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Competitive Reactivity of Stabilizers and Ballistic Modifiers During Simulated Aging of Propellants

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The competitive efficiencies of solid double-base propellant stabilizers, namely, para-nitro-N-methylaniline, and 2-nitrodiphenylamine and ballistic modifiers to react during the aging of nitroglycerin, have been investigated in an attempt to gain knowledge of the reactions that take place in propellant systems. It was found that ballistic modifiers greatly differ in their effect. Significant differences between aliphatic-acids-based lead salts were not detected, while lead salts of aromatic acids caused a better effect. Introduction of a hydroxyl group and an increase in the number of hydroxyls in aromatic monocarboxylic-acid-based lead salts caused a superior effect. This suggests that the competition for nitroglycerin degradation products between the lead compound and the stabilizer and the organic moiety of the ballistic modifier have an important influence on the reactions of the stabilizers. The relative reactivity of lead-based ballistic modifiers vs stabilizers toward the individual reactive species known to be generated during double-base propellant decomposition, namely, NO_2, HNO_2, and HNO_3, has also been thoroughly investigated. It was found that the various ballistic modifiers and stabilizers differ in their reactivity toward these reactive species. The basis of evaluation of the effect of the different ballistic modifiers on both the reaction of stabilizers and the properties of the propellants is well defined. This has helped to give a clear picture of the chemistry occurring during the aging of solid double-base propellants.

I. Introduction

BALLISTIC modifiers are used in nitrocellulose (NC)-based propellants to modify the ballistic characteristics of rocket motors, reducing the variability in motor performance over the operational temperature range.

A great deal of work has been performed on the way in which a ballistic modifier affects the ballistics of rocket propellants, but there have been few published works[1–3] on the effects these modifiers may have on the chemical stability. Some of these researches already indicated that the chemical stability of double-base propellants is influenced directly by different ballistic modifiers.

Systematic investigations should be carried out to obtain a deeper insight into this phenomenon. These investigations were carried out on nitroglycerin (NG) solution in acetonitrile containing identical quantities of different ballistic modifiers in the form of lead salts, which are commonly used in double-base propellants. NG, the main nitrate ester constituents of double-base propellants, has been found[4] to decompose 5–6 times faster than NC. Acetonitrile was chosen as the solvent for these experiments partly because it is reported[5] to have a dielectric constant similar to that of NG, and should therefore approximate to the conditions existing inside a double-base propellant matrix, and also because further experiments have shown that acetonitrile is unreactive toward NG decomposition products.

The thermal decomposition of nitrate esters is generally agreed to involve the generation of nitrogen dioxide, which can react with the degradation products of the nitrate esters, or with other propellant ingredients, so that the final products may include nitrogen oxides and nitrous and nitric acids.

A study of the effect of ballistic modifiers on the reactions of stabilizers with propellant degradation products, namely, NO_2, HNO_2, and HNO_3 could also indicate how the ballistic modifiers themselves react with either these reactive species or the by-products of the reaction of stabilizers with them. Studying the reaction of these compounds with these decomposition products is very important to understand the mechanism of double-base propellant decomposition.

The mechanism reaction of ballistic modifiers with NO_2, HNO_2, and HNO_3 is outside the scope of this investigation, and the main concern in this paper is to identify the relative efficiency of ballistic modifiers vs stabilizers to react with the well-known generated decomposition products during the aging of double-base propellants. The aim was to deduce some key parameters for the best stabilizer or stabilizer mixture that would be effective in improving the chemical stability of the propellant matrix.

The effect of the different ballistic modifiers on the consumption of the commonly used stabilizers para-nitro-N-methylaniline (pNMA) and 2-nitrodiphenylamine (2NDPA) in double-base rock propellants was investigated. The ability of these ballistic modifiers to decrease the consumption of stabilizers was taken as a measure of the relative efficiency of the ballistic modifiers to retard NG decomposition, and hence improve the chemical stability of double-base propellants.

II. Experimental

A. Materials, Standard Solutions, and Reaction Formulations

The ballistic modifiers were washed with acetonitrile (HPLC grade), dried at 80°C for 12 h, and then stored in well-sealed bottles. The other materials used for the preparation of the reaction formulations were obtained from the Aldrich Chemical Co., Ltd, in the United Kingdom and were used without further purification. NG solution was prepared in acetonitrile by the same procedure as described in Ref. 6.

All of the reaction formulations shown in Tables 1–3 were prepared at the required concentration in NG solution in acetonitrile by the same procedure as described in Ref. 6. The reaction formulations were aged at 75°C in a fan-assisted oven for different reaction periods.

The standard solutions of stabilizers and ballistic modifiers were prepared in dry acetonitrile and stored in the dark at room temperature in 20-ml sealed vials.

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Table 1 Effect of ballistic modifiers on *p*NMA reactions during NG aging

		*p*NMA (%C),[a] day		N.NO.*p*NMA (%F),[b] day	
No.	Formulation	7	14	7	14
1	*p*NMA (0.05)	40	73	15	29
2	*p*NMA (0.05) + LBR	27	54	24	47
3	*p*NMA (0.05) + LS	31	58	27	50
4	*p*NMA (0.05) + LC	36	67	15	30
5	*p*NMA (0.05) + LP	36	67	15	30
6	*p*NMA (0.05) + LSt	36	66	17	35
7	*p*NMA (0.05) + HRes	31	55	23	39
8	*p*NMA (0.05) + HSal	33	61	26	44

[a] Percent consumption with respect to the initial concentration.
[b] Percent formation of the derivative with respect to the initial concentration of the original stabilizer.

