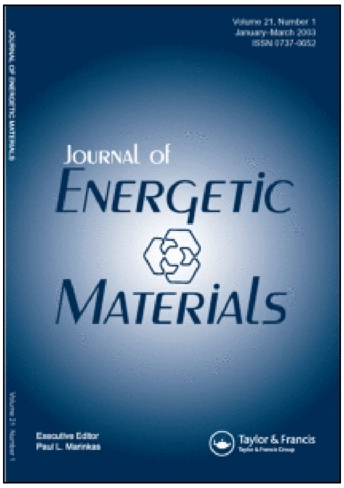

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REACTIONS OF 2- AND 4-NITRODIPHENYLAMINE AND THEIR COMBINATION IN SINGLE BASE PROPELLANTS: EVIDENCE FOR AN INTERACTION BETWEEN STABILIZERS AT 80°C

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ABSTRACT

Reverse phase HPLC has been used to determine concentration profiles for the stabilizers and derivatives in three experimental single base propellants stabilized by 1% 2-nitrodiphenylamine (2NDPA), 1% 4-nitrodiphenylamine (4NDPA) and 0.5% 2NDPA/0.5% 4NDPA during aging at 80°C over 28 days. In the single-stabilizer compositions 2NDPA is converted mainly into 2,2'- and 2,4'-dinitrodiphenylamine while 4NDPA initially gives N-nitroso-4-nitrodiphenylamine (NO-4NDPA). The same derivatives, but with different concentration profiles, are observed in the dual-stabilizer propellant. It is concluded that the differences result from

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the interaction of N-nitroso-2-nitrodiphenylamine (NO-2NDPA) and 2NDPA with nitrogen oxides arising from NO-4NDPA dissociation. There is evidence that dinitrodiphenylamines derived from 2NDPA are formed by rearrangement of N,2-dinitrodiphenylamine while those derived from 4NDPA are generated in reactions which follow NO-4NDPA dissociation.

INTRODUCTION

Stabilizers are added to NC-based propellants to react with the initial nitrate ester breakdown products, thereby delaying the onset of autocatalytic decomposition during storage[1]. Among the most widely used stabilizers are aromatic secondary amines such as diphenylamine (DPA) which react rapidly with oxides of nitrogen and other species arising from nitrate ester decomposition, initially to give primarily N-nitrosamines. It is generally assumed[2] that the latter derivatives then independently undergo rearrangement and oxidation to produce the C-nitro compounds observed in aged propellants. Recently however it has been suggested[3] that an N-nitrosamine formed during the accelerated aging of a dual-stabilizer Cast Double Base (CDB) propellant may also be reacting with stabilizers and other derivatives in the composition. It was therefore of interest to examine evidence for possible similar interactions during the accelerated aging of a single base propellant stabilized by a mixture of two different aromatic secondary amines.

EXPERIMENTAL

Propellant Aging and Sample Preparation for HPLC Analysis

Three propellants were investigated. Each was made in the form of 1 mm diameter graphite-glazed discs using manufacturing facilities at MRL and contained a nominal 99% nitrocellulose (NC, 12.6% N) and 1% stabilizer. Propellant A was stabilized with 2-nitrodiphenylamine (2NDPA), Propellant B with 4-nitrodiphenylamine (4NDPA) and Propellant AB with a mixture of 0.5% 2NDPA and 0.5% 4NDPA.

A separate quantity of propellant was used for each aging period, the sample (approx. 5 g) being sufficient almost to fill a small glass tube 5 mm in diameter x 16 mm deep. Each tube was sealed with a tight-fitting polyethylene cap and then aged for between 1 and 28 days at 79.9±0.1°C in an aluminium block heater.

At the end of the aging period a small amount (approx. 0.5 g) of the aged propellant sample was ground up and extracted with technical grade dichloromethane (60 cm^3) for 2.5 hours in a conventional Soxhlet extractor. The resulting solution was evaporated nearly to dryness on a steam bath and the residue redissolved in methanol (approx. 15 cm^3) and quantitatively transferred to a 25 cm^3 volumetric flask. Internal standard solution (2.5 cm^3) was then added and the volume was made up to 25 cm^3 by the addition of further methanol. All solvents were HPLC Grade (Ajax Chemicals, Auburn, NSW) unless indicated.

