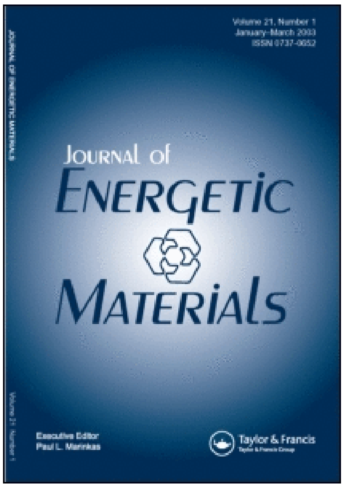

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EFFECT OF CERTAIN LEAD AND COPPER COMPOUNDS AS BALLISTIC MODIFIER FOR DOUBLE BASE ROCKET PROPELLANTS

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SUMMARY

During our search for better burn rate catalysts and platonizers the effect of lead oxide with lead copper salts of organic acids was studied. Basic lead and copper salts of aliphatic acids have been found to produce more or less similar catalytic and plateau effects, whereas basic copper salts of aromatic acids were comparatively more effective in producing higher burn rates than basic lead salts, although reduction of pressure index values was more pronounced with basic lead salts. The results have been explained in the light of existing theories on catalysis and platonization.

1. INTRODUCTION

The burning rate - pressure relationship is one of the major criteria in the selection of propellants for any specific application. Propellants having lower pressure index value (0 to 0.2) are pressure insensitive and are popularly known as platonised propellants. These propellants are often temperature insensitive as well. In view of consistant ballistics produced by platonised/mesonic propellants at extreme conditions of temperature, they are the preferred choice for propulsion of rockets/missiles.

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A number of lead and copper salts and their combinations are reported to produce pressure and temperature insensitivities[1-6]. Most of the studies carried out so far reveal that while copper salts produce higher catalytic effect, lead salts work as platonizer. We have reported the effect of a number of lead and copper salts of aliphatic and aromatic acids and metallic oxides on burning rate pressure relationship of double base propellant[5-6]. A number of other research workers have also used various different combinations of lead and copper salts to obtain catalytic/plateau effects in practical double base formulations. During our search for better catalyst/platonizer, the effect of lead oxide with lead and copper salts of organic acids was studied. The effectiveness of the ballistic modifiers was evaluated in the pressure range 35-140 kg/cm^2, which is generally chosen for rocket propulsion. A double base propellant composition having Cal-Val of 860 cal/g was selected as the base composition for study of ballistic modification.

2. EXPERIMENTAL

Basic lead salicylate (BLSa) and Basic Cupric Sterate (BSC) were prepared as per method described by Kebrich[7] and Kuss et al[8]. Mono basic cupric salicylate (MBCSa) was prepared by reacting an aqueous solution of salicylic acid with basic cupric carbonate at 60°C. After completion of the reaction, the reaction product floated on the surface leaving clear greenish solution at the bottom. The salt was filtered, washed with water and alcohol and dried. Copper content estimated was 28.4% as against 30.4% calculated. Basic lead resorcylate (BLR) was prepared by reacting PbO with β-resorcylic acid. The mixture was stirred at ambient temperature under the current of air for five hours. The salt was filtered, washed with ice cold 50% ethanol and dried in the oven at 100°C. Lead content obtained was 40% (40.35% theoretical). Basic Cupric-β-Resorcylate (BCR) was prepared by reacting basic cupric carbonate with resorcylic acid at 60°C. The stirring and heating was continued for three hours after the addition of resorcylic acid. The product was filtered, washed and dried at 70-75°C. The copper content was 28% (28.3 % calculated).

Propellant compositions were made by Solventless method and strands extruded by extrusion technique [9]. The cal-val was determined on Julius Peters apparatus at a loading density of 0.016g/cc, while the burn rates at different pressures were determined on Crawford Bomb. Burn rate data reported is the average of the analysis carried out in triplicate. The variation of burn rate for the same formulation was 0.1mm/s. Catalytic acitivity was calculated as the ratio of catalyzed burn rate to uncatalyzed burn rate.