Table 2 Effect of ballistic modifiers on 2NDPA reactions during NG aging

		2NDPA (%C),[a] day		2,4'-DNDPA (%F),[b] day	
No.	Formulation	7	14	7	14
9	2NDPA (0.05)	16	35	14	30
10	2NDPA (0.05) + LBR	2.1	6.9	3.5	5.9
11	2NDPA (0.05) + LS	25	51	21	39
12	2NDPA (0.05) + LC	16	37	14	31
13	2NDPA (0.05) + LP	15	40	14	31
14	2NDPA (0.05) + LSt	12	31	10	26
15	2NDPA (0.05) + HRes	4.2	15	4	11
16	2NDPA (0.05) + HSal	28	50	21	36

[a] Percent consumption with respect to the initial concentration.
[b] Percent formation of the derivative with respect to the initial concentration of the original stabilizer.

Table 3 Effect of equimolar concentration of ballistic modifiers on the reactions of *p*NMA and 2NDPA during NG aging

		*p*NMA reactions				2NDPA reactions			
		*p*NMA (%C),[a] day		N.NO. *p*NMA (%F),[b] day		2NDPA (%C),[a] day		2,4'-DNDPA (%F),[b] day	
No.	Formulation	7	14	7	14	7	14	7	14
17	[*p*NMA (0.025) + 2NDPA (0.01)]	43	74	34	65	34	67	25	52
18	[*p*NMA (0.025) + 2NDPA (0.01)] + LBR	59	93	51	85	8	19	4	13
19	[*p*NMA (0.025) + 2NDPA (0.01)] + LS	77	100	68	94	5.2	67	3.6	49
20	[*p*NMA (0.025) + 2NDPA (0.01)] + LC	42	83	32	73	25	54	19	43
21	[*p*NMA (0.025) + 2NDPA (0.01)] + LP	40	79	31	69	30	61	25	47
22	[*p*NMA (0.025) + 2NDPA (0.01)] + LSt	40	72	33	65	14	43	9.5	31
23	[*p*NMA (0.025) + 2NDPA (0.01)] + HRes	58	90	47	77	9.2	28	7.3	20
24	[*p*NMA (0.025) + 2NDPA (0.01)] + HSal	80	100	71	90	8.3	69	6.2	44

[a] Percent consumption with respect to the initial concentration.
[b] Percent formation of the derivative with respect to the initial concentration of the original stabilizer.

The standard solution of NO_2 was prepared in dry acetonitrile to the required concentration, and stored in a sealed 20-ml vial at room temperature in the dark. To avoid any loss of gas, the requisite amount of NO_2 for each reaction was removed through the vial septum using a 50-μl HPLC syringe and rapidly introduced into a sealed 10-ml reaction vial through its septum.

The HNO_2 used for this investigation was prepared to the required concentration by the addition of HCl (as a standard solution in acetonitrile) to sodium nitrite (added as an aqueous standard solution), dissolved in the reaction formulation in acetonitrile.

The standard solution of anhydrous HNO_3 was prepared in dry acetonitrile to the required concentrations and stored in the dark at room temperature in sealed 20-ml vials. To avoid any loss of acid, the requisite amount of HNO_3 for each reaction was removed through the septum using a 50-μl high performance liquid chromatography (HPLC) syringe and rapidly introduced into a sealed 10-ml reaction vial through its septum.

For convenience, the figures for the molar concentrations of the reacting compounds, in Tables 4–6, will be shown as follows: 1 unit concentration = 3.29×10^{-4} mol/l.

The concentration of each compound in each formulation will be given in units of concentration. The amount of added NO_2, HNO_2, or HNO_3 in each formulation will represent the molar equivalent with respect to the unit concentration of the stabilizers.

The reaction formulations were prepared to the required concentrations in 25-ml volumetric flasks, and the solution was then distributed into 10-ml sealed vials and stored under the required reaction conditions in the dark. The volume of a 10-ml solution in 10-ml sealed vials was chosen to minimize the effect of the free space volume. These vials contain a certain amount of oxygen and may affect the results.

Table 4 Effect of ballistic modifiers on the reaction of stabilizers with NO_2

No.	Formulation (unit concentration)	NO_2 mol eq	2NDPA (%C)[a]	NO.2N (%F)[b]	2,4'-DNDPA (%F)[b]	2,2'-DNDPA (%F)[b]	*p*NMA (%C)[a]	N.NO.*p*NMA (%F)[b]
33	2NDPA (2)	4.0	96	63	6.3	5.4	——	——
34	2NDPA (2) + LBR (2)	4.0	30	24	2.4	1.1	——	——
35	2NDPA (2) + LS (2)	4.0	48	34	1.9	1.9	——	——
36	2NDPA (2) + LP (2)	4.0	43	29	2.7	2.1	——	——
37	2NDPA (2) + PbO (2)	4.0	96	62	7.1	5.7	——	——
38	2NDPA (2) + *p*NMA (2)	4.0	27	18	2.5	2.0	——	——
39	*p*NMA (2)	1.5	——	——	——	——	69	66
40	*p*NMA (2) + LBR (2)	1.5	——	——	——	——	21	20
41	*p*NMA (2) + LS (2)	1.5	——	——	——	——	49	47

[a] Percent consumption with respect to the initial concentration.
[b] Percent formation of the derivative with respect to the initial concentration of the original stabilizer.

