J Forensic Sci, Apr. 1977, Vol. 22, No. 2

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Thermal Decomposition of Nitrocellulose Propellants

Most smokeless propellant powders for small arms use are either single base or double base types. Single base powders consist of nitrocellulose with small amounts of additives such as tin to reduce barrel fouling and muzzle flash, graphite to improve handling, and a stabilizer such as diphenylamine. Double base powders contain nitrocellulose with 10 to 15% of nitroglycerin added [*1*].

While there have been numerous calorimetric studies on the combustion of propellants to determine their heat content, the results of such studies are not readily available. Combustion at high pressure more closely resembles the combustion in a closed breech firearm. Under these conditions of use, the heat of combustion of single base propellants is about 875 cal/g (3.66 MJ/kg), while that of double base propellants is about 1075 cal/g (4.498 MJ/kg).

Although the heats of combustion vary somewhat with degree of nitration, the major differences between powders of the same type is the burning rate, which depends on the size and shape of the granules as well as the composition. For analytical purposes, combustion at high pressures cannot be conveniently and quickly carried out in a routine way. Although there is a need for such information, very limited data are available on the decomposition of nitrocellulose propellants at ambient pressure. In a recent study, the decomposition of nitrocellulose powders at atmospheric pressure was studied with differential thermal analysis (DTA) [*2*]. Unfortunately, the decomposition energies reported for a given propellant frequently varied by as much as a factor of more than two, thus failing to establish reliable thermal limits for reference analytical purposes. Additionally, great variation was found for the whole series of powders used with the average decomposition energies ranging from 255 to 490 cal/g (1.07 to 2.05 MJ/kg). In view of the foregoing, the decomposition of nitrocellulose propellants was studied by using differential scanning calorimetry (DSC) to establish reliable heats of decomposition at atmospheric pressure.

Experimental Procedures

The nitrocellulose propellants used in this work were commercially available canister powders used in reloading small arms ammunition. Experience has shown the noncanister lots of propellants used in commercial ammunition behave similarly. Commercially available powders usually have granular shapes of (1) cylindrical rods; (2) flat disks; (3) short cylinders with an axial hole; (4) short cylinders without holes; and (5) spheres or slightly flattened spheres. The powders chosen for use in this work represent these five

Received for publication 21 June 1976; accepted for publication 20 Aug. 1976.
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types and are shown in Figs. 1*a* through *e*. Thermal data are reported here for each of these propellants. The propellants include both single base and double base types.

