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PROPERTIES OF BIS(2,2-DINITROPROPYL)ACETAL AND BIS(2,2-DINITROPROPYL)FORMAL, EUTECTIC MIXTURE

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nitro compound

I. INTRODUCTION

The eutectic composition of bis(2,2-dinitropropyl)acetal and bis(2,2-dinitropropyl)formal (BDNPA/F), a 50/50 wt.% mixture, has received considerable attention as a plasticizer in Plastic Bonded Explosives. Both LLL and LASL have looked extensively at the nitro plasticizer, BDNPA/F, for use in improved PBX formulations. BDNPA/F is somewhat energetic, has good thermal and chemical stability, and is a relatively good plasticizer for thermally stable polymeric binders such as poly 2,2-dinitropropylacrylate (PDNPA) and Estane*. The collected properties of BDNPA/F are tabulated below. The data was collected from such sources as Aerojet General Corp., Naval Ordnance Lab. and Naval Ordnance Station.

II. PROPERTIES OF PDNPA/F

1. Specification

WS-1141A Amendment 1, January 22, 1964, "Weapons Specification bis(2,2-dinitropropyl)acetal - bis(2,2-dinitropropyl) formal, mixture of." Polaris Fleet Ballistic Missile, Department of the Navy, Bureau of Naval Weapons.

2. Physical and Chemical Properties

Composition: Bis(2,2-dinitropropyl)acetal - bis(2,2-dinitropropyl)formal, a mixture of in the weight ratio of 45/55 to 55/45.

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"Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Atomic Energy Commission to the exclusion of others that may be suitable."

Appearance: A straw-colored liquid.

Freezing point, °C: Below -5, large tendency to supercool, (see phase diagram, Figure 1)

Boiling Point: Approximately 150°C at 0.01 mm HG (determined in a 2 in. Rodney Hunt wiped-film still.)

Refractive Index at 25°C: 1.462 - 1.464.

Density, g/ml at 25°C: 1.383 - 1.397.

Viscosity:

Temperature, °C	Viscosity, cp
66	20
54	40
43	65
32	130
21	260
10	1135

Heats of Formation and Fusion(1)

BDNPF:

ΔH_f° (liquid) = -45.72 kcal/100 g (ρ = 1.415 g/cc)

ΔH_f° (solid) = -47.51 kcal/100 g (ρ = 1.43 g/cc)

ΔH^{298}(fusion) = 5.6 ± 1.2 kcal/mole

BDNPA:

ΔH_f° (liquid) = -47.03 kcal/100 g (ρ = 1.343 g/cc)

ΔH_f° (solid) = -48.45 kcal/100 g ($\rho \sim$ 1.36 g/cc)

ΔH^{298}(fusion) = 4.6 ± 0.6 kcal/mole

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(1) JANAF Thermochemical Data on Propellant Ingredients.

Plasticization

The plasticizing ability of BDNPA/BDNPF eutectic in 2,2-dinitropropylacrylate, polymer is given by:

$$1000\ Tg\ (°K) = 5.718 - 2.350\sqrt{W_2}$$

where Tg = glass transition temperature

W_2 = weight fraction of plasticizer

Solubility

1. Insoluble in water,
2. Sparingly soluble in aliphatic hydrocarbons
3. Soluble in benzene and toluene
4. Completely miscible with methanol, acetone, ethylacetate, methylenechloride and ethylene-chloride.

Stability

Low temperature storage tests on BDNPA/F mixtures were performed. Based on these results no significant changes are expected in the composition of nitroplasticizers when subjected to freezing and thawing which occur during temperature extremes.

High temperature stability has been found to be very good, as reported by the Naval Ordnance Laboratory.(2)

Hydrolytic stability is excellent. Prolonged heating of separate components BDNPA and BDNPF at 120°F resulted in no evidence of hydrolysis. The materials are thought to be resistant to hydrolysis because of their low solubility,

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(2) Private communication from H. Heller, Naval Ordnance Laboratory.

particularly of the acetal, in water. The hydrolysis effect might be heightened in the presence of organic solvents.

Although the long term stability is thought to be excellent, a stabilizer is added as a precaution. The stabilizer is Neozone D, phenyl naptha β amine, and is present in 0.16% concentration. Its principal role is to prevent acidic buildup which, if it took place, could catalyze further decomposition. (A small percentage of acetic acid impurity is sometimes present.) Because of the presence of Neozone D, the BDNPA/F gets darker with time, turning from straw colored to coffee brown.

The chemical stability of the BDNPA/F is thought to be excellent. Only strong alkali or reducing agents attack it. It is a poor solvent for most materials of construction.