Results for Propellants A and B were each obtained from a single series of extractions and analyses. A second series was undertaken for Propellant AB and agreement between the two sets of results was good.

HPLC Equipment and Analysis Procedure

Quantitative HPLC analyses were carried out at room temperature (21±2°C) using a Millipore Waters 600E System Controller and WISP 712 auto-injector (10 μl injection volume). Separations were performed on a Millipore Waters C18 Resolve column (15 cm, 5 μm particle size) using a mobile phase consisting of 45% acetonitrile/10% methanol/45% water[4,5] flowing at a rate of 1.2 cm^3 min^{-1}. A 2 cm C18 Resolve guard column was used with the analytical column. The separated components were detected at 270 nm using a Millipore Waters 490E UV detector.

These HPLC conditions gave excellent separation for 2NDPA and its derivatives. That for 4NDPA and its derivatives was less satisfactory, with complete baseline separation of peaks due to 4NDPA and N-nitroso-4-nitrodiphenylamine (NO-4NDPA) not being achievable. Furthermore, 4NDPA could not be quantified beyond 14 days because of the possible co-elution with 2,4,4'-trinitrodiphenylamine, which is expected to start appearing in the aged propellant after this time[6].

HPLC calibration curves based on peak area measurements were prepared using three different standard solutions of the stabilizers and their derivatives in methanol. 4-Nitroanisole was used as the internal standard and was added to sample solutions and calibration standards as a solution in methanol (1.613×10^{-3} g cm^{-3}). The derivatives were synthesised using methods previously described[2,7]. Chromatography data handling was performed on an industry standard personal computer using Millipore Waters Maxima 820 software.

RESULTS AND DISCUSSION

Propellant A (2NDPA-stabilized)

Concentration profiles in Propellant A aged at 80°C are shown in Figure 1. Depletion of 2NDPA occurs steadily over most of the 28 day aging period and the principal derivatives observed are 2,2'- and 2,4'-dinitrodiphenylamine (22'DNDPA and 24'DNDPA), the ratio between the two being approximately 1:3 throughout. Apparently anomalous HPLC analysis results were recorded for 2NDPA and 22'DNDPA between 21 and 28 days. The reason for this is unknown although stabilizer recovery was slightly low for the 25 day sample. Analysis of the 21, 25 and 28 day samples was repeated twice and the results shown in Figure 1 are reproducible. It is possible that ineffective sealing of the glass tube used for aging the 25 day sample resulted in it being subjected to slightly different aging conditions.

Only small amounts of N-nitroso-2-nitrodiphenylamine (NO-2NDPA) were detected in Propellant A over the course of 28 days, a finding which is in line with previous results[7,8] and which suggests that the derivative is labile and readily converted into dinitrodiphenylamines at 80°C. Possible pathways for the conversion of N-nitrosamines into C-nitro compounds in propellants have been discussed[2,8,9].

Propellant B (4NDPA-stabilized)

The concentration profiles for species in Propellant B aged at 80°C are presented in Figure 2. It is apparent that 4NDPA is consumed more rapidly in this composition than is 2NDPA in Propellant A under the same conditions, suggesting that it reacts faster with the initial products of NC decomposition. In this respect 4NDPA can be said to be a more effective stabilizer than 2NDPA.

A feature of the results for Propellant B is the relatively large amount of NO-4NDPA formed. The concentration of dinitrodiphenylamines therefore remains low compared to the situation in Propellant A. Also of note is the fact that the 44'DNDPA/24'DNDPA ratio changes over the 28 day aging period, in contrast to the constant 1:3 ratio observed for 22'DNDPA/24'DNDPA during aging of Propellant A. This may indicate that NO-2NDPA and NO-4NDPA are converted into dinitrodiphenylamines by different mechanisms.

