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EFFECTS OF HNS ON CAST TNT

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Crystal modifier

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The existence of a complex of TNT and HNS has been confirmed and its presence promotes TNT casts of superior quality. Its presence, however, is apparently not required for superior casting of TNT. Good casts can be produced by adequate dispersal of HNS in the melt, either by ultrasonic mixing or by dissolution.

TABLE OF CONTENTS

FIGURES

INTRODUCTION

The 2,4,6-trinitrotoluene (TNT) is used extensively in munitions either alone or as one of several energetic materials in various compositions. The low melting point of 82°C leads to casting from the melt as the method of choice when producing charges. Extensive supercooling in casting molten TNT, however, invariably leads to the formation of large crystallites which produce very poor quality casts. It is known (ref. 1) that adding a small amount of 2,2',4,4',6,6'-hexanitrostilbene (HNS) and cycling the melt through two temperatures produces a very uniform cast having a matrix of very fine, randomly oriented grains. The present study is aimed at understanding the essential features which are operative in the above process. Several experimental techniques have been applied, including neutron and x-ray diffraction, optical microscopy, and differential scanning calorimetry.

Neutron Diffraction

The TNT can exist in two crystal phases; viz, an orthorhombic and a monoclinic modification. From the known crystal structure (ref. 2) of these two phases, one can calculate the expected neutron diffraction pattern. Figure 1 shows the calculated (vertical bars) and measured neutron diffraction pattern for the two phases in a region of scattering angle in which they are sufficiently different that the technique is useful as a quantitive measure of the presence of each phase in a sample. Neutron diffraction is here employed because it is a bulk measurement (neutrons having much higher penetrating power than x-rays) and thus reflects the composition of the entire sample. The diffraction patterns were obtained on a spectrometer on the National Bureau of Standards research reactor. Both military grade and recrystallized TNT samples were used and the results were essentially the same.

A series of measurements was performed to determine the conditions under which each phase was produced from the melt. In these, TNT was heated to 85°C in a thin wall aluminum cylinder 1.27 cm in diameter and then either allowed to cool slowly to ambient temperature, or poured onto an aluminum plate held in an ice bath. The sample which was quenched crystallized entirely in the orthorhombic phase, while the slowly cooled sample crystallized in the monoclinic phase. The orthorhombic form could be transformed to the monoclinic by raising the sample temperature to 75°C and maintaining this temperature for 1/2 hour. This confirmed the results of a previous study (ref. 3). The monoclinic phase is thus the more stable phase, but the orthorhombic can be stabilized by reducing the temperature quickly below that required for the phase transition.

The procedure (ref. 1) for obtaining high quality casts of TNT is to heat a mixture of TNT and 0.5% HNS to about 100°C until the HNS is

