THE EFFECT OF FILLERS ON CHLOROPOLYESTER BLEND CPB 4 AND INHIBITION OF DOUBLE-BASE PROPELLANTS

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Summary

A direct bonding inhibition system based on chloropolyester blend CPB 4 has recently been developed for inhibition of double-base rocket propellants. The effect of alumina trihydrate ($Al_2O_3 \cdot 3H_2O$) and antimony trioxide (Sb_2O_3) on various properties of CPB 4 has been studied, such as effect on gel time, exotherm peak temperature, tensile strength, per cent elongation, water absorption, nitroglycerine absorption, heat resistance, and flame retardant characteristics. The data on flame retardance and other characteristics indicate that CPB 4 with 30% $Al_2O_3 \cdot 3H_2O$ and CPB 4 with 20% Sb_2O_3 are suitable for inhibition of double-base propellants. The double-base propellant sustainers (containing 2-NDPA) have been inhibited with CPB 4 containing 30% $Al_2O_3 \cdot 3H_2O$ and CPB 4 containing 20% Sb_2O_3 separately (without the application of any barrier coating), and statically fired at ambient, sub-zero (after conditioning at −40°C for 18 h) and high (after conditioning at +50°C for 18 h) temperatures. The pressure—time profiles were found to be smooth and flat in all cases, indicating that the pressure level was the same throughout the combustion duration, inferring the suitability of these systems for inhibition of double-base propellants without the application of any barrier coating.

Introduction

The use of unsaturated polyesters [1,2] and chloropolyesters [3] for inhibition of double-base rocket propellants has been reported in the literature. Chloropolyesters based on tetrachlorophthalic anhydride (TCPAn) with propylene glycol, polyethylene glycol (M. W. 200) and maleic anhydride have been synthesized in this laboratory [4] and, based on various characteristics, a chloropolyester blend designated as CPB 4 has been selected for inhibition of double-base rocket propellants. The object of the present investigation is to study the effect of alumina trihydrate and antimony trioxide fillers on gel time, exotherm peak temperature, tensile strength, per cent elongation, water absorption, nitroglycerine absorption, heat resistance and flame retardance of CPB 4, and to carry out an examination of inhibition and a static evaluation of double-base propellant sustainers inhibited with CPB 4 based filled systems.

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Materials and methods

The materials used in this work were tetrachlorophthalic anhydride (m.p. 255—258°C, chlorine content 48.45%), propylene glycol (BDH, LR) polyethylene glycol, M. W. 200 (BDH, LR), maleic anhydride, technical grade (m.p. 51 ± 2°C, purity 98.5%), styrene monomer (b.p. 145 ± 2°C, specific gravity 0.9055 at 25°C), alumina trihydrate (purity minimal 99.5%, all passing through 400 BSS), antimony trioxide (purity minimal 99.5%, all passing through 200 BSS), and curing agents cobalt naphthenate (3% in methylene chloride) and methyl ethyl ketone peroxide (50% in diethyl phthalate). All were procured from trade and used as such without further purification. Alumina trihydrate and antimony trioxide were sieved and dried at 100 ± 2°C for 2 to 3 hours.

Preparation of chloropolyester blend CPB 4: It was prepared by a two-step process, according to a method described earlier [4].

Gel time and exotherm peak temperature: Gel time and exotherm peak temperature were determined by the method reported earlier [2].

Tensile strength and per cent elongation: Tensile strength and per cent elongation were determined by an ASTM method [5].

Water absorption: Water absorption was also measured by an ASTM method [6].

Nitroglycerine absorption: Nitroglycerine absorption was measured using liquid absorption [7,8].

Heat resistance: Heat resistance was measured by the method reported earlier [9].

Flame retardance: Flame retardance was also measured by ASTM test method D 635-63, with some minor modifications as described in our earlier communication [2].

Infrared spectra: Infrared spectra of different compositions were recorded at room temperature by the smear method using a Perkin—Elmer Model 457 spectrophotometer.

Inhibition and static evaluation trials: The cast double-base propellant sustainers (containing 2-NDPA as stabiliser) were inhibited by CPB 4—30% alumina trihydrate and CPB 4—20% antimony trioxide as filler by casting [7]. Three numbers of propellant sustainers were inhibited, machined, X-rayed and statically evaluated after conditioning for 18 h at ambient, low (−40°C) and high (+50°C) temperatures.

