JOURNAL OF PROPULSION AND POWER
Vol. 16, No. 1, January–February 2000

Improvements in the Chemical Stability of Double-Base Solid Rocket Propellants

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The effect of copper, compared with lead salt-based ballistic modifiers on the reaction of the propellant stabilizers, *para*-nitro-N-methylaniline and 2-nitrodiphenylamine, during the aging of nitroglycerin solutions and on the reactions of these stabilizers with the individual reactive species known to be generated during double-base propellant decomposition, namely NO_2, HNO_2, and HNO_3, have been thoroughly investigated in an attempt to deduce some key parameters that influence the reactions that take place in these propellant systems during aging. It was found that copper modifiers greatly differ from lead ones in their effect on the depletion of stabilizers and in their reactivity toward the reactive species. All of the copper salts have a dramatic effect on the reactions of propellant stabilizers. They cause more rapid depletion of stabilizers when compared with that produced by lead salts, the effect of basic copper salicylate being more dramatic than that of copper oxide. The results have shown that the organic moiety of the ballistic modifier plays an important role in its influence on the reactions of stabilizers with propellant degradation species, and that the higher reactivity of copper salts compared with that of lead salts is attributable to the combined effect of both the copper ion and the salt anion. In particular, this investigation has helped contribute information on the propellant compositions that should fulfill the requirements for propellant service use. To overcome the deleterious effect of some copper modifiers on the chemical stability of double-base propellants, the stabilizer system must include resorcinol and the copper salt should be used at a low level.

I. Introduction

COPPER salts, in combination with lead salt-based ballistic modifiers, are used in nitroglycerin-(NC)-based propellants to modify the combustion characteristics of solid rocket propellants.

Nearly all solid propellants based on nitrate esters contain a uniformly distributed stabilizer. The function of the stabilizer is the removal of NO_2, which is formed as a primary decomposition product during the storage of propellants,[1] and which would otherwise autocatalytically accelerate the decomposition. Stabilizer mixture systems are widely used in double-base rocket propellant formulations, where they have been found[2] to be most effective in prolonging the crack-free life of the propellant grain during storage. It is generally assumed that the more reactive stabilizer reacts rapidly with the propellant degradation products during the early stages of aging, whereas the second stabilizer reacts more slowly.

Stabilizers like resorcinol, and the combination of resorcinol with other stabilizers, are reported to be useful.[3,4] The effectiveness of resorcinol has been explained[5] as being a result of activated aromatic ring formation, which helps in the absorption of nitrogen oxides quickly and more effectively, resulting in further control of growth of autocatalytic reactions.

It was indicated[6] that the chemical stability of double-base propellants is significantly influenced by different lead-based ballistic modifiers, and that the organic moiety of the ballistic modifier is an important influence on the reactions of the stabilizers.

In this work, systematic investigations have been carried out to obtain a deeper insight into 1) a comparison of the effect of lead and copper salt-based modifiers on the reaction of stabilizers commonly used in the cast double-base (CDB) rocket propellants, namely *para*-nitro-N-methylaniline (*p*NMA) and 2-nitrodiphenylamine (2NDPA), during the aging of NG solutions in acetonitrile-containing identical quantities of the ballistic modifiers that are also commonly used in the propellant matrix, and 2) a study of the effect of copper modifiers on the reactions of the stabilizers with propellant degradation products (namely NO_2, HNO_2, and HNO_3). Studying the reaction of these compounds is very important to improve the understanding of the mechanism of double-base propellant decomposition.

The detailed mechanism of the reaction of copper-based ballistic modifiers is outside the scope of this investigation, and the main concern in this paper is to identify the relative efficiency of copper–salt modifiers vs lead-based modifiers to react with the well-known decomposition product generated 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 and be compatible with the ballistic modifiers required for producing the desired burning characteristics of double-base propellants.

II. Experiments

The ballistic modifiers were washed with acetonitrile, dried at 80°C for 12 h, and then stored in well-sealed bottles. The stabilizers and 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. The NG solution was prepared in acetonitrile, by the same procedure as described in Ref. 7.

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. The standard solutions of NO_2, HNO_2, and anhydrous HNO_3 were prepared in dry acetonitrile to the required concentrations by the same procedure as previously described in Ref. 6, and stored in 20-ml sealed vials at room temperature in the dark. The requisite amount of each was removed through the vial septum, using a 50-μl high-performance liquid chromatography (HPLC) syringe and rapidly introduced into a 10-ml sealed reaction vial through its septum to avoid any loss.

For convenience, the figures for the molar concentrations of the reacting compounds in Tables 1–9 will be shown as follows: 1 unit concentration (1 u.c.) $= 0.01$ molar ratio with respect to NG $= 3.29 \times 10^{-4}$ mol/l. The concentration of each compound in each formulation will be given in units of concentration (u.c.). The concentration of added NO_2, HNO_2, and HNO_3 in each formulation will represent the molar equivalent of any with respect to the unit concentration of stabilizers.

The reaction formulations were prepared to the required concentrations in 25-ml volumetric flasks, and the solution was then

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Received 30 December 1997; revision received 2 May 1998; accepted for publication 18 December 1998.

