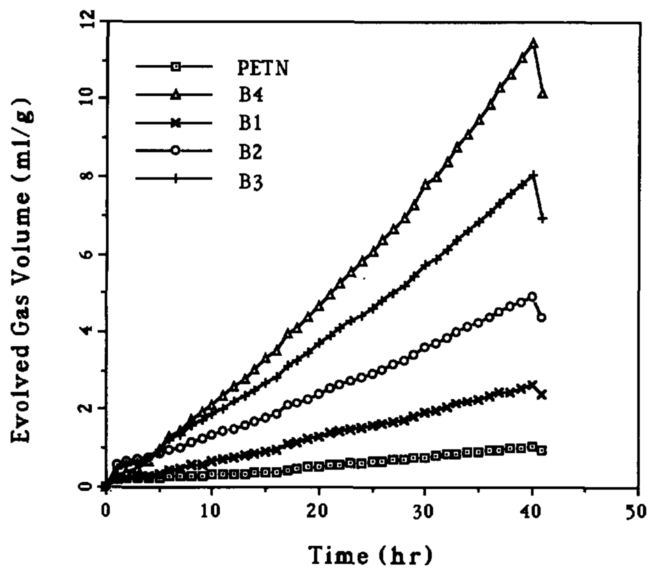

Fig. 4. Comparison of decomposition curves of PETN, NC (13.4% N) and their mixtures at 120°C, testing started in vacuo.

Table 2 gives the results of the vacuum stability test (after cooling to room temperature). The gas volumes liberated by PETN, NC (12.6% N), and NC (13.4% N) at 100°C are 0.245, 0.223, and 0.799 ml g^{-1}, respectively. At the same temperature, ref. 11 reported 0.1, 0.2, and 0.3 ml g^{-1} evolved by PETN, NC (12.6% N), and NC (13.45% N), respectively. Gibbs and Popolato [12] reported a vacuum stability result for PETN of 0.2–0.5 ml g^{-1} after 48 h heating at 100°C. After heating at 120°C, the

TABLE 2

Final results of the modified vacuum stability tests

Sample no.	Evolved gas volume after cooling (ml g^{-1})			E_a (kcal mol^{-1})
	100°C	110°C	120°C	
PETN	0.245	0.380	0.947	31.3
A1	0.006	0.800	1.733	35.4
A2	0.111	1.133	3.177	49.1
A3	0.220	1.222	3.828	44.1
A4	0.223	1.979	5.510	44.8
B1	0.333	1.178	2.399	31.1
B2	0.555	1.666	4.377	32.3
B3	0.660	2.155	6.931	34.3
B4	0.799	3.739	10.175	36.6
Detasheet C	0.633	1.412	19.860	57.7

evolved gas volume of the aforementioned three compounds was 0.947, 5.510, and 10.175 ml g^{-1}, respectively. Reference 11 reported that the results for all three compounds were somewhat larger than 2.2 ml g^{-1} at 120°C; however, these experiments were not for 40 h of heating, because of the limits of the apparatus employed. As seen in Table 2, the effect of temperature on the evolved gas volume was significant; for instance, a change from 110°C to 120°C produced an approximately three-fold increase for all samples. The amounts of gas produced from the decomposition of mixtures containing PETN and NC were intermediate between that of PETN and NC. This implies that PETN and NC are compatible. It should be noted that the amount of gas evolved from the mixtures increases as the NC content increases.

Because the extent of the reaction studied in this paper was small, the decomposition reaction was reasonable assumed to be a pseudo-zeroth-order reaction. The decomposition rate might be calculated as the first-order derivative of the function describing the time dependence of the volume. The calculation was based on the experimental data during the 10th and 40th hours. Using the Arrhenius' law, the activation energy was estimated according to the decomposition rates in the temperature range 100–120°C. The values of the calculated activation energies are given in Table 2. Kučera and Havránková [13] reported activation energies for NC (13.31% N and 11.0% N) in the temperature range of 115–140°C of 40.4 and 42.8 kcal mol^{-1}, respectively. Wilfong et al. [14] also studied the NC decomposition and obtained an activation energy value of 46.67 kcal mol^{-1} in the temperature range 84–162°C. Smith [15] examined the thermal decomposition of NC (11.8% N) within the range 165–200°C and determined a value of 43 kcal mol^{-1}. The activation energy value obtained for PETN was 31.3 kcal mol^{-1}. Van der Merwe et al. [16] reviewed the literature on the stability of PETN and pointed out that its activation energy values range from 30 to 70 kcal mol^{-1}. They explained this wide range of results by the complexity of the PETN decomposition and the diversity of the methods used to determine them. Therefore, the calculated activation energies of NC and PETN by the MVST method approximate reasonably to the literature data. As listed in Table 2, the activation energies obtained for the mixtures range between those of PETN and NC. Therefore, it can be said that PETN and NC are compatible.