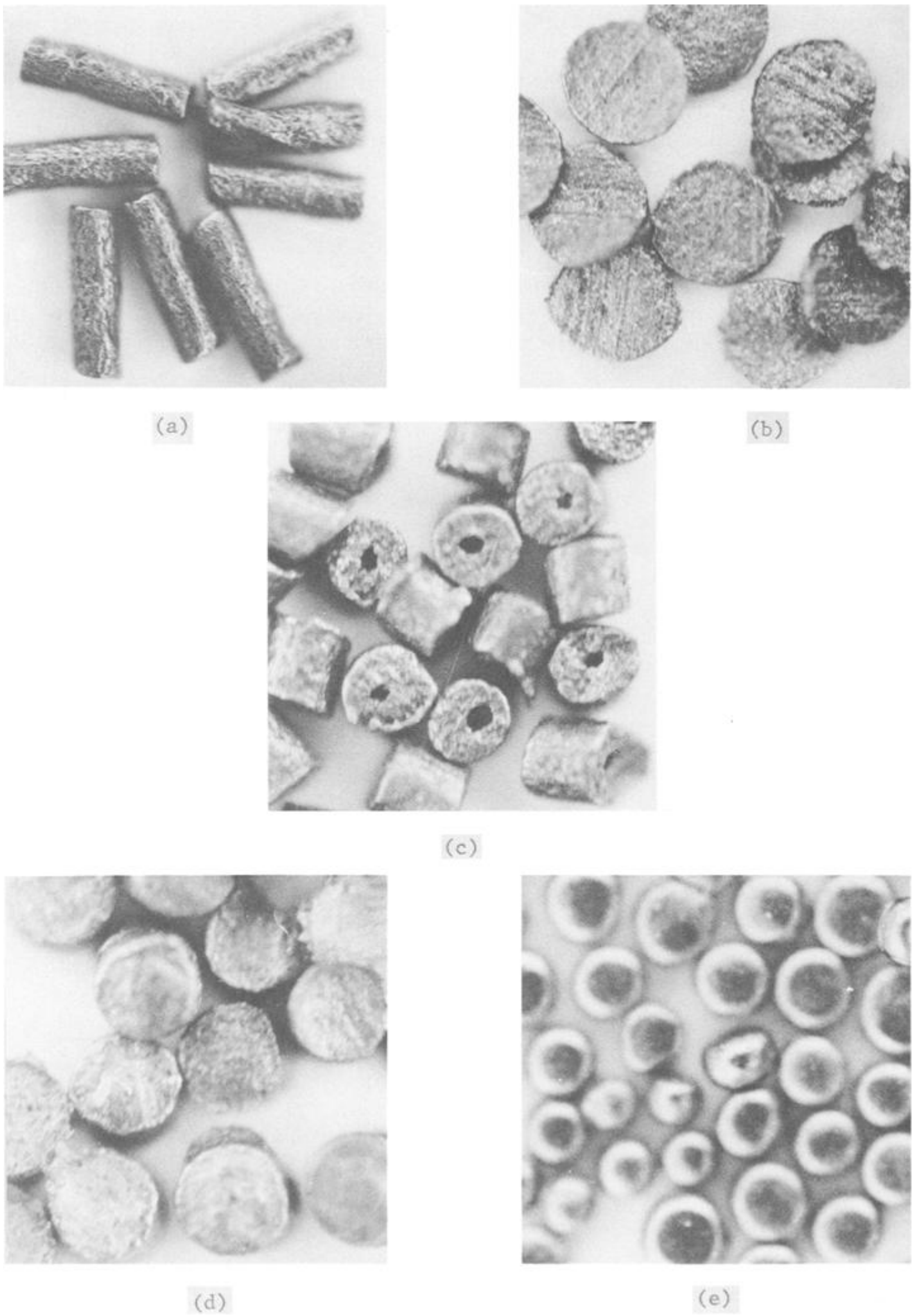

FIG. 1—*Granules of propellants showing the most common configurations:* (a) *Du Pont IMR 4198, single base;* (b) *Hercules Unique, double base;* (c) *Du Pont IMR 4227, single base;* (d) *Hercules 2400, double base; and* (e) *Hodgdon BL C-2, double base.*

Thermal studies were carried out with a Perkin-Elmer differential scanning calorimeter, Model DSC-1B. Calibration of the instrument was accomplished with the fusion of tin having a heat of fusion of 14.6 cal/g (61.1 kJ/kg). All runs were made with the sample compartment purged with dry nitrogen at a flow rate of 30 cm^3/min. Samples were weighed to the nearest microgram and were generally in the range of 1 to 2 mg. The samples were contained in aluminum pans, and a heating rate of 20°C/min was used. For most powders, six to eight individual samples were studied. Peak areas were determined by means of a planimeter with several traces being determined for each peak so that accurate average values could be determined.

Results

The DSC curves obtained during the decomposition of the propellants show only a single exothermic peak beginning around 185°C. Generally, the peaks exhibited the characteristics shown in Fig. 2. However, some samples yielded curves having profiles

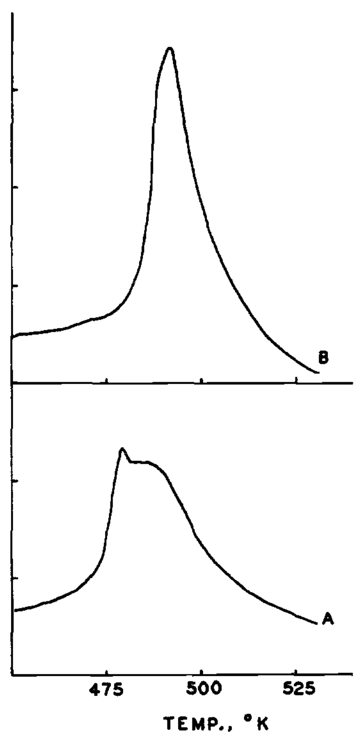

FIG. 2—*Differential scanning calorimetric curves for decomposition of Hercules Unique* (A) *and Du Pont IMR 4198* (B) *propellants.*

intermediate between those types shown. These peak shapes are not reliable for identification purposes owing to the more than one propellant giving a particular shape of the exothermic peak. Also, separate samples of the same propellant gave widely differing peak shapes, although the heat of decomposition values showed good precision.

