

LA-UR- 97 - 3341

Title: Stabilizers in PBX 9501

CONF-970982--

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Submitted to: 21st Aging, Compatibility and Stockpile Stewardship  
Conference at Sandia National Lab in Albuquerque  
9-30 - 10-02-97

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STABILIZERS IN PBX 9501

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20 min oral presentation preferred.

## STABILIZERS IN PBX 9501

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### ABSTRACT

An analysis of the analytical data from initial acceptance of PBX 9501 at Pantex and the current analysis of the library samples of the same lots show that the amount of Irganox has reduced linearly with time in the library samples. Data from the cycle reports show no negative trend in a sealed inert atmosphere. We also find that the stockpile return samples show very little change, both by thermal analysis with the ARC and chemical analysis by NMR, and can be said to be aging gracefully.

### INTRODUCTION

Our current objective is to understand the aging of the explosive in the stockpile and to assure that the lifetime of the PBX 9501 can be extended. The component of PBX 9501 most subject to change is its binder. Changes in the molecular weight of the estane binder have been observed in aging studies caused by hydrolysis of the ester linkages and radical attack, which can both break the polymer into shorter chains and cause cross linking that results in an insoluble fraction of unknown molecular weight. Either change is undesirable because it produces changes in the mechanical properties of the explosive. Radical attack is ameliorated by the inclusion of a stabilizer in the formulation. Either diphenylamine (DPA) or Irganox 1010 is added. DPA has a long history of use with explosives and is especially useful for removing any nitrogen oxide radicals formed. Irganox is a hindered phenoxy radical collector with four independent rings. It has been shown to protect the binder from radicals in the air.<sup>1</sup> The nominal amount of Irganox in PBX 9501 is  $0.1 \pm 0.04$  wt %. Some lots were accepted with the amount of Irganox less than 0.07 wt %. Faubion found that increasing the temperature accelerated the loss of the Irganox.<sup>2</sup> Matuszak and Loughran found that the loss of compressive strength was related to temperature by first order Arrhenius kinetics.<sup>3</sup> In the current study the data from the stockpile returns is analyzed to evaluate the stability of the explosive in the normal environment of the stockpile.

### RESULTS AND DISCUSSION

The amount of Irganox or DPA is found by extracting the sample and determining concentration by comparing with standards by reverse-phase high performance liquid chromatography (HPLC). This method measures the amount of only the unreacted stabilizer. Because Irganox has four independent rings, the complete loss of the parent peak does not eliminate its ability to stabilize the estane. The amount of Irganox in PBX 9501 decreases linearly with time when stored in the conventional manner in the magazine. When the difference between the original acceptance analysis and the current analysis is plotted against time as in Fig. 1, a least squares fit to the data can be used to approximate the amount of Irganox in a specific lot at the time it was sealed in an inert atmosphere. The difference between the calculated amount of Irganox at the time sealed in an inert atmosphere and the analysis after removal shows that no loss of Irganox has occurred while in the stockpile (Fig. 2). This indicates that in the sealed environment, radicals are not present that would react with the binder. However, if the rate of loss of Irganox in the library samples is applied to the current analysis, a date when the lot will have less than 0.06 wt %, the lower limit of the PBX 9501 specification, can be found. The last of the 730 lots will fall below this amount in approximately two years. A new lot should be WR certified to have material within specification for replacement of charges in the future, and it should be stored without exposure to the atmosphere. The loss of DPA in the library samples because there were only two lots with acceptance analyses. These two lots show no loss within experimental error.

Another factor in aging is the migration of materials. Analyses of samples machined from cores of a charge show that the stabilizer and the plasticizer will move away from the warmer areas and be found within all available materials. Figure 3 shows the spatial analysis of Irganox on stockpile return charge A76-1081037. Shields from several charges were analyzed and found to contain 0.08 to 0.13 wt % DPA or Irganox.

A bulk sample of the above charge was also analyzed by accelerating rate calorimetry (ARC) and NMR. Isothermal ARC runs showed very little difference in the sample compared to its library sample. Both were heated isothermally at 180°C. The ARC followed a small exotherm adiabatically to 182 °C and then held that temperature until the exotherm due to the decomposition of HMX began. The small exotherm is due to the exotherm of the nitroplasticizer. Fig. 4 illustrates the temperature and pressure profile. The difference between the library and stockpile sample is within the experimental variation of the baseline slope for long isothermal runs. The NMR on the aged samples showed about the same ratio of aromatic to aliphatic protons of the estane as its library sample, and it had no insoluble fraction. Analysis by NMR of a binder without Irganox aged at 50°C under Argon for 72 weeks showed change. First the binder had 28 % insoluble material and second the soluble material had a significantly larger aliphatic to aromatic fraction than the binder stored at ambient temperature. Table I has the NMR results.