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Table 1 Relative reactivity of stabilizers during NG aging

		2NDPA reactions					*p*NMA reactions			
		2NDPA, %C[a]			2,4′-DNDPA, %F[b]		*p*NMA, %C[a]		N.NO.*p*NMA, %F[b]	
Number	Formulation (u.c.)[c]	5[d]	11	16	5	11	5	11	5	11
1	2NDPA (2)	31	81	100	24	61	—	—	—	—
2	2NDPA (1) + *p*NMA (2)	25	59	82	24	47	22	60	20	51
3	2NDPA (1) + Res[e] (2)	3	27	82	3	20	—	—	—	—
4	2NDPA (1) + *p*NMA (1) + Res (1)	2.7	18	71	3.6	13	43	100	43	54

[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.
[c] Unit concentration (1 u.c.) = 0.01 molar ratio with respect to NG = 3.29×10^{-4} mol/l.
[d] Aging periods 5, 11, and 16 days at 75°C.
[e] Resorcinol.

Table 2 Relative reactivity of stabilizers during NG aging

		*p*NMA reactions			
		*p*NMA, %C[a]		N.NO.*p*NMA, %F[b]	
Number	Formulation (u.c.)	5	11	5	11
5	*p*NMA (2)	38	87	20	39
6	*p*NMA (2) + Res (2)	25	56	27	51

[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 Comparison of the effect of lead and copper oxides on stabilizer reactions

		*p*NMA, %C,[a] day		N.NO.*p*NMA, %F,[b] day		2NDPA, %C,[a] day	
Number	Formulation (u.c.)[c]	7[d]	14	7	14	7	14
7	Control[e]	43	74	34	65	34	67
8	Control + PbO (3)	41	73	33	64	33	66
9	Control + CuO (3)	52	100	30	63	56	100
10	Control + Res (2)	35	70	30	59	0	3.4
11	Control + CuO (3) + Res (2)	41	80	33	72	0.3	3.2

[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.
[c] Unit concentration (1 u.c.) = 0.01 molar ratio with respect to NG = 3.29×10^{-4} mol/l.
[d] Aging periods 7 and 14 days at 75°C.
[e] *p*NMA (2) + 2NDPA (1).

Table 4 Effect of copper-based ballistic modifiers on stabilizer reactions[a]

		*p*NMA, %C,[b] day		N.NO.*p*NMA, %F,[c] day		$N.NO_2$.*p*NMA and 2,4-DNMA, %F,[c] day	
Number	Formulation (u.c.)[d]	5[e]	9	5	9	11	11
12	*p*NMA (2)	38	87	20	39	23	2.3
13	*p*NMA (2) + LS (1)	33	58	33	60	0	0
14	*p*NMA (2) + BCS (1)	100	100	17	3.8	40	29
15	*p*NMA (2) + LBR (1)	30	54	30	53	0	0
16	*p*NMA (2) + LBR (.5) + BCS (.5)	85	100	73	83	21	2.9
17	*p*NMA (2) + CuO (1)	45	93	19	36	39	4.4

[a] *p*NMA-based formulations.
[b] Percent consumption with respect to the initial concentration.
[c] Percent formation of the derivative with respect to the initial concentration of the original stabilizer.
[d] Unit concentration (1 u.c.) = 0.01 molar ratio with respect to NG = 3.29×10^{-4} mol/l.
[e] Aging periods 5, 9, and 11 days at 75°C.

distributed into 10-ml sealed vials and stored under the required reaction conditions in the dark. The volume of 10-ml solutions in 10-ml sealed vials was chosen to minimize the effect of the free volume. These vials contain a certain amount of oxygen and may affect the results.

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 are described in Ref. 8. The data obtained from the HPLC were statistically analyzed to obtain data for stabilizer consumption and the formation of their derivatives at the end of each reaction period. For simplicity, results that contributed little to the discussion are not presented in the tables.

III. Results and Discussion

A. Relative Reactivity of Resorcinol with Respect to *p*NMA and 2NDPA Stabilizers During Aging of Nitroglycerin

The effect of resorcinol on the reactions of propellant stabilizers *p*NMA and 2NDPA has been investigated during the aging of NG solutions in acetonitrile at 75°C. A study of the consumption of

Table 5 Effect of copper-based ballistic modifiers on stabilizer reactions[a]

		2NDPA, %C,[b] day		2,4′DNDPA, %F,[c] day		2,2′DNDPA, %F,[c] day
Number	Formulation (u.c.)[d]	5[e]	11	5	11	16
18	2NDPA (2)	31	81	24	61	5
19	2NDPA (2) + LS (2)	58	98	43	70	4
20	2NDPA (2) + BCS(2)	100	100	70	ND[f]	30
21	2NDPA (2) + LBR (2)	12	52	8.7	38	0
22	2NDPA (2) + LBR (1) + BCS (1)	100	100	66	ND	2
23	2NDPA (2) + Cu_2O (2)	100	100	68	ND	30
24	2NDPA (2) + CuO (2)	48	100	36	69	19
25	2NDPA (2) + CuO (2) + Res (2)	0.6	20	2.3	15	0

[a] 2NDPA-based formulations.
[b] Percent consumption with respect to the initial concentration.
[c] Percent formation of the derivative with respect to the initial concentration of the original stabilizer.
[d] Unit concentration (1 u.c.) = 0.01 molar ratio with respect to NG = 3.29×10^{-4} mol/l.
[e] Aging periods 5, 11, and 16 days at 75°C.
[f] Not determined.

