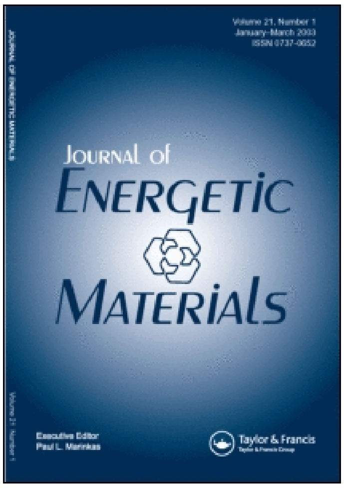

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INFLUENCE OF METAL SALTS OF 4-(2,4,6-TRINITROANILINO) BENZOIC ACID ON THE BURNINING RATE OF DOUBLE BASE PROPELLANTS

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ABSTRACT

Cobalt, Nickel, Copper and Lead salts of 4-(2,4,6-trinitroanilino) benzoic acid have been evaluated as ballistic modifiers in double base propellant formulations. Measurements showed considerable increase in burning rate over the control propellant, in presence of salts at all pressures in the range 3.43 - 8.82 MPa. The effect of the lead salt, however, was more pronounced and showed a burning rate increase of 50 - 60%; the lower pressure ranges showing higher burning rate enhancement. The salts decompose exothermically: cobalt salt at 270°C (initiation), nickel salt at 300°C, copper salt at 240°C and lead salt at 260 °C.

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The calorimetric value of the salts are: cobalt salt, +608; nickel salt, +662; copper salt, 679 and lead salt, 839 cal/g. The salts are insensitive to impact and friction and thus safe for processing.

INTRODUCTION

There are a lot of additives incorporated in a propellant mix to facilitate processing and modify performance[1]. Ballistic modifiers are prominent among them. Metal salts of carboxylic acids (like basic lead salicylate and lead stearate) have been in use[2] for the purpose, conventionally. However, the quest for improving the overall energetics of the propellants have lead to the idea of introducing energetic groups like the nitro or azido in all additives and ingredients. Energetic ballistic modifiers, thus contain nitro or azido groups as part of the otherwise inert organic moiety of metal salts of carboxylic acids. Incorporation of energetic modifiers can improve the total heat output, as these compounds possess a positive calorimetric value (cal. Val.). The presence of energetic groups like nitro also enhance rate of decomposition of these salts thereby giving an impetus to the catalysis of the burning process. This paper discusses the results of the evaluation of four energetic ballistic modifiers, viz. cobalt, nickel, copper and lead salts of 4-(2,4,6-trinitroanilino) benzoic acid (TABA)[designated CoTABA, NiTABA, CuTABA and PbTABA, respectively] in a double base propellant matrix. The results of the evaluation, details of the thermal stability and impact and friction sensitivity of these salts, and the processing of the propellant mix are also described.

EXPERIMENTAL

Synthesis: Synthesis of these salts has been carried out as described elsewhere.[3, 4]

Propellant processing: Processing of the propellant mix has been carried out according to the reported method[5].

Control composition (NC: 54.0%, NG: 32.0%, RDX: 10.0%, Carbamate: 4.0% of cal.val.: 1098 cal/g)

DTA was carried out in static air, using a locally fabricated DTA apparatus at a heating rate of 10^0C/min. Impact sensitivity measurements were carried out using a locally fabricated drop hammer (2.0 kg weight) apparatus. Friction sensitivity was determined by using a Julius Peter apparatus. Cal. val. was determined by a Parr adiabatic bomb calorimeter and the burning rates were measured by a strand burner assembly.[6]

RESULTS AND DISCUSSION

The cal. val. of the cobalt, nickel, copper and lead salts were +608, +662, +679 and +839 cal/g respectively. This indicates the salts are energetic and when incorporated in the propellant would contribute to the total heat output.

This can be seen from a comparison of the cal. val. of the control and the formulations containing the salts (Table 1).

TABLE 1

Cal. Val. and Stability of TABA Salts Containing Double Base Propellants

Composition	Cal. Val. (cal/g)	BJ Test (ml/5g at 120^0C)
Control	1098	2.2
Control + 2 parts BLS	1060	2.2
Control + 2 parts PbTABA	1096	3.6
Control + 4 parts PbTABA	1090	3.5
Control + 2 parts CuTABA	1084	3.5
Control + 4 parts CuTABA	1079	3.3
Control + 2 parts CoTABA	1074	3.2
Control + 4 parts CoTABA	1070	3.3
Control + 2 parts NiTABA	1086	3.0
Control + 4 parts NiTABA	1078	3.2

