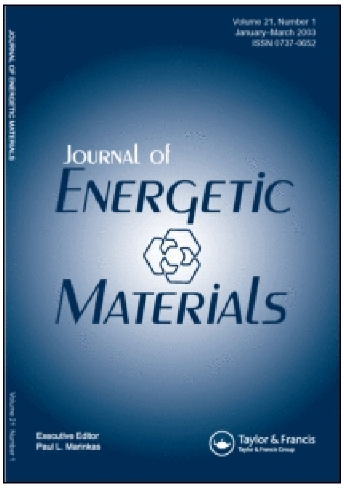

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III. Chemical compatibility study of gap based propellant by the DVST

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GAS EVOLUTION ANALYSIS: III. CHEMICAL COMPATIBILITY STUDY OF GAP BASED PROPELLANT BY THE DVST

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ABSTRACT

To produce a clean propellant, we must use new energetic materials, whose effect on the chemical stability during long-term storage is unknown. A formulation including ammonium nitrate (AN), GAP, and BDNPAF was studied. This study was based on accelerated aging and gas evolution, using the vacuum stability test in conjunction with gas chromatography.

Incompatibility between AN and the other ingredients was found to be responsible for the chemical degradation. The effect of various stabilizers was evaluated and N-methyl-4-nitroaniline proved to be the most efficient stabilizer for the formulation investigated.

INTRODUCTION

Ammonium nitrate (AN) is becoming increasingly interesting for its use in rocket propellants because of characteristics such as low smoke and low toxic emissions(1). The low energetic content of AN may be compensated by the use of energetic binder and energetic plasticizer in the propellant. However, such propellants exhibit serious incompatibility between the energetic groups as well as moisture sensitivity and gas evolution(2). Consequently, a fast and reliable test is required to evaluate the compatibility and stability of these energetic materials and their effect on the chemical stability during long-term storage. The vacuum stability test (VST), which combines accelerated aging and gas evolution analysis, was the first step used to identify the source of the problem and to understand the mechanism of degradation.

EXPERIMENTAL

The study was performed on a propellant formulation including ammonium nitrate (AN), glycidyl azide polymer (GAP), and bis-2,2-dinitropropylacetal/formal (BDNPAF). The curing agent was an isocyanate (N100). The AN was phase stabilised by 3% NiO (PSAN)(3).

The gases evolved upon heating of these mixtures were measured and analyzed by the VST method, which is described in part 1, in conjunction with gas chromatography (GC).

Sample preparation

All ingredients were dried at 100°C under vacuum to get rid of the volatiles. The sample size was 5g for stability evaluation of single ingredients; compatibility determinations on binary mixtures used 2.5g of each ingredient. Each sample was stored in the vacuum tube at 100°C for 48 hours.

RESULTS AND DISCUSSIONS

A block of propellant aged at 60°C for three months showed gassing and cracks, which was indicative of a chemical decomposition. This gassing was confirmed by the VST results which indicate a gas evolution of 9 ml/g, as shown in table 1.

TABLE 1. Gas evolution for AN and AP based propellant. Comparison with BDNPAF/GAP/N100 mixture.

Formulation	*Vol. (ml/g)*	N_2%	N_2O%	CO%	CO_2%
BDNPAF/GAP/N100	0.6	60	5	0	35
BDNPAF/GAP/N100/AN	9	55	20	1	24
BDNPAF/GAP/N100/AP	0.4	60	5	0	35

The first attempt to elucidate this problem consisted of simultaneous aging of a sample of propellant and a mixture of ingredients free of AN and analyzing the gas evolved. As illustrated in table 1, the mixture of GAP, N100, and BDNPA/F showed no signs of decomposition since the volume of gases evolved is very low (0.6 ml/g) . Table 1 also shows the results obtained from a compatibility study of two different oxidizers (ammonium perchlorate and ammonium nitrate) with the different ingredients. The volume of evolved gas is still very low (0.4 ml/g) when ammonium perchlorate (AP) is added to the mixture. It is clear that the gas composition is unchanged, (table 1) which indicates that AP does not interfere chemically with the other ingredients. However, in the formulation including AN, extensive gas evolution occurred. The combination of PSAN with BDNPAF and GAP was found to be responsible for this chemical incompatibility. One consequence was a change in the gas composition and in particular, a 20% rise in the N_2O content. The autocatalytic effect of nitrogen oxide(4) on the propellant decomposition is well known and must be prevented. Once the problem had been identified and associated with the incorporation of AN into the formulation, further testing of this material with all other ingredients was necessary. Table 2 shows the VST results at 100°C for various combinations of AN with the other ingredients. The amount of gas evolved with the mixtures AN/BDNPAF and AN/GAP in comparison with that evolved with the individual ingredients indicates a serious incompatibility problem between AN and the two other materials. In contrast there were no signs of incompatibility between BDNPAF and GAP.