Table 6 Effect of copper-based ballistic modifiers on stabilizer reactions[a]

		*p*NMA, %C,[b] day		N.NO.*p*NMA, %F,[c] day		2NDPA, %C,[b] day	
Number	Formulation (u.c.)[d]	7[e]	14	7	14	7	14
26	Control[f]	45	87	44	83	33	72
27	Control + LS (1)	79	100	71	98	14	74
28	Control + BCS (1)	100	100	14	19	100	100
29	Control + Cu_2O (1)	100	100	15	36	100	100
30	Control + CuO (1)	48	98	37	90	38	97
31	Control + Res (2)	39	78	40	76	0	4.5
32	Control + Cuo (1) + Res (2)	42	80	41	72	0.5	2.2

[a] (*p*NMA + 2NDPA)-based formulations.
[b] Percent consumption with respect to the initial concentration.
[c] Percent formation of the derivative with respect to the initial concentration of the original stabilizer.
[d] Unit concentration (1 u.c.) = 0.01 molar ratio with respect to NG = 3.29×10^{-4} mol/l.
[e] Aging periods 7 and 14 days at 75°C.
[f] *p*NMA (2) + 2NDPA (1).

both *p*NMA and 2NDPA stabilizers, and of the formation of their corresponding derivatives, is reported. This enables the relative reactivities of the different stabilizers toward the NG decomposition products to be determined.

The formulations shown in Tables 1 and 2 were aged in an NG/acetonitrile solution at 75°C for different periods. 2NDPA (in formulations 1–4) and *p*NMA (in formulations 5 and 6) were used as the primary stabilizer, whereas the other compounds were used as secondary stabilizers.

It is clear from Tables 1 and 2 that resorcinol is more efficient than *p*NMA in decreasing the consumption of the primary stabilizer 2NDPA.

*p*NMA reacts with the NG decomposition products to form N-nitroso-*para*-nitro-N-methylaniline (N.NO.*p*NMA) as the major product. Aging for the third aging period caused the complete consumption of *p*NMA, and the further reaction of some of the N.NO.*p*NMA, with the formation of traces of N-nitro-*para*-nitro-N-methylaniline ($N.NO_2$.*p*NMA) and N-methyl-2,4-dinitroaniline (2,4-DNMA). 2NDPA formed 2,4′-dinitro-diphenylamine (2,4′-DNDPA) as the major product, together with traces of 2,2′-dinitro-diphenylamine (2,2′-DNDPA).

During the first aging period, negligible consumption of 2NDPA occurred when resorcinol was present compared with that when *p*NMA was present, but during the third aging period, the 2NDPA consumption was the same in both cases. This observation suggests that the resorcinol reaction products, formed by reaction with the NG decomposition products, enhance the nitrosation/nitration reactions of 2NDPA during the later stages of aging. This effect was also apparent in formulation 4, where an equimolar mixture of *p*NMA and resorcinol was used as the secondary stabilizer. The 2NDPA consumption during the final aging period was much more than that during the first two aging periods combined.

In formulation 6, resorcinol decreased the consumption of *p*NMA and was itself consumed to a high degree. The reason for this may be related either to the ability of resorcinol to undergo side reactions with its own reaction products, hence causing higher self-consumption without depleting the primary stabilizer *p*NMA, or even to a catalytic effect of the products of the reaction of resorcinol with NG decomposition products.

From the preceding text, it was found that resorcinol is more efficient than *p*NMA in decreasing the consumption of 2NDPA. This order may be taken as a measure of the relative reactivities of these stabilizers toward NG decomposition products, and consequently, of their ability to improve the chemical stability of double-base propellants in which NG is the most labile component.

B. Relative Reactivity of Lead and Copper Modifiers During Aging of Nitroglycerin

1. Comparison of the Effect of Lead and Copper Oxides on Stabilizer Reactions

The formulations shown in Table 3 were based on a mixture of *p*NMA (2 u.c.) and 2NDPA (1 u.c.) as the stabilizer. Resorcinol was added to the stabilizer mixture in equimolar concentration to *p*NMA. Lead and copper oxides were added in concentrations as shown in Table 3. These formulations were aged at 75°C for 7 and 14 days. The results obtained for stabilizer consumption and the formation of the corresponding derivatives are shown in Table 3.

The following facts are clearly seen from Table 3:

1) *p*NMA was consumed with the formation of N.NO.*p*NMA. An observable amount of $N.NO_2$.*p*NMA was formed. 2NDPA reacted

Table 7 **Effect of copper-based ballistic modifiers on stabilizer reactions with nitrogen dioxide**

		2NDPA reactions				*p*NMA reactions	
Number	Formulation (u.c.)[c]	2NDPA, %C[a]	N.NO.2NDPA, %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)	96	63	6.3	5.4	——	——
34	2NDPA (2) + LS (2)	47	34	2	1.9	——	——
35	2NDPA (2) + BCS (2)	35	27	0	0	——	——
36	2NDPA (2) + LBR (2)	31	24	2.4	1.2	——	——
37	2NDPA (2) + LBR (1) + BCS (1)	36	32	0	0	——	——
38	2NDPA (2) + PbO (2)	98	62	7.1	6.7	——	——
39	2NDPA (2) + Cu_2O (2)	44	34	1.8	1.6	——	——
40	2NDPA (2) + CuO (2)	88	46	3.5	4.1	——	——
41	2NDPA (2) + CuO (2) + Res (2)	43	35	1.6	1.5	——	——
42	*p*NMA (2)	——	——	——	——	69	66
43	*p*NMA (2) + LS (2)	——	——	——	——	49	47
44	*p*NMA (2) + LBR (2)	——	——	——	——	21	20
45	*p*NMA (2) + LBR (1) + BCS (1)	——	——	——	——	19	19
46	*p*NMA (2) + CuO (1)	——	——	——	——	66	64

Note: 2NDPA formulations [NO_2 (4 molar equivalent to 2 u.c.) to react at 20°C for 5 min]. *p*NMA formulations [NO_2 (1.5 molar equivalent to 2 u.c.) to react at 20°C for 5 min].

[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.