The initiation temperature, the temperature at the exothermic peak maximum, and the temperature at termination were determined from the DSC curves. Since the DSC determines heat capacity as a function of temperature, the peak areas give the enthalpy of decomposition ΔH directly. The various decomposition temperatures and ΔH values are shown in Table 1. The mean ΔH values are given as well as the average deviation from the mean for the several determinations.

Discussion

The temperatures shown in Table 1 for the decomposition of the propellants indicate that under the conditions of this study, there are only minor variations between the powders used. Initiation temperatures for different propellants frequently differ less than different samples of the same propellant.

TABLE 1—*Temperatures and thermal values for decomposition of nitrocellulose propellants.*

					$-\Delta H$, cal/g[a]	
Propellant	Type	T_i, °C	T_m, °C	T_f, °C	Mean	± Avg Deviation
Hercules 2400	double base	177	192	262	519	18
Hercules Unique	double base	177	192	262	504	20
DuPont IMR 4227	single base	192	202	262	518	24
DuPont IMR 4198	single base	177	217	367	520	16
Hodgdon BL C-2	double base	187	217	252	501	14

[a] 1 cal/g = 4184.000 J/kg.

The ΔH values for the decomposition of the propellants were found to be reproducible to within about ± 4%. Mean values for the ΔH for different propellants were found to be about the same regardless of which propellant was used. All the propellants gave mean ΔH values of slightly over 500 cal/g (2.09 MJ/kg). Burning of propellants under conditions of actual use at high pressure liberates about 875 and 1075 cal/g (3.66 and 4.498 MJ/kg), respectively, for single and double base types. The values found in this work show no significant difference between the single and double base types. The reason for the low ΔH values lies in the fact that complete, efficient combustion of nitrocellulose takes place only under high pressure. At a pressure of 1 atm (0.1 MPa), there is a substantial residue and decomposition is not complete although it is reproducible.

Previously reported data for decomposition of propellants showed that a large range of values was obtained for the heat of decomposition of a given powder [*2*]. In this work, we found no such behavior although it was observed that 1 sample of perhaps 15 showed an anomalous behavior and gave a significantly lower ΔH. For example, one sample of Hercules Unique® gave a value of 264 cal/g (1.10 MJ/kg), while eight other samples averaged 504 cal/g (2.11 MJ/kg), with an extreme variation of 80 cal/g (0.33 MJ/kg) and an average deviation from the mean of ± 20 cal/g (0.08 MJ/kg). Similarly, a single sample of Du Pont 4198® gave a ΔH of 239 cal/g (1.00 MJ/kg), while eight others averaged 520 cal/g (2.18 MJ/kg), with an average deviation from the mean of ± 16 cal/g (0.07 MJ/kg). No reason could be found for this behavior and it was not observed for all the propellants.

Two of the five powders used in this work, Hercules Unique and 2400®, were among those previously studied using DTA [*2*]. Different lots of Hercules 2400 were reported as having heats of decomposition of 290 and 310 cal/g (1.21 and 1.30 MJ/kg). For these two batches, the range of values for individual samples was reported as 290 to 665 cal/g (1.21 to 2.78 MJ/kg) in one case and 240 to 515 cal/g (1.00 to 2.15 MJ/kg) in the other. The value obtained in this work is 519 ± 18 cal/g (2.17 ± 0.08 MJ/kg). For Hercules

Unique the average heat of decomposition was reported to be 255 cal/g (1.07 MJ/kg), with a range of values of 205 to 380 cal/g (0.86 to 1.59 MJ/kg) [2]. Using DSC, we have determined the heat of decomposition of this powder to be 504 ± 20 cal/g (2.11 ± 0.08 MJ/kg).

The results obtained in this work indicate that there is little likelihood of being able to differentiate between propellants on the basis of thermal decomposition heats. Values for ΔH of decomposition are all very similar and decomposition temperatures do not differ by much, even for powders having greatly differing physical characteristics. This is not surprising in view of the fact that the various powders differ much more in their physical properties than they do in their chemical composition. However, a large exothermic peak in the range 180 to 260°C during thermal analysis of a solid sample would be indicative of the presence of a nitrocellulose propellant in the sample. If the propellant granules are recovered intact from samples, visual examination is usually sufficient to determine that a propellant is present. The data presented in this report do provide reference values against which heats of decomposition of nitrocellulose propellants can be compared for identification.

References

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