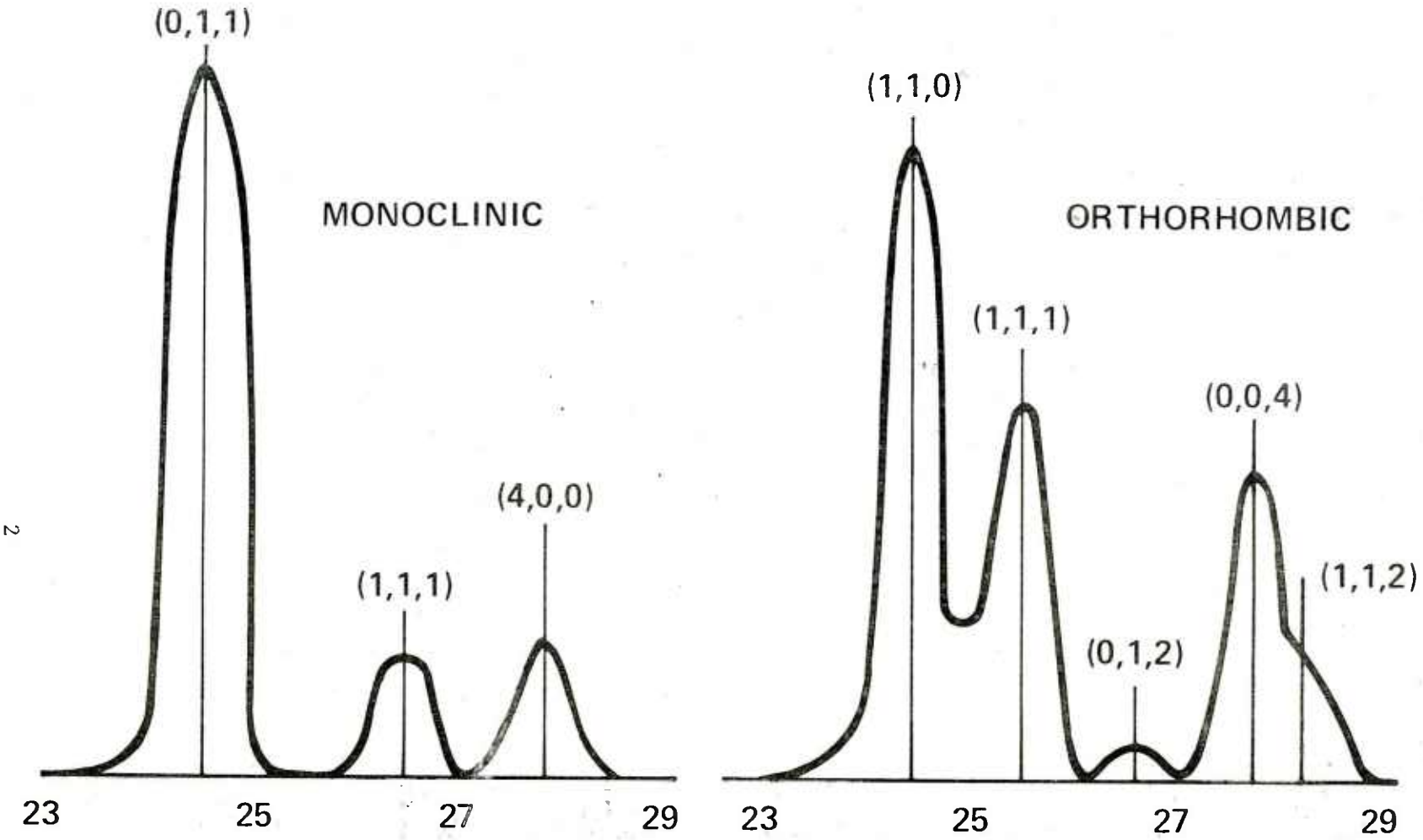

Figure 1. Neutron diffraction pattern of the two phases of solid TNT.

completely dissolved, allow the melt to cool until it stiffens, reheat to slightly below 85°C and then cast. The question arises as to whether the first temperature cycle in which HNS dissolves is required in order to obtain (1) an adequate dispersion of the HNS, (2) complex formation or (3) chemical interaction. In order to obtain a good dispersal of the HNS without dissolving it in the TNT, a sample was suspended in an ultrasonic vibrator for 15 minutes in a water bath maintained at 85°C, a temperature at which essentially no dissolution of the HNS occurs. The sample treated in this manner and one in which the two temperature cycles were followed were then used in the casting experiments described above. The results were identical for both samples; viz, that under no circumstances of casting could the orthorhombic phase be produced. Whatever mechanism is operative in the two-temperature process, is probably also present in the ultrasonically produced dispersion.