3. RESULTS AND DISCUSSIONS

3.1 Effect of Lead Oxide(PbO)

Preckel[1] has reported that lead oxides render burning rates of double base propellant independent of pressure over certain range. According to Kubota et al[10], PbO produced mesa effect, which shifted to lower pressure range with increase in the concentration of PbO. With a view to find out an optimum concentration of PbO to act as an effective catalyst its effect in different concentrations was studied, as earlier studies concentrate only at a fixed concentration. The results of burning rates are given in Table-1. The results of Cal-Val, heat test and presssure index are also included in the table.

Results obtained indicate that incorporation of 0.5 parts of lead oxide increased burning rate upto 70 kg/cm^2 pressure along with a considerable reduction in pressure index (n) values. As the percentage of lead oxide was increased further in increments of 0.5 parts per 100 parts of base composition, the catalytic activity remained around 1.5 $\pm$ 0.02 while the pressure index values were reduced. Plateau behaviour was observed with 2.0 parts of lead oxide in 35-70 kg/cm^2 pressure range. Incorporation of 2.5 and 3.0 parts of lead oxide resulted in mesa burning. However, this was not observed with 3.5 parts lead oxide. These results bring out that lead oxide while being an effective catalyst at lower pressures produces plateau effect upto 2 parts composition and a mesa effect between 2.5 and 3 parts concentration.

3.2 <u>Effect of Carbon black with PbO</u>

It has been reported that incorporation of carbon black along with lead salts increases burning rates further and shifts plateau effect to higher pressure side[5]. Further, 0.5 part carbon black per 100 parts of base composition produces the best results in terms of catalysis. Hence,studies were carried out with 0.5 part of fine carbon black of average particle size 400°A(Carbolac obtained from Cabot Corporation, USA). The results are given in Fig. 1.

Inclusion of carbon black produced higher catalytic effect and burning rates were increased with increase in concentration of PbO. However, plateau effect disappeared with 1.5 parts PbO and 0.5 part carbon black, although burning rate was increased by 140% at 35 kg/cm^2pressure. 2 parts PbO and 0.5 parts carbon black produced plateau effect in 70-105 kg/cm^2 pressure range. These results suggest that by judicious selection of the concentration of PbO and carbon black desired catalytic and plateau effects can be obtained in the required pressure range.

3.3 <u>Effect of basic Lead salts in pressure of PbO</u>

In view of high catalytic and mesa behaviour observed with PbO, further experiments were carried out using combinations of PbO with lead salts of aliphatic and aromatic acids. We have reported earlier that among lead salts of aromatic acids, lead salicylate and lead-β-resorcylate are very effective as catalyst and platoniser. Further, the monobasic lead salts are more effective than their corresponding normal lead salts[5]. Hence, the effect of typical three lead salts namely, monobasic lead stearate (MBLSt), Mono basic lead salicylate (MBLSa) and basic lead resorcylate (BLR) was studied in the presence of PbO (2 parts). The results are given in Fig. 2.

MBLSt(2 parts) along with PbO (2 parts) increased burning rates upto 70 kg/cm^2 and the catalytic activity was increased from 1.5 to 2. In case of 2 parts MBLSa and 2 parts PbO, higher catalytic effect was observed in the entire pressure range studied. The catalytic activity of 2.35 was obtained at 35 kg/cm^2 pressure with this combination. Mixture of BLR and PbO gave highest catalytic effect and burning rates were about 175%. This combination produced mesa effect in the pressure range 70-105 kg/cm^2. These results bring out that combination of BLR and PbO is a potential ballistic modifer to achieve higher burning rates along with plateau/mesa effect, followed by combination of MBLSa and PbO.