The table also shows that the formulations are chemically stable within the accepted levels. Upto 12 ml/5g of gas evolution in the B and J test[7] is empirically accepted as indicative of a stable formulation. The impact sensitivity data of the salts show that all salts have a $h_{50}\%$ of >170 cm except for lead salt (77 cm). The friction sensitivity of all salts were > 36 kg. These sensitivity data[7] indicate that these salts are insensitive to external stimuli[7] and are safe for processing in a propellant matrix. The burning rates of the propellant samples without and with the salts are presented in Table 2. It is clear from the table that in the presence of the salts, the burning rate of the propellant is more compared to the control propellant. This is more pronounced in the case of the lead salt and at lower pressures; 60% increase at 3.43 MPa and 50 % increase at 8.82 MPa and showing a consistent trend throughout the range of pressures studied. Copper salts (both 2 and 4 parts) effect a 10 - 20 % enhancement in burning rate which is at par with that obtained by using non-energetic ballistic modifiers like basic lead salicylate (BLS) for a RDX - containing double base formulation. But, lead salt effects a much higher increase in burning rate. 2 parts induce 25 - 40 % increase and 4 parts 50 - 60 %, which is a big leap in the burning rate. The TGA curve of Pb salt shows 95% weight loss in a single step between 160 -185^{0}C. This shows that in the temperature range of propellant decomposition the Pb salt decomposes completely. This would enhance the burning rate considerably, as indeed is the experimental observation. The other salts show weight losses to the extent of 80 - 85% only and it may be the reason for the lesser increase in burning rate observed in the case of these salts. The pressure exponent at low pressure ranges, i.e. 3.43 - 6.86 MPa was lower compared to the control, but at 8.82 MPa it is higher. The DTA results of the formulations are given in Table 3. The inception and peak temperatures of the formulations are lowered slightly compared to the control, but the decomposition is spread over a wider range of temperature than the control.

CONCLUSIONS

Metal salts such as cobalt, nickel, copper and lead salts of 4-(2,4,6-trinitroanilino) benzoic acid have been evaluated as energetic ballistic modifiers in nitramine containing double base propellant formulations. The stability and the sensitivity of the control propellant formulation are not adversely affected by the incorporation of these salts. The cal.val. shows increase over the control confirming energetic nature of the slats. More significantly, the burning rates are enhanced by the incorporation of these salts in the propellant formulation. 4 parts of the lead salt enhances the burning rate by a drastic 50 - 60 % compared to 20 ~ 30 % obtained by using conventional ballistic modifiers (Table 2).

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TABLE 2

Effect of TABA Salts on the Burning Rates of RDX Containing Double Base Propellants

Composition	Burn rate (mm/s) at pressures (MPa)				n value over pressure range (MPa)		
	3.43	4.89	6.86	8.82	3.43-4.89	4.89-6.86	6.86-8.82
Control	6.3	7.7	9.4	11.0	0.56	0.59	0.63
Control + 2 parts BLS	10.0	11.0	11.7	12.3	0.27	0.18	0.20
Control + 2 parts PbTABA	9.2	10.4	12.2	13.5	0.41	0.47	0.40
Control + 4 parts PbTABA	10.6	11.8	13.8	15.3	0.40	0.46	0.41
Control + 2 parts CuTABA	7.8	8.5	9.9	11.5	0.24	0.45	0.47
Control + 4 parts CuTABA	8.3	9.2	10.7	12.3	0.29	0.45	0.55
Control + 2 parts CoTABA	7.2	8.0	9.3	11.0	0.30	0.45	0.67
Control + 4 parts CoTABA	7.4	8.6	10.0	12.0	0.42	0.45	0.72
Control + 2 parts NiTABA	6.9	8.0	9.2	10.8	0.41	0.42	0.64
Control + 4 parts NiTABA	7.2	8.3	9.7	11.4	0.40	0.43	0.64

TABLE 3

DTA Results of TABA Salts Containing formulations

Composition	T_i (^0C)	T_{max} (^0C)	T_f (^0C)	Impact (cm)	Friction (kg)
Control	174	193	228	22	19.2
Control + 2 parts BLS	170	188	222	22	19.2
Control + 2 parts PbTABA	165	186	230	24	21.6
Control + 4 parts PbTABA	160	184	235	23	21.6
Control + 2 parts CuTABA	165	192	215	30	21.6
Control + 4 parts CuTABA	167	190	212	28	19.2
Control + 2 parts CoTABA	164	192	235	23	21.6
Control + 4 parts CoTABA	162	189	237	23	19.2
Control + 2 parts NiTABA	162	191	230	29	21.6
Control + 4 parts N TABA	159	188	235	27	19.2