[c] Unit concentration (1 u.c.) = 3.29×10^{-4} mol/l.

Table 8 **Effect of copper-based ballistic modifiers on stabilizer reactions with nitrous acid**

		2NDPA reactions				*p*NMA reaction
		2NDPA, %C[a]		N.NO.2NDPA, %F[b]		*p*NMA, %C[a]
Number	Formulation (u.c.)[c]	I[d]	E[e]	I	E	I
47	Control[f]	92	98	74	13	100
48	Control + LS (2)	1.7	44	0.8	14	83
49	Control + BCS (2)	5.5	54	3.4	15	100
50	Control + LBR (2)	1.2	71	0.7	23	100
51	Control + LBR (1) + BCS (1)	83	93	54	20	100
52	Control + CuO (2)	96	98	63	11	100
53	Control + Cu_2O (2)	8	23	5.5	9	100

[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.

[c] Unit concentration (1 u.c.) = 3.29×10^{-4} mol/l.

[d] Two h at 20°C.

[e] Seven days at 20°C.

[f] *p*NMA (2) + 2NDPA (1).

with the NG decomposition products and formed 2,4′-DNDPA as the major product with traces of 2,2′-DNDPA.

2) Copper oxide (CuO) had a significant effect on *p*NMA and 2NDPA reactions, whereas lead oxide (PbO) did not cause a noticeable effect when compared with that occurring in the control formulation (in the absence of ballistic modifiers).

CuO increased both *p*NMA consumption and the formation of the corresponding derivatives, N.NO_2.*p*NMA and 2,4-DNMA. The observed ratio of N.NO.*p*NMA formed/*p*NMA consumed was much smaller than that observed for the other formulations. 2,4-DNMA was formed only in the presence of CuO. CuO also increased both 2NDPA consumption and the formation of 2,4′-DNDPA, particularly during the second aging period. This indicates that CuO may promote the nitrosation/nitration reactions of *p*NMA and 2NDPA with NG decomposition products, e.g., nitric oxide, nitrite ion, etc., none of which would react with these stabilizers in the absence of CuO. This will be discussed in detail in a later section.

3) Because of the problems with the HPLC analysis, it was not possible to follow the consumption of resorcinol during aging. However the main concern was to compare the effect of CuO on the consumption of both *p*NMA and 2NDPA, in the presence of resorcinol.

Addition of resorcinol to the control formulation, in the absence of ballistic modifiers, gave an interesting result. The reaction of *p*NMA was not significantly affected, but the reaction of 2NDPA was totally suppressed. 2NDPA consumption by the end of the second aging period was negligible. This indicates the higher reactivity of both *p*NMA and resorcinol vs 2NDPA toward NG decomposition products. This has been thoroughly investigated.[9]

Observe that the inclusion of resorcinol also suppressed the effect of CuO on the reactions of *p*NMA and 2NDPA. CuO caused a slight increase in *p*NMA consumption without affecting 2NDPA consumption. It is therefore suggested that the inclusion of resorcinol in double-base propellants containing CuO may have a significant beneficial effect on the chemical stability of these propellants.

2. *Comparison of the Effect of the Other Lead and Copper Modifiers on Stabilizer Reactions*

a. pNMA-based formulations. The formulations shown in Table 4 were based on *p*NMA as the sole stabilizer, which was used in 2 u.c. copper- and lead-based ballistic modifiers were added in half the concentration of the stabilizer. These formulations were aged at 75°C for 5, 9, and 11 days.

Analysis of Table 4 shows the following:

1) *p*NMA was consumed with the formation of N.NO.*p*NMA. An observable amount of N.NO_2.*p*NMA was formed.

Table 9 Effect of copper-based ballistic modifiers on stabilizer reactions with nitric acid

		2NDPA reactions			*p*NMA reactions			
Number	Formulation (u.c.)[c]	2NDPA, %C[a]	2,4′.DNDPA, %F[b]	2,2′.DNDPA, %F[b]	*p*NMA, %C[a]	N.NO.*p*NMA, %F[b]	2,4-DNMA, %F[b]	N.Salt[d] *p*NMA, %F[b]
54	2NDPA (2)	64	22	18	——	——	——	——
55	2NDPA (2) + LS (2)	24	9.9	1.7	——	——	——	——
56	2NDPA (2) + BCS (2)	48	6.7	5.9	——	——	——	——
57	2NDPA (2) + LBR (2)	11	6	0	——	——	——	——
58	——	52	19	3.2	——	——	——	——
59	——	31	13	5.7	——	——	——	——
60	2NDPA (2) + CuO (2)	100	42	33	——	——	——	——
61	——	38	16	7.2	——	——	——	——
62	*p*NMA (2)	——	——	——	62	6.9	1.8	246
63	*p*NMA (2) + LS (1)	——	——	——	14	0.9	0	0
64	*p*NMA (2) + LBR (2)	——	——	——	2.4	0	0	0
65	——	——	——	——	18	3	0	0
66	*p*NMA (2) + CuO (1)	——	——	——	100	4.2	24	506

2) All of the copper salts, CuO, basic copper salicylate (BCS), and the combination [lead β-resorcylate (LBR) and BCS], had a dramatic effect on the reactions of *p*NMA. They caused more rapid consumption of *p*NMA, even during the early stages of aging, when compared with that produced by LBR and lead salicylate (LS).

3) CuO caused a noticeable increase in the rate of formation of N.NO$_2$.*p*NMA compared with that occurring in the control formulation, in good agreement with the earlier results (Table 3).