3.4 Effect of basic Copper Salts in the presence of PbO

It was reported earlier that combination of lead and copper salts produce synergistic effect on burning rates and hence the effect of basic copper salts in the presence of PbO was studied. The results are given in Figure-3. The combination of BCSt and PbO gave higher burning rate upto 50 kg/cm^2 pressure. Significantly, this combination reduced 'n' value to -0.14 in 35-70 kg/cm^2 region and reduced 'n' value to 0.17 in 70-105 kg/cm^2 pressure region. Mixture of MBCSa and PbO gave higher catalytic activity than the earlier combinations and burning rate was increased by 160% at 35 kg/cm^2 pressure. In case of the mixture of BCR and PbO, highest burning rates were obtained and catalytic activity was raised to 3.7 and thus burning rate enhancement of the order of 270% was obtained at 35 kg/cm^2 presssure.These results indicate that at the same concentration of ballistic modifiers, while basic lead and copper salts of aliphatic acids produce more or less similar catalytic and plateau effects, basic copper salts of aromatic acids are more effective in producing catalytic effect as compared to basic lead salts of aromatic acids, although reduction of pressure index values were much more pronounced with basic lead salts.

As regards the mechanism of the action of lead and copper salts on the burning behaviour of double base propellant, a number of theories have been proposed . However, carbon or carbonaceous matter formation theory explains most of the observed facts satisfactorily. According to Singh and Rao[11], catalysis and platonisation are dependent on C/NO ratio in the fizz zone. So long as this ratio is greater than one, super rate burning is obtained, followed by plateau effect, where C/NO is reduced to unity. Ultimately, C/NO ratio goes down to less than one, resulting in post- plateau effect. The experimental data of the present study support this mechanism. The catalytic and plateau effects observed with PbO may be due to its carbon forming tendency in the flame. On the basis of the results of high speed photography, microthermocouples and scanning election microscopy (SEM), Sheng et al[12] proposed that PbO plays the role of an active agent in the catalytic combustion and the carbon formed on the burning surface performs the role of a carrrier for the PbO. Superior catalytic and plateau effects with basic lead salts in general and aromatic lead salts in particular may be due to higher heat of reaction during combustion[13]. The difference on the influence of lead and copper salts may be due to the difference in their carbon forming tendency and due to the fact that lead salts promote early appearance of H_2O, resulting in higher carbonaceous species, whereas copper salts promote formation of carbon oxides.

CONCLUSION

Our studies on the effectiveness of various lead and copper compounds on the combustion rate of double base propellant indicate that lead oxide is an effective catalyst and platoniser. Desired catalytic and plateau effects can also be obtained by the judicious selection of lead oxide and carbon black concentration while lead salts of aromatic acids produce enhanced burn rates in the presence of lead oxide than the lead salts of aliphatic acids and, combination of basic copper salts with lead oxide produces superior ballistic effect than combination of basic lead salts with PbO.

TABLE-1 : EFFECT OF PbO ON THE BURNING RATES OF DOUBLE BASE PROPELLANTS

Propellant Composition	Additives	Cal-val	Abel's Heat test at 160oF, min	Burning rate(mm/s) at pressures (kg/cm2)				Catalytic activity at pressures (kg/cm2)				'n' values over pressure range (kg/cm2)		
				35	70	105	140	35	70	105	140	35-70	70-105	105-140
NC-59.5	NIL	865	23	4.8	7.2	10.2	12.5	-	-	-	-	0.59	0.84	0.74
NG-30.5	0.5 PbO	850	23	7.0	7.6	9.2	11.9	1.46	1.05	0.90	0.95	0.12	0.46	0.92
Carbamite - 3.0	1.0 PbO	845	24	7.1	7.5	9.2	11.5	1.48	1.04	0.90	0.92	0.08	0.49	0.81
DEP - 7.0	1.5 PbO	827	24	7.2	7.3	9.4	11.7	1.50	1.01	0.92	0.94	0.01	0.61	0.77
	2.0 PbO	829	25	7.3	7.3	9.5	11.8	1.52	1.01	0.93	0.94	0	0.65	0.75
	2.5 PbO	818	25	7.3	7.1	9.7	12.2	1.52	0.98	0.98	0.98	-0.04	0.77	0.80
NC-59	NIL	860	23	3.7	6.8	9.1		-	-	-	-	0.88	0.72	
NG-29	3.0 PbO	853	27	7.5	7.3	9.9		2.03	1.07	1.09		-0.01	0.75	
Carbamite - 3.0	3.5 PbO	850	27	7.2	7.4	10.2		1.95	1.09	1.12		0.04	0.79	
DEP-7.0														