The amount of NO-4NDPA generated in Propellant B and its rapid disappearance after about 17 days appear to be in conflict with the results of Curtis[2] who detected lower levels of the derivative in a similar composition at 80°C but found significant amounts remaining even after 28 days. In the latter case aging was undertaken in an open tube. When the experiments were repeated and the HPLC analysis carried out using the reverse phase method described above there was good agreement with Curtis's results. It therefore appears that NO-4NDPA survives for longer in a propellant exposed to the atmosphere. This is probably due mainly to the ease with which nitrogen oxides can escape from an open tube but it may also be associated with oxygen availability. The effect of oxygen on stabilizer and derivative profiles during aging of propellants has been demonstrated[10,11,12].

Thus, HPLC analysis results indicate that in 4NDPA- and 2NDPA-stabilized propellants of otherwise similar composition NO-4NDPA is initially generated in much greater concentrations than NO-2NDPA but, over a comparable aging period at 80°C, is not converted into less reactive C-dinitro compounds to the same extent. On this basis 4NDPA must be considered a less effective stabilizer than 2NDPA.

Propellant AB (2NDPA/4NDPA-stabilized)

The concentration profiles for the primary stabilizers and their N-nitroso derivatives during aging of Propellant AB at 80°C are shown in Figure 3. In the early stages (to about 6 days) the 4NDPA depletion rate is similar to that observed in Propellant B and NO-4NDPA is again a major product. However, 2NDPA is consumed at a lower rate than in

Propellant A. It would therefore appear that 2NDPA is less effective than 4NDPA in competing for NC decomposition products during the early stages of aging of Propellant AB.

The depletion profiles for the two primary stabilizers begin to deviate from their initial course after about 6 days and thereafter show considerable differences from those for the same compounds in the single-stabilizer propellants. This suggests that reactions are taking place in Propellant AB which are not occurring in Propellants A or B over the same period. It is reasonable to conclude that these involve interactions between the stabilizers or species derived from them.

A major feature of the change in the depletion profiles of the primary stabilizers in Propellant AB is a marked reduction in the rate of loss of 4NDPA. The rate is similar in Propellants B and AB over the first 6 days of aging but by 14 days the level of 4NDPA had fallen to approximately 25% of its original value in Propellant AB compared to 15% in Propellant B. It is possible that the continued rapid loss of 4NDPA in Propellant AB is being masked by an increase in the level of 2,4,4'-trinitrodiphenylamine since the latter is known to co-elute with 4NDPA under the HPLC conditions employed. However, this is not supported by the calculated stabilizer recovery which is close to the expected 0.95% throughout the 6-14 day aging period. Furthermore, as noted above, 2,4,4'-

trinitrodiphenylamine is not expected to appear in the propellant until about 15 days at 80°C[6].

It is suggested that the fall in the rate of depletion of 4NDPA in Propellant AB results from the regeneration of the stabilizer from accumulated NO-4NDPA. Schroeder et al[8] showed by isolating 4NDPA from a double base composition stabilized with NO-4NDPA that denitrosation of the latter occurs in an NC propellant at 71°C. It is therefore not unreasonable to assume that NO-4NDPA will undergo the same reaction in Propellant AB at 80°C. The aging conditions and the nature of the N-nitrosamine[13] are likely to favour initial thermolysis of the N-N bond to give NO and the 4-nitrodiphenylamino radical in a reversible process[14]. Such a dissociation would be consistent with the fact that less NO-4NDPA is formed in Propellant B in an open system where ready loss of NO can occur. In a sealed tube in the presence of oxygen NO will be oxidised to NO_2 which can react with the 4-nitrodiphenylamino radical to give dinitrodiphenylamines[14]. Alternatively, the radical could abstract a hydrogen atom from a suitable propellant ingredient to regenerate 4NDPA[15]. Radical formation during the aging of NC-based compositions stabilized by NO-4NDPA has been confirmed by ESR[16].

The increased regeneration of 4NDPA in Propellant AB after 6 days is attributed to competition for NO_2 between the 4-nitrodiphenylamino radical and 2NDPA or a species derived from it. This competition is postulated to lead to a reduction in the rate of reaction between the radical and NO_2 and hence to an increase in hydrogen abstraction. The involvement of 2NDPA or a derivative would account for the absence of similar changes in Propellant B.