A study was performed on AN/BDNPAF and AN/GAP mixtures in order to understand the mechanism of degradation and to select an appropriate stabilizer.

Table 2. Compatibility between AN, BDNPAF, and GAP.

Sample	Vol. (ml/g)	N_2%	N_2O%	CO%	CO_2%
AN	0.1	-	-	-	-
BDNPAF	0.6	68	0	0	32
GAP	0.3	88	0	0	12
AN/BDNPAF	6.6	76	13	1	10
AN/GAP	5.8	97	1	1	2
BDNPAF/GAP	0.8	84	10	0	6

Cause of the incompatibility between AN and BDNPAF

Figure 1 shows the effect of various stabilizers on the AN/BDNPAF mixtures. Resorcinol was found to be the most efficient stabilizer, in agreement with the work of Asthana(5). This is due to a strong electron donating mesomeric effect of the OH groups(5). In contrast, phenyl-beta-naphthylamine (PBNA) which was used by the manufacturer to stabilize BDNPAF, showed no stabilizing effect. On the contrary, PBNA seems to have a negative effect on the compatibility between AN and BDNPAF as illustrated by figure 2, where the volume of gas evolved by AN/BDNPAF was plotted as a function of PBNA concentration. This figure shows that the volume of evolved gas increases with the PBNA content. This is a sign of incompatibility between the AN/BDNPAF mixture and the amine function of PBNA.

Since resorcinol is not a base, its stabilizing effect suggests that the acidity of AN is apparently not involved in the mechanism of decomposition. This mechanism is nonetheless unclear. The individual chemical stabilities of AN and BDNPAF are excellent, as illustrated in table 2. The stability of the nitro group in BDNPAF is due to its resonance hybrid(6). However, the stabilizing effect of resorcinol and the nature of the evolved gases indicate that the incompatibility could be caused by the decomposition of AN according to equation 3.

$$NH_4NO_3 \;\; \text{--->} \;\; N_2O + 2H_2O \qquad (3)$$

This result is not in agreement with those obtained by Meulenbrugge' study(7) where the cause of the incompatibility was attributed to the acidity of AN.

Although resorcinol is very effective in the removal of N_2O, it was not considered in the propellant formulation since its hydroxyl groups may interfere in the curing reaction.

Figure 3 shows the effect of MNA as a stabilizer. A high gas evolution was observed when the initial 0.5% of MNA was added. This contradiction may be explained by a chemical incompatibility between the components of the mixture and the amine function of MNA. This confirms the incompatibility observed with PBNA. However, the figure also indicates that the volume of evolved gas decreases when the MNA content was increased further.

Cause of the incompatibility between AN and GAP

A similar study was performed on AN/GAP mixture in order to select the most efficient stabilizer. AN is an ester of a weak base and a strong acid (equation 1). The nitric acid may catalyze the reaction with the azide group of the GAP to produce imine and nitrogen (equation 2).

AN : $NH_4NO_3 + H_2O \text{ ------> } NH_4OH + HNO_3$ (1)

GAP: $R\text{-}CH_2N_3 \text{ ------> } RCH{=}NH + N_2$ (2)

This mechanism is confirmed by the results of figure 4 which show that the addition of a small amount of a strong base (KOH) was sufficient to prevent the chemical degradation. Thus, the use of a weak base such as DPA or MNA to neutralise the acidity was considered a possibility. Of all the stabilizers used, N-methyl-4-nitroaniline (MNA) and diphenylamine (DPA) were found to be the most efficient. Resorcinol which is not a base, proved to not be effective in this case. The basic nature of these additives is a strong evidence that the incompatibility was caused by an acid.