4) BCS had a more dramatic effect on the reactions of *p*NMA than CuO. During the first aging period, BCS caused complete consumption of *p*NMA, with a corresponding increase in the formation of the other derivatives. In this formulation it was noticed that the N.NO.*p*NMA initially formed was rapidly consumed, with subsequent formation of large amounts of N.NO$_2$.*p*NMA and 2,4-DNMA. During the later stages of aging, another HPLC peak, close to the 2,4-DNMA peak, was observed; this might be a higher nitrated derivative of *p*NMA. This observation indicates that BCS has a high catalytic effect on the nitrosation/nitration reactions of *p*NMA.

5) A comparison of the effects of copper salts with those of lead salts and the combination of lead and copper salts might enable the reason for the catalytic behavior of copper salts as well as that of the salicylate anion to be identified.

LBR decreased *p*NMA consumption compared with that occurring in the control formulation, with the corresponding formation of N.NO.*p*NMA as the major product, and prevented the formation of the other derivatives, N.NO$_2$.*p*NMA and 2,4-DNMA. Nevertheless, the combination (LBR and BCS) caused the rapid consumption of *p*NMA with the subsequent formation of N.NO.*p*NMA and N.NO$_2$.*p*NMA, together with traces of 2,4-DNMA during the later stages of aging.

The addition of LBR to BCS caused a large increase in the ratio of N.NO.*p*NMA formed/*p*NMA consumed compared with that observed when BCS was used solely. This suggests that LBR reacts preferentially with the same species that causes the formation of the higher derivatives of *p*NMA, i.e., N-nitration of *p*NMA and/or the oxidation of N.NO.*p*NMA, whereas *p*NMA reacts preferentially with nitrogen dioxide and forms the N.NO.*p*NMA. It also suggests that the combination formulation was able to react, although to a limited extent, with the reaction products formed from the catalytic effect of BCS on the reactions of the stabilizer. This follows the observation that the addition of BCS to LBR had a dramatic effect on *p*NMA consumption and the subsequent formation of N.NO$_2$.*p*NMA, compared with that occurring in the case of the LBR-based formulation.

Although BCS and LS are structurally related, the effect on the reactions of *p*NMA produced by the former was quite dramatic compared with that produced by the latter. LS caused a lower consumption of *p*NMA compared with that occurring in the control formulation, it gave N.NO.*p*NMA as the major product, and it prevented the formation of the higher derivatives N.NO$_2$.*p*NMA and 2,4-DNMA; whereas BCS caused the catalytic consumption of *p*NMA with a subsequent increase in the formation of the higher derivatives.

From the preceding text it is concluded that the much higher reactivity of BCS over LBR and that of BCS over the structurally related LS, toward NG decomposition products, leading to an enhancement of the rate of nitrosation/nitration of the stabilizer, is caused by the combined effect of both the copper ion and the associated anion. This is supported by results in the following sections.

b. 2NDPA-based formulations. The formulations shown in Table 5 were based on 2NDPA as the sole stabilizer, which was used in 2 u.c. Resorcinol was added in equimolar concentration to 2NDPA. Ballistic modifiers were added in equimolar concentration to the stabilizer. These formulations were aged at 75°C for 5, 11, and 16 days.

The following facts are clearly seen from Table 5:

1) 2NDPA reacted with the NG decomposition products and formed 2,4′-DNDPA as the major product with traces of 2,2′-DNDPA, but the presence of the copper salts enhanced the formation of the tri-nitro-derivatives of 2NDPA.

2) BCS had a dramatic effect on the reactions of 2NDPA, causing very rapid consumption of 2NDPA, even during the first aging period, with subsequent formation of the di- and tri-nitro-derivatives of 2NDPA.

3) In formulation 22, where the combination (LBR and BCS) was used, 2NDPA consumption and the subsequent formation of the derivatives were as high as that occurring in the formulation containing BCS alone, with complete consumption of 2NDPA occurring during the first aging period. This observation clearly indicates that the effect of BCS on the reactions of 2NDPA outweighs that of LBR. LBR significantly reduced the consumption of 2NDPA compared with that occurring in the control formulation.

4) Copper (II) oxide [Cu_2O] had a similar effect on the reactions of 2NDPA as that occurring in the BCS-based formulation. This observation supports the earlier suggestion that the copper ion contributes to the catalytic effect on the stabilizer reactions observed with the copper-based formulations.

5) CuO showed the same trend in influence on the reactions of 2NDPA as that observed in the former results (see Table 3 formulations). This observation provides further support for the earlier suggestion that CuO may catalyze the consumption of secondary amine stabilizers by enhancing the nitrosation/nitration reactions of these compounds with NG decomposition products.

6) The reaction of 2NDPA was totally suppressed when resorcinol was added to the CuO-based formulation. 2NDPA consumption during the first aging period was negligible, much lower than that produced by LBR. This indicates the higher reactivity of resorcinol toward the catalytic NG decomposition products. Once again, this provides further evidence for the suggestion made earlier that the inclusion of resorcinol in double-base propellants containing CuO has a significant beneficial effect on the chemical stability of these propellants.

From the preceding text it is concluded that because *p*NMA is more reactive than 2NDPA, the former is capable of competing with the ballistic modifiers during the early stages of aging, whereas the latter is only affected by the catalytic behavior of the copper salts. This conclusion will be further supported by the results presented in the following section.

c. (pNMA + 2NDPA)-based formulations. The formulations shown in Table 6 were based on *p*NMA and 2NDPA stabilizer mixtures, which were used in 2 and 1 u.c., respectively. Resorcinol was added to the stabilizer mixture in equimolar concentration to *p*NMA. Ballistic modifiers were added in equimolar concentration to 2NDPA. These formulations were aged at 75°C for 7 and 14 days.

