

Role of Carbonates of Ca(II), Ba(II) & Sr(II) & of Calcium Oxide as Burning Rate Inhibitors for Composite Solid Propellants (Polystyrene + Ammonium Perchlorate)

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Received 20 October 1976; accepted 10 February 1977

The role of calcium carbonate, barium carbonate, strontium carbonate and calcium oxide as burning rate inhibitors for polystyrene + ammonium perchlorate propellant has been investigated. Considerable decrease in burning rate has been observed when calcium oxide and calcium carbonate are used as inhibitors. The propellant samples, at higher percentages of inhibitors, do not burn at all. The flame temperature (T_f) and surface temperature (T_s) for propellants + inhibitors have been measured. These are invariably lower than those for propellants without inhibitors. TGA studies show that the rate of decomposition of polymer, AP and propellants is lowered by inhibitors. It has been found that the real inhibitors are the oxides which are produced by the thermal decomposition of the corresponding carbonates. Further, it appears that these inhibit the gas phase reactions in the combustion zone although the exact mechanism is not known.

CONSIDERABLE amount of work has been reported¹⁻⁶ on the decomposition and combustion of ammonium perchlorate (AP) and composite propellants in the presence of catalysts. Very little work, regarding the effect of inhibitors on AP^{2,7} and the propellants seems to have been done. Humphery⁸ reported that reduction in burning rate up to 50% of composite solid propellant was obtained by (i) increasing particle size of the oxidizer, (ii) addition of endothermic combustion modifiers and (iii) inclusion of flame retardants. Additional reduction was obtained by incorporating binder soluble organophosphate and binder insoluble oxamide. Boggs *et al.*² have also reported that MnO_2 , TiO_2 , SnO_2 , ZnO , ammonium orthophosphate ammonium hydrogen fluoride and ammonium oxalate, etc. reduce the burning rate of AP pellets. However, the mechanism of action of the inhibitors has not been examined in detail so far.

Glaskova⁹ has made a comprehensive study on the inhibiting action of different types of additives. His study leads to following conclusions: (i) 1% of salts of ammonia reduce burning rate by a factor of 3-4 at low pressures, (ii) halogenides of lead or cadmium have the same effect, and (iii) double additives of ammonium salts and halogenides of metals intensify the inhibiting effect.

The following explanations for the decelerating action were put forward by Glaskova: (i) ammonium salts decompose producing ammonia which shifts equilibrium of dissociation of NH_4ClO_4 to the left, (ii) some of the additives bind the perchloric acid or products of its decomposition into less reactive compounds than perchloric acid itself or original AP and (iii) the additives inhibit the decomposition of perchloric acid.

However it should be noted that the shift in dissociation equilibria of NH_4ClO_4 would hardly be significant since the inhibiting action is marked even when the inhibitor concentration is only 1%. Similarly the extent of formation of lead or cadmium perchlorates would also be small. The third explanation is attractive but more data are needed.

In view of the above, it was planned to make a comprehensive investigation on the polystyrene (PS)-AP-inhibitor systems. For this purpose, burning rate, surface and flame temperatures and TGA studies were undertaken. The results are discussed in this paper.

Materials and Methods

(i) Styrene monomer (Synthetics & Chemical Ltd, Bareilly, India) was purified by fractional distillation under reduced pressure after removing the inhibitor. AP (Central Electrochemical Research Institute, Karaikudi), calcium carbonate (S. Merck), calcium oxide (S. Merck), barium carbonate (BDH), strontium carbonate (S. Merck) and benzoyl peroxide (BDH) were used as such without further purification.

Preparation of propellants—Styrene was polymerized by adding benzoyl peroxide (10 g/litre) and keeping the reaction mixture in a thermostat maintained at 50° as reported earlier¹⁰. The prepolymer thus obtained was used for the preparation of the propellant samples. AP (100-200 mesh) was mixed with prepolymer and various inhibitors (fine powder) and homogenized. The mix was filled in glass moulds (0.4 in. diam. and 4.0 in. length). The samples were cured in an incubator maintained at 50° for 10-12 days. The glass moulds were broken to obtain propellant samples.

Burning rate measurements at ambient pressure — The propellant samples were inhibited by applying PVC tape to protect them from side burning. The burning rate was measured as reported earlier¹⁰.