The next step was that of optimizing the most efficient stabilizer, by testing the AN/GAP mixture with increasing amounts of MNA. Figure 5 indicates that a low gas evolution is obtained by adding 0.5 % of MNA, although the minimum is observed at 2%.

The final step in this study was to test the propellant formulation with MNA as a stabilizer. MNA seems to have an excellent global stabilizing effect since the volume of gas dropped from 9.0 to 0.5 ml/g as shown in table 3. The N_2O content dropped from 20 to 2%, indicating that the autocatalytic effect was inhibited.

TABLE 3. Stabilizing effect of methylnitroaniline (MNA) on the formulation AN/BDNPAF/GAP.

Formulation	*Vol. (ml/g)*	N_2%	N_2O%	CO%	CO_2%
AN/BDNPAF/GAP/N100	9	55	20	1	24
AN/BDNPAF/GAP/N100 +MNA	0.5	53	2	0	44

CONCLUSIONS

Gas evolution analysis, which was performed on propellant components as well as on AN/GAP and AN/BDNPAF mixtures, indicated an incompatibility problem between AN and the other ingredients. The acidity of AN in the AN/GAP mixture was found to catalyze the chemical decomposition of the GAP. In the case of AN/BDNPAF mixtures, the autocatalytic effect of nitrogen oxide seems to be the cause of the incompatibility. N-methyl-4-nitroaniline was found to be very effective in its role of neutralizing the acidity as well as removing nitrogen oxide.

The discontinuous VST method used in conjunction with gas chromatography proved to be a fast and economical way to study compatibility problems between energetic materials.

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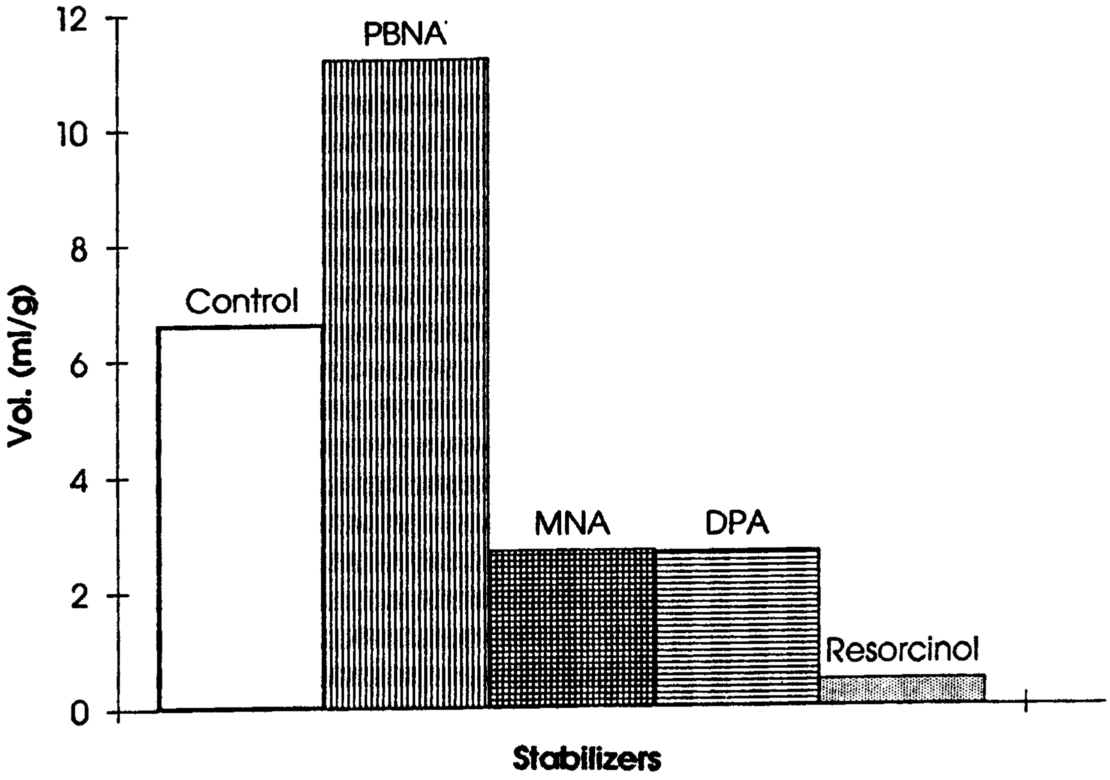