Analysis of Table 6 shows the following:

1) The reaction of *p*NMA and 2NDPA with the NG decomposition products gave the same derivatives as were observed in the preceding text.

2) BCS caused complete consumption of *p*NMA, even during the first aging period, with the formation of much less N.NO.*p*NMA than was formed in the presence of the corresponding lead salt LS. On the other hand, BCS caused large amounts of $N.NO_2$.*p*NMA and 2,4-DNMA to be formed. Simultaneously, the complete consumption of 2NDPA took place, even during the first aging period, with the formation of 2,4′-DNDPA and 2,4,4′-trinitro-diphenylamine (2,4,4′-TNDPA).

3) Cu_2O had the same effect on the reactions of *p*NMA and 2NDPA as that observed for BCS. On the other hand, CuO did not exhibit the same deleterious effect on stabilizer reactions as that produced by Cu_2O. Nevertheless, that CuO should be used in propellant composition at very low levels.

4) Once again, the addition of resorcinol to a CuO-based formulation gave a similar effect to that produced earlier, suppressing the catalytic effect of CuO on the reactions of *p*NMA and 2NDPA. It caused a slight increase in *p*NMA consumption, compared with the control formulation, and negligible consumption of 2NDPA during both aging periods. This provides further evidence that the inclusion of resorcinol in double-base propellants containing CuO has a significant beneficial effect on the chemical stability of these propellants.

The mechanism of reaction of these copper salts with NG decomposition products is beyond the scope of this investigation. Brackman and Smit[10] found that copper complexes catalyze the reactions of nitric oxide, one of the possible NG decomposition products that is not a nitrosating agent itself, with secondary amines. Keefer[11] explained the roles played by metal atoms in catalyzing the nitrosation reactions, and it is expected that copper atoms would fulfill most of these roles, thus enhancing the consumption of the stabilizers.

From the preceding text it may be concluded that copper salts greatly enhance the nitrosation/nitration reactions of stabilizers. This indicates that copper salts, commonly used as ballistic modifiers in CDB propellants, greatly decrease the chemical stability of these propellants. This is in agreement with the observations[12,13] that double-base propellants containing copper salt modifiers, particularly BCS and the combination (LBR and BCS), have high rates of stabilizer consumption and high rates of gas evolution, with consequent lower crack-free lives.

C. Effect of Copper-Based Ballistic Modifiers on the Reaction of Stabilizers with Propellant Reactive Species

1. Reactions with Nitrogen Dioxide

a. 2NDPA-based formulations. In the formulations shown in Table 7, ballistic modifiers were used in equal molar concentrations to 2NDPA. Four molar equivalent (to 2 u.c.) of NO_2 were added to each formulation and allowed to react for 5 min at 20°C in the dark. Resorcinol was added in equal concentrations to 2NDPA.

It was previously shown[6] that lead-based ballistic modifiers 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 be significant.

The following facts are clearly seen from Table 7:

1) 2NDPA reacted with NO_2 and formed N-nitroso-2-nitrodiphenylamine (N.NO.2NDPA) as the major product with traces of the nitro-derivatives 2,4′-DNDPA and 2,2′-DNDPA.

2) The order of efficiency of the different ballistic modifiers investigated in decreasing 2NDPA consumption is as follows: LBR > BCS > (LBR + BCS) > Cu_2O > LS > PbO > CuO.

It is not known definitely whether the effect of the ballistic modifiers on the reactions of 2NDPA is caused by their direct reaction with NO_2, or by their reaction with the HNO_3 produced from the reaction of 2NDPA with NO_2. It was previously shown that lead-based ballistic modifiers have great reactivity toward HNO_3.[6]

3) The presence of BCS totally inhibited the formation of the C-nitro-derivatives of 2NDPA. Only N.NO.2NDPA was formed as the major product. The inclusion of BCS in combination with LBR as a ballistic modifier mixture caused the same effect. This feature emphasizes the great reactivity of both BCS and LBR toward both NO_2 and HNO_3. The inclusion of LBR in formulation 37 increased the formation of N.NO.2NDPA, compared with formulation 35, 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, as shown previously,[6] does not necessarily mean that they are unreactive toward NO_2. This is not expected to be the case for those having a reactive aromatic structure like LBR, LS, BCS, etc. LBR when used alone in formulation 36 caused the formation of small amounts of the C-nitro-derivatives of 2NDPA, even though it gave the lowest 2NDPA consumption among the other ballistic modifiers. This clearly reflects a high reactivity of LBR toward NO_2.

The large difference in the efficiency of BCS and LS in decreasing 2NDPA consumption, because they have the same anion, was explained previously. It was shown that LS showed a marked effect in increasing 2NDPA consumption during the later stages of aging.[6] 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. BCS is, as shown in Table 7, more reactive than LS toward NO_2. The difference may be caused by the basicity of BCS, which will make it more reactive toward the HNO_3 produced during the reaction of 2NDPA with NO_2. However, the difference may be rationalized in terms of the combined effect of both the copper ion and the associated salicylate anion, leading to an enhancement of the rate of nitrosation/nitration of the stabilizer (the same conclusion was reached in the preceding text).

4) PbO did not have any noticeable effect on 2NDPA consumption, whereas Cu_2O decreased the consumption of 2NDPA more than CuO. A possible reason for this may be that some NO_2 is consumed by the oxidation of Cu_2O to CuO, producing nitric oxide as the reduction product, the latter being unable to nitrosate/nitrate 2NDPA.