Results and discussion

Gel time and exotherm peak temperature

The gel time and exotherm peak temperature data for CPB 4 containing 10—60% alumina trihydrate and antimony trioxide are given in Tables 1a and 1b, respectively, and time versus temperature curves (exotherms) are shown in Figs. 1a and 1b, respectively. It is seen from these data that gel time increases in both the systems.
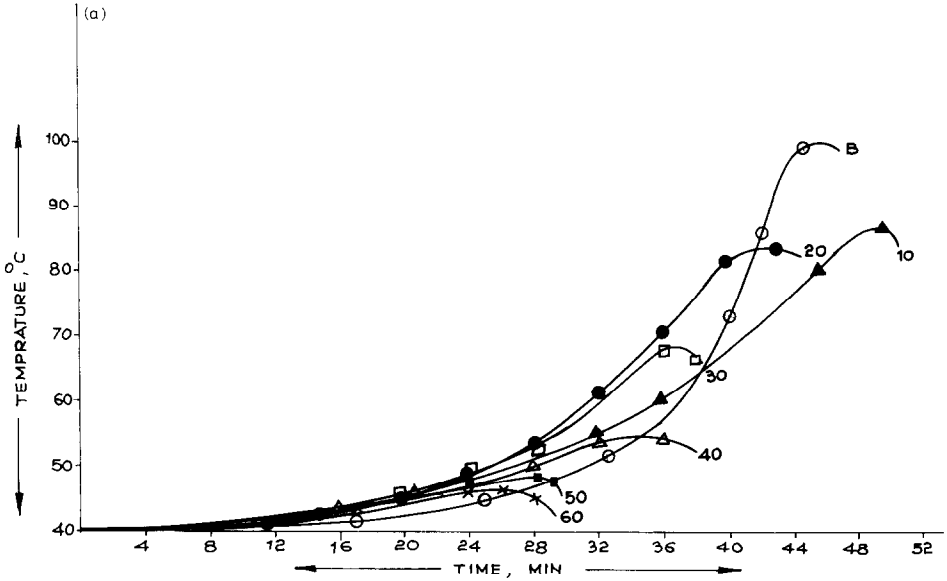
Fig. 1a. Exotherm curves for CPB 4 with different percentages of alumina trihydrate. B: no alumina trihydrate added; numbers refer to the percentage alumina trihydrate in the system.
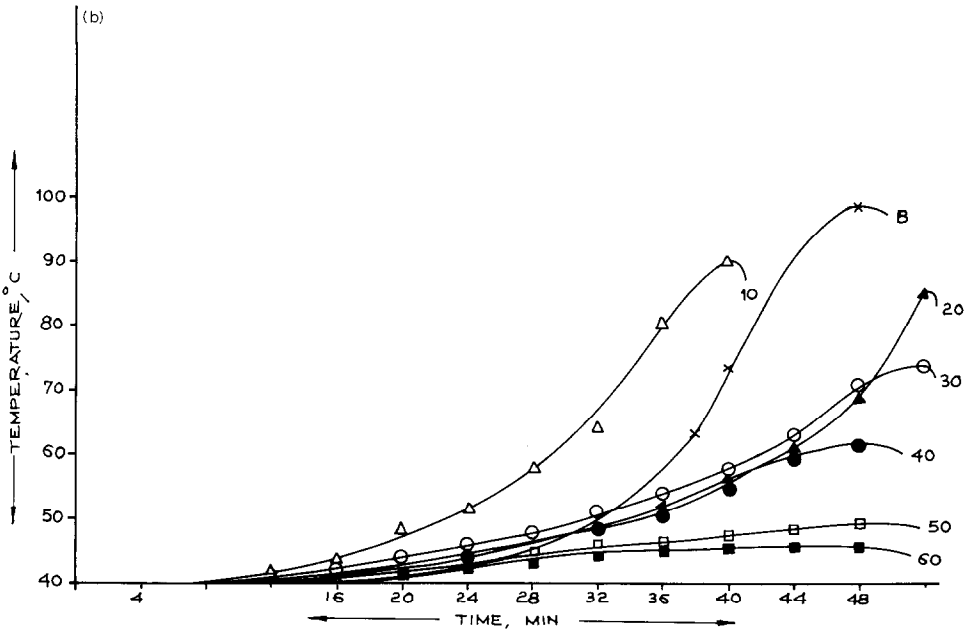

Fig. 1b. Exotherm curves for CPB 4 with different percentages of antimony trioxide. B: no antimony trioxide added; numbers refer to the percentage antimony trioxide in the system.

TABLE 1a

Gel time and exotherm peak temperature of chloropolyester blend CPB 4 with different percentages of alumina trihydrate

Alumina trihydrate (%)	Gel time (min ± 10 s)	Exotherm peak temperature (°C ± 2°C)
0	16.0	97
10	16.4	87
20	17.1	84
30	17.6	67
40	18.2	54
50	18.7	47
60	19.1	46

TABLE 1b

Gel time and exotherm peak temperature of chloropolyester blend CPB 4 with different percentages of antimony trioxide

Antimony trioxide (%)	Gel time (min ± 10 s)	Exotherm peak temperature (°C ± 2°C)
0	16.0	97
10	17.6	90
20	18.1	80
30	19.0	74
40	20.2	62
50	21.1	49
60	22.2	46

In general, addition of fillers increases the gel time of a resin as a result of hindered diffusion due to increased viscosity. This is in agreement with the data reported by Zhestous Kii in the case of a urea—formaldehyde resin formulation [10]. It is seen further that exotherm peak temperature decreases as the percentage of filler increases. This is due to the fact that weight of resin (which is the only source of heat liberation on polymerization because of conversion of C=C to C—C) decreases as the percentage of filler increases.