FIGURE 1
Stabilizing effect of different additives on AN/BDNPAF mixture. (2% of stabilizer, 48h at 100°C)

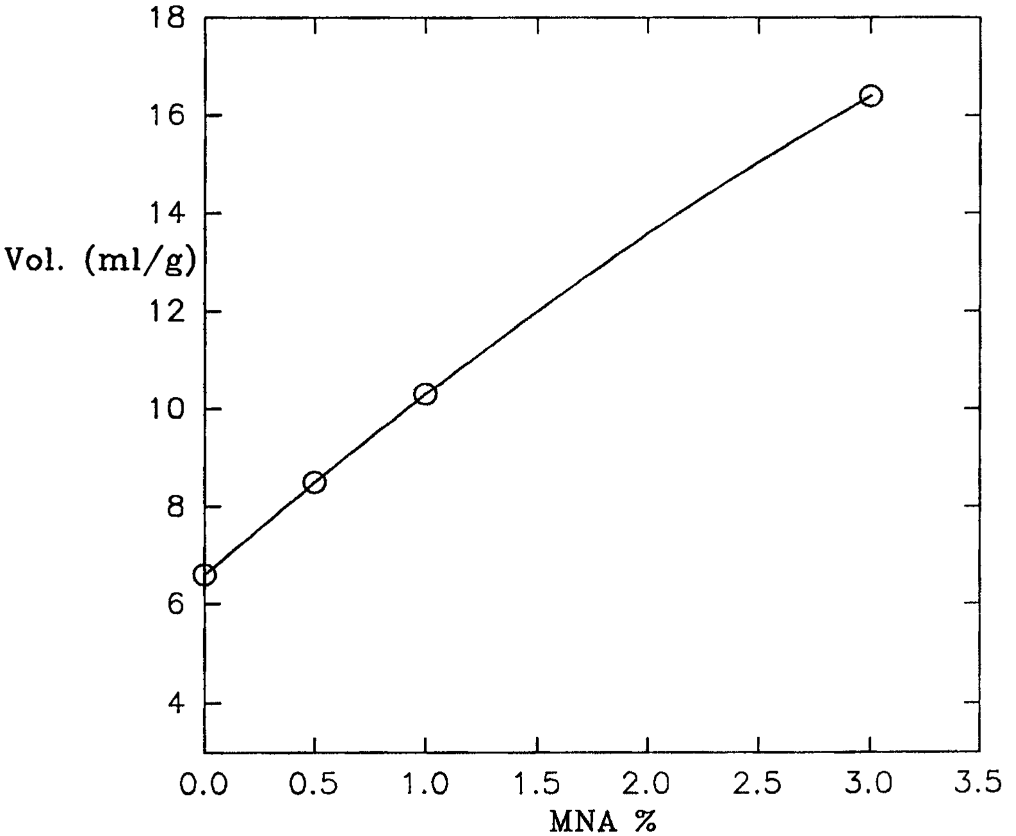

FIGURE 2
Volume of gas evolved by AN/BDNPAF mixture as a function of PBNA content.

