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SPHEROIDAL PROPELLANT STABILIZER STUDIES

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The stabilization effectiveness of diphenylamine, ethyl centralite and arkadit II is being evaluated in spheroidal propellant formulations ranging from 0 to 35% nitroglycerin. German stability, stabilizer depletion rates, pH, NO_2/NO_3 ion chromatography and microcalorimetry are being used to assess stabilizer effectiveness.

INTRODUCTION

In a joint effort sponsored by the U. S. Army Mortar Program Management Office; the U.S. Army Research Development and Engineering Center (ARDEC) and St. Marks Powder are evaluating the performance of various stabilizers in spheroidal propellants.

A matrix of nine propellant formulations is being extensively analyzed to evaluate and compare the stabilizing effects of three stabilizers. Results to date are presented here.

SAMPLES MATRIX

Three basic propellant formulations were selected, and each was manufactured with the three selected stabilizers for a total sample matrix of nine propellants. The three formulations selected are:

I. Single base
II. Low nitroglycerin double base deterred
III. High nitroglycerin double base undeterred

Each of the three formulations was stabilized with diphenylamine (DPA), ethyl centralite (EC) and akardit II (AK).

The nominal compositions for each of these three formulations are summarized in “Table 1”. The sample matrix nomenclature used through out this report is depicted in “Table 2”.

Table 1. Nominal compositions of propellants formulations

	Formulation		
	I	II	III
Nitrocellulose	96	90	62
% N in Nitrocellulose	13.1	13.1	13.1
Nitroglycerin	0	10	35
Deterrent	0	5.0	0
Moisture & Volatiles	1.5	1.0	.5
Potassium Salts	1.0	2.0	1.0
Stabilizer (DPA, EC or AK)	1.3	1.3	1.3
All values in weight %.			

Table 2. Sample matrix nomenclature

Formulation	Stabilizers		
	DPA	EC	AK
I – Single base	ID	IE	IA
II – Low NG Double Base Deterred	IID	IIE	IIA
	IIID	IIIE	IIIA

EVALUATION TESTS

The sample matrix is being subjected to a battery of tests to evaluate the stabilization properties of the three stabilizers for the varying formulations. The tests are being conducted at ARDEC, NSWC–Crane and/or St. Marks Powder.

Tests conducted and summarized here include:

- German Heat Tests – A reference test for propellant stability.
  – Salmon Pink Time (135°C. for single base and 120°C. for double base samples).
  – Time to Explosion at (135°C. for single base and 120°C. for double base samples).
- Stabilizer Depletion Rate – Stabilizer depletion rates are being measured at 65°C. over a period of 12 weeks.
- Microcalorimetry – Heat flow microcalorimetry measurements are being made at 50°, 65.5° and 80°C.
- pH and NO_3/NO_2 ion concentrations.

TEST RESULTS

To date, tests have been completed on the DPA and EC stabilized samples (ID, IID, IE and IIE). Evaluation of the high nitroglycerin undeterred samples is partially completed, and evaluation of the akardit stabilized samples is planned for 2001.

German Heat Tests

Salmon pink test results are shown in "Table 3". All samples tested exceeded the 300-minute minimum explosion time criteria.

Table 3. Salmon pink test results

SAMPLE	S. P. TEMP. (°C)	S. P. TIME (MINUTES.)
ID	135	55
IE	135	40
IID	120	80
IIE	120	65
IIID	120	55
IIIE	120	45

Stabilizer Depletion Rates

Stabilizer depletion rates at 65.5°C for the DPA and EC stabilized samples were measured for a period of 12 weeks at St. Marks Powder and ARDEC. The St. Marks Powder results are summarized in "Figures 1 and 2". ARDEC results show similar depletion rates.

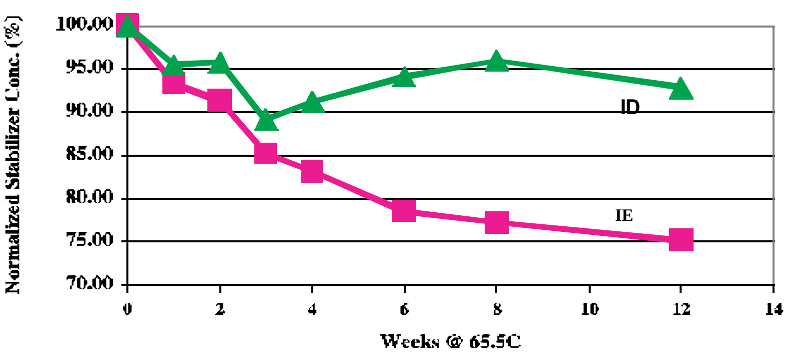

Figure 1. 65.5°C stabilizer depletion rates for the single base formulation – samples ID and IE.

