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MEMORANDUM REPORT ARLCD-MR-80001

GRAIN MODIFICATION ADDITIVES FOR TNT AND
ITS COMPOSITIONS. A PRELIMINARY SCREENING
VIA SUPPRESSION OF SUPERCOOLING

S. PORTNOY

JUNE 1980



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER
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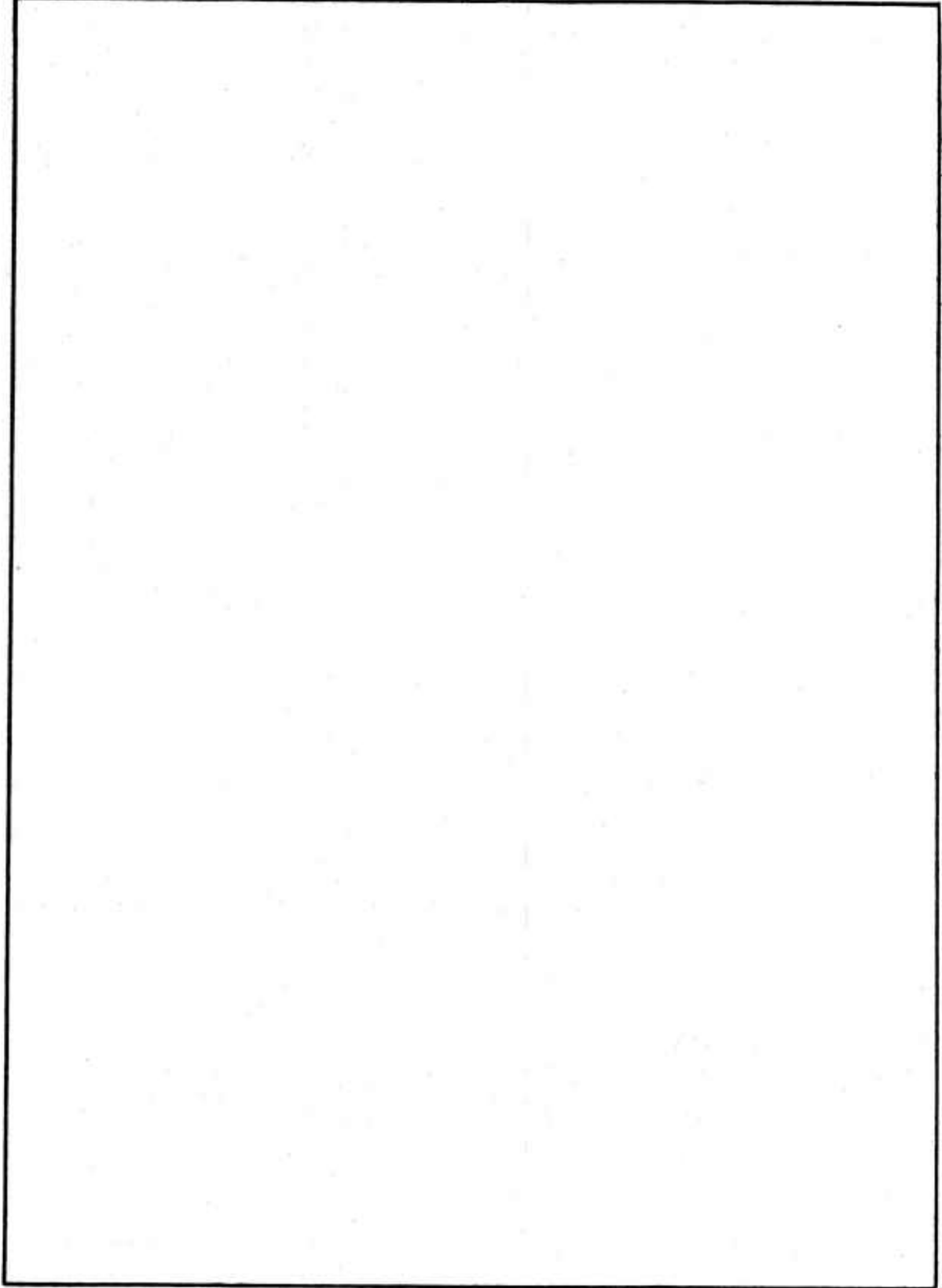
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A preliminary search for alternatives to 2,2',4,4',6,6'-hexanitrostilbene, as grain modification additives for TNT and its compositions, has been made. Screening of candidate additives was based upon the determination, via differential scanning calorimetry (DSC), of the suppression of supercooling by 0.5% of additive. A cast of good quality was obtained with 5-nitrobarbituric acid trihydrate.		