Beach and Canfield [7] suggested an extent of reactivity of a mixture R to judge the compatibility of highly energetic materials in various admixtures of polymers. The extent of reactivity is estimated by eqn. (1) for a mixture with a weight ratio of 1:1 (explosive:polymer)

$$R = Q - \frac{M+N}{2} \qquad (1)$$

where R is the difference in the gas volume generated by the thermal decomposition of the mixture over the sum of that generated by decomposition of the components, Q is the standard volume of gas evolved from the mixture, and M and N are the standard volumes of gas liberated from the pure components of explosive and polymer, respectively. Ger et al. [17] proposed eqn. (2) for when the weight ratio of explosive to binder is $\alpha:1$ rather than 1:1

$$R = Q - \frac{\alpha M + N}{\alpha + 1} \tag{2}$$

If R is less than 0.6 ml g^{-1}, the mixture is compatible; otherwise the mixture is incompatible. The second term on right-hand-side of eqns (1) and (2) is a theoretical gas volume that might be released by decomposition of the mixtures. Figure 5 shows a typical compatibility test for PETN and NC (12.6% N) mixtures. It is found that the experimental evolved gas volumes of the mixtures are slightly less than those predicted by theoretical calculations. A similar result was found for NC with 13.4% nitrogen. Thus, it is confirmed that PETN and NC are apparently compatible.

Typical DTA and TG thermograms for PETN and NC (13.4% N) are shown in Fig. 6. It can be seen that a distinct endothermic melting point peak occurs before the strong exothermic decomposition peak on the PETN DTA curve. However, there is only one exothermic peak on the

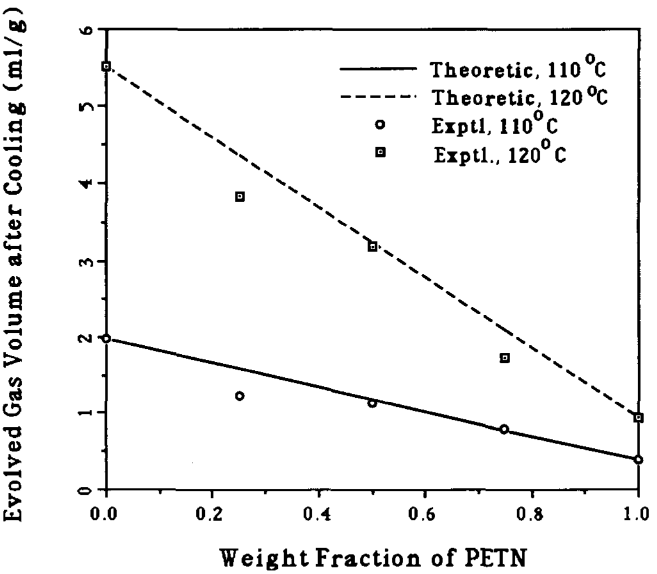

Fig. 5. Compatibility test of PETN and NC (12.6% N) by the vacuum stability test method.