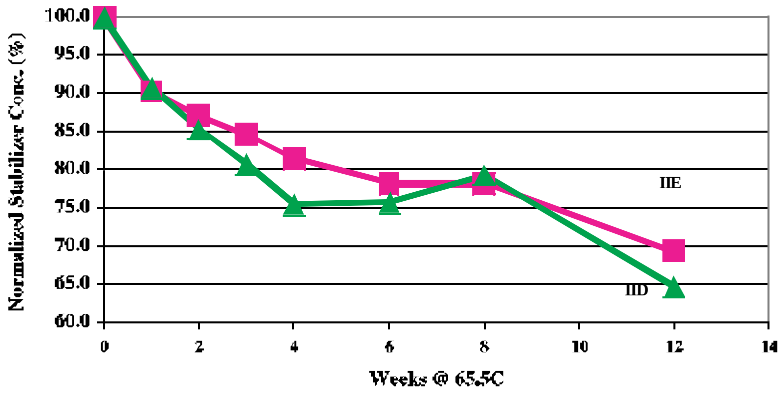

Figure 2.65.5°C stabilizer depletion rates for low the NG, deterred double base formulation-samples IID and IIE.

DPA is reported as the combined total of DPA and daughter products using the formula:

$$DPA = DPA + .854\ NNDPA + .790\ (2nDPA + 4nDPA)$$

Values were normalized to % using the formula:

$$\text{Normalized \% Stabilizer} = \text{Stabilizer (t)/Stabilizer } (t_o) * 100\%$$

Analyses were conducted using high-pressure liquid chromatography (HPLC).

pH and NO_3/NO_2 Ion Concentrations

Samples conditioned at 65.5°C storage were subjected to pH, and NO_2 and NO_3 ion concentration analysis. Samples were stored for eight weeks at 65.5°C and analyzed at weeks 0, 1, 2, 3, 4 ,6 and 8.

All samples were held and analyzed for pH at the same time. The procedure was adapted from an NSWC-Crane method for testing pH of propellants after accelerated aging storage. The samples were ground to increase surface area and extracted with deionized water for 24 hours. The pH was taken directly from the water/propellant slurry.

No differences in pH were noted for the EC and DPA stabilized high NG formulations. However the single base samples showed distinct pH differences between the EC and DPA stabilized samples. Likewise the NO_2 anion concentration (measured by chromatography) showed a marked difference of NO_2 presence between the DPA and EC stabilized single base propellants.

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"Figures 3 and 4" depict the pH and NO_2 comparison for the single base propellants. The DPA stabilized formulation shows higher pH and lower NO_2 concentration as compared to the EC stabilized formulation. The pH drop and the presence of increased levels of NO_2 should be considered negative stability indicators.

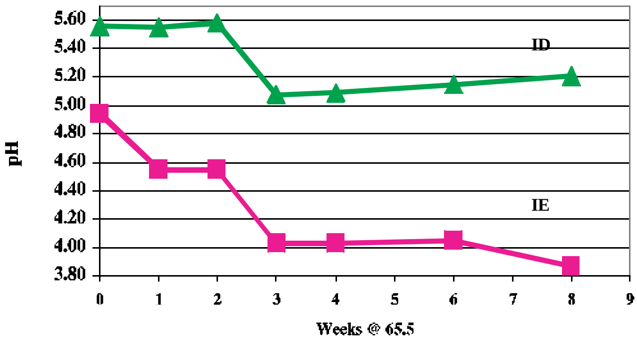

Figure 3. pH shift as a function of 65.5°C storage time for the single base formulation.

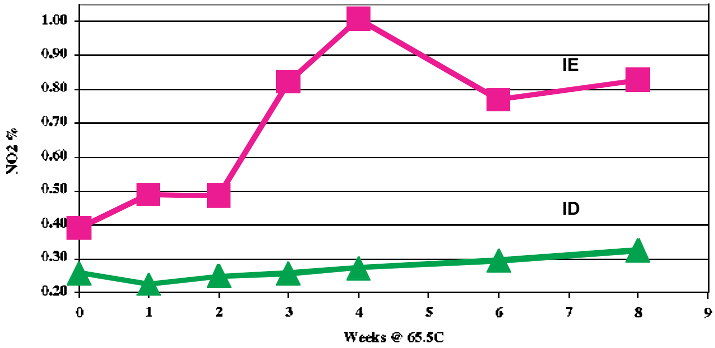

Figure 4. NO_2 ion concentration as a function of 65.5°C storage time for the single base formulation.

