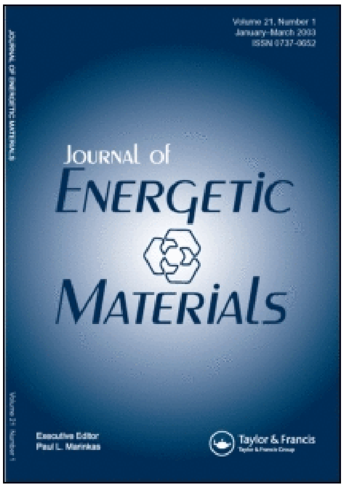
This article was downloaded by:
On: *16 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Development of reverse phase HPLC techniques for determination of stabilizer depletion rates in high energy gas generator propellants

D. D. Ryder[a]; G. D. Knowlton[a]
[a] Chemical and Propulsion Sciences Dept., Talley Industries of Arizona, Mesa, Arizona

To cite this Article Ryder, D. D. and Knowlton, G. D.(1983) 'Development of reverse phase HPLC techniques for determination of stabilizer depletion rates in high energy gas generator propellants', Journal of Energetic Materials, 1: 4, 349 — 365

To link to this Article: DOI: 10.1080/07370658308012325

URL: http://dx.doi.org/10.1080/07370658308012325

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

DEVELOPMENT OF REVERSE PHASE HPLC TECHNIQUES FOR DETERMINATION OF STABILIZER DEPLETION RATES IN HIGH ENERGY GAS GENERATOR PROPELLANTS.

D.D. Ryder and G.D. Knowlton

Chemical and Propulsion Sciences Dept., Talley
Industries of Arizona, P.O. Box 849, Mesa, Arizona

ABSTRACT

Reverse phase high performance liquid chromatographic methods have been developed for determining the stabilizer content in a nitrate ester plasticized gas generator propellant. The accuracy and precision of these methods are demonstrated by the results of stabilizer depletion rate determinations obtained over a three month accelerated aging period. The stabilizers investigated included diphenylamine (DPA), 2-nitrodiphenylamine (2-NDPA), 4-nitrodiphenylamine (4-NDPA), resorcinol and ethyl centralite (EC). Details of the analytical technique and methods development will be discussed.

Downloaded At: 14:11 16 January 2011

Journal of Energetic Materials Vol. 1, 349-365 (1983)
(c) 1983 Dowden, Brodman & Devine, Inc.

0737-0652/83/0104-$4.25

INTRODUCTION

One of the critical factors in the aging of propellants containing nitro and nitrato compounds is the slow, spontaneous degradation of these compounds to give NO and NO_2 [1-3]. Accumulation of these oxides of nitrogen in a propellant can ultimately lead to a number of undesirable effects, specifically: (1) self-heating and autoignition of the propellant, (2) excessive internal gas generation with subsequent grain cracking and fissuring, and (3) degradation with deterioration of propellant mechanical properties [1,4-7]. The occurrence of the above effects can be delayed by the addition of selected aromatic amines, substituted ureas, and phenols that scavenge the nitrogen oxides [1,5,7-9].

To evaluate the effectiveness of various stabilizers in a specific propellant, it is desirable to determine the rate of depletion of these stabilizers in the propellant stored under accelerated (elevated temperature) aging conditions [1,4,7,8]. Stabilizer depletion rates have been studied in a number of ways utilizing existing chromatographic techniques--e.g. liquid, gas, thin layer [10-14].

Downloaded At: 14:11 16 January 2011

The depletion rates and behavior of selected stabilizers in a nitrate ester plasticized gas generator propellant were investigated. The study required the development of several reverse phase high performance liquid chromatographic (RPHPLC) methods for the separation and quantitative determination of the stabilizers in the new propellant. The following discusses methods development work, interpretation of analytical results, and determination of stabilizer depletion rates.

