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(7) ~~HEAT RESISTANT EXPLOSIVES, EX:~~ ~~PRODUCTION OF GRADE II HNS~~ (C). (8)

(1) Technical rept.,

(10) Francis Taylor, Jr. and R. E. Oesterling.

(11) 26 Aug 65, (12) 9p.

ABSTRACT: A purified high bulk density form of HNS, 2,2',4,4', 6,6'-hexanitrostilbene, has been produced from Grade I HNS in a continuous extraction-recrystallization apparatus using a mixed solvent system of acetonitrile-toluene. Three extractors of one liter capacity have been operated continuously to produce about 100 g/day of HNS with a bulk density of 0.50 g/ml or greater. Both the melting point and the vacuum stability of HNS are improved by this process. This product has been designated "Grade II HNS." Scale-up of the process is considered to be entirely feasible. (C)

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NOLTR 65-142 26 August 1965

This report describes the production of high bulk density 2,2',4,4',6,6'-hexanitrostilbene, Grade II HNS. This heat resistant explosive has been proposed for use in mild detonating fuse and flexible linear shaped charge components for high speed aircraft and space vehicles. The work reported here was carried out under Task RUME-4E-000/212-1/F008-08-11 (Study of Explosives Properties).

J. A. DARE
Captain, USN
Commander

for Albert Lightbody

ALBERT LIGHTBODY
By direction

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ILLUSTRATIONS

INTRODUCTION

The bulk density of 2,2',4,4',6,6'-hexanitrostilbene, HNS, depends on particle size and shape, and these may become critical factors in some applications. Grade I HNS[1] is a light tan powder with small particle size and low bulk density; ranging from 0.25 to 0.30 g/ml. This material has been reported to be quite suitable in end boosters for mild detonating fuse.[2]

Under the polarizing microscope HNS indicates a monoclinic crystal form;[3] however, because of its tendency to recrystallize in clusters of needles which are highly twinned, no single crystals sufficiently large for thorough study have been obtained. The solubility of HNS in most organic solvents is extremely low. Recrystallization from high boiling polar solvents such as nitrobenzene, dimethylformamide and dimethyl sulfoxide tend to give thin needles with bulk densities in the range of 0.20 to 0.25 g/ml.

The goal of this study has been to produce a high bulk density HNS with physical and explosive properties desirable for loading into mild detonating fuse and flexible linear shaped charge systems. Such a product, designated Grade II HNS, has been produced from Grade I HNS by continuous extraction-recrystallization in the apparatus described for the production of high bulk density DIPAM.[4] It was found that acetonitrile-toluene as a double solvent system was effective for HNS in the continuous apparatus. The process combines a low boiling fair solvent with a higher boiling poor solvent. The recrystallization solution is stirred to promote equal rates of growth of the crystal faces, seeded to minimize spontaneous nucleation and refluxed continuously. The condensing solvent is passed through the Grade I HNS in the upper body of the extractor and filtered back into the boiling flask as a continuous feed for the growing crystals of Grade II.

Approximately eight pounds of Grade II HNS have been produced during this study and an evaluation of its explosive properties is currently being done by the Explosion Dynamics Division of these laboratories.

DISCUSSION AND RESULTS

Screening of solvent pairs for use with HNS showed acetone-carbon tetrachloride, tetrahydrofuran-toluene and methyl ethyl ketone-toluene to have extremely slow extraction rates and therefore to be impractical for scaled-up production. Mixtures of acetonitrile-toluene were found to give better rates

and improved crystal shapes. A mixture of 2:1, acetonitrile: toluene, was selected for the original recrystallization experiments using 1000 ml flasks with the apparatus shown in Figure 1. In the body of the extractor, constructed from a 90mm coarse fritted glass funnel, was placed 100 gm of HNS. Both Grade I HNS (Figure 2) and HNS-R (Figure 3), recrystallized from nitrobenzene, were used as starting materials for these experiments and gave identical Grade II HNS products.

The upper body of the extraction apparatus was fitted with a reflux condenser and a ground shaft glass stirrer with Teflon blade. It was found necessary to operate this stirrer only when the filtration rate slowed because of partial plugging of the coarse frit causing a liquid level build-up in the extractor. For all experiments these stirrers were turned off overnight and used only intermittently when attended.