NO_3 analysis did not yield conclusive results for the single base samples, and the double base sample results were skewed by the presence of NG, which interfered with NO_2 and NO_3 quantification.

Microcalorimetry

Microcalorimetry provides a measure of the total heat generation rate of a material. Propellant chemical stability is determined by the rates of denitrification reactions of nitrate esters. If these denitrification reactions are the predominant source of heat generation in aging propellant, then microcalorimetry can provide a good indication of relative stability.

Extensive heat flow microcalorimetry analyses are being conducted by NSWC-Crane Division. Heat generation rates are being measured at 50°C, 65.5°C and 80°C, to gather information about the relative stability of the samples.

Microcalorimetry measurements for the single base samples ID and IE show similar heat flows at 50°C. The 65.5°C tests show the DPA stabilized sample (ID) has a lower rate of heat generation for the first 10 weeks. After approximately 10 weeks the heat generation curves for samples ID and IE intersect, and the EC stabilized sample shows a lower rate of heat generation at 65.5°C. Results at 80°C show similar trends as those at 65.5°C.

The low nitroglycerin deterred samples (IID and IIE) show almost equivalent heat generation rates at the three temperatures tested (50°C, 65.5°C and 80°C.).

"Figures 5 and 6" depict the total heat generation as a function of time at 80°C. for the three formulations.

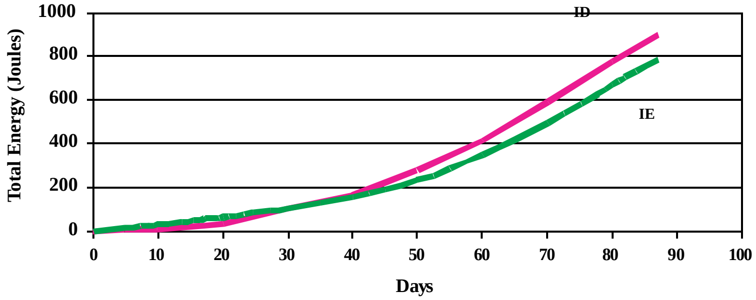

Figure 5. Total energy released at 80°C. As a function of time for the single base samples ID and IE.

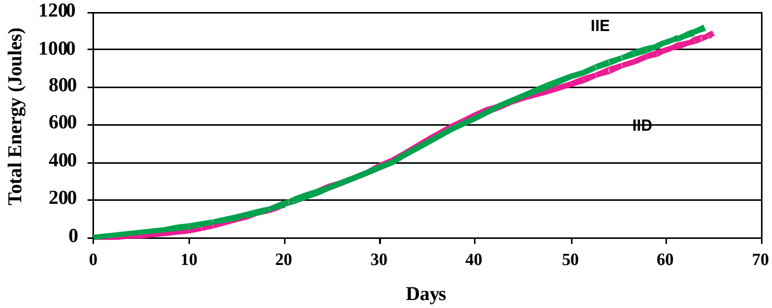

Figure 6. Total energy released at 80°C. As a function of time for low nitroglycerin deterred samples IID and IIE.

CONCLUSIONS

All data on the stabilizer test matrix evaluation is not available. As testing is ongoing, no definitive conclusions have yet been drawn.

However from the available data the following observations and preliminary conclusions can be drawn.

- In multiple sampling of all formulations, the EC stabilized samples demonstrate a lower Salmon pink time than their DPA stabilized counterparts.
- With the exception of the microcalorimetry test, all of the stability indicators evaluated (salmon pink time, pH, ion chromatography and stabilizer depletion rates) point to DPA as more suitable for single base formulations than EC. No conclusions are drawn from the microcalorimetry results of samples ID an IE, as further interpretation and analyses are required.
- For the low NG deterred formulation (samples IID and IIE) the stability indicators evaluated do not show significant differences between the stabilization effects of DPA and EC.

ON-GOING/FUTURE WORK

Work is ongoing to complete the testing of the sample matrix described in “Table 1”:

- Completion of the high nitroglycerin and akardit samples (IA, IIA, IIIA, IIID and IIIE) evaluation is planned for 2001.
- Ballistic evaluations will be conducted with selected samples.

Future areas of planned work include an evaluation of the effects of potassium flash suppressants (KNO_3, K_2SO_3) on the chemical stability of single and double base propellants.

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