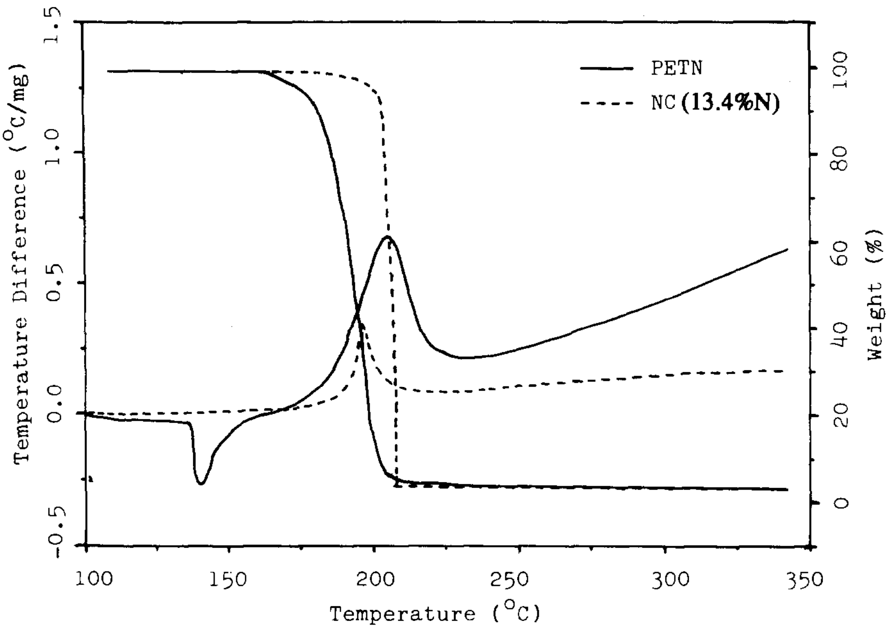

Fig. 6. DTA and TG thermograms of PETN and NC (13.4% N) at a heating rate of 10°C min^{-1} and an N_2 flow rate of 50 ml min^{-1}.

DTA curve of NC. This indicates that NC would decompose in a solid phase. Newman [18] estimated the melting point of NC (12.6% N) indirectly by determining those of mixtures of NC and γ-butyrolactone. By extrapolation, he calculated the melting point of NC to be 617°C. Also from Fig. 6, it can be seen that the TG curve of PETN is quite different from that of NC (13.4% N). PETN starts to decompose at 155.0°C, its weight loss occurring relatively slowly. However, NC starts to decompose at 180.0°C, its weight loss occurring comparatively rapidly. Comparing the DTA and TG curves for PETN, there is an exothermic decomposition reaction reaching a maximum rate at 206.1°C associated with a weight loss of 92%. Conversely, the DTA curve of NC reaches an exothermic peak at 196.4°C, where only 7% of the NC has decomposed. This shows that below the temperature of initiation, the decomposition of NC is relatively slow, but that an explosive decomposition takes place if the temperature is high enough.

The results obtained by TG and DTA for PETN, NC, and their mixtures are summarized in Table 3. From the TG curves, the temperatures at which the weight loss commences and those at 20% weight loss of the samples are given in Table 3: the commencing point decreased when PETN was mixed with NC, or vice versa. The temperatures at 20% weight loss for the mixture samples were near to that of PETN, but were about 15°C lower than that of NC. Except for pure NC samples (A4 and B4),

TABLE 3

Results obtained from TGA and DTA for PETN, NC and their mixtures

Sample no.	TGA		DTA			
	Start of wt. loss T_0 (°C)	20% wt. loss T_{20} (°C)	Endothermic peak T (°C)	Exothermic peak T_m (°C)	E_a (kcal mol^{-1})	Reaction order n
PETN	155.0	185.1	141.6	206.1	46.6	1.24
A1	149.5	186.6	140.2	205.0	43.7	1.15
A2	143.3	188.2	141.7	204.3	44.6	1.45
A3	145.1	189.9	142.7	194.2	42.9	4.00
A4	178.0	203.0	–	195.3	43.2	2.92
B1	143.3	187.1	139.2	205.8	44.7	0.94
B2	148.6	189.0	139.2	201.7	41.9	1.08
B3	140.0	191.3	139.7	191.9	42.6	4.84
B4	180.0	203.6	–	196.4	43.5	2.99
Detasheet C	139.4	193.3	134.7	204.6	58.8	0.96

the endothermic peak temperatures (melting point) on the DTA curves of the mixture samples were close to that for PETN. The exothermic peak temperatures for the mixtures were located between those for PETN and NC. Based on the model proposed by Huang et al. [19], the kinetic parameters of the decomposition reaction were determined from a single DTA curve. The activation energy (E_a) of PETN was 46.6 kcal mol^{-1}, which is in very good agreement with the literature data [12]. The activation energies of NC (12.6% N) and NC (13.4% N) were 43.2 and 43.5 kcal mol^{-1}, respectively. Reich [8] calculated a value of 180 kcal mol^{-1} for NC using the method he developed from DTA curves. As mentioned above, however, the literature values for the E_a of NC are generally much lower than Reich's data. The obtained activation energies of NC decomposition in Table 3 are in quite good agreement with the literature data. As listed in Table 3, the E_a values for the mixtures change only slightly and, therefore, PETN and NC must be considered compatible. As discussed above, the same conclusion is reached from the results of the MVST method.

