LONG-TERM STABILITY OF THE EDNPF/BDNPA
NITROPLASTICIZER SYSTEM - AN NMR ANALYSIS

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DEVELOPMENT DIVISION

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ABSTRACT

NMR analysis of the BDNPF/BDNPA eutectic system reaffirms the molecular integrity of the constituents, the stability of their molar ratios, and the effective retardant effect of the phenyl-beta-naphthylamine antioxidant. Additional work on the analysis of the PBX 9501 system is underway at the present time.

DISCUSSION

The nitroplasticizer system used in PBX 9501 is a 50/50 weight percent eutectic composed of bis-2,2-dinitropropylformal (BDNPF) and bis-2,2-dinitropropylacetal (BDNPA). The system, including both the eutectic mixture and its individual components, was analyzed through NMR procedures to confirm spectral and molecular correlations, molar ratio of the components, and stability of the eutectic system with prolonged storage. Samples were run on a Varian HA-100, using d-6 acetone as solvent and tetramethylsilane (TMS) and benzene as integral lock materials.

SPECTRAL CORRELATIONS

bis-2,2-dinitropropylformal (BDNPF)

The spectrum of this material (Fig. 1a) displays no unusual spectral characteristics, with three isolated proton groups appearing as singlets and $\Delta\nu$ about as expected; isolated terminal methyl ~ 230 Hz, the isolated propyl methylene ~ 453 Hz, and isolated formal methylene ~ 495 Hz. Integration values are consistent - 6/4/2.

bis-2,2-dinitropropylacetal (BDNPA)

The spectrum of the acetal homolog (Fig. 1b) is predominantly first order in its expected and actual splitting patterns; acetal methyl doublet at ~ 135 Hz, isolated terminal methyl at ~ 230 Hz, and the acetal proton quartet at ~ 505 Hz, indicating strong deshielding of the acetal proton, brought about by its location in the plane of both etheral linkages. The isolated propyl methylene protons show magnetic non-equivalence, resulting in two doublets centered at ~ 450 Hz. There is considerable mixing of the energy states by the magnetic field, with $J/\Delta\nu \rightarrow 1.0$, with non 1st order AB spectral characteristics. Integration values are consistent - 1/4/6/3.

The 50/50 weight percent mixture (eutectic) of BDNPF/BDNPA produces a spectral pattern indicating a non-reactive miscible system (Fig. 2a). Spectral integration of the acetal methyl group of BDNPA and the composite singlet of the isolated terminal methyls of BDNPF and BDNPA, produce 1 to 4 ratio. This system was made from LASL standard BDNPF and

BDNPA for use in the composition of the eutectic. No phenyl-beta-naphthylamine (antioxidant) was added, with the mixture dissolved in d-6 acetone, maintained at 21 C and run within one hour of makeup.

The spectrum of the BDNPF/BDNPA eutectic (Aerojet AF-OCP-XB-9/8) containing an antioxidant and having undergone long-term storage (manufactured in 1964), shows no apparent change in the molecular integrity of either BDNPF or BDNPA, and no apparent change in the molar ratio of the eutectic constituents (Fig. 2b) within the limits of the Miller integrator at this percentage level (50/50 wt %, $\pm 1\%$).

A mixture comparable to the Aerojet material (50/50 wt % BDNPF/BDNPA) but without phenyl-beta-naphthylamine added, and stored for four years at ~ 25 C, was spectrally analyzed to determine the stability of the system (Fig. 3). A considerable degree of decomposition and/or acetal reversion has occurred. Reversion is indicated by the appearance of formyl proton (~ 805 Hz) and alcoholic OH (565 Hz). The shift of a portion of the isolated terminal propyl methyl is quite prominent (230 Hz $\longrightarrow$ 230, 220 Hz), as well as the shift upfield and the general spectral deterioration of the acetal proton quartet (505 $\longrightarrow$ 490 Hz).

COMMENTS

NMR analysis of the BDNPF/BDNPA system has reaffirmed the retention of molecular integrity and the stability of the molar ratios of the system, and effectively displayed the retardant affect of the phenyl-beta-naphthylamine as a system antioxidant.

The application of NMR procedures for analysis of this system is quantitatively limited ($\pm 0.5\%$). However, the system is uniquely applicable to a qualitative appraisal of the molecular integrity of the system components, as a possible cross check of the constituent performance and behavior.

The application of NMR to study the PBX 9501 system is under investigation at this time.

(a) bis-2,2-dinitropropylformal (BDNPF)

(b) bis-2,2-dinitropropylacetal (BDNPA)

Fig. 1. HA-100 Spectra of BDNPF and BDNPA (TMS Lock)

(a) Pantex - Unaged

(b) Aerojet - Extended Aging

Fig. 2. HA-100 Spectral Comparison of BDNPF/BDNPA
50/50 Weight Percent Eutectic Samples
(Benzene Lock)

Fig. 3. HA-100 Spectra of Aged BDNPF/BDNPA Without Antioxidant (TMS Lock)