Table 5 Effect of ballistic modifiers on the reaction of stabilizers with HNO_2

No.	Formulation (unit concentration)	HNO_2 mol eq	2N (%C)[a]		NO.2N (%F)[b]	
			Initial	Extended	Initial	Extended
	2NDPA-based formulation					
42	2NDPA (1.5)	1.0	78	90	64	71
43	2NDPA (1.5) + LBR (2)	1.0	0.2	75	0.4	46
44	2NDPA (1.5) + LS (2)	1.0	1.0	45	1.0	30
45	2NDPA (1.5) + LC (2)	1.0	68	85	46	56
46	2NDPA (1.5) + LP (2)	1.0	1.3	98	1.1	64
47	2NDPA (1.5) + *p*NMA (2)	1.0	0	89	0	62
	*p*NMA + 2NDPA-based formulation					
48	Control	3.0	92	98	74	13
49	Control + LBR (2)	3.0	1.7	71	0.7	23
50	Control + LS (2)	3.0	1.2	44	0.8	14
51	Control + LC (2)	3.0	76	89	49	24
52	Control + LP (2)	3.0	20	40	15	15

Note: Initial = 2 h/20°C, Extended = 7 day/20°C, further 1 mol eq HCl, 2 h/20°C.
[a] Percent consumption with respect to the initial concentration.
[b] Percent formation of the derivative with respect to the initial concentration of the original stabilizer.

Table 6 Effect of ballistic modifiers on the reaction of stabilizers with HNO_3

No.	Formulation (unit concentration)	HNO_3 mol eq	2NDPA (%C)[a]	2,4'-DNDPA- (%F)[b]	2,2'-DNDPA- (%F)[b]	*p*NMA (%C)[a]	N.NO.*p*NMA (%F)[b]
53	2NDPA (2)	1.0	43	14	8.1	——	——
54	2NDPA (2) + LBR (2)	1.0	6.0	2.5	0	——	——
55	2NDPA (2) + LS (2)	1.0	12	4.5	0.9	——	——
56	2NDPA (2) + LP (2)	1.0	21	8.0	6.2	——	——
57	2NDPA (2) + PbO (2)	1.0	42	12	7.3	——	——
58	2NDPA (2) + *p*NMA (2)	1.0	34	9.3	7.8	——	——
59	*p*NMA (2)	1.0	——	——	——	62	6.9
60	*p*NMA (2) + LBR (1)	1.0	——	——	——	2.4	0
61	*p*NMA (2) + LS (1)	1.0	——	——	——	14	0.9

[a] Percent consumption with respect to the initial concentration.
[b] Percent formation of the derivative with respect to the initial concentration of the original stabilizer.

Table 7 Effect of nitrite ion on reactions of *p*NMA

No.	Formulation	*p*NMA (%C),[a] day		N.NO. *p*NMA (%F)[b]	
		7	14	7	14
25	[*p*NMA (0.02) + 2NDPA (0.02)]	0	0	0	0
26	[*p*NMA (0.02) + 2NDPA (0.02)] + LBR	20	20	18	18
27	[*p*NMA (0.02) + 2NDPA (0.02)] + LS	46	46	44	44
28	[*p*NMA (0.02) + 2NDPA (0.02)] + LC	16	14	13	12
29	[*p*NMA (0.02) + 2NDPA (0.02)] + LP	48	46	46	43
30	[*p*NMA (0.02) + 2NDPA (0.02)] + LSt	0	0	0	0
31	[*p*NMA (0.02) + 2NDPA (0.02)] + HRes	0	0	0	0
32	[*p*NMA (0.02) + 2NDPA (0.02)] + HSal	0	0	0	0

[a] Percent consumption with respect to the initial concentration.
[b] Percent formation of the derivative with respect to the initial concentration of the original stabilizer.

B. HPLC Quantitative Analysis

At the end of each reaction period, the solutions were filtered through 0.2-μl filters and then injected onto the HPLC. The HPLC conditions were as described in Ref. 7.

The data obtained from the HPLC were statistically analyzed to obtain data for stabilizer reactions. The results obtained for stabilizer consumption and the formation of their derivatives at the end of each reaction period are presented in Tables 1–7. For simplicity, some of these results, especially those which do not contribute much to the discussion, are not presented in Tables 1–7.

III. Results and Discussion

A. Reactions of Stabilizers and Ballistic Modifiers During Nitroglycerin Aging

1. Effect of Ballistic Modifiers on Stabilizer Reactions (pNMA-Based Formulations)

The formulations shown in Table 1 were based on *p*NMA, which was used in a 0.05 molar ratio with respect to NG. The different ballistic modifiers, resorcylic acid (HRes) and salicylic acid (HSal), were added in equimolar concentration to the stabilizer. These formulations are aged at 75°C for 7 and 14 days. The results obtained for the consumption of *p*NMA and for the formation of its derivatives are shown in Table 1.