Figures 7 and 8 present the DTA and TG results, respectively, for the mixture samples A1, A2, and A3. Comparing the DTA curves for mixtures to that for PETN, the melting endothermic peak is small, as anticipated. For sample A3, which contains 75 wt.% NC, the exothermic peak temperature dropped to 194.2°C. Furthermore, the onset of the decomposition curve occurred comparatively rapidly, and after a peak temperature was attained, a rather gentle decline in ΔT was observed.

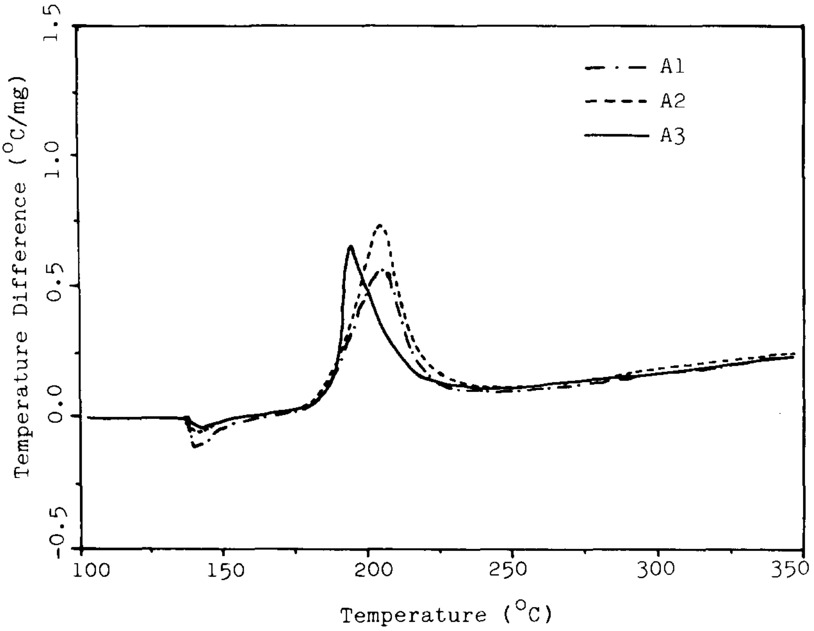

Fig. 7. DTA thermograms of samples A1, A2, and A3 at a heating rate of 10°C $\min^{-1}$ and 50 ml $\min^{-1}$ nitrogen purge.

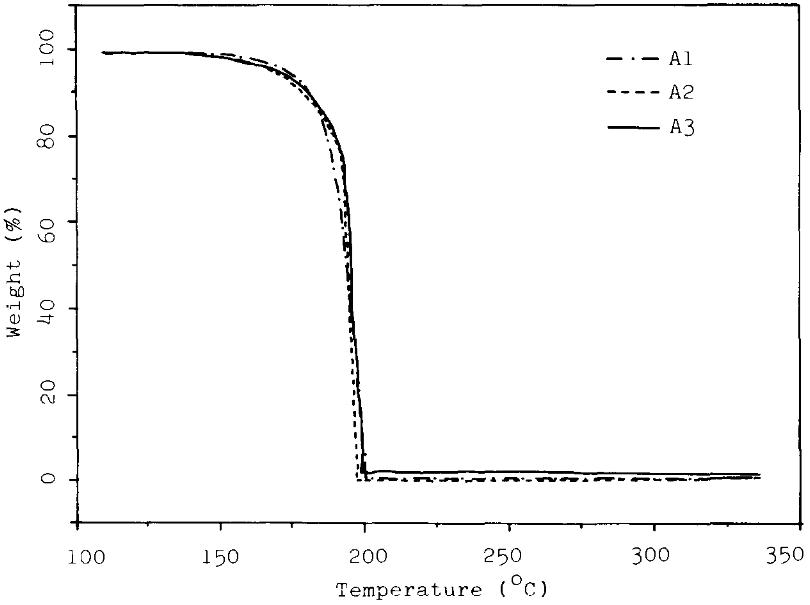

Fig. 8. TG thermograms of samples A1, A2, and A3 at a heating rate of 10°C $\min^{-1}$ and 50 ml $\min^{-1}$ nitrogen purge.