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INTRODUCTION

One of the difficulties encountered in casting 2,4,6-trinitrotoluene (TNT) or TNT-containing explosives is the columnar growth of large TNT crystals. This can produce fracture planes throughout the cast, causing cracks. The phenomenon has been attributed to supercooling of the melt and subsequent slow initial crystallization at the melt surface by insufficient numbers of crystal nuclei.

Casts of TNT having a matrix of very fine, randomly oriented grains have been achieved by the "creaming process." This involves the addition of solid TNT, with stirring, to the melt prior to casting, and results in the solidification of the slurry of solid and liquid TNT into the desired product. The need for fine temperature control and the high viscosities encountered in this process led to the search for other methods of grain modification.

The use of nucleating agents proved to be most promising. By far, the most efficient additive found to date is 2,2',4,4',6,6'-hexanitrostilbene (HNS), the use of which is covered by a Bofors patent (ref 1). Small additions (less than 2%) minimize supercooling of TNT, give larger percentages of the monoclinic form, and produce fine casts (ref 2). In the absence of HNS, more of the orthorhombic polymorph is present. The patent describes two methods for modifying the TNT cast with HNS; a double thermal cycling process and a single stage process. It has been reported that the latter gives casts of poorer quality (ref 3) or shows no improvement over casts without HNS (ref 4).

Recent work (ref 3,4) has brought to light evidence of complex formation between TNT and HNS (2:1) and that this complex is the actual nucleating and grain modification agent, and not HNS alone. Parry and Thorpe (ref 4) have isolated the crude complex and demonstrated its existence via Differential Scanning Calorimetry. This work was confirmed on pure complex (ref 5), the free TNT having been removed in a modified sublimation apparatus at 80°C/4-5.3 pascals.

The presence of the complex, however, may not be required for good casting of TNT. Recent work (ref 6) has shown that good casts can also be produced by adequate dispersal of HNS in the melt, either by ultrasonic mixing or by dissolution.

In view of the present high cost and low availability of HNS, the patent restriction on its use, and the cost of the thermal cycling necessary for the Bofors process, a program was initiated,

excluding consideration of possible complex formation, to obtain alternative grain modifier additives. One approach was based upon the similarity of crystal structure of HNS and TNT (ref 2). A computer search of all x-ray and neutron diffraction data of organic and organo-metallic compounds having the same or similar space group symmetry and similar lattice dimensions as HNS was made by the National Bureau of Standards (NBS) via use of the NBS-Cambridge University Reduced Cell Search Program.

The initial computer print-out, based upon lattice dimensions within a specified range, provided a list of possible alternatives to HNS, as well as the means for determining whether the similarity of the crystal structure between HNS and monoclinic TNT is an important factor in the excellent nucleating ability of HNS. A parallel approach involved substituent and/or ring modification of compounds that showed activity in suppressing supercooling and tested as additives.

Recent work (ref 7,8) indicates that nucleating agents such as HNS minimize supercooling of TNT and produce a matrix of fine, randomly oriented grains. The efficacy of these additives have been generally studied by observing the supercooling of melts in the hot stage of a microscope or by use of differential scanning calorimetry (DSC). DSC was chosen in this work as the method of screening.