Analysis of the results presented in Table 1 shows the following.

1) The ballistic modifiers lead β-resorcylate (LBR), and lead salicylate (LS) had a significant effect on *p*NMA reactions, while the others, lead phthalate (LP), lead citrate (LC), and lead stearate (LSt) did not cause a noticeable effect when compared to that occuring in the control formulation (in the absence of ballistic modifiers). The order of efficiency of the different ballistic modifiers in decreasing the consumption of *p*NMA was as follows: LBR > LS > LP = LC = Lst > control, whereas the corresponding order of efficiency toward the formation of *p*NMA derivatives was different. This observation will be discussed in detail for each formulation.

2) In all of the formulations *p*NMA was consumed with the formation of N-nitrosopara-nitro-N-methylaniline (N.NO.*p*NMA). In most of the formulations, an observable amount of N-nitro-para-nitro-N-methylaniline (N.NO$_2$.*p*NMA) was formed, and the ratio of N.NO.*p*NMA formed/*p*NMA consumed was about 0.4. The quantitative formation of N.NO$_2$.*p*NMA was not followed because an authentic sample of this derivative was unavailable; the information on this derivative was based solely on the increase in its HPLC peak area during aging.

3) LBR and LS decreased the consumption of *p*NMA and increased the percentage formation of N.NO.*p*NMA compared to the control formulation. The *p*NMA consumption results, caused by the presence of LBR and LS, are in agreement with reported previously results.[1] In addition, these two lead salts appeared to prevent the formation of N.NO$_2$.*p*NMA. It is known that the reaction of *p*NMA with nitrogen dioxide generates N.NO.*p*NMA and nitric acid. If the latter is not removed from the system, its accumulation will cause either further N-nitration of *p*NMA or the oxidation of the N-nitroso derivative of *p*NMA, both leading to the formation of N.NO$_2$.*p*NMA. It is possible that both LBR and LS may react with the generated nitric acid, thus favoring the formation of N.NO.*p*NMA as observed.

4) Note that resorcylic acid and salicylic acid gave comparable effects on both *p*NMA consumption and N.NO.*p*NMA formation to that produced by their corresponding salts, LBR and LS, respectively. This suggests that the reactivity of ballistic modifiers pertains to their ions.

5) Although *p*NMA cannot be used alone in double-base propellants, it is mixed in the casting powder with NC and the ballistic modifiers, LBR and LS, and it is expected that *p*NMA will undergo reactions with NC decomposition products during the processing of the casting powder. These reactions, as already observed in the preceding text, would be affected by the presence of LBR and LS.

2. Effect of Ballistic Modifiers on Stabilizer Reactions (2NDPA-Based Formulations)

The formulations shown in Table 2 were based on 2NDPA, which was used in a 0.05-molar ratio with respect to NG. The different ballistic modifiers and resorcylic and salicylic acids were added in equimolar concentration to the stabilizer. These formulations were aged at 75°C for 7 and 14 days.

Analysis of the results presented in Table 2 shows the following:

1) In all of the formulations 2NDPA reacted with the NG decomposition products and formed 2,4′-dinitro-diphenylamine (2,4′-DNDPA) as the major product with traces of 2,2′-dinitro-diphenylamine (2,2′-DNDPA).

2) LBR and LS produced a significant effect on the 2NDPA reactions, while the other modifiers, LSt, LP, and LC did not cause a noticeable effect compared to that occurring in the control formulation. The order of efficiency of the different ballistic modifiers in decreasing the consumption of 2NDPA was as follows: LBR >> LSt > LP = LC = control > LS. The corresponding order of efficiency in decreasing the formation of 2,4′-DNDPA mirrors that for 2NDPA consumption.

3) Note that the effect of LBR and LS on 2NDPA reactions, although approximately similar toward *p*NMA reactions, is quite different. LBR greatly reduced 2NDPA consumption, whereas LS increased the consumption of 2NDPA during both aging periods. The results obtained for the formation of 2,4′-DNDPA complement those obtained for 2NDPA consumption. This unexpected observation requires further investigation to determine the reason why the behavior of LBR and LS, although structurally related as salts of hydroxyl-substituted benzoic acid, differ in this situation. This will be dealt with in detail in the following section.

Resorcylic acid and salicylic acid had approximately the same effect on both 2NDPA consumption and the formation of 2,4′-DNDPA as that produced by their corresponding salts, LBR and LS, respectively. This provides support for the earlier suggestion that the organic moiety of lead salts plays an important role in the reactivity of these salts toward NG decomposition products.

3. Effect of Ballistic Modifiers on Stabilizer Reactions (Stabilizer Mixture-Based Formulations)

The formulations shown in Table 3 were subjected to the same preparation, aging, and analysis conditions as given earlier. These formulations were based on the stabilizer mixture *p*NMA and 2NDPA. *p*NMA and 2NDPA were used in 0.025 and 0.01 molar ratios with respect to NG, respectively. The different ballistic modifiers and resorcylic and salicylic acids were added in equimolar ratio (0.03 with respect to NG).