3. Energy

From cylinder test experiments we have established the contribution of the BDNPA/F nitro plasticizer to the energy of an HMX based PBX. For each volume percent of HMX replaced by the BDNPA/F, the energy of the PBX would be decreased 0.75%. For comparison, bis(2,2-dinitro-2-fluoroethyl)formal (FEFO) decreases the energy 0.3% and Viton+ decreases the energy 1.0% for each volume percent of HMX they replace.

+ Trade Mark for a fluoroelastomer produced by duPont Chemical Co.

4. Sensitivity

4.1 Shipping Classification

Mixtures of BDNPA and BDNPF have an ICC shipping classification of "Propellant Explosives (liquid), Class B." Material is shipped in polyethylene bottles or in steel drums with polyethylene liners.

4.2 Detonability

The blend of BDNPA and BDNPF in a steel sleeve, 8 in. in diameter by 32 in. long will not detonate when subjected to a number 8 blasting cap and 30 grams of tetryl booster. However, the material will partially explode under these conditions. One of the components, BDNPF, in a solid state, will detonate when subjected to the 30 gram tetryl booster test. These tests were conducted at 35°F with approximately 80 to 90 lbs of test material contained in a 8 in. O.D. by 32 in. long schedule 40 iron pipe sleeve and initiated by a 30 gram tetryl booster. The specific results of the tests are tabulated in Table I below.

Explosive Classification Tests

Sample	Temperature	Results
BDNPF	35°F	Two positive
	35°F	Three negative (J2 cap alone)
BDNPA	35°F	Five negative (including 4 partials)

Sample	Temperature	Results
50/50 BDNPA/ BDNPF	35°F	Four negative (including 4 partials)
	0°F	One negative
		Negative with a No. 8 blasting cap[a]

[a] 3.5 in. diameter by 7 in. long steel sleeve.

4.3 Propagation Tests

Tests to determine the propagation of fire and detonation in a solution of 50/50 BDNPA/BDNPF were conducted.

Propagation and Extinguishment of Fire

The propagation of fire in tubes and in open pans at ambient and elevated temperatures and the most suitable means for extinguishing the resulting fires were investigated. It was determined that fire would not propagate in the 1 in. or 1/2 in. diameter tubes, even though the samples were heated as high as 210°F. The nitroplasticizer cannot burn as a mono propellant, and air is required to support combustion. Also it is believed that the nitroplasticizer must be in a vapor state before burning will occur. The test results also indicated that the combustion of the nitroplasticizer would not transit from deflagration to a detonation or violent explosion under the test conditions.

For the investigation of satisfactory modes of extinguishment of fires, a 1 in. layer of BDNPA/BDNPF was placed in a shallow pan (20 inches x 20 inches x 3 inches). The ignition of the mixture was accomplished by a layer of acetone or a gasoline ignited by a squib. Of 3 various methods of extinguishment, it was found that a water fog was the most satisfactory even though extinguishment by means of a CO_2 fire extinguisher was quite rapid. The use of a water stream was less satisfactory even though extinguishment was achieved.

4.4 Propagation of Detonation

Detonation propagation tests of the 50/50 BDNPA/BDNPF solution were performed to provide information concerning the characteristics of this mixture during distillation, in which the material is exposed to elevated temperatures (100°F and 200°F) under ambient and reduced pressure conditions. The tests were conducted in 1/2 in. O.D. (0.025 in. wall) and 1 in. O.D. (0.035 in. wall), type 304 stainless steel tubes in order to simulate conditions of actual use. The desired heating was obtained through the use of electric heating tapes wound around the sample tubes with the temperature measured by means of thermocouples inserted directly into the test liquid. A detonator assembly was attached to the test assembly in such a manner as to preserve the pressure seal at reduced pressures.

The specific results of the test are tabulated as follows:

Sample Size	Temperature	Results
1" x 6" long[a]	ambient	6 negative (incl. 1 partial)
1" x 8" long	ambient (25" vacuum)	5 negatives
1" x 6" long	160°F	6 negatives and 4 positives
1/2" x 6" long[b]	200°F	6 negatives and 1 positive

[a] 1" diameter by 2", 33 gram composition C-4 booster.

[b] 1/2" diameter by 2", 8 gram composition C-4 booster.

The test results show that the elevated temperatures increase the detonability of the material; and in four out of 10 tests at 160°F in the 1" tube, detonations occurred. For the 1/2" diameter tests at 200°F, one detonation occurred in seven tests. At ambient temperature and pressure, no detonations had occurred. The application of vacuum did not affect the detonability. These tests results serve to indicate that the material is not completely inert, and adequate precautions must be taken.