5) It was not possible to follow the consumption of resorcinol during aging. However, the main concern was to compare the effect of CuO on the reaction of the stabilizer with NO_2 in the presence of resorcinol.

It is clear that the addition of resorcinol suppressed the effect of CuO, and thus decreased the consumption of 2NDPA. This indicates the higher reactivity of resorcinol vs 2NDPA toward NO_2, as previously investigated in the preceding text.

b. pNMA-based formulations. In this investigation, ballistic modifiers were added to *p*NMA in equal molar amounts as shown in Table 7. These formulations were allowed to react with a 1.5 molar equivalent (to 2 u.c.) of NO_2 for 5 min at 20°C in the dark.

The following facts are clearly seen from Table 7:

1) *p*NMA was consumed with the formation of N.NO.*p*NMA as the major product.

2) The order of efficiency of the different ballistic modifiers, in decreasing *p*NMA consumption, is as follows: (LBR + BCS) > LBR > LS > CuO.

Once again, LBR, and the combination of LBR and BCS, had a significant effect on decreasing *p*NMA consumption. LS gave a higher *p*NMA consumption than when either LBR or the combination of LBR and BCS were used, as also happened in the case of the 2NDPA-based formulations. This feature again furnishes evidence for the role of the hydroxyl groups in the reactivity of the ballistic modifiers.

3) The presence of CuO did not have any noticeable effect on *p*NMA consumption, suggesting the much higher efficiency of *p*NMA vs 2NDPA to react with NO_2.

In conclusion, the effect of copper-based ballistic modifiers on the reactions of 2NDPA and *p*NMA with NO_2 is quite significant and cannot be ignored.

2. *Reactions with Nitrous Acid*

In the formulations shown in Table 8, a mixture of *p*NMA (2 u.c.) and 2NDPA (1 u.c.) was used as the stabilizer. The ballistic modifiers were present at 2 u.c. These formulations were allowed to react with 1 and then 3 molar equivalent (to 2 u.c.) HNO_2 at 20°C for 2 h in the dark. Following an analysis after 2 h at 20°C, the samples were left for an additional 7 days at 20°C in the dark.

The following facts are clearly seen from Table 8:

1) For the first reaction period, the presence of the ballistic modifiers LBR, LS, and BCS, resulted in a negligible consumption of 2NDPA.

A possible rationalization for this observation is as follows: during the 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 on the relative rate of protonation of the ballistic modifier. The reactivity of the corresponding acid that is generated may then affect the 2NDPA consumption during the second reaction period. The carboxyl groups, in the structure of ballistic modifiers, is expected to be protonated rapidly. The presence of the resulting acid may be undesirable and may cause the catalytic consumption of 2NDPA.

2) The combination of LBR and BCS gave results different from those obtained from formulations, where these ballistic modifiers were used individually. Although 2NDPA consumption was high during the first reaction period, the increase in its consumption when going from the first to the second reaction period was much lower than the initial consumption.

An explanation for this is as follows: before the initial addition of HCl, some of the LBR and BCS may interact and release their corresponding free acids. Thus, the addition of HCl will result mainly in the formation of HNO_2. However, some of the HCl will also cause protonation of that part of the ballistic modifiers that has not been affected initially. Comparing the 2NDPA consumption during the first reaction period for formulation 51 with that in control formulation 47 supports this explanation.

The effect that is suspect to be more deleterious on 2NDPA consumption of resorcylic acid compared with salicylic acid is confirmed by a comparison of the increase in 2NDPA consumption between the first and the second reaction periods, cf. formulations 50 and 48.

3) 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 again supports the suggestion that salicylic acid, formed from LS protonation, reacts with HNO_2. The reactivity toward HNO_2 of the acids formed from ballistic modifiers is discussed in Ref. 14.

4) Although the presence of LBR caused the lowest 2NDPA consumption during the first reaction period, its presence in formulations 50 and 51 seems to be responsible for the large increase in 2NDPA consumption during the second reaction period. This observation supports the earlier suggestion for the protonation of ballistic modifiers.

5) The suggestion of protonation of ballistic modifiers by the initial addition of HCl is supported by the results for the effect of several ballistic modifiers on *p*NMA consumption. It has been shown that *p*NMA reacts rapidly with HNO_2.[7]

It is clear that the protonation of LS and BCS, which would result in the formation of salicylic acid, is not as important in its effect on 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.

6) CuO did not give any change in 2NDPA consumption from that in the control formulation, whereas Cu_2O caused a much lower 2NDPA consumption. This may be a result of the reduction of N_2O_3 (from $2\ HNO_2 === N_2O_3 + H_2O$) by Cu_2O, thus decreasing the efficiency of the former.

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

3. *Reactions with Nitric Acid*

In this investigation, the different formulations of the 2NDPA stabilizer mixtures with some known ballistic modifiers, as shown in Table 9, were reacted with 1 molar equivalent (to 2 u.c.) of anhydrous HNO_3 at 70°C for 20 h. The ballistic modifiers were used in equal molar amounts to the stabilizer. The formulation containing LBR + BCS as ballistic modifier mixture contains 1 u.c. of each.

The following facts are clearly seen from Table 9:

1) CuO caused complete consumption of 2NDPA. There is a wide difference in the efficiency of Cu_2O and CuO toward HNO_3. In contrast to CuO, Cu_2O gave a very low 2NDPA consumption.

2) BCS had a very favorable effect on 2NDPA consumption. This would suggest a higher reactivity of BCS toward HNO_3, as found earlier for NO_2. The available data do not suggest an explanation for the much smaller quantity of the C-nitro derivatives of 2NDPA formed vs the 2NDPA consumed, in the presence of BCS.