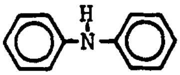
EXPERIMENTAL

Stabilizers

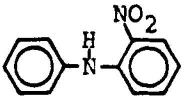
The following stabilizers were selected for evaluation in the propellant aging program:

Downloaded At: 14:11 16 January 2011

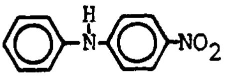
Diphenylamine (DPA)



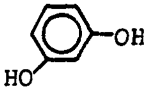
2-nitrodiphenylamine (2-NDPA)



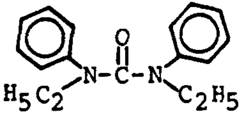
4-nitrodiphenylamine (4-NDPA)



1,3-benzenediol (Resorcinol)



N,N'-diethyl,N,N'-diphenylurea (Ethyl centralite)



One pint propellant mixes containing 0.6% by weight of each stabilizer were prepared in a vertical planetary Baker-Perkins mixer. One hundred gram cubes of each cured mix were placed in a 160°F oven for accelerated aging. At certain aging time intervals, samples of each cube were removed and the stabilizer concentrations determined. The rest of the mix was stored at ambient conditions for evaluation of initial stabilizer concentrations.

Sample Preparation

The solubility of the stabilizers was evaluated in several solvents to determine the best solvent for extraction of the stabilizers from the propellant. The solvents tested included: tetrahydrofuran (THF), acetonitrile, methanol, dichloromethane, chloroform, acetone, methyl ethyl ketone, trichloroethylene, hexane and water. THF was found to be the most suitable solvent.

Downloaded At: 14:11 16 January 2011

Unaged propellant samples containing each stabilizer were extracted with THF. One gram samples from each cube were prepared as slices and transferred into 50 ml beakers. The samples were initially extracted in 25 ml of THF for 12 hours. After decanting the extract, three to four additional extractions were performed by adding 20-25 ml portions of fresh solvent to the beakers. Each of the extracts were combined in a 100 ml volumetric flask and diluted to volume with THF.

Chemical Reagents/Standards

The purity of the stabilizers, as certified by the vendor, ranged from 98-99.9% pure. All solvents used were Burdick and Jackson high purity solvents (99.9% pure). Standard solutions of each stabilizer were prepared in THF at concentrations of 0.02, 0.04, and 0.06 mg/ml.

Equipment/Instrumentation

All analyses were performed on a Waters Liquid Chromatograph equipped with a Model 6000A pump, UK-6 injector system and a Model 440 absorbance detector set at a wave length of 254 nm. The column was a Regis Hi-Chrom (reversible) packed with five micron Spherisorb coated with octadecyl silane II(C-18). Data from all analyses were recorded on a Perkin-Elmer Sigma 15 processor/plotter interfaced with the Waters Chromatograph.

Downloaded At: 14:11 16 January 2011

Propellant Physical Testing

Physical characteristics of each propellant mix were determined weekly. Propellant hardness was measured using a Shore type A-2 hardness tester. Propellant mass loss was determined on a Sartorius top loading balance accurate to ± 0.01 grams.

RESULTS AND DISCUSSION

The determination of stabilizer depletion rates in the nitratoplasticized propellant studied required the development of a liquid chromatographic method capable of separating and quantitatively measuring the stabilizers of interest.

The initial analytical methods development involved the selection of a solvent for extraction of the stabilizers from unaged propellant samples. All five stabilizers studied were found to be soluble in THF, acetonitrile, methylene chloride, chloroform, acetone, and methyl ethyl ketone. THF was selected as the extraction solvent because it had several desirable characteristics including: polarity, miscibility with water, and minimal U.V. absorbance at 254 nm. Standard solutions of each of the five stabilizers were prepared in THF for development of the reverse phase high performance liquid chromatographic (RPHPLC) method.

Downloaded At: 14:11 16 January 2011

A five micron C-18 column was selected for the separation of the stabilizers, nitratoplasticizers and other propellant ingredients. Initially, the separation of the stabilizers and nitratoplasticizers was determined over a range of concentrations in three binary solvent systems--acetonitrile/ water, THF/water and methanol/water. The methanol/water and acetonitrile/ water systems provided the best separation of the components of interest. The methanol/water system was selected for refinement of the RPHPLC method. A concentration of 75% methanol and 25% water provided optimum separation of the stabilizers and nitratoplasticizers (See Fig. 1).