4.5 Toxicity

Accumulated experience of over 5 years and several (up to 5) million pounds handling experience by Aerojet General Corp. and Naval Ordnance Station has yielded no toxicological incident. This applies to the prime

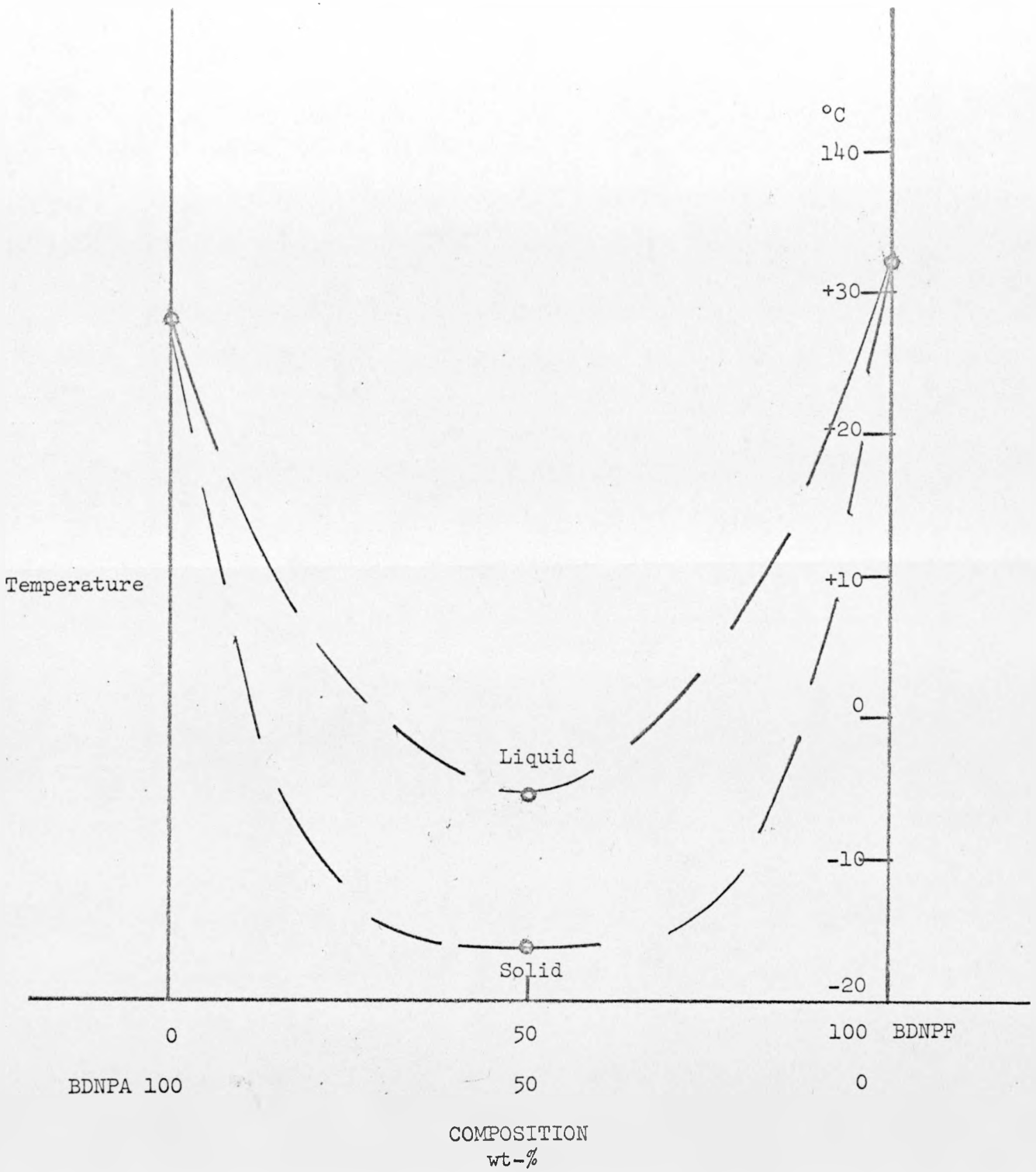
intermediate, 2,2-dinitropropanol (DNPOH) and each of the components of the final eutectic mixture, BDNPA and BDNPF. There have been no incidents of dermatitis; no people sensitized; no allergic reaction; no corrosion causing secondary incidents; no headaches and no congestion from inhalation. Normal laboratory practice over several years has yielded no incident of a toxicological nature. Simple precautions of wearing gloves with solvents and avoiding gross contact or injestion are the only warnings required.

Preliminary animal screening tests on the components of the nitroplasticizer indicate:

BDNPF - By intraperitoneal administration - no effects were seen in rats at the 100 mg per kg level. Gross pathological examination two (2) weeks subsequent to intraperitoneal administration revealed no abnormalities. Direct irritant effects to eye and skin were absent.

BDNPA - No effects were found in rats or guinea pigs at the level used with BDNPF.

Figure 1. BDNPA/F PHASE DIAGRAM



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