Analysis of the results presented in Table 3 shows the following:

1) In all of the formulations *p*NMA reacted with the NG decomposition products and formed N.NO.*p*NMA as the major product; 2NDPA reacted and formed 2,4′-DNDPA as the major product together with traces of 2,2′-DNDPA. Note that *p*NMA did not form N.NO$_2$.*p*NMA as occurred in the case of *p*NMA-based formulations (Table 1). This is mainly because of the presence of 2NDPA in the stabilizer mixture, as was observed previously[6] in stabilizer reactions in the NG solution in acetonitrile. During the investigation of the reaction of stabilizers with the individual NG decomposition products, it was shown[8] that 2NDPA is more likely than *p*NMA to react with the nitric acid (produced from the reaction of *p*NMA with nitrogen dioxide), which otherwise would cause the formation of N.NO$_2$.*p*NMA as previously suggested.

2) During the first aging period most of the ballistic modifiers, except LBR and LS, did not show significant effects on

the *p*NMA reactions, compared to those that occurred in the control formulation. LBR and LS caused a significant increase in *p*NMA consumption, and consequently, an increase in the formation of N.NO.*p*NMA during both aging periods.

3) During the second aging period there was a difference, although not very significant, between the effect on the *p*NMA reactions caused by the other different ballistic modifiers LSt, LC, and LP, and the control formulation. As observed earlier for *p*NMA-based formulations, the effect of LBR and LS on *p*NMA reactions was very significant compared to those in the control formulation. Thus, the major attention will be directed toward investigating the effect of LBR and LS on *p*NMA reactions with NG decomposition products.

4) LBR and LS allowed higher consumption of *p*NMA compared to that which occurred in the control formulation, and this was reflected in higher formation of N.NO.*p*NMA. This observation is in contrast to that observed when *p*NMA was used as the sole stabilizer (Table 1 formulations), where LBR and LS both decreased the consumption of *p*NMA compared to the control formulation. The reason for this may be because of the higher concentration of LBR and LS in Table 1 formulations with respect to that in the current formulations, which might compete with *p*NMA for the NG decomposition products, hence decreasing the consumption of *p*NMA.

Any mechanistic investigation into the competing reactions of the different compounds *p*NMA, 2NDPA, LBR, or LS, and their reaction products with the different NG decomposition products, is likely to be very difficult. In the present context, the main concern is to determine the effect of the different ballistic modifiers, commonly used in double-base propellants, on the reactions of either *p*NMA or 2NDPA, or a mixture of both in the double-base propellant matrix.

The order of efficiency of the different ballistic modifiers in decreasing 2NDPA consumption was as follows: LBR >> LSt > LP > LC > LS > control. This order indicates that there is a significant difference between the effect of LBR and LS on 2NDPA reactions; the other ballistic modifiers did not show noticeable differences.

As found for 2NDPA-based formulations (Table 2), LBR and LS produced different effects on 2NDPA reactions. LBR caused a significant decrease in 2NDPA consumption during both aging periods, while LS, although causing a significant decrease in 2NDPA consumption (even more than that occurred in the case of LBR), during the first aging period, had no effect on 2NDPA consumption during the second aging period. It would be expected that the consumption of 2NDPA would be much higher if the aging were to be continued, judging from the much higher rate of increase in 2NDPA consumption during the second aging period with respect to that which occurred during the first aging period.

In the Table 2 formulations, in which 2NDPA was the sole stabilizer, LS allowed a higher consumption of 2NDPA than that occurring in the control formulation during both aging periods. This suggests that the large effect caused by LS in decreasing the consumption of 2NDPA during the first aging period in Formulation 19, Table 3, might mainly be caused by the presence of *p*NMA. This is further supported by the observation that *p*NMA was largely consumed during the first aging period, and thus, LS almost solely affects the 2NDPA reactions during the second aging period.

It seems that LBR and LS have a high reactivity toward NG decomposition products. The by-products of the reactions of LBR and LS with the NG decomposition products have different effects on the *p*NMA and 2NDPA stabilizers. Those produced from LS caused catalytic consumption of the stabilizers by enhancing the nitrosation/nitration reactions of both stabilizers. In contrast, although the by-products resulting from the reactions of LBR with the NG decomposition products enhanced the nitrosation/nitration reactions of *p*NMA, it did not affect those of 2NDPA. The reason for this contradiction between the effect of LBR and LS, although structurally related, may be related to the number of the hydroxyl groups in each.

As previously observed in both *p*NMA- and 2NDPA-based formulations (Tables 1 and 2, respectively), resorcylic and salicylic acids gave approximately the same effect on both *p*NMA and 2NDPA consumption and the formation of their derivatives as that produced by their corresponding salts, LBR and LS, respectively. This provides further evidence for the earlier suggestion that the organic moiety of lead salts plays an important role in the reactivity of these salts toward NG decomposition products.

Further investigations were undertaken to determine the reactivity of LBR, LS, and their corresponding acids toward one of the possible NG decomposition products, nitrite ion. The ultimate aim was to obtain support for the suggestion made earlier that LBR and LS promote the nitrosation/nitration reactions of stabilizers by decomposition products, which otherwise, in the absence of these lead salts, would not occur.

The formulations shown in Table 7 were based on the *p*NMA and 2NDPA stabilizer mixture in acetonitrile solution with aqueous sodium nitrite in molar excess concentration. The ballistic modifiers and resorcylic and salicylic acids were used in equimolar concentration to that used in Table 3 formulations.