Optical Microscopy

A hot-stage microscope with a magnification of 65X was used in this part of the study. The TNT was heated on a glass slide to both 85°C and 100°C and the sample temperature lowered at a rate of 2°/min. It was found that the liquid supercooled by approximately 20°C before crystallization occurred, and then it occurred at very few sites, producing large grains as shown in figure 2a. When the sample in which the ultrasonically dispersed HNS was heated to 85°C and then cooled at the same rate, supercooling was suppressed, and many nucleating sites were observed in the cast produced (fig. 2b). The size of the particles in figure 2b is between 0.1 and 0.25 mm. In contrast to the grain size in figure 2a, this is a reduction by much more than an order of magnitude. A mixture of TNT and 0.5% HNS which was not treated ultrasonically was subjected to the two-temperature process described above. In the initial heating, small particles (presumably HNS, which is insoluble at 85°C) were observed to dissolve at 110°C. The sample temperature was lowered at 2°/min and nucleation was observed, as with the ultrasonically treated sample of figure 2b. The sample was reheated to 85°C and particles whose morphology had not previously been observed appeared (fig. 2c). When recrystallization occurred as the temperature was lowered, the cast shown in figure 2d was produced. These particles are approximately half the size of those in figure 2b. Reheating the sample to 85°C again produced the particles of figure 2c, which disappeared when the sample temperature was raised to 95°C. A cast of the quality of figure 2b was obtained upon subsequent crystallization of this last sample.

Studies on the HNS-TNT Complex

Differential Scanning Calorimetry

Recent work (refs. 4,5) has brought to light evidence of complex formation between TNT and HNS. Parry and Thorpe (ref. 5) have prepared

c d

Figure 2. Microphotographs of the crystals produced by casting TNT

and isolated the crude complex and demonstrated its existence via Differential Scanning Calorimetry (DSC). This work was confirmed on pure complex (ref. 6), the free TNT being removed in a modified sublimation apparatus at 80°C/4-5.3 pascals.

Pure TNT exhibits an endotherm at about 82°C, corresponding to its melting point, as shown in the lower curve in figure 3. Sublimed TNT, which was collected on a cold finger, produced an identical curve. A small amount of the sublimation residue was found to exhibit the 82°C endotherm characteristic of the free TNT. Sublimation was continued until no evidence, or very little evidence, of this peak remained. The DSC thermogram of this sample is shown as the upper curve in figure 3 and exhibits an endotherm, attributed to the complex at 117°C. The temperature was then lowered to 30°C, and a second DSC scan produced the lower trace of figure 3, showing a reappearance of the TNT endotherm and the absence of the endotherm attributed to the complex. We interpret these results as confirming the existence of the HNS-TNT complex. Disappearance of the 117°C endotherm indicates decomposition of the complex into TNT and HNS, and the reappearance of the endotherm at 82°C represents TNT formerly bound in the complex.

X-Ray Diffraction:

Approximately 20 milligrams of the complex were obtained by the method of vacuum sublimation described above. This is insufficient for obtaining a neutron diffraction pattern, but quite adequate for x-ray diffraction. The powder x-ray diffraction pattern obtained from this sample was completely different from that obtained from either TNT or HNS (fig. 4), and we take this as further evidence of the existence of the complex.

In addition, from the widths of the diffraction lines, which were measurably broader than the resolution of the diffractometer, one can estimate the particle size to be in the order of 50-100 Å. This last observation may explain the enhanced nucleating power of the complex.

CONCLUSIONS

The present work has confirmed the existence of a complex of TNT and HNS which is formed when the melt containing dissolved HNS is crystallized. In addition, it has been shown that HNS produces superior casts of TNT by providing many nucleating sites for crystallization. The presence of the complex, however, is apparently not required for good casting of TNT. Good casts also can be produced by adequate dispersal of HNS in the melt, either by ultrasonic mixing or by dissolution. The slightly better casts obtained with the complex may be due not to chemical interaction with the complex but rather to the presence of a greater number of nucleating sites because of the small particle size of the complex.