This implies that a much more complex mechanism might be involved for the decomposition of sample A3 (as listed in Table 3, the reaction order is 4.0). As shown in Fig. 8, all three TG curves are quite similar. The samples were almost completely decomposed at around 200°C, which is obviously lower than for PETN and NC. Comparing the TG curves in Figs. 8 and 6, it is found that the shape of the TG curves for mixtures is a combination of those for PETN and NC. At the start of the TG curves, the rate of weight loss from mixture samples matches that from PETN. At the end of the TG curves, the mixture samples decomposed completely and rapidly, as did NC. It is noted that in the presence of PETN, the starting decomposition temperature of NC would fall. However, a small amount of NC might cause a fast, complete decomposition of PETN.

Figure 9 shows the DTA and TG thermograms of Detasheet C at a heating rate of 10°C min^{-1}. The DTA scan of Detasheet C is quite similar to that of sample A1 (see Fig. 7), except for a slight fall in the melting endothermic peak temperature. However, the TG curve of Detasheet C is different from that of mixtures of PETN and NC, particularly in the final part. This is reasonable because besides PETN and NC there is a plasticizer contained in Detasheet C. The activation energy and the reaction order for the decomposition of Detasheet C were determined from the DTA results as 58.8 kcal mol^{-1} and 0.96, respectively. The decomposition of Detasheet C was also studied under vacuum by the MVST method. The experimental data are listed in Table 2. The

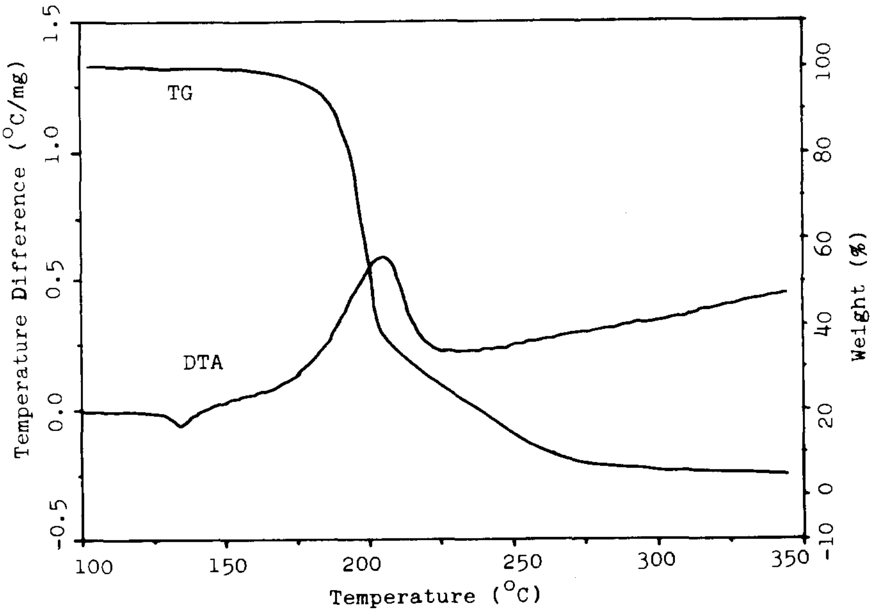

Fig. 9. DTA and TG thermograms of Detasheet C at 10°C min^{-1} heating rate and an N_2 flow rate of 50 ml min^{-1}.

activation energy obtained by the MVST method is 57.7 kcal mol^{-1}, in good agreement with that obtained by the DTA method. The evolved gas volume of Detasheet C was found to be very high on heating at 120°C, but low at 110 and 100°C. This indicates that Detasheet C is stable at lower temperatures and becomes unstable if the temperature is higher than 120°C.

CONCLUSIONS

The thermal decomposition of PETN, NC, and their admixtures was investigated by a manometric stability testing (MVST) apparatus under vacuum, and by DTA and TGA. The activation energies for the decomposition of the mixtures obtained by the MVST and DTA methods were reasonably consistent. From the DTA results, the activation energies and the exothermic peak temperatures of the mixtures were only slightly different from those of PETN and NC. From the results of the MVST experiments, the evolved gas volumes of the mixtures were less than those predicted by theoretical calculations. Thus, it can be concluded that PETN and NC are essentially compatible. A commercial product, Detasheet C, a mixture of PETN and NC with a plasticizer, was also studied by the same methods. The activation energy of Detasheet C was found to be 58.8 kcal mol^{-1}.

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