Note that only LBR, LS, and their corresponding acids caused the consumption of *p*NMA with the formation of N.NO.*p*NMA as the major product. The other ballistic modifiers, LP, LC, and LSt, did not affect the stabilizers. The magnitude of the effect of resorcylic and salicylic acids on the stabilizer reactions were similar to that produced by their corresponding salts LBR and LS, respectively.

It was further observed that during the second aging period, *p*NMA consumption and the formation of N.NO.*p*NMA did not change from that which occurred during the first aging period. This may indicate that the available nitrite ions were limited by the efficiency of each salt to act as an acid site toward nitrite ion. It was shown[9] that under more conventional nitrosation conditions (H^+, NO_2^-), the nitrite ion must react with two hydrogen ions before it can be attacked by the secondary amine. It may be that LBR, LS, resorcylic acid, and salicylic acid have an acid effect toward the nitrite ion, thus activating it for the nitrosation reaction of the secondary amine stabilizer. It was also shown[6] that *p*NMA reacts much more rapidly than 2NDPA with the nitrosating agent.

The catalytic effect in increasing the 2NDPA consumption, caused by the presence of LS in formulations 11 and 19, was supported by the results obtained in formulation 27, in which LS allowed consumption of only traces of 2NDPA. For LBR in formulation 26, the consuption of both stabilizers was even lower.

The results obtained from the comparison of the effect of LBR, LS, and their corresponding acids on stabilizer reactions, and also from the study of the effects of LBR, LS, and their corresponding acids on the promotion of stabilizer nitrosation by nitrite ion, led to the conclusion that the organic moiety of the ballistic modifier plays an important role in its influence on the reactions of stabilizers.

During burning studies of double-base propellant, it was observed[10] that the catalytic and plateau behavior of lead salts depend largely on the nature and structure of the organic moiety of the lead salt. Thus, it would seem reasonable to suggest that the organic moiety plays a similar role in influencing the chemical stability of a double-base propellant during aging.

B. Reactions of Stabilizers and Ballistic Modifiers with Propellant Decomposition Products

It was shown in the preceding text that ballistic modifiers have a significant effect on the reaction of stabilizers during the aging of NG. It was therefore envisaged that a study of the effect of ballistic modifiers on the reactions of stabilizers with propellant degradation products (namely, NO_2, HNO_2, and

HNO_3) might also indicate how the ballistic modifiers themselves react with either these reactive species or the by-products of the reaction of stabilizers with them. Studying the reaction of these compounds with these decomposition products is very important to an understanding of the mechanism of double-base propellant decomposition.

1. *Effect of Ballistic Modifiers on the Reaction of Stabilizers with Nitrogen Dioxide*

In the formulations shown in Table 4 ballistic modifiers were used in equal molar amounts to stabilizers. 4 and 1.5 molecular equivalent (mol eq) (to 2 unit concentration) of NO_2 were added to 2NDPA and a *p*NMA-based formulation, respectively, and allowed to react for 5 min at 20°C in the dark.

It has previously been thought[1,2] that a ballistic modifier will not compete with the very reactive additives like secondary amines for NO_2, and thus, that the effect of a ballistic modifier on the chemical stability of double-base propellants would not be significant. It is clear, however, from Table 4 that some ballistic modifiers have a significant effect on the reactions of 2NDPA. Comparison of the effects of ballistic modifiers with those of secondary stabilizers,[8] on the reactions of 2NDPA, indicates that the ballistic modifier LBR produces a slightly smaller effect than that of *p*NMA, the most reactive stabilizer toward NO_2.

The relative efficiency of the different ballistic modifiers and stabilizers investigated in decreasing 2NDPA consumption is as follows: *p*NMA > LBR > LP > LS > PbO = Control.

*p*NMA gave the lowest consumption of 2NDPA, and completely consumed and quantitatively converted to its corresponding N-nitroso-derivative.

The effect of the ballistic modifiers on the reactions of 2NDPA is caused by either their direct reaction with NO_2 or by their reaction with the HNO_3 produced from the reaction of 2NDPA with NO_2. It will be shown from the investigation of the effect of ballistic modifiers on 2NDPA reactions with HNO_3 that ballistic modifiers have great reactivity toward HNO_3.

The inclusion of LBR in formulation 34 considerably decreased the consumption of 2NDPA and increased the formation of N.NO.2NDPA, compared with formulation 33, which lacked LBR. This suggests that LBR reacts with HNO_3 to form HNO_2, which in turn causes an increase in the N.NO.2NDPA formed.

The greater reactivity of some ballistic modifiers toward HNO_3 does not necessarily mean that they are unreactive toward NO_2. This is not expected to be the case for those modifiers having a reactive aromatic structure like LBR, LS, LP, etc. LBR when used alone in formulation 34 caused the formation of small amounts of the C-nitro-derivatives of 2NDPA, even though it gave the lowest 2NDPA consumption among the other balllistic modifiers. This clearly reflects a high reactivity of LBR toward NO_2.

The large difference between the effect of LBR and LS on 2NDPA consumption may be related to the number of hydroxyl groups present in each. It is anticipated that the reactivity of these structures toward HNO_3 and NO_2 is derived from the presence of the hydroxyl group. Thus, the higher efficiency of LBR compared to LS in retarding the consumption of 2NDPA may be caused by 1) the larger number of hydroxyl groups, and 2) the orientation of the two hydroxyl groups in LBR molecule, which make it more susceptible to electrophilic substitution by either NO^+ or NO_2^+.