The solvent mixture was placed in the recrystallizing flask, stirred with a Teflon covered magnetic stirring bar, and refluxed for periods of 20 to 50 hours. The initial experiments without seeding gave material with bulk densities between 0.3 and 0.4 g/ml. In subsequent experiments the flask was seeded with 10 grams of the highest bulk density material available. Depending on the total time of operation and the bulk density of the seeding material, conversions to Grade II varied from 30 to 60% and bulk densities varied from 0.4 to 0.62 g/ml (Figure 4).

After 48 hours of operation the solvent mixture became dark in color. It was found that the filtrates could be treated with activated charcoal and re-used to give satisfactory Grade II HNS. Examination of the filtrate, by evaporation, revealed a concentration of 0.2 g of solids per 100 ml of solvent. A thin layer chromatogram of this solid residue showed two spots of approximately equal size. One was identified as HNS and the other as 2,2',4,4',6,6'-hexanitrobibenzyl[1].

All samples of Grade I HNS which were checked by thin layer chromatography (TLC) showed faint spots of the hexanitrobibenzyl as an impurity. None of the Grade II HNS samples showed any impurities by TLC. It was possible to make a rough estimate of the amount of bibenzyl present in a 100 g charge of Grade I HNS after 48 hours in the continuous extractor. Because the hexanitrobibenzyl is much more soluble than the HNS, it can be assumed that nearly all of this impurity would be in solution in the recrystallizing flask. Thus with 950 ml of

solution containing 0.2 g/100 ml, half of which is the bibenzyl, a total of at least 0.95 g was present originally in the 100 gram charge; or approximately a 1% impurity. No other impurities were apparent in the Grade I HNS and it is reasonable that the presence of 1 to 2% of the bibenzyl could cause the lower melting point of Grade I compared to Grade II HNS.

Several of the later experiments using 700 ml of acetonitrile and 250 ml of toluene (2.8:1 ratio) gave the highest bulk density products (Figure 5). No study was made of the minimum amount of toluene required to produce Grade II HNS. Also, no substitutes for toluene were tried. It is possible that other high-boiling, stable solvents would have the desired effect on crystal shape and give high bulk density products.

Operation of the three 1000 ml recrystallizers shown in Figure 1 gave an average of 100 gm of Grade II HNS per day. A blend of 3.8 lbs of Grade II HNS was prepared and designated X-528. This blend had a bulk density of 0.55 g/ml. A minimum bulk density of 0.50 g/ml was established for qualification of HNS as Grade II. Table 1 compares X-528 with Grade I HNS and HNS-R (recrystallized from nitrobenzene).

ACKNOWLEDGMENT

The authors wish to thank Dr. J. M. Rosen for preparing the photomicrographs reproduced here. Impact sensitivities were determined by Mrs. Sarah Duck. Vacuum stability determinations were made by Mr. H. T. Simmons.

FIG. 1 A. GRADE I HNS IN BODY OF EXTRACTOR
B. GRADE II HNS CRYSTALS GROWING IN 1000 ml FLASK
C. 25mm O.D. VAPOR DELIVERY SIDE ARM

FIG. 2 GRADE I HNS, 50X
BULK DENSITY = 0.25 g/ml

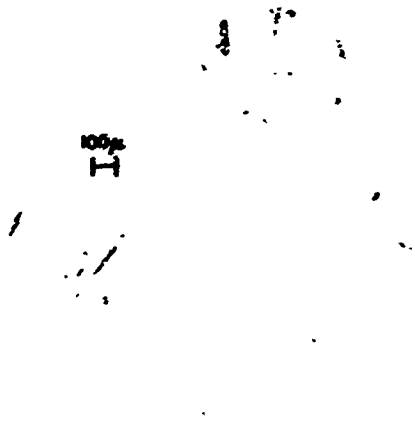

FIG. 3 HNS-R FROM NITROBENZENE: 50X
BULK DENSITY = 0.25 g/ml

FIG. 4 GRADE II HNS 50X
BULK DENSITY 0.50 g/ml

FIG. 5 GRADE II HNS 50X
BULK DENSITY = 0.62 g/ml

[redacted] I

	[redacted] I [redacted] (Fig. 2)	[redacted]-2 (Nitrobenzene) (Fig. 3)	[redacted] II [redacted] X-538 (Fig. 4 and 5)
Bulk Density g/ml	0.25	0.24	0.55
Melting Point (dec.) (uncorrected)	312-314°C	314-316°C	318-319°C
Vacuum Stability cc/g/hr, 260°C	1.68[1]	0.50[1]	0.23
Impact Sensitivity [redacted] Machine Type 12 Tools (Tetryl = 32 cm)	40 cm[1]	45 cm[1]	61 cm

EXPERIMENTAL

CAUTION! In the preparation and processing of heat resistant explosives extreme care must be taken to avoid contamination of the products. The presence of fibers from filter paper or cloth, or contamination by grease, dust or other extraneous matter may seriously affect the heat resistance of these compounds and cause them to be unsuitable for the applications proposed.