Downloaded At: 14:11 16 January 2011

The expected elution of 4-NDPA, 2-NDPA and DPA in the order of decreasing polarity was not observed in the three binary solvent systems investigated. Although reversal of the expected elution order of DPA and 2-NDPA has been reported in work performed by J.G. Carver [10] and B.R. Richardson [11], no explanation for the reversal was provided. It is proposed that the observed elution order of the stabilizers is due to varying degrees of hydrogen bonding with the mobile phase. It is possible that intramolecular hydrogen bonding in 2-NDPA (amine hydrogen to nitro oxygen) reduces the sites available for intermolecular hydrogen bonding with the mobile phase. Thus 2-NDPA would have a lower affinity for the mobile phase than either the DPA or 4-NDPA, and therefore elute last. This would also explain the lower solubility observed for 2-NDPA in methanol.

With the successful development of a method for separating and quantitating the five stabilizers and nitratoplasticizers, it was necessary to obtain maximum extraction efficiency of each stabilizer from the propellant. Standard solutions of each stabilizer and the propellant extracts containing each stabilizer were analyzed using the RPHPLC method developed. It was found that optimum extraction efficiency of DPA, 2-NDPA, 4-NDPA and ethyl centralite was achieved with THF using 4 successive extractions over a 15 hour period. The extraction efficiency could not be determined for resorcinol due to a coeluting species that was strongly absorbing U.V. radiation at 254 nm.

The observed interference of a coeluting species during resorcinol determination required the development of an alternate method of analysis. A ternary solvent system consisting of 50% H_2O, 25% CH_3CN, 25% THF, provided the desired separation of

Downloaded At: 14:11 16 January 2011

resorcinol from the coeluting species (See Fig. 2). With the interference problem resolved, it was found that resorcinol could be isolated from the propellant slices with the previously developed extraction techniques. It was later discovered that nitroguanidine was the interfering species.

The data generated in the method development was subjected to an error analysis to determine the maximum error and precision of the RPHPLC techniques. The results of an error analysis performed on 4-NDPA standards and extracts of unaged propellant samples are shown in Table 1. The maximum error was determined by adding the percent variation in the response factor to the error, at the 99% confidence limit, for each data set (minimum 3 determinations). This resulted in a maximum error of ± 3.0% for 2-NDPA and resorcinol. The maximum error for 4-NDPA and DPA samples was less than 2.5%. This applies to all unaged and aged propellant samples analyzed.

Downloaded At: 14:11 16 January 2011

TABLE 1.

Error Analysis for Reverse Phase HPLC Determination of 4-NDPA in Propellant

Mass of propellant sample (g)	Number of injections	Area counts	Standard deviation	Concentration (Wt %)
1.0396	6	1.9070	0.018	0.598
1.016	6	1.8594	0.026	0.597
1.1109	6	2.0632	0.015	0.606
1.3047	6	2.4118	0.021	0.603

Average 4-NDPA concentration (Wt %) = 0.601
Percent variation of the four samples = 1.5

Actual propellant stabilizer concentration(Wt %) = 0.60

Average response factor for three
4-NDPA Standards (μg/area count) = 0.3262 ± 0.0026

Downloaded At: 14:11 16 January 2011

The newly developed analytical techniques were utilized to determine the depletion rates of selected stabilizers in the propellant undergoing accelerated aging at 160^{o}. The initial concentration of each stabilizer in unaged propellant samples was established during the analytical methods development. The stabilizer content in aged (160^{o}F) propellant samples was then determined at intervals over a three month period. Ethyl centralite stabilized propellant was eliminated from the study because of rapid propellant deterioration. The depletion rates of the remaining four stabilizer/propellant systems were represented by the slopes of the stabilizer concentration plots (see Fig. 3). The rates varied from -0.00277 Wt %/day for 2-NDPA to -0.00158 Wt %/day for resorcinol. The high degree of precision and accuracy obtained when using the newly developed RPHPLC methods are substantiated by the calculated correlation coefficients for the plotted stabilizer depletions which ranged from 0.940 to 0.996.