It was shown in the preceding text that LS had a marked effect in increasing 2NDPA consumption. The consumption of 2NDPA was decreased during the early stages of aging, but it was greatly increased during the later stages. An explanation of this may be related to the possibility of forming HNO_2 and HNO_3 from the direct reaction of LS with HNO_3 and NO_2, respectively. However, the difference may be rationalized in terms of the associated salicylate anion, leading to an enhancement of the rate of nitrosation/nitration of the stabilizer.

PbO did not have any noticeable effects on 2NDPA consumption, suggesting that any reactivity of ballistic modifiers toward NO_2 is because of their reactive aromatic structures.

LP, although not having hydroxyl groups in its structure, exhibited a moderate effect on decreasing 2NDPA consumption. It is not clear whether LP reacts directly with NO_2, or with the HNO_3 produced from the reaction of 2NDPA with NO_2. It will be shown later that LP exhibits a significant reactivity toward HNO_3.

It is also clear from Table 4 that ballistic modifiers have significant effect on decreasing *p*NMA consumption. The order of efficiency of the different ballistic modifiers, in decreasing *p*NMA consumption, is as follows: LBR > LS > Control.

LS gave a higher *p*NMA consumption than when LBR was used, as also happended in the case of 2NDPA-based formulations. This feature again furnishes evience for the role of the hydroxyl groups in the reactivity of the ballistic modifiers.

2. *Effect of Ballistic Modifiers on the Reaction of Stabilizers with Nitrous Acid*

The formulations shown in Table 5 were based on 2NDPA (1.5 unit concentration), and on stabilizer mixture [*p*NMA (2 unit concentration) + 2NDPA (1.5 unit concentration)] as primary stabilizers. The ballistic modifiers were present at 2 unit concentration. HNO_2 was allowed to react with each formulation as shown in Table 5.

It is clear from Table 5 that *p*NMA is efficient toward HNO_2, as judged from their ability to reduce 2NDPA consumption.

It is also clear that some ballistic modifiers compete with the very reactive additive, such as *p*NMA for HNO_2. These ballistic modifiers have a significant effect on the reactions of 2NDPA. The results for the first reaction period indicate that the presence of the ballistic modifiers LBR, LS, and LP resulted in negligible consumption of 2NDPA. They produced a similar effect to that of *p*NMA, the most reactive stabilizer toward NO_2. LC led to only a modest decrease compared to that in the control formulation.

Addition of a further 1 mol eq (to 2 unit concentration) HCl gave results that led to the following conclusions:

1) The relative efficiency of ballistic modifiers and stabilizers in decreasing 2NDPA consumption, when comparing the second reaction period with the first, is as follows: LS > LBR > LC > *p*NMA.

2) Although LP gave negligible 2NDPA consumption during the first reaction period, it gave the highest consumption (even higher than that of the control formulation) during the second reaction period. The same behavior occurred in the presence of LBR, but to a lesser degree.

A possible rationalization for these observations is as follows: during the initial addition of HCl, the ballistic modifier may become protonated more rapidly than the nitrite ion, thus preventing the formation of HNO_2. Consequently, 2NDPA consumption would depend upon the relative rate of protonation of the ballistic modifier. The reactivity of the corresponding acid that is generated might then affect the 2NDPA consumption during the second reaction period. LP, because it has two carboxyl groups, is expected to be protonated rapidly, but the presence of the resulting phthalic acid may be undesirable and may cause catalytic consumption of 2NDPA. The same explanation may also be applied in the LBR and LS cases.

A further investigation was designed to identify the reaction pathway for the reaction of ballistic modifiers with excess HNO_2 and their effect on stabilizer reactions. The reaction formulations based on a mixture of *p*NMA and 2NDPA (shown in Table 5) were allowed to react with 3 mol eq (to 2 unit concentration) HNO_2 at 20°C for 2 h in the dark. Following the analysis after 2 h at 20°C, the samples were left for a further 7 days at 20°C in the dark.

The aforementioned behavior of LBR, LS, and LP is supported by the results obtained here. These results support the suggestion that some protonation of the ballistic modifier is caused by the initial addition of HCl.

Of all the ballistic modifiers investigated, LS was the only one that prevented the complete consumption of *p*NMA during the first reaction period, and gave the lowest 2NDPA consumption during the combined reaction periods. This observation suggests that salicylic acid, formed from LS protonation, reacts with HNO_2. The reactivity toward HNO_2 of the acids formed from ballistic modifiers will be discussed later.

It is clear that the protonation of LS, which would result in the formation of salicylic acid, is not as important in its effect upon stabilizer consumption as in the case of resorcylic acid from LBR. It appears that salicylic acid is more reactive than resorcylic acid toward HNO_2. However, resorcylic acid appears to be undesirable in other respects.

From the preceding text it is obvious that ballistic modifiers have a significant effect on the reaction of stabilizers with HNO_2.

An investigation[11] was performed to clarify the effect of acids generated from ballistic modifiers. The results showed that resorcylic acid gave a 2NDPA consumption that was even higher than that in the control formulations, whereas salicylic acid and the combination of resorcylic acid and salicylic acid gave negligible 2NDPA consumption.