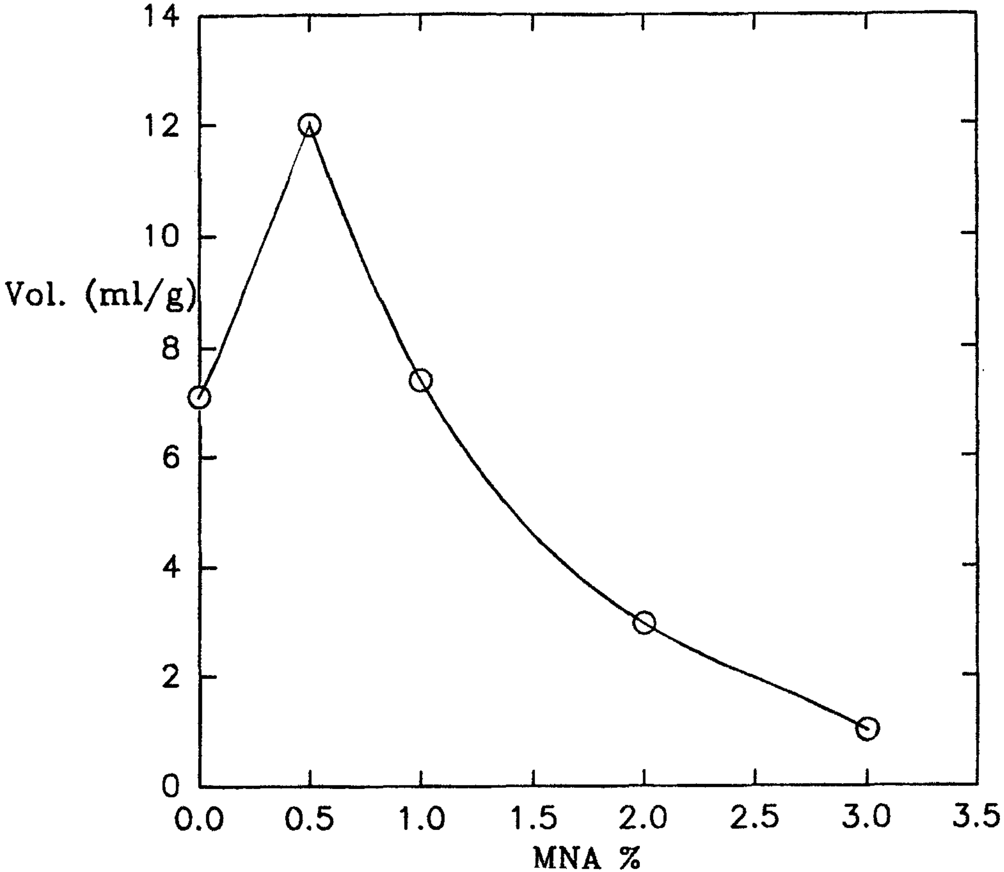

FIGURE 3
Volume of gas evolved by AN/BDNPAF mixture as a function of MNA content.