EXPERIMENTAL PROCEDURE

Preparation of Sample

To 995 mg of TNT, recrystallized from isopropyl alcohol, was added 5 mg of the candidate additive. The mixture was slowly heated in an oil bath until liquification, after which slow heating was continued with magnetic stirring until dissolution was attained at a temperature of between 100°C and 130°C (approximately one hour). Heating and stirring were continued for another hour at that temperature and then the mixture was poured into a platinum dish heated to 98°C in an oven. The oven was immediately shut off and the dish removed after five minutes and allowed to cool at room temperature until solidification. The sample was carefully ground to a fine powder and stored overnight in a desiccator.

Determination of Degree of Supercooling

Supercooling was determined on a Perkin-Elmer DSC 1B instrument. Settings were scan speed (5°C/min), chart speed (20 mm/min), range (4 or 8) and pen range (20mV). Perkin-Elmer Sample Pan Kit No. 219-0062 was used with a suitable lid-crimping instrument. Vanillin and azobenzene were the calibrants used.

A sample was heated from 30°C to 82°C, held at 82°C for three minutes and cooled at the same scan rate until the appearance of the TNT exotherm. Supercooling was determined from the difference in endo- and exotherm peak temperature values. A sample containing 0.5% hexanitrobibenzyl (11) was used to check the operation of the DSC. At least five runs were made per determination.

DISCUSSION

The compounds tested in this preliminary screening of grain modification additives are listed in table 1. Untreated TNT, and TNT containing 0.5% HNS were included for comparison purposes. Hexanitrooxanilide (12) was previously examined by Davies and Lee (ref 7) and was found to suppress supercooling and to have an effect as a nucleant. It did not appear, however, to produce casts of the same quality as those obtained with HNS (ref 9).

To date, under the conditions used in this work to determine supercooling, ten new additives were found to suppress supercooling, although for some it was very slight. TNT and 0.5% 5-nitrobarbituric acid trihydrate (27), the most active of this group, gave a cast of good quality. Average TNT crystal diameter was 0.09 mm. In comparison, a cast similarly made with HNS gave a value of 0.05 mm. A disclosure on this additive has been submitted for filing with the US Patent Office.

CONCLUSIONS

Examination of table 1 indicates possible types of compounds worth pursuing in a continued screening program. Such types are as follows:

1. Barbituric acid derivatives unsubstituted on the ring nitrogens and having electron-withdrawing substituents in the 5-position.
2. Procurement or synthesis of 5,5'-dinitro-5,5'-bibarbituric acid. This is based on the relatively good suppression of supercooling (13.6°C) by the 5,5'-dihydroxy analogue (28) in conjunction with the decrease of supercooling (4.8°C) by 5-nitrobarbituric acid trihydrate (27) in comparison to 5-hydroxybarbituric acid (26).
3. Other heterocyclics containing ring NH and CO and substituted as above such as 5-nitrouracil, 5-nitrothiobarbituric acid, etc. The cooperative program with NBS for computer search for alternatives to HNS should also be continued.

Table 1. Supercooling of TNT containing 0.5% nulceant

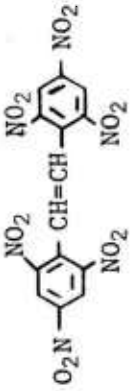
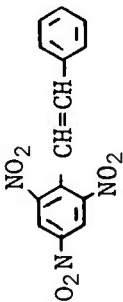
No.	Additive	Name	M.P.(°C)	Super-cooling (°C)
1.	0	-	-	20.2
2.		Hexanitrostilbene	316	7.2
3.		2,4,6-trinitrostilbene	152	>25
4.		Tetraphenylethylene	222-224	>25
5.		Tetra-p-nitrophenylethylene	298-300	24.2
6.		<u>trans-1,2-Bis(4-pyridyl)</u> ethylene	150-153	20.5