It is also concluded that 1) the higher efficiency of LBR and LS in decreasing 2NDPA consumption is caused by both the reactivity of resorcylate and salicylate anions toward HNO_2 and the protonation of the salts by the initial addition of HCl, and 2) resorcylic acid catalyzes the reaction of 2NDPA with HNO_2, whereas salicylic acid reacts with HNO_2, therefore reducing 2NDPA consumption.

3. *Effect of Ballistic Modifiers on the Reaction of Stabilizers with Anhydrous Nitric Acid*

In this investigation the different formulations of the stabilizer mixtures with some ballistic modifiers (as shown in Table 6), were reacted with 1 mol eq (to 2 unit concentration) of anhydrous HNO_3 at 70°C for 20 h. The concentration of the stabilizers and ballistic modifiers were also shown in Table 6.

It is clear from Table 6 that 2NDPA forms nitration products, the C-nitro derivatives 2,4′-DNDPA and 2,2′-DNDPA, whereas *p*NMA was consumed to a lower extent than 2NDPA, but produced traces of the known nitrosation/nitration products, namely, N.NO.*p*NMA, N.NO_2.*p*NMA, and 2,4-DNMA.

It is also clear from Table 6 that some ballistic modifiers have a significant effect on 2NDPA consumption. Some lead salts have a larger effect on decreasing 2NDPA consumption than some of the secondary stabilizers as studied previously.[8] The relative efficiency in decreasing 2NDPA consumption of the different stabilizers and lead salts studied is as follows: LBR > LS > LP > *p*NMA > PbO. This order again highlights the importance of the organic moiety as the source of reactivity of lead salts, cf. reactions with NO_2. The presence of hydroxyl groups, and their number and position, seems to be a decisive factor in this reactivity.

The results of the effect of some ballistic modifiers on *p*NMA consumption support the results presented for 2NDPA formulations. LBR showed the highest efficiency in decreasing *p*NMA consumption, the latter being almost negligible.

Two conclusions may be drawn: 1) LBR is the most reactive of all the ballistic modifiers toward HNO_3, and b) 2NDPA is more reactive toward HNO_3 than *p*NMA, because *p*NMA consumption was much less than that of 2NDPA when each was used in combination with LBR under the same reaction conditions.

A comparison of these results with those obtained earlier for the reactivity of LS toward the possible NG decomposition products, shows that LS has a high reactivity toward these reactive species during the early stages of aging, but during the later stages LS shows a catalytic effect on the reaction of the stabilizer. The reaction products from LS enhance the nitrosation/nitration reaction of the stabilizer, causing rapid consumption, compared to that occurring in the control formulation, i.e., in the absence of LS.

The absence of the formation of significant amounts of N.NO.*p*NMA in formulations using both ballistic modifiers and *p*NMA may be of help in explaining the mode of action of ballistic modifiers with HNO_3. It is known that *p*NMA is very reactive toward HNO_2, forming N.NO.*p*NMA as the major product. Indeed, *p*NMA reacts very rapidly with HNO_2 even at temperatures below room temperature, whereas 2NDPA reacts with HNO_2 rather slowly. Therefore, the absence of significant amounts of N.NO.*p*NMA in the formulations studied in Table 6 suggests that 1) the direct reaction of ballistic modifiers with HNO_3 does not produce any HNO_2, or 2) the higher the consumption of 2NDPA with respect to *p*NMA may be explained by direct nitration of 2NDPA, the latter having a structure that is more susceptible toward this type of substitution than *p*NMA.

From the preceding text, it is obvious that ballistic modifiers have a significant effect on the reaction of stabilizers with HNO_3.

IV. Conclusions

The organic moiety of lead salt-based ballistic modifiers play an important role in the reactivity of these salts toward NG decomposition products.

LBR and LS, have a significant effect on the reactions of *p*NMA and 2NDPA, whereas the other modifiers, LSt, LP, and LC, do not have a noticeable effect. Although LBR and LS have approximately similar effects on the *p*NMA reactions, their effect on the 2NDPA reactions is quite different. They cause an increase in the formation of N.NO.*p*NMA and prevent the formation of N.NO_2.*p*NMA. The effect of LS is greater than that exhibited by LBR. LBR greatly reduces 2NDPA depletion, whereas LS increases the consumption of 2NDPA.

Some ballistic modifiers have a significant effect on the reactions of stabilizers with NO_2, HNO_2, and HNO_3.

Indeed, some lead salts have a higher effect in decreasing 2NDPA depletion with HNO_3 than some of the secondary stabilizers. LBR produces a slightly smaller effect than that of *p*NMA, the most reactive stabilizer toward NO_2. Of all the ballistic modifiers investigated, LS has the largest effect on stabilizer reactions with HNO_2, giving the lowest consumption of both *p*NMA and 2NDPA. This is attributed to the reactivity of salicylic acid toward HNO_2, and contrasts with the undesirable effect produced by resorcylic acid.

The reactivity of LBR and LS toward NO_2, HNO_2, and HNO_3 appears to derive from the presence of hydroxyl groups in the molecule, and their relative efficiency may be related to the number of hydroxyl groups and their orientation. The other ballistic modifiers based on phthalic acid and citric acid have not shown significant effects on stabilizer reactions with these reactive species.

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