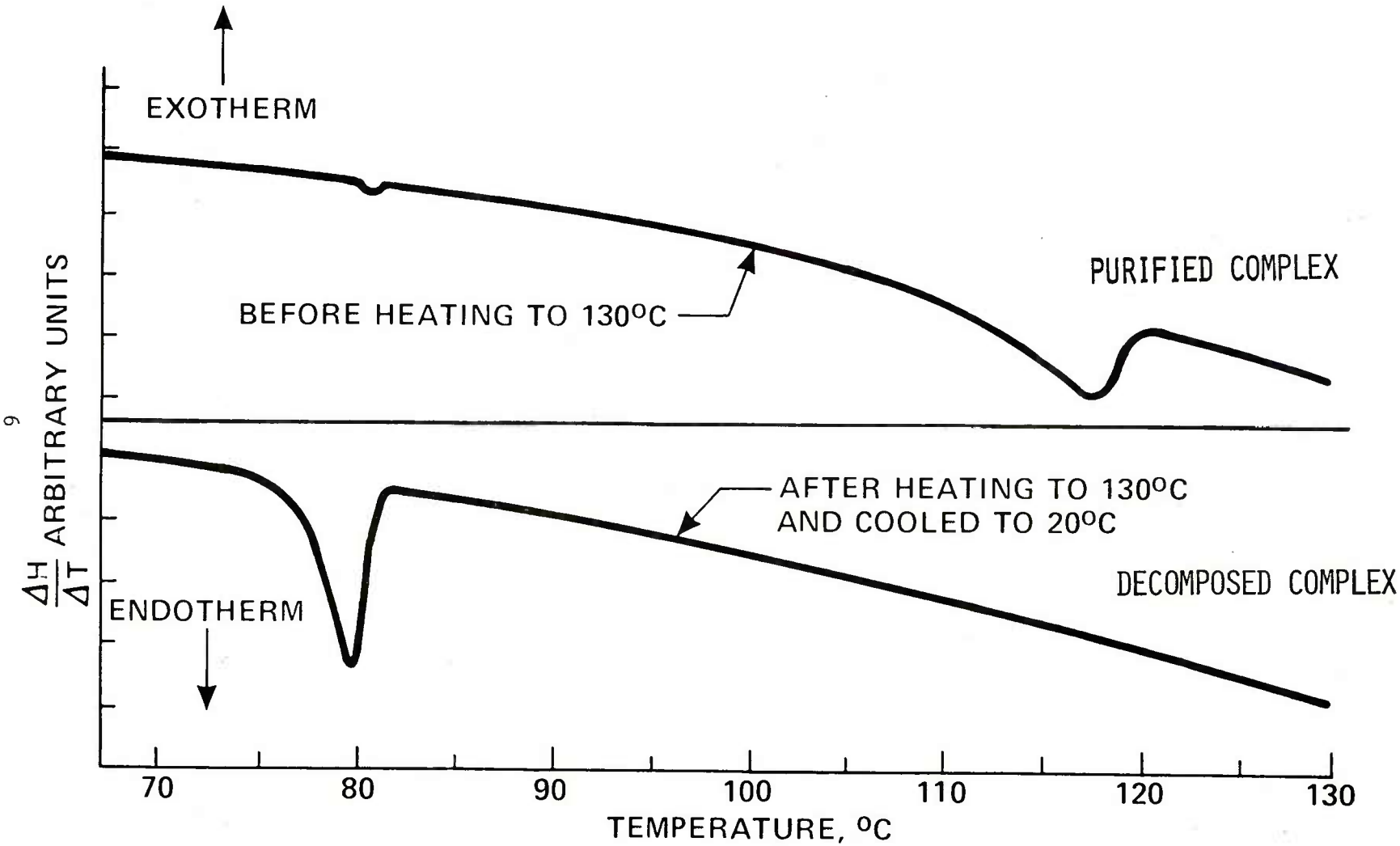

Figure 3. DSC scans of the purified HNS-TNT complex and the decomposed complex.