TGA studies on PS, AP and propellants in presence of inhibitors — TGA studies on AP (particle size 100-200 mesh) + inhibitors (wt ~ 0.14 g), PS + inhibitors (wt ~ 0.15 g) and PS + AP + inhibitors (wt ~ 0.20 g) were undertaken by dynamic thermogravimetric analyser (P & D Division, Sindri, India) at a heating rate of 4° min⁻¹ as reported earlier¹. The sample weight was taken approximately constant for each run. The AP + inhibitors were taken in powdered form whereas PS + inhibitors and propellant + inhibitors were taken in pellet forms. The shape and size of the pellets were kept the same in each case.

Surface temperature measurements — The surface temperatures of pure and inhibitor containing propellants were measured with platinum-platinum (Rh = 13%) thermocouple (diam. = 0.45 mm) by lamp and scale arrangement as reported earlier¹⁰.

Measurement of flame temperature — The flame temperatures of PS + AP and PS + AP + inhibitors propellants were measured by sodium-line reversal technique by the procedure applied earlier¹⁰. The temperature was noted at a point 2.5 cm above the surface of the propellants.

Results and Discussion

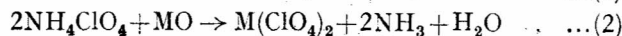
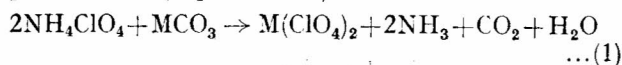
The data on burning rate at various percentages of inhibitors, recorded in Table 1 show that burning rate is lowered when calcium carbonate, barium carbonate, strontium carbonate and calcium oxide are used as inhibitors. Burning rate is lowered by 50% with calcium carbonate (4% by wt) whereas propellant sample does not burn at all with 8% calcium carbonate. Similarly, burning rates decrease by 50 and 70% with 1 and 2% calcium oxide respectively. A propellant sample containing 4% CaO did not burn.

Many investigators have reported that the thermal decomposition of AP⁶ and polymeric fuel binders¹¹⁻¹³ play an important role in the burning of propellants. Thus burning rate would be lowered on account of the inhibition of any one of the following processes: (i) PS degradation; (ii) AP decomposition, and (iii) propellant decomposition.

In order to find out which of the above processes is inhibited, TGA studies on PS + inhibitors, AP + inhibitors and PS + AP + inhibitors were undertaken.

The data reported in Tables 2-4 clearly show that the percentage decomposition of PS, AP and the corresponding propellants is lowered with all the inhibitors examined except calcium oxide and barium carbonate. CaO enhances the decomposition of AP and propellants up to 300° and at temperatures higher than 300°, the percentage decomposition is lowered. It has also been observed that the percentage decomposition of AP is enhanced between 360° and 420° when barium carbonate is used as inhibitor.

The inhibition of AP and the propellants decomposition may be due to the formation of metal perchlorates (Eqs. 1 and 2):



where M is calcium, barium or strontium.

It has been observed that ammonia is evolved even at room temperature when AP is mixed with CaO. The metal perchlorates are more stable to decomposition as compared to AP which is apparent from their heat of formation data¹⁴. Formation of metal perchlorates is supported by the fact that

TABLE 2 — TGA OF PS+INHIBITORS (4% BY WT)

(Heating rate = 4° min⁻¹)

Temp. °C	Decomposition (%)				
	PS	PS + CaCO ₃	PS + BaCO ₃	PS + SrCO ₃	PS + CaO
140	1.36	—	0.32	0.63	0.63
160	—	0.96	1.30	0.93	1.20
180	2.72	1.92	1.52	1.87	1.89
200	—	2.56	2.27	3.12	2.52
220	3.74	—	2.60	3.44	3.15
240	4.08	3.20	2.92	—	3.78
260	5.10	—	3.25	4.69	5.04
280	6.12	3.84	—	5.31	—
300	—	4.80	3.57	5.93	6.73
320	7.14	5.76	4.55	6.56	—
340	8.84	6.72	5.20	8.25	8.82
360	9.52	9.28	6.17	9.00	—
380	11.90	—	6.50	—	10.71
400	13.68	12.16	9.75	12.81	—
420	26.52	21.12	20.15	25.62	18.90
440	30.60	26.00	26.00	28.12	24.57
460	70.04	57.60	39.00	63.12	39.06
480	97.92	83.20	96.20	97.12	65.52
500	97.92	96.00	96.20	97.12	95.87