All processes described here were carried out in clean glassware. The recrystallizing apparatus with ground joints was assembled without grease. Large fritted glass funnels were used for filtration and drying was done in clean glass dishes in a clean stainless steel forced-air oven. The dried Grade II HNS was stored in wide-mouth brown glass bottles with Teflon cap liners.

Continuous Extraction-Recrystallization, Grade II HNS.

A mixture of 250 ml of toluene and 200 ml of acetonitrile[8] was placed in the 1000 ml boil-up flask of the extraction apparatus. For the initial experiments no Grade II HNS was available for seeding; however, all subsequent experiments were seeded by adding 10 grams of Grade II HNS to the flask. A slurry of 100 g of Grade I HNS or HNS-R in 500 ml of acetonitrile was poured into the upper section of the apparatus and allowed to filter by gravity into the boil-up flask which was stirred with a Teflon covered magnetic bar and heated with a Glas-col mantle.

The upper section of the extractor was fitted with a Teflon blade ground shaft stirrer and a reflux condenser. An electric heating tape was placed around the extractor body to maintain a temperature of 75-78°C, just below the boiling point of acetonitrile. The solvent mixture was refluxed continuously for 24 to 48 hours. The reflux rate was adjusted to avoid a liquid level build-up in the body of the extractor. The liquid level in the boil-up flask was maintained well above the level of contact of the heating mantle to avoid local overheating and possible darkening of the recrystallized product.

After the reflux period the mixture was allowed to cool to room temperature and the Grade II HNS was collected on a vacuum funnel with coarse fritted disc. The product was washed on the funnel with 200 ml of absolute methanol, then dried in a forced air oven at 140°C for 16 to 18 hours. A typical experiment gave 60 g of Grade II HNS with a bulk density of 0.52 g/ml and a melting point of 318°C (dec.).

The initial experiments, without seeding, gave material with a bulk density of 0.35 t 0.40 g/ml. The experiments using 10 g of Grade II HNS for seeding and operating for 48 hours gave a bulk density range of 0.50 to 0.62 g/ml. After correcting for the weight of seeding, the conversions to Grade II HNS ranged from 50 to 60%. The percent conversion could be increased by extending the extraction time; however, the extraction rate decreased when smaller amounts of material remained in the extractor. Thus, it was arbitrary and more a matter of convenience as to when the operation should be discontinued and the product filtered. Any material remaining in the extractor was used in the next experiment.

Recovery of Solvents.

The acetonitrile-toluene solvent mixture became dark brown in color after a 48 hour extraction-recrystallization period with an original charge of 100 g of Grade I HNS. The filtrate, 950 ml, was treated with 10 g of Darco G-60 activated charcoal then filtered twice through glass fiber filter pads. This solution was used again in the next continuous recrystallization and gave similar, good quality Grade II HNS.

An aliquot of 100 ml of a charcoal treated acetonitrile-toluene filtrate was evaporated to dryness to give 0.20 g of residue indicating the loss of material due to solubility to be 1.9 g/100 g experiment. Thin-layer chromatographic analysis of this residue was carried out on Silica gel-G plates (Research Specialties Co., Richmond, Calif.). The sample was applied to the plate as a saturated acetone solution, developed with benzene and visualized by spraying with an alcoholic solution of potassium hydroxide. Two spots of approximately equal size were present. One spot was identical to that for pure HNS and the other to pure 2,2',4,4',6,6'-hexanitrobibenzyl.

Because each re-use of the solvent mixture allows a slight increase in the concentration of the hexanitrobibenzyl impurity, it is recommended that the acetonitrile be recovered by distillation where practical, and that the toluene and residues be discarded.

Bulk Density Measurement.

A ten gram sample of dry HNS was introduced into a clean, dry 50 ml graduated cylinder through a 50° glass funnel of 65 mm top diameter with a one inch stem of about 11 mm I.D. Low bulk density samples were sifted slowly through the funnel to avoid.

plugging. The cylinder was held securely on the bench top and tapped lightly several times with a wooden pencil to level the powder surface. The volume was read to the nearest milliliter and divided into the sample weight to give bulk density in grams/ml.

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1. Explosives, Heat-resistant
2. Hexanitro-stilbene
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II. Taylor, Francis H., jr.
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