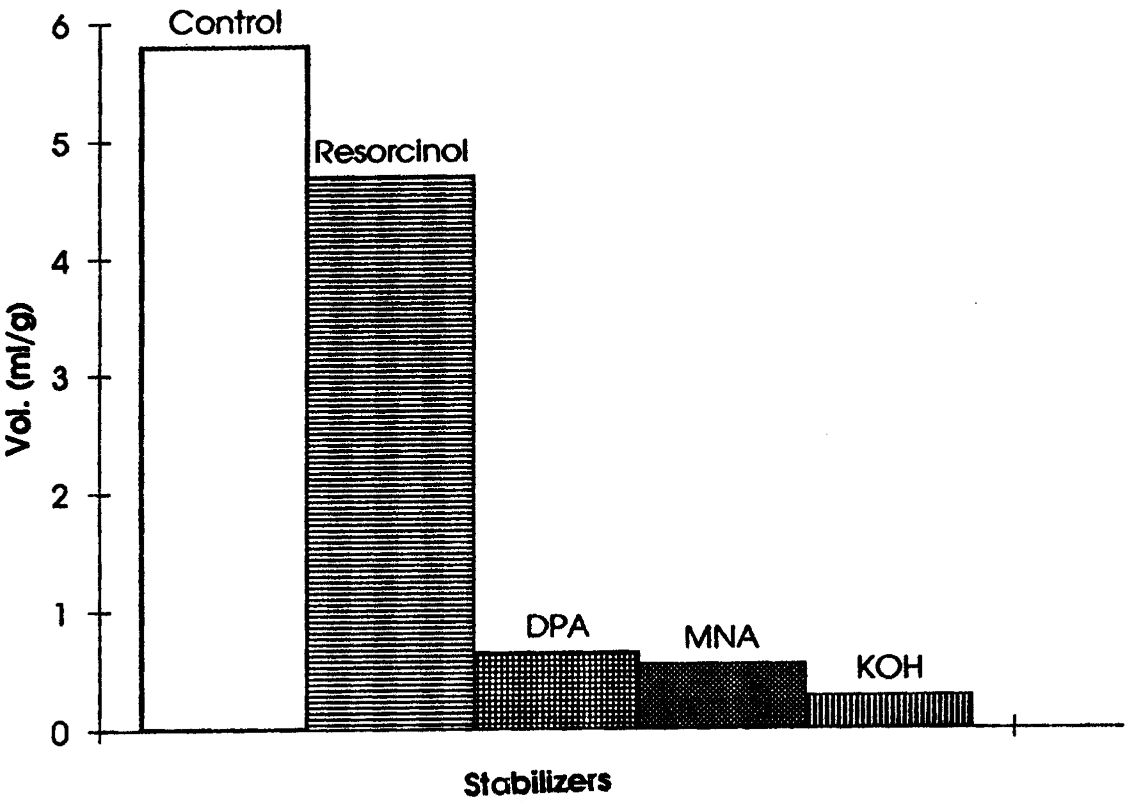

FIGURE 4
Stabilizing effect of different additives on AN/GAP mixture.

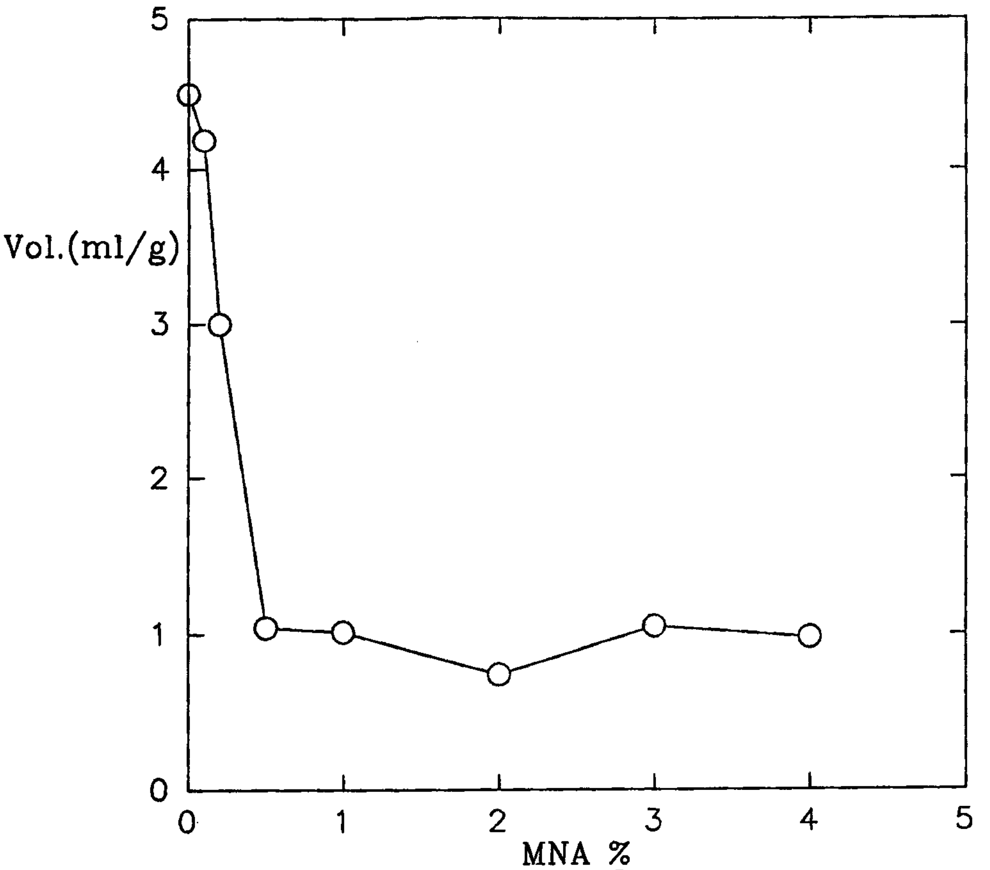

FIGURE 5
Volume of gas evolved by AN/GAP mixture as a function of MNA content.