Concentration profiles (Figure 3) suggest that NO-2NDPA may be the principal species competing for NO_2 with the 4-nitrodiphenylamino radical in Propellant AB. This derivative is expected to be the major product of the reaction between 2NDPA and NC decomposition products but its concentration does not increase in line with the fall in the level of 2NDPA, suggesting that it is rapidly transformed either by rearrangement or by reacting with another propellant ingredient. The latter is thought more likely since conditions in a propellant do not in general favour direct rearrangement of aromatic N-nitrosamines[2,9].

The nature of the proposed reaction between NO_2 and NO-2NDPA is not entirely clear but there are indications that the latter undergoes oxidation in the propellant. Thus between 8 and 10 days only 22'DNDPA, of the expected C-dinitrodiphenylamines, shows evidence of an increase in concentration (Figure 4), indicating that N,2-dinitrodiphenylamine (NO_2-2NDPA), which is known to rearrange initially to give exclusively 22'DNDPA[2,17], may be formed in Propellant AB at this time. If this is so it seems most likely to arise from the oxidation of NO-2NDPA by NO_2 or possibly HNO_3. The former is known to react with NO-2NDPA at room temperature, both in solution[9] and in a propellant[18], and HNO_3 is able to convert NO-2NDPA into 22'DNDPA, the reaction being thought to occur via NO_2-2NDPA[9]. The formation of 22'DNDPA and 24'DNDPA, the latter by a cartwheel mechanism[19] during the later stages of aging, via the intramolecular rearrangement of NO_2-2NDPA may account for the constant 22'DNDPA/24'DNDPA ratio found during aging of Propellant A.

The acceleration in the rate of depletion of 2NDPA in Propellant AB after about 10 days (the new rate being similar to that seen from the outset in the aging of Propellant A) is thought to be due to the increased availability of N_2O_3, a more reactive nitrosating agent than N_2O_4[20], which would be generated by the proposed reduction of NO_2/N_2O_4 or HNO_3 by NO-2NDPA and from reactions of NO released by dissociation of NO-4NDPA. The reaction of 2NDPA with N_2O_3 which contains NO derived from NO-4NDPA amounts to a transnitrosation[20] from NO-4NDPA to 2NDPA, the existence of which could help to explain differences between the NO-4NDPA profiles in Propellant B (Figure 2) and Propellant AB (Figure 3). Thus an increase in 4NDPA regeneration resulting from NO removal by 2NDPA, leading to the formation of more NO-4NDPA, may account for the slower decline in the concentration of the latter in Propellant AB than in Propellant B.

The 44'DNDPA concentration profile in Propellant AB (Figure 4) may lend support to the proposed transnitrosation. An increase in the concentration of this derivative is observed during the first 20 days of aging, as in Propellant B (Figure 2), but the concentration in Propellant AB remains constant from this point until the aging is terminated at 28 days. This suggests that NO-4NDPA, which continues to be depleted (Figure 3), is not being converted into 44'DNDPA over this period and is therefore undergoing other reactions. There is a possibility that it is rearranging exclusively to 24'DNDPA but this is considered unlikely. Direct nitration of the ring by HNO_3 to give N-nitrosodinitrodiphenylamines is also possible but derivatives of this type are expected to denitrosate readily, giving 44'DNDPA among other products. It is therefore suggested that, in the later stages of aging of Propellant AB, NO-4NDPA undergoes denitrosation rather than oxidation and rearrangement and that the released NO then reacts indirectly with 2NDPA, resulting in transnitrosation.

CONCLUSIONS

HPLC analysis has shown that the stabilizers 2NDPA and 4NDPA give different types of derivative in single base propellants during the early stages of aging in a closed system at 80°C, the former yielding mainly dinitrodiphenylamines and the latter mainly the N-nitrosamine. Changes in the concentration profiles of the stabilizers and their derivatives in a propellant containing a 2NDPA/4NDPA mixture indicate that interactions between stabilizers occur in this case. Examination of the profiles has enabled the reaction pathways of the individual stabilizers to be tentatively identified and has led to the conclusion that reactions of 2NDPA and NO-2NDPA with oxides of nitrogen arising from the dissociation of NO-4NDPA are responsible for the different concentration profiles in the dual stabilizer composition.