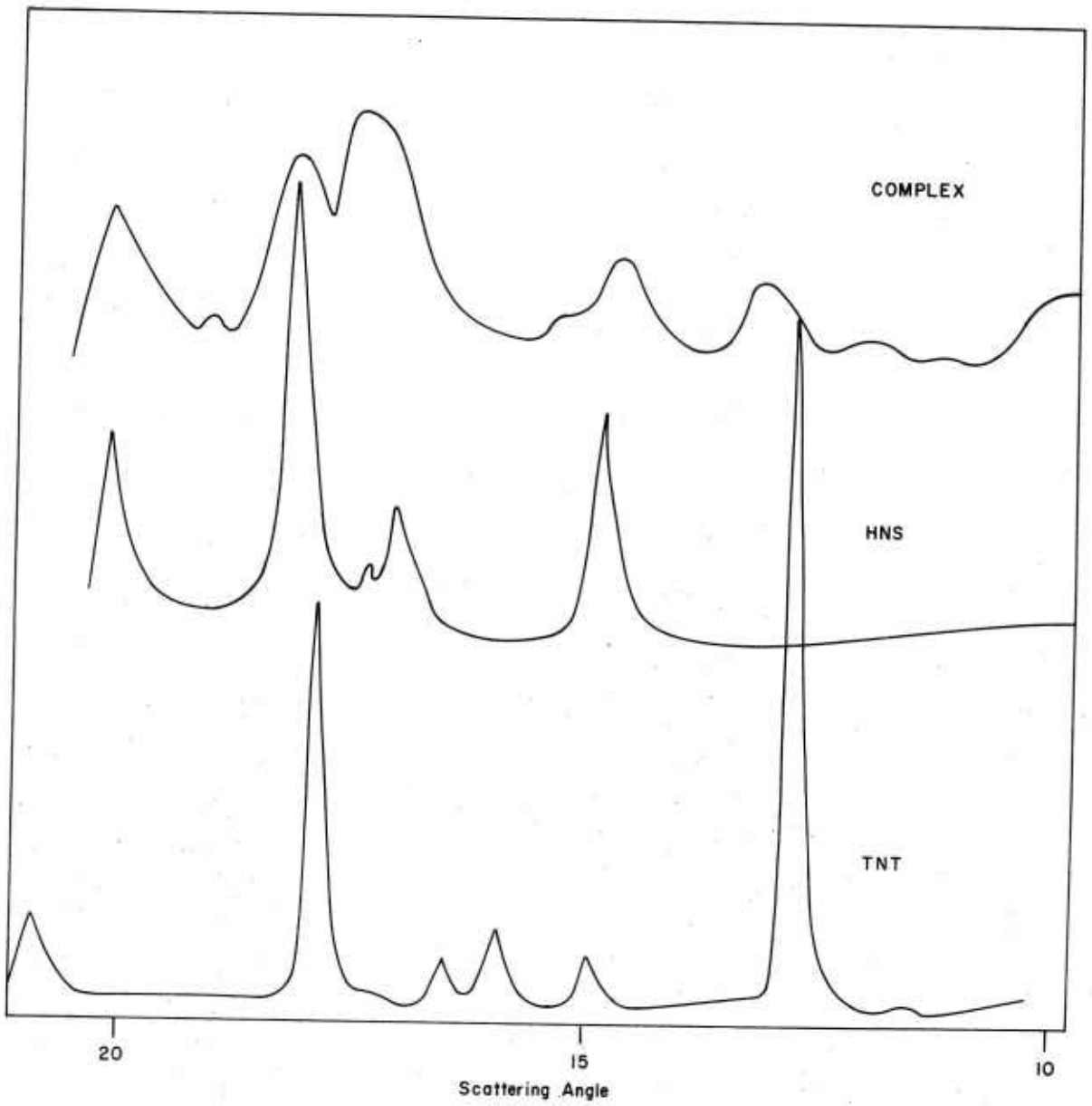

Figure 4. Powder x-ray diffraction patterns of TNT, HNS, and the HNS-TNT complex.

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