TABLE 1 — BURNING RATE OF PROPELLANTS AT VARIOUS PERCENTAGES OF INHIBITORS

(PS/AP = 1/3; room temp. = 31°)

Inhibitors	Burning rate (cm/sec) at [inhibitor] (%)			
	1	2	4	8
Nil	0.114 ± 0.003	0.114 ± 0.003	0.114 ± 0.003	0.114 ± 0.003
Calcium carbonate	—	0.075 ± 0.003	0.059 ± 0.004	*
Barium carbonate	—	—	0.095 ± 0.002	0.072 ± 0.003
Strontium carbonate	—	—	0.083 ± 0.003	0.055 ± 0.003
Calcium oxide	0.066 ± 0.002	0.034 ± 0.005	*	*

*Did not burn.

TABLE 3 — TGA OF AP+INHIBITORS (4% BY WT)

 (Heating rate = 4° min⁻¹)

Temp. (°C)	Decomposition (%)				
	AP	AP +CaCO ₂	AP +BaCO ₃	AP +SrCO ₂	AP +CaO
140	0.35	0.35	0.36	0.36	0.35
160	0.71	0.69	—	—	2.85
180	1.07	—	0.73	1.09	4.28
200	2.14	1.75	1.10	—	5.35
220	2.50	2.10	—	1.46	7.14
240	2.85	—	1.47	2.56	—
260	3.21	2.45	2.94	2.93	7.50
280	3.57	—	3.67	3.29	8.57
300	3.92	3.15	4.41	4.39	10.00
320	14.64	11.22	5.88	8.05	12.50
340	24.21	16.49	15.07	19.41	21.42
360	28.92	18.58	36.02	21.24	—
380	30.71	20.00	41.17	23.07	22.85
400	32.50	21.75	44.85	26.73	27.14
420	39.64	27.01	54.04	33.33	32.14
440	56.07	*	*	51.81	35.71
460	*	—	—	58.34	39.28
480	—	—	—	*	*

*Sudden deflagration.

TABLE 4 — TGA OF PROPELLANT+INHIBITORS (4% BY WT)

 (Heating rate = 4° min⁻¹)

Temp. (°C)	Decomposition (%)				
	PS+AP	PS+AP +CaCO ₃	PS+AP +BaCO ₃	PS+AP +SrCO ₃	PS+AP +CaO
120	0.47	—	0.46	0.23	0.47
140	0.94	0.70	0.92	0.47	1.17
160	1.18	0.94	1.16	0.70	1.88
180	1.42	1.31	—	—	2.58
200	1.89	1.88	1.63	1.31	3.52
220	2.60	2.11	2.36	—	4.23
240	3.07	2.58	2.99	1.88	—
260	3.78	3.05	3.40	2.35	5.17
280	4.49	3.26	4.28	2.68	5.88
300	5.44*	4.76	5.31	3.76	6.58
320	—	13.16	10.97	8.46	7.05

*Sudden deflagration occurs after 320°.

anhydrous perchlorates of Zn, Cd, Pb, Ca can be prepared by heating AP with the corresponding oxides or carbonates¹⁴⁻¹⁹. The formation of perchlorate salts has also been observed in the presence of barium carbonate and calcium carbonates^{20,21}. It has also been pointed out by Schumacher¹⁴ that the above perchlorates simply decompose to give metal chlorides which are quite stable.

The decrease in the percentage decomposition of PS in the presence of inhibitors (Table 3) may be due to formation of some species which inhibit the oxidative degradation. It is known that chain terminators or metal deactivators are effective in inhibiting the polymer oxidation²².

Surface and flame temperatures of propellants with and without inhibitors were found to be lowered for propellants having inhibitors (Table 5).

It is pertinent to identify the actual species which act as inhibitors in the combustion reactions before

TABLE 5 — SURFACE AND FLAME TEMPERATURES OF PROPELLANTS

[PS/AP = 3/7; inhibitor = 4% (by wt); room temp. = 30°]

Inhibitor	Flame temp. (T _f) (°C)	Surface temp. (T _s) (°C)	(T _f -T _s) (°C)	(T _s -T ₀) (°C)
Nil	1660±26	1004±13	656±39	974±13
CaCO ₂	1303±18	781±12	522±30	751±12
BaCO ₃	1402±18	770±11	632±29	740±11
SrCO ₃	1427±16	760±5	667±21	730±5
CaO (2%)	1317±18	762±7	555±25	732±7

discussing any mechanism of inhibition. Following experiments were performed for this purpose. The propellant samples containing carbonate of metals were burnt and the white particles falling out of the flame were collected. These were found to be oxides of the respective metals by chemical analysis and flame tests.