Table 1. Cont'd

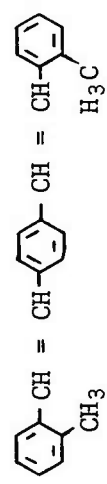
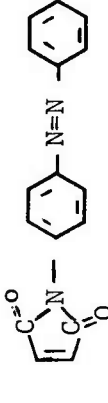
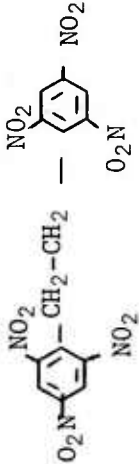
No.	Additive	Name	M.P. (°C)	Super-cooling (°C)
7.		Bis(MSB)	178-179	24.8
8.		4-nitrochalcone	158-160	24.0
9.		Curcumin	176-177	23.4
10.		p-phenylazomaleinanil	162-165	19.8
11.		Hexanitrobiphenyl	218-220	15.6

Table 1. Cont'd

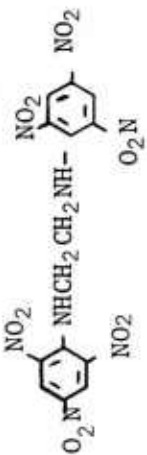
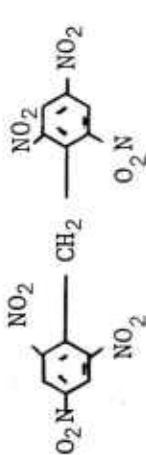
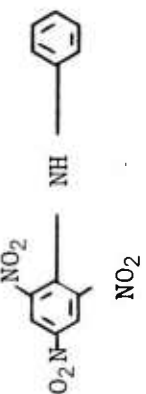
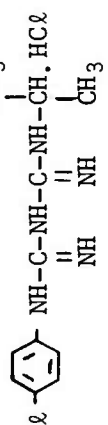
No.	Additive	Name	M.P. (°C)	Super-cooling (°C)
12.		Hexanitrooxanilide	300-315	10.8
13.		N,N'-dipicryl-ethylenediamine	230	>25
14.		Hexanitro-benzophenone	278, dec	23.7
15.		Dipicrylmethane	232, dec	>25
16.		2,4,6-trinitro-diphenylamine	179-180	23.3
17.		1-(p-chlorophenyl)-5-isopropylbiguanide hydrochloride	248-50	23.0

Table 1. Cont'd

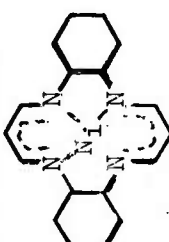
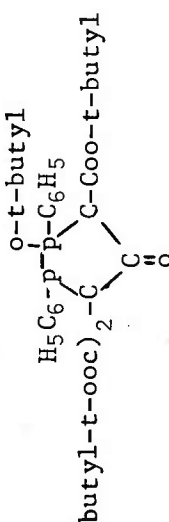
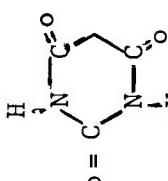
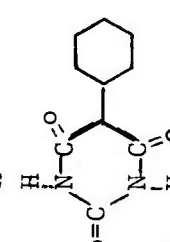
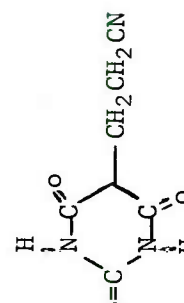
No.	Additive	Name	M.P. (°C)	Super-cooling (°C)
18.		dibenzo [b,i] [1,4,8,11] tetraaza [14] annulenenickel (II)	>350	23.7
19.		1-t-butoxy-1,2-diphenyl-3,3,5-tricarbo-t-butoxy-1,2,-diphosphacyclopentene-5-one	88-91	23.8
20.		Barbituric acid	252, dec	18.1
21.		5-cyclohexyl barbituric acid	252-4, dec	24.1
22.		5 [1-(2-cyanoethyl)] barbituric acid	195-7	>25