3) The main difference between the effects of BCS and LS on 2NDPA consumption is that 2NDPA consumption is higher with BCS. Because there are many variables controlling this difference in reactivity, e.g., basicity, solubility in the solvent acetonitrile, the amount of water present, and the copper catalytic reactivity, it is difficult to make a comparison between the two systems. A thorough investigation would be required to find the reaction pathway for each, and this is outside the scope of this investigation.

4) The addition of LBR to BCS had nearly the same effect as using BCS solely. This suggests that BCS suppressed the effect of LBR, again most likely because of its higher reactivity. The combination (LBR + BCS) produced an increase in 2,4′-DNDPA formation.

5) The result obtained from the addition of resorcinol to CuO-based formulation indicates the higher reactivity of resorcinol vs HNO_3, the main difference here being that resorcinol consumption was increased in the presence of CuO. This suggests that CuO has a catalytic effect in nitrosation/nitration reactions in these systems. Nevertheless, the results emphasizes the conclusion reached earlier that the inclusion of resorcinol in propellants containing CuO has a substantial beneficial effect on the chemical stability of these propellants.

Different formulations of the *p*NMA stabilizer mixtures with some ballistic modifiers, as shown in Table 9, were reacted with 1 molar equivalent (to 2 u.c.) of anhydrous HNO_3 at 70°C for 20 h. The concentration of the *p*NMA was 2 u.c., whereas that of the ballistic modifiers was 1 u.c.

The results of the effects that ballistic modifiers have on *p*NMA consumption, as reported in Table 9, supports the results presented earlier for 2NDPA formulations:

1) LBR showed the highest efficiency in decreasing *p*NMA consumption, the latter being almost negligible. Two conclusions may be drawn: LBR is the most reactive of all the ballistic modifiers toward HNO_3; and 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.

2) *p*NMA consumption in the formulation where a combination of LBR and BCS was used, was higher than when LBR was used

solely. It is probable that the higher consumption of *p*NMA in this formulation was caused by the presence of BCS. The effect of BCS solely was not studied, but comparing its effect in the 2NDPA formulation clearly indicates that the probable reason for the higher *p*NMA consumption in the (LBR + BCS) combination is because of the dominant effect of BCS.

3) The question of why the addition of BCS to LBR increases the consumption of both *p*NMA and 2NDPA, although LBR when used solely decreased the consumption markedly, may be answered as follows: the observation that the consumption of the stabilizers is nearly the same in the (LBR + BCS) combination as in the BCS formulation suggests that the effect is a result of BCS being more reactive than LBR. However, if BCS consumes HNO_3 faster and yet causes higher stabilizer consumption, this suggests that the product of reaction of BCS with HNO_3 is catalytic. The probable product from BCS would be salicylic acid and this might cause a higher consumption of stabilizer than the resorcylic acid formed from LBR. The latter was shown to react slowly. This explanation raises another question, namely, why is there a difference in stabilizer consumption between the formulations containing LS and BCS individually, because they give the same acid? The answer to this might be related to a possible catalytic activity of copper, and the most likely easier formation of salicylic acid from BCS.

4) 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 at temperatures that are even 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 suggests that the direct reaction of ballistic modifiers with HNO_3 does not produce any HNO_2, or the higher 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.

5) It is clear that CuO causes a much higher consumption of *p*NMA, and the catalytic consumption of *p*NMA forming a significant amount of the C-nitro-derivative of *p*NMA (2,4-DNMA), which was not seen in more than trace amounts in all other formulations. This supports the supposition mentioned earlier in connection with 2NDPA formulations, that CuO has a catalytic effect in its reaction with HNO_3 or NO_2, increasing stabilizer consumption. All ballistic modifiers except CuO prevented *p*NMA from forming its nitrate salt. This again indicates the superiority of LBR, LS, and BCS over *p*NMA in their rate of reaction with HNO_3. The catalytic behavior of CuO was once more demonstrated by the large peak area for *p*NMA nitrate salt.

IV. Conclusions

Copper–salt-based ballistic modifiers greatly decrease the chemical stability of double-base propellants. CuO, BCS, and the combination of BCS with LBR, have a dramatic effect on the reactions of propellant stabilizers *p*NMA and 2NDPA, even during the early stages of aging, when compared with that produced by lead salts, the effect of BCS being more dramatic than that of CuO.

The much higher reactivity of BCS vs LBR, and that of BCS vs the structurally related LS, toward NG decomposition products, leading to an enhance of the rate of nitrosation/nitration of the stabilizer, is because of the combined effect of both the copper ion and the associated salicylate anion.

Copper-based ballistic modifiers have a significant effect on the reactions of stabilizers with NO_2, HNO_2, and HNO_3. BCS shows large reactivity toward both NO_2 and HNO_3. The inclusion of BCS in combination with LBR as a ballistic modifier mixture causes the same effect. Although using LBR or BCS individually shows higher reactivity toward HNO_2, their use in combination gives high stabilizer consumption; this increase is a result of the generation of resorcylic acid. There is a wide difference in the reactivity of Cu_2O and CuO. Cu_2O significantly affected stabilizer reactions with both NO_2 and HNO_2 more than CuO. Cu_2O gave a much lower stabilizer consumption, because of the reduction effect produced by Cu_2O.

Resorcinol suppresses the dramatic effect produced by copper salts. Although CuO has a dramatic effect on stabilizer reactions, the addition of resorcinol to CuO-based formulations overcomes the effect of CuO on 2NDPA reactions. Therefore, the inclusion of resorcinol in double-base propellants containing CuO is a great beneficial effect for the chemical stability of these propellants.

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