Interactions of the type described above may contribute to the stabilizer depletion processes during aging of other nitrate ester propellants since both 2NDPA and 4NDPA are intermediates in reactions associated with the aging of DPA-stabilized compositions[21]. Similar interactions may occur in propellants containing other stabilizers. A better understanding of such processes may therefore lead to more reliable propellant safe-life predictions from accelerated aging and to the development of more effective dual stabilizer systems[22].

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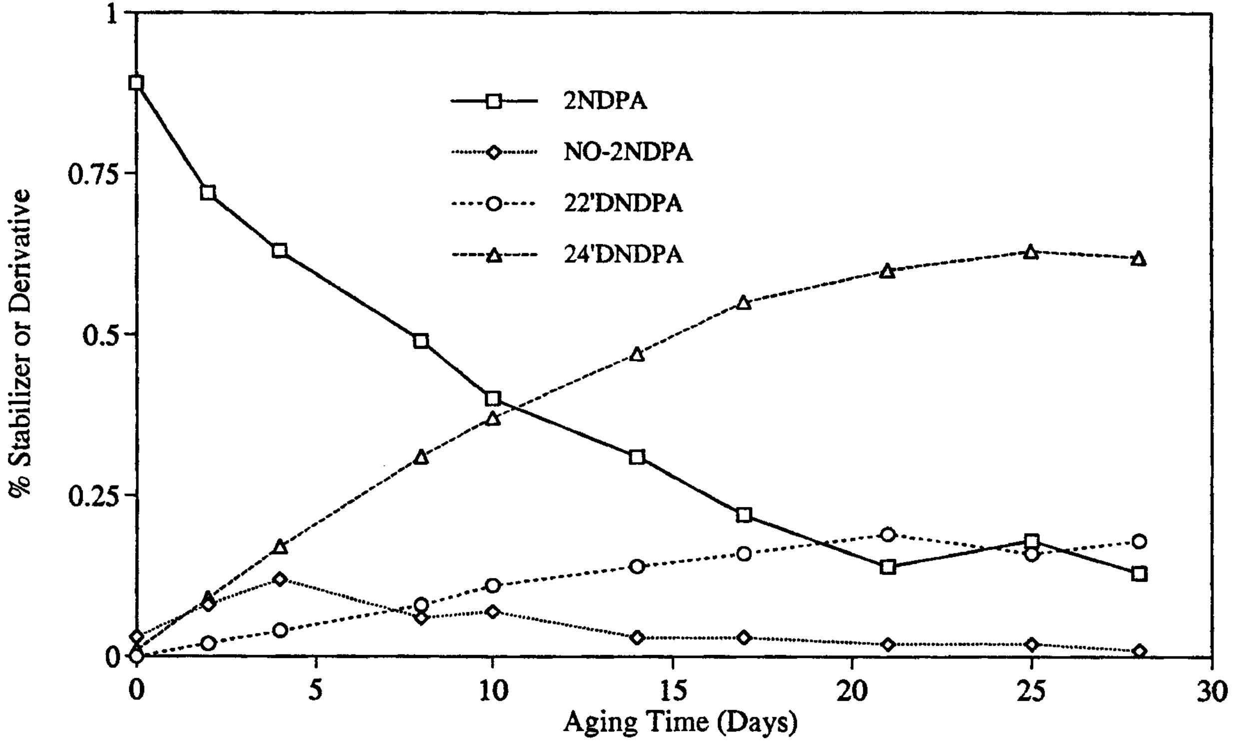