Table 1. Cont'd

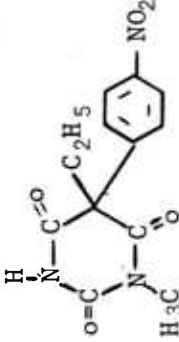
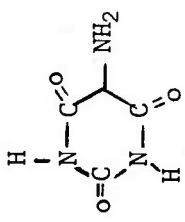
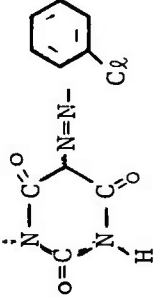
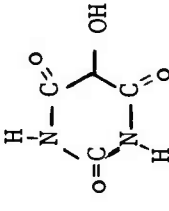
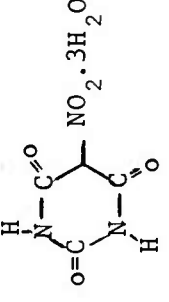
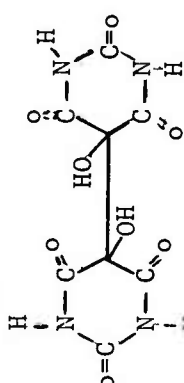
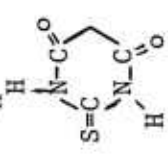
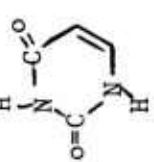
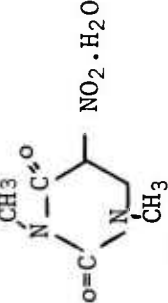
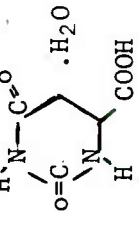
No.	Additive	Name	M.P. (°C)	Super-cooling (°C)
23.		1-methyl-5-ethyl-5-(p-nitrophenyl)-barbituric acid	158-61	>25
24.		5-aminobarbituric acid	>400	>25
25.		o-chlorophenylazo-5-barbituric acid	312, dec	>25
26.		5-hydroxybarbituric acid	224	17.0
27.		5-nitrobarbituric acid trihydrate	180-181	12.2

Table 1. Cont'd

No.	Additive	Name	M.P. (°C)	Super-cooling (°C)
28.		5,5'-dihydroxy-5,5'-bibarbituric acid (alloxantin)	210, dec	13.6
29.		2-thiobarbituric acid*	244, dec	15.3
30.		Uracil	335, dec	>25
31.		1,3-dimethyl-5-nitrouracil monohydrate	155-157	16.0
32.		Orotic acid monohydrate	>300	14.9

*May exist as the 4,6-dihydroxy-2-mercaptopyrimidine tautomer in the screening sample.

Table 1. Cont'd

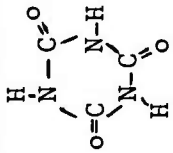
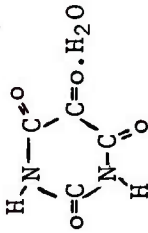
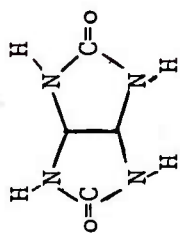
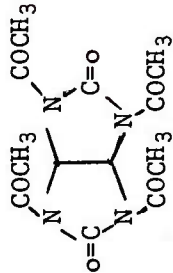
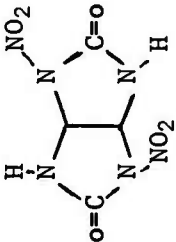
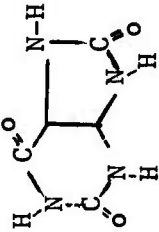
No.	Additive	Name	M.P. (°C)	Super-cooling (°C)
33.		Cyanuric acid	360	15.9
34.		Alloxan	243, dec	>25
35.		Glycoluril	>300	16.6
36.		Tetraacetylglycoluril	231-232	>25

Table 1. Cont'd

No.	Additive	Name	M.P. (°C)	Super-cooling (°C)
37.		Dinitroglycoluril**	253, dec; exp	>25
38.		Uric acid	>300	19.9

**Position of two nitro groups undetermined.

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