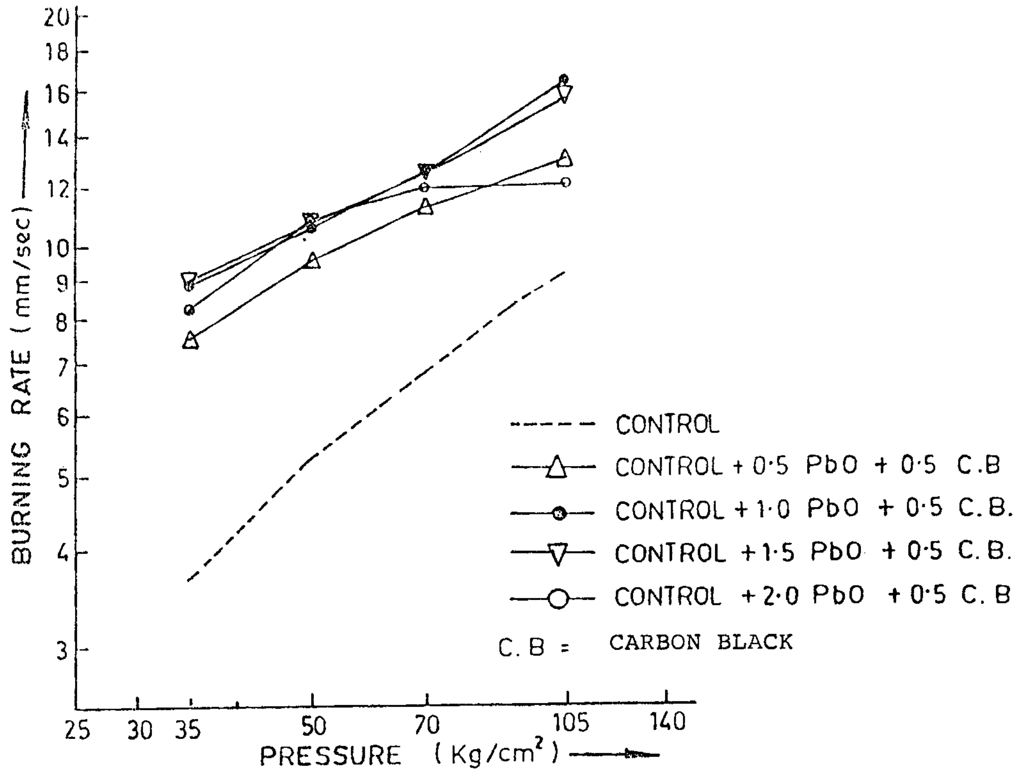

FIG. 1 EFFECT OF CARBON BLACK AND PbO ON THE BURNING RATES OF DOUBLE BASE PROPELLANTS

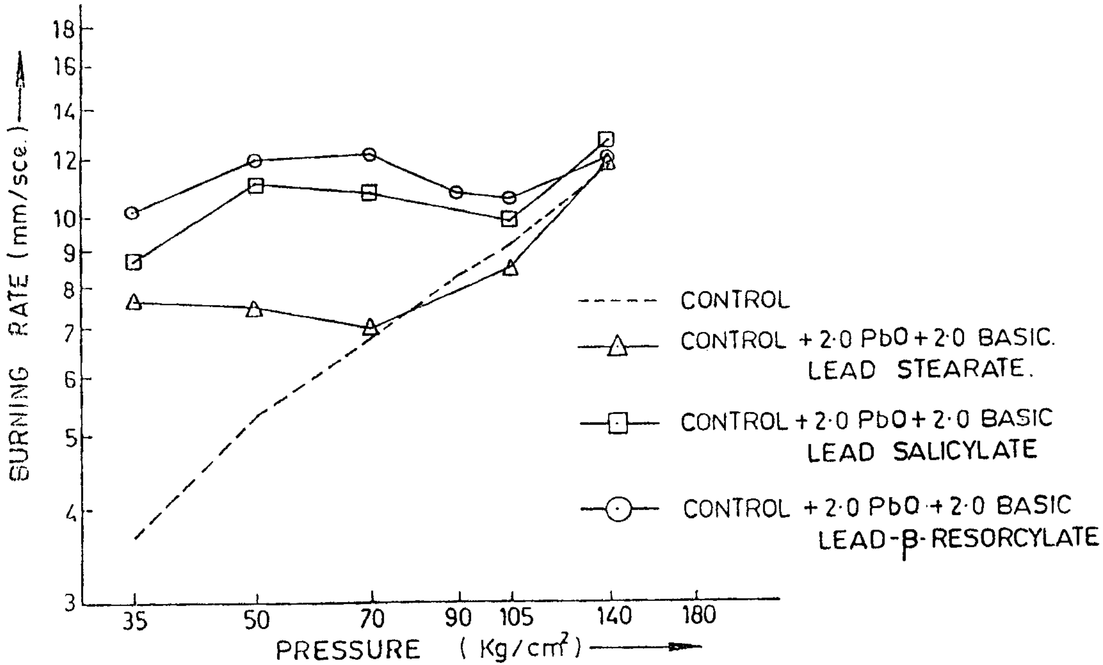

FIG. 2 EFFECT OF LEAD SALTS OF ALIPHATIC