FIGURE 1
Concentration profiles for 2NDPA and derivatives in Propellant A

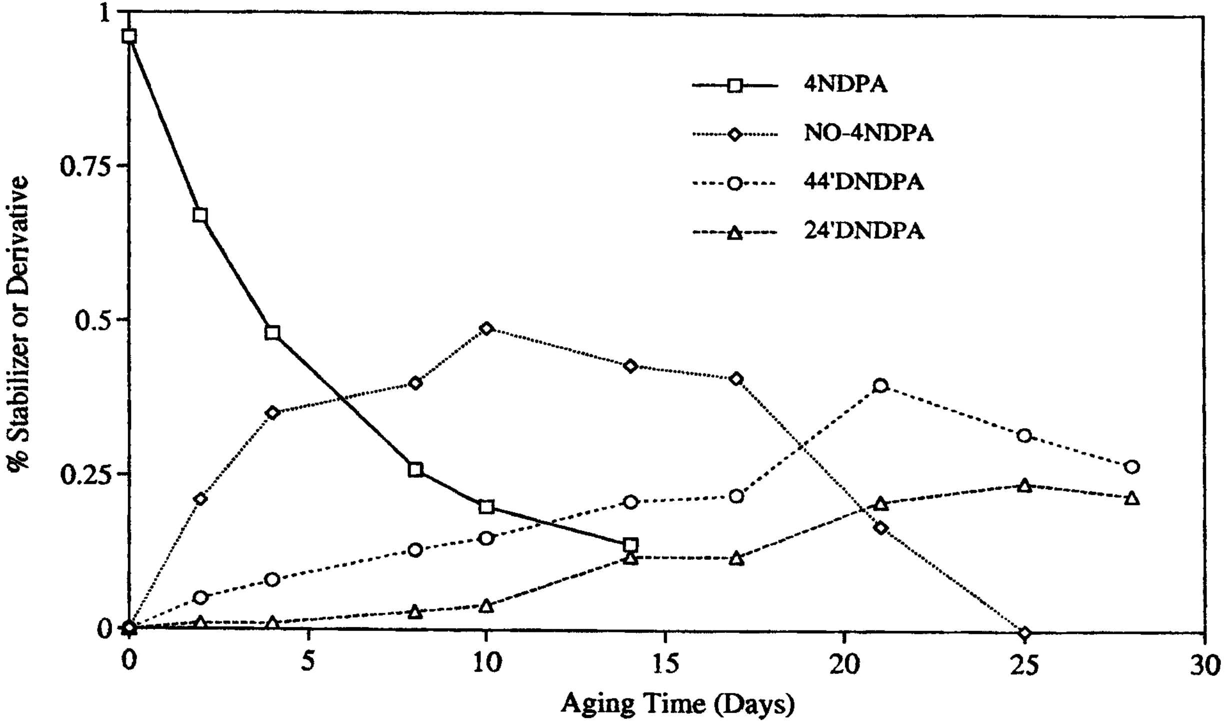

FIGURE 2
Concentration profiles for 4NDPA and derivatives in Propellant B (4NDPA not determined beyond 14 days)