The results of this study showed that the resorcinol stabilizer was depleting at the slowest rate in the propellant system. The resorcinol stabilized propellant also exhibited the lowest mass loss and the best retention of original mechanical properties (determined by Shore A hardness testing) when compared to the other stabilizer/propellant systems (see Table 2). These latter results lend support to the outcome of the RPHPLC analyses.

Downloaded At: 14:11 16 January 2011

TABLE 2.

Changes in Propellant Physical Properties with Aging at 160°F

Propellant stabilizer	Total Aging time (days)	Average mass loss (g) per day	ΔShore A hardness per day
DPA	106	2.2×10^{-3}	-0.05
2-NDPA	100	2.8×10^{-3}	-0.12
4-NDPA	101	3.8×10^{-3}	-0.14
Resorcinol	106	2.2×10^{-3}	-0.02

CONCLUSIONS

Good precision and accuracy was obtained with the RPHPLC methods developed for determining the depletion rates of DPA, 2-NDPA, 4-NDPA and resorcinol stabilizers in a nitrate ester plasticized propellant. Reversal in the expected elution order of certain stabilizers (DPA and 2-NDPA) was observed and attributed to hydrogen bonding of the stabilizers with the mobile phase.

Stabilizer depletion rates were determined for DPA, 2-NDPA, 4-NDPA and resorcinol stabilized propellant which had undergone accelerated aging at 160°F for three months. The results indicated that resorcinol provided the best stabilization of the propellant. This was supported by Shore A hardness and mass loss data collected over the three month study. Further studies involving resorcinol and dual stabilizer systems are in progress.

Downloaded At: 14:11 16 January 2011

ACKNOWLEDGMENTS

The authors would like to thank Dr. Michael T. Donohue of Talley Industries of Arizona for his helpful suggestions and review of this paper.

REFERENCES

1. L.H. Layton, L.L. Jones, and R.C. Raisor, ARFPL Report No. TR-82-062, December 1982.

2. P.M. Stevens, "ADPA Symposium on Compatibility of Plastic and Other Materials With Explosives, Propellants, and Pyrotechnics," NOS, Indian Head, Maryland, April 1976, p. II-B-1.

3. J.R. Spencer, R.W. Dalton, C.D. Chandler, and W.T. Bolleter, "7th JANNAF Propellant Characterization Meeting," Picatinny Arsenal, Dover, New Jersey, June 1976, p. 3.

4. R.P. Corina and J.K. Webb, AFRPL Report No. TR-79-36, August 1979.

5. P.A. Silver, J.W. Morton, K.O. Hartman, and R. Baczuk, "JANNAF Propulsion Meeting," Vol. I; New Orleans, Louisiana, May 1981, p. 287.

6. R.W. Arhart, K.P. McCarty, and T.H. Rytting, "JANNAF Propulsion Meeting," Vol. VI; New Orleans, Louisiana, May 1981, p. 255.

7. A.E. Oberth, "JANNAF Propulsion Meeting," Vol. II; Incline Village, Nevada, February 1978, p. 25.

8. R.J. Baczuk, R.W. Arhart, and S.W. Beckwith, "JANNAF Propulsion Meeting," Vol. V.; New Orleans, Louisiana, May 1981, p. 1.

9. R.D. Barefoot and C.L. Whitman, "ADPA Symposium on Compatibility of Plastic and Other Materials With Explosives, Propellants, and Pyrotechnics;" NOS, Indian Head, Maryland, April 1976, p. I-E-1.

10. J.G. Carver, Technical Report No. RK-83-4, U.S. Army Missile Command, Redstone Arsenal, Huntsville, Alabama, March 1983.