In another experiment, the flame of the propellant sample was dipped in water taken in a beaker and the white residue which collected at the bottom was found to be the metal oxide. Analysis of water gave positive tests for Ca²⁺, Ba²⁺ and Sr²⁺. Since only 2% CaCO₃ is effective in suppressing the burning rate, it is obvious that only a small fraction of ammonium perchlorate is converted into calcium perchlorate, if at all. Unless some additional inhibiting mechanism is there, the formation of calcium perchlorate alone cannot explain the results. It seems likely that alkaline earth metal oxides may inhibit the decomposition of HClO₄.

The results have been examined from a semi-quantitative angle. The heat balance equation (3) can be written following Summerfield *et al.*²³.

$$\dot{m}C_s(T_s - T_0) = \frac{\lambda g(T_f - T_s)}{L} + \dot{m}Q_s \quad \dots(3)$$

where \dot{m} = mass burning rate; C_s = specific heat of solid propellant; T_s = surface temperature of propellant; T_0 = ambient temperature; T_f = flame temperature of propellant; Q_s = net heat release for gasification of the propellant; λg = average thermal conductivity of the gas; and L = thickness of the reaction zone.

If the heat produced (Q_i) due to reaction on the inhibitor surface is also taken into account, Eq. (3) can be rewritten as Eq. (4).

$$\dot{m}C_s(T_s - T_0) = \frac{\lambda g(T_f - T_s)}{L} + \dot{m}(Q_s + Q_i) \quad \dots(4)$$

Hence burning rate would be given by:

$$r = \frac{\lambda g(T_f - T_s)}{a\rho_p L [(C_s(T_s - T_0) - (Q_s + Q_i))]} \quad \dots(5)$$

where 'a' is the area of the burning surface and ρ_p is the density of the propellant.

Apparently, burning rate would decrease if (i) $(T_f - T_s)$ decreases or (ii) $[C_s(T_s - T_0) - (Q_s + Q_i)]$ increases or (iii) L increases on the addition of inhibitors. It may be noted that in the experiments a is kept constant λg and ρ_p may be assumed to be

constant. Experimental data shows that $(T_f - T_s)$ decreases on addition of inhibitors. However, the decrease in $(T_f - T_s)$ cannot completely account for decrease in burning rate.

Now, if L remains the same, burning rate would depend on α , the ratio of $(T_f - T_s)/[C_s(T_s - T_0) - (Q_s + Q_i)]$ for inhibited and uninhibited propellants. Hence, it can be reasonably expected that α would not vary appreciably since both $(T_f - T_s)$ and $(T_s - T_0)$ decrease in the case of inhibited propellants (Table 5).

Let us now try to assess to what extent L is affected when the inhibitors are added. The thickness of the reaction zone (L) represents the distance which the reactants have to travel for the completion of the gas phase reaction. L would be smaller, if the reaction rate is faster and vice versa. Further L would be inversely proportional to the rate constant k or $A \exp(-E/RT_g)$ where E is energy of activation, A is frequency factor, R is universal gas constant, and T_g is the temperature of effective gas phase reactions. If energy of activation is increased as it happens in the case of negative catalysts (inhibitors), L would increase by a large amount.

Summarizing, the present results show that the extent of inhibition by alkaline earth carbonates cannot be simply explained by the possible formation of metal perchlorates or metal halides, unless these act as negative catalysts which seems unlikely. Further, it follows that the real inhibitors are the alkaline earth oxides since CaO decreased the burning rate much more than the corresponding carbonates. The oxide can act as a negative catalyst on the propellant surface or in the gaseous phase when it is finely dispersed. The former possibility seems remote since the surface temperature is not high enough to decompose the carbonate appreciably. However, the exact mechanism of inhibition of reactions occurring in the gas phase combustion zone is not known and future research would be needed to settle this point.

Acknowledgement

Thanks are due to the UGC and CSIR, New Delhi, for supporting the investigation. Thanks are also

due to Shri H. K. Khatri for his help in the preliminary stage of the work.

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