TABLE I. RATIO OF ALIPHATIC TO AROMATIC PROTONS IN ESTANE

| <u>Sample</u>  | <u>Ratio 4.0 to 7.3 PPM Proton Resonance in DMSO</u> |
|----------------|--|
| 730-004        | 5.02   |
| 76-1081037A    | 5.71   |
| Estane /NP     | 4.85   |
| Aged Estane/NP | 7.93 (ppt removed)                                   |

## CONCLUSIONS

The binder of the PBX 9501 is more stable when a stabilizer is used and when stored under an inert atmosphere at less than 30°C. The amount of Irganox in the library samples has decreased linearly with age while the amount from samples sealed under an inert atmosphere shows little correlation with age, implying the rate of stabilizer loss is very dependent on storage conditions. The lifetime of the explosive stored in magazines could be lengthened with improved storage conditions. In addition, migration of the plasticizer and stabilizer may cause a reduction in the analysis of the stabilizer. Additional analysis shows that the PBX 9501 has good thermal and chemical stability and large changes in estane seen in an artificially aged sample without stabilizer have not occurred.

## ACKNOWLEDGMENTS

HPLC analysis of the library samples were done by Wayne King, at LANL and Rusty Vincent of Pantex. ARC and NMR studies were done by Danielle Garcia, summer student from NMSU. Thanks to Greg Buntain for data retrieval from the cycle reports and organizing the enhanced surveillance project between Los Alamos and Pantex chemists.

## REFERENCES

1. M. Matuszak, K. Firestone, "PBX Thermal Stability Study, Comparative Study of Antioxidants," WX-2-MR-77-11, (1977)
2. Billy D. Faubion, "Inhibitor Life in PBX 9501", MHSMP-86-24 (1986).
3. M. L. Matuszak and E. D. Loughran, "Thermal Stability of PBX 9501," Los Alamos Scientific Laboratory report, LA-8156-MS (February 1980).

# FIGURES

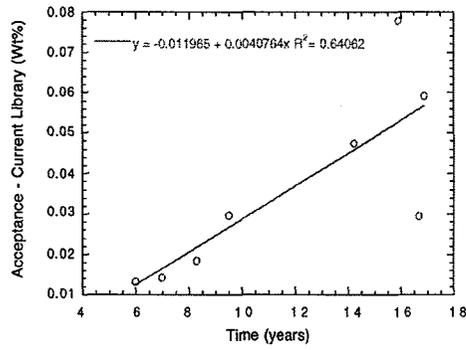


Fig. 1. Loss of Irganox from Library Samples.

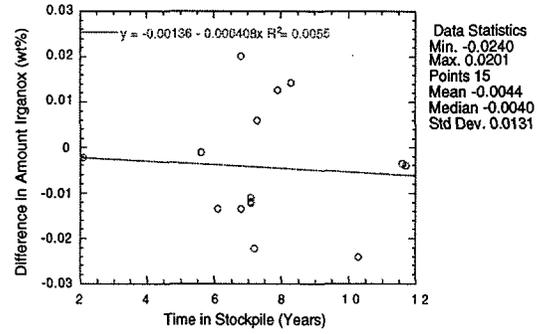


Fig. 2. Loss of Irganox in Stockpile.

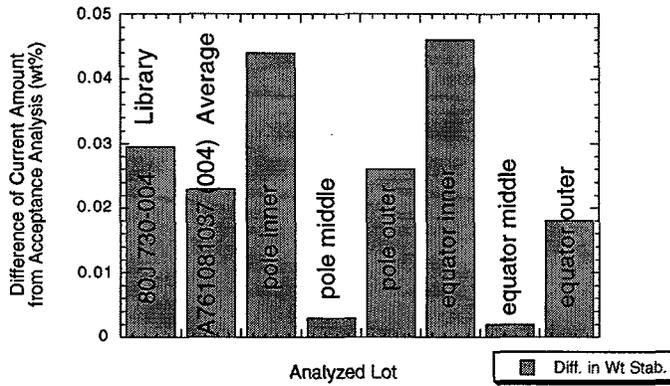


Fig. 3. Spatial variation of Irganox analysis within charge.

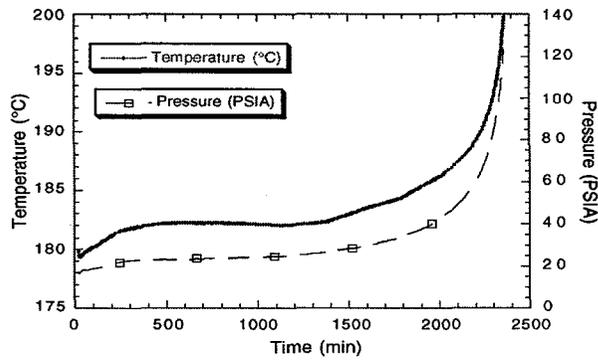


Fig. 4. ARC analysis of 76-1081037A, isothermal age at 180 °C.