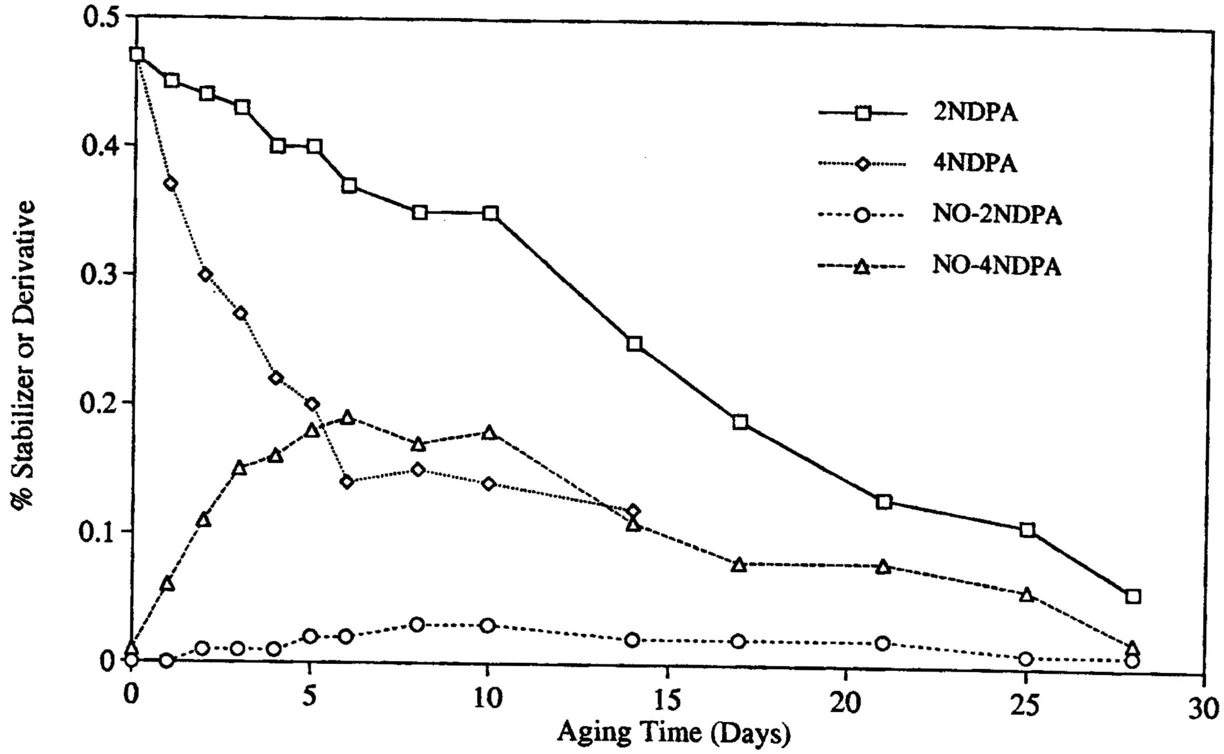

FIGURE 3
Concentration profiles for 2NDPA, 4NDPA and their N-nitroso derivatives in Propellant AB (4NDPA not determined beyond 14 days)

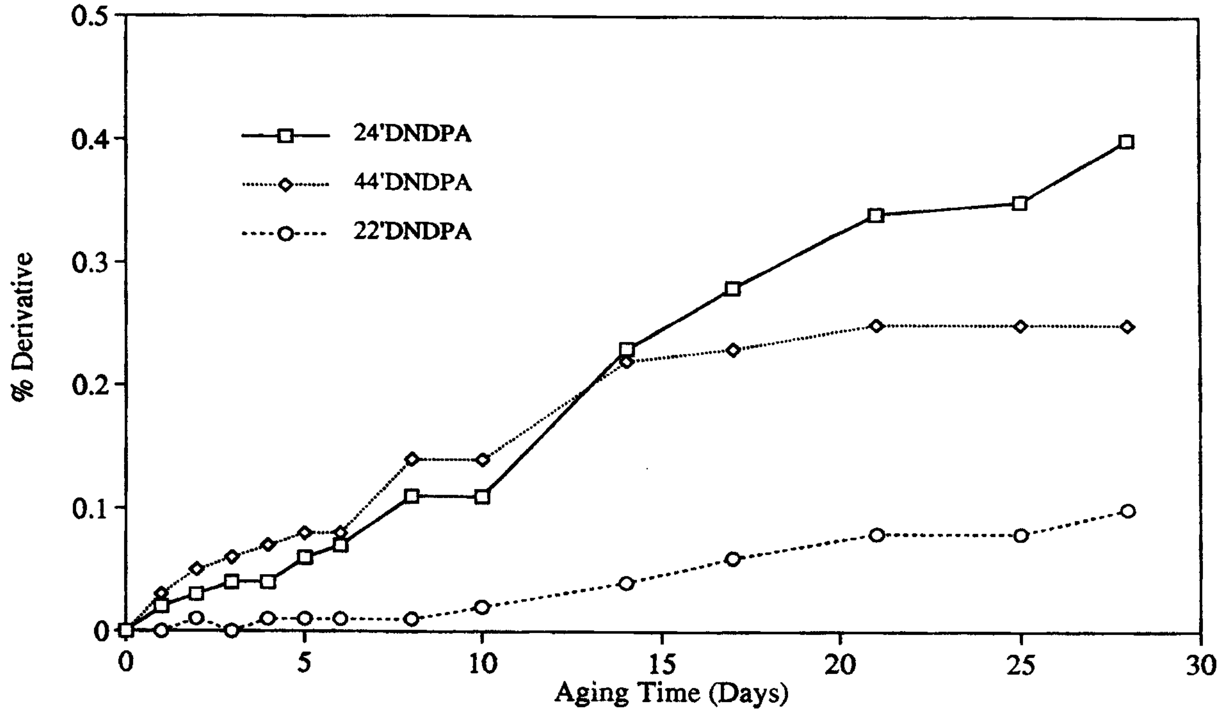

FIGURE 4
Concentration profiles for dinitrodiphenylamines in Propellant AB

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