11. B.R. Richardson, Report No. MHSMP-82-11, Mason and Hanger, Silas Mason Co., Amarillo, Texas, March 1982.

Downloaded At: 14:11 16 January 2011

12. B.J. Alley and W.H. Dykes, "JANNAF Propellant Characterization Subcommittee Handbook," September 1982.

13. F. Volk, Propellants and Explosives **1**, 59 (1976).

14. F. Volk, Propellants and Explosives **1**, 90 (1976).

Downloaded At: 14:11 16 January 2011

Downloaded At: 14:11 16 January 2011

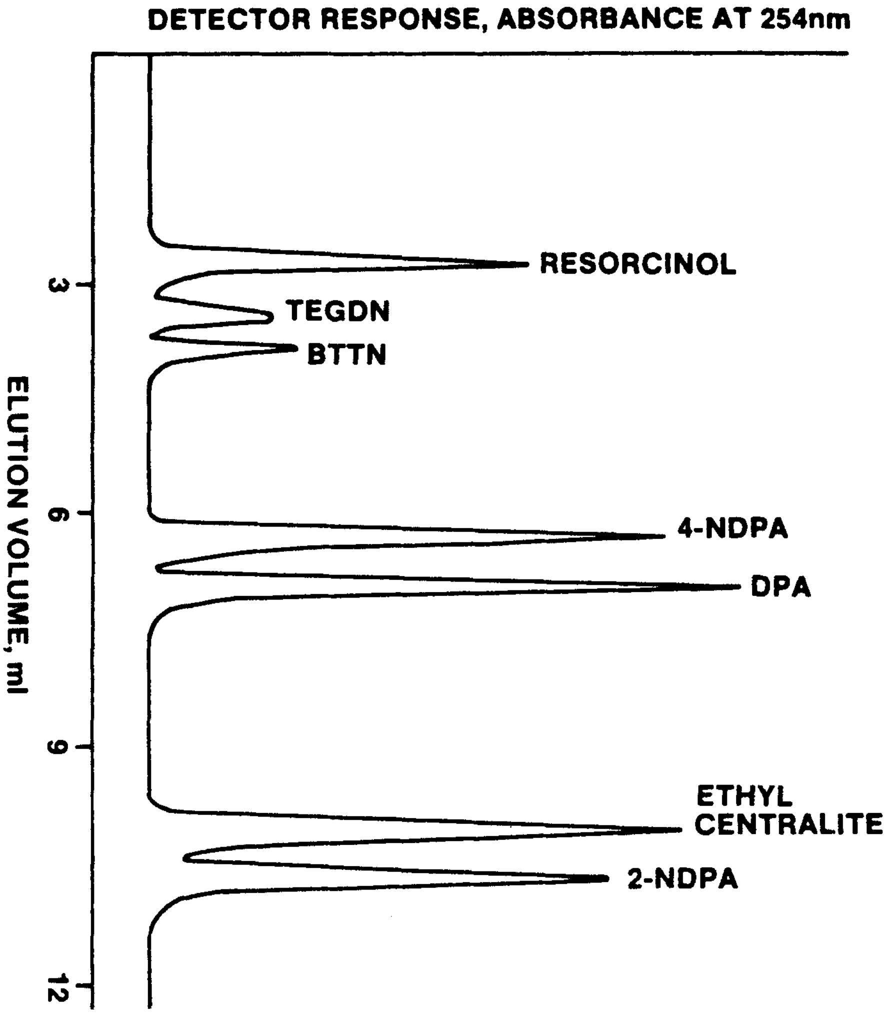


FIGURE 1.