ACIDS AND AROMATIC ACIDS WITH PbO

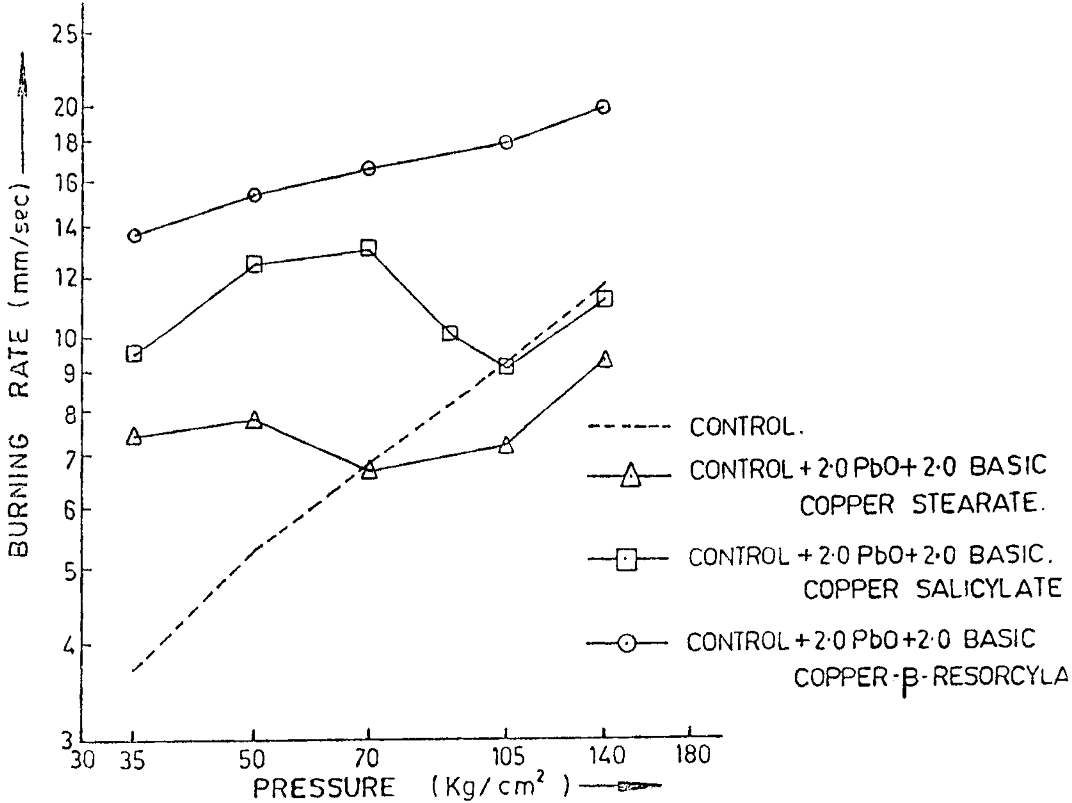

FIG.3 EFFECT OF COPPER SALTS OF ALIPHATIC ACIDS AND AROMATIC ACIDS WITH PbO

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