Reverse Phase HPLC Separation of Stabilizers and Nitratoplasticizers

Downloaded At: 14:11 16 January 2011

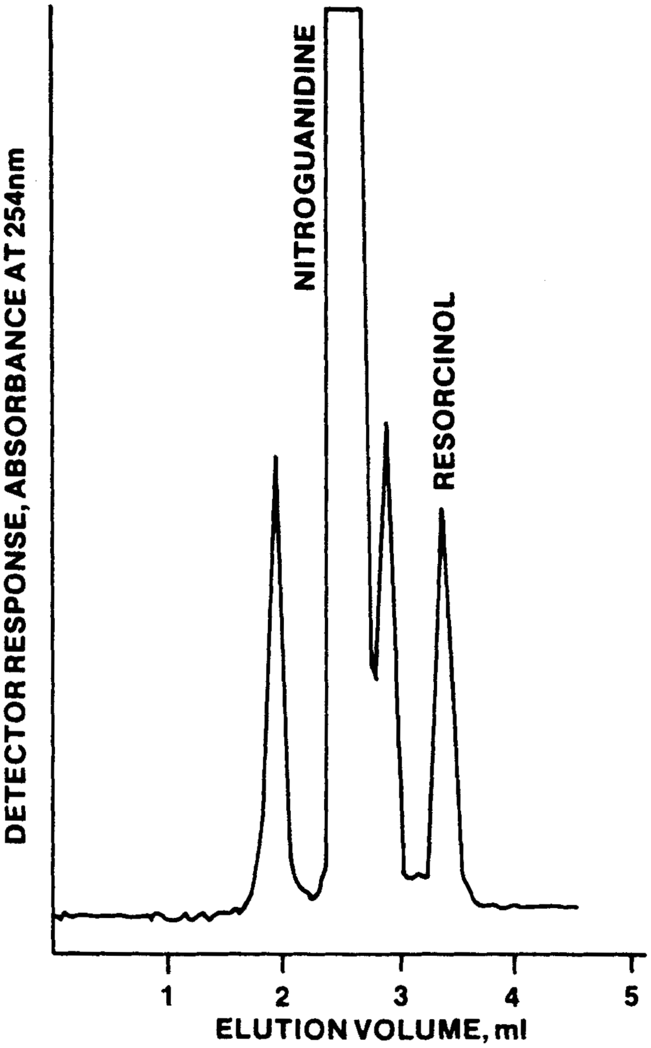


FIGURE 2.

Reverse Phase HPLC Separation of Resorcinol from Nitroguanidine

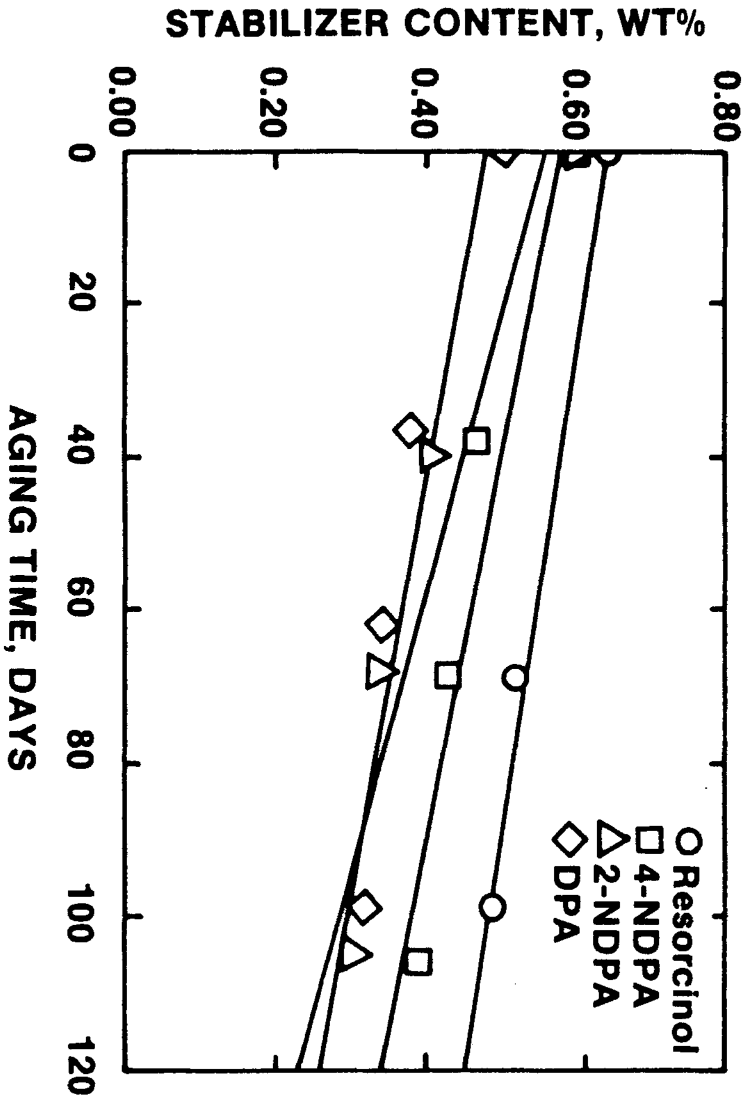


FIGURE 3.

Stabilizer Depletion from Propellant Samples Aged at 160°F