Tensile strength and per cent elongation

Tensile strength and per cent elongation data are shown in Tables 2a and 2b, respectively. In case of the CPB 4—alumina trihydrate system, tensile strength increases with increase of percentage of filler, but per cent elongation decreases. This is a shared general characteristic of both polyesters and most other crosslinked polymers. However, in case of the CPB 4—antimony trioxide system, there is no specific trend in tensile strength. Specific gravity of alumina trihydrate is 2.42 and of antimony trioxide 5.3—5.8, respectively, i.e., antimony trioxide is heavier than alumina trihydrate; therefore, this

effect is probably due to a higher tendency to settle of the heavier antimony trioxide during the process of polymerization of the system CPB 4—Sb_2O_3 as compared to the system CPB 4—$Al_2O_3 \cdot 3H_2O$ However, the trend of per cent elongation of CPB 4—antimony trioxide is similar to that of the CPB 4—alumina trihydrate system.

TABLE 2a

Tensile strength and per cent elongation of chloropolyester blend CPB 4 with different percentages of alumina trihydrate

Alumina trihydrate (%)	Tensile strength (kg/cm^2)	Elongation (%)
0	58 2	19 0
10	60 0	17 6
20	61 8	15 9
30	63 7	14 1
40	66 9	13 0
50	69 2	12 2
60	86 5	6 5

TABLE 2b

Tensile strength and per cent elongation of chloropolyester blend CPB 4 with different percentages of antimony trioxide

Antimony trioxide (%)	Tensile strength (kg/cm^2)	Elongation (%)
0	58 2	19 0
10	43 5	16 8
20	47 18	15 2
30	57 17	14 1
40	51 19	10 3
50	51 5	9 2
60	53 2	7 3

Nitroglycerine and water absorption

   Tables 3a and 3b show the influence of nitroglycerine on CPB 4 systems filled with alumina trihydrate and antimony trioxide, and Tables 4a and 4b show influence of water absorption on filled CPB 4 systems. The variation in nitroglycerine and water absorption of filled systems are shown in Figs 2a and 2b, and 3a and 3b, respectively It is observed that both nitroglycerine and water absorption decrease as the percentage of alumina trihydrate and antimony trioxide increase, and at the same time increase with the increase in number of days This is due to the fact that the percentage of CPB 4, which is mainly responsible for nitroglycerine and water absorption, decreases as the percentage of filler increases. This is similar to the observations

TABLE 3a

Nitroglycerine absorption of chloropolyester blend CPB 4 with different percentages of alumina trihydrate

Alumina trihydrate (%)	Nitroglycerine absorption (%) at time (h)						
	24	48	96	144	192	240	288
0	1.98	2.61	3.23	3.77	4.25	4.60	4.74
10	1.63	2.06	2.45	3.00	3.47	3.66	3.77
20	1.50	1.93	2.31	2.73	3.28	3.56	3.63
30	1.23	1.61	2.18	2.26	2.58	2.73	2.86
40	1.12	1.30	1.71	1.86	2.13	2.25	2.34
50	0.95	1.20	1.51	1.71	2.03	2.19	2.27
60	0.90	1.19	1.31	1.64	1.71	1.75	1.80

TABLE 3b

Nitroglycerine absorption on chloropolyester blend CPB 4 with different percentages of antimony trioxide

Antimony trioxide (%)	Nitroglycerine absorption (%) at time (h)						
	24	48	96	144	192	240	288
0	1.98	2.61	3.23	3.77	4.25	4.60	4.74
10	1.52	2.77	2.45	3.41	3.98	4.25	4.35
20	1.42	1.80	2.31	3.11	3.11	3.80	3.81
30	1.21	1.54	2.18	2.69	3.08	3.25	3.32
40	1.08	1.44	1.71	2.21	2.46	2.54	2.58
50	1.00	1.35	1.51	1.88	2.39	2.50	2.56
60	0.68	0.93	1.20	1.25	1.43	1.50	1.60

TABLE 4a

Water absorption of chloropolyester blend CPB 4 with different percentages of alumina trihydrate

Alumina trihydrate (%)	Water absorption (%) at time (days)					
	1	2	3	4	5	6
0	1.89	2.61	3.02	3.20	3.34	3.42
10	1.72	2.36	2.83	2.94	3.22	3.32
20	1.38	2.11	2.53	2.77	2.88	2.95
30	1.36	2.08	2.37	2.56	2.65	2.68
40	1.28	1.99	2.27	2.27	2.47	2.53
50	1.01	1.54	1.85	1.99	2.06	2.10
60	0.96	1.21	1.45	1.81	1.88	1.92

TABLE 4b

Water absorption of chloropolyester blend CPB 4 with different percentages of antimony trioxide

Antimony trioxide (%)	Water absorption (%) at time (days)					
	1	2	3	4	5	6
0	1.89	2.61	3.02	3.20	3.44	3.45
10	1.68	2.44	2.83	3.11	3.20	3.25
20	1.58	2.11	2.67	2.77	2.98	3.07
30	1.25	2.08	2.20	2.36	2.47	2.52
40	0.97	1.99	2.10	2.27	2.32	2.42
50	0.90	1.54	1.67	1.79	1.85	1.88
60	0.74	1.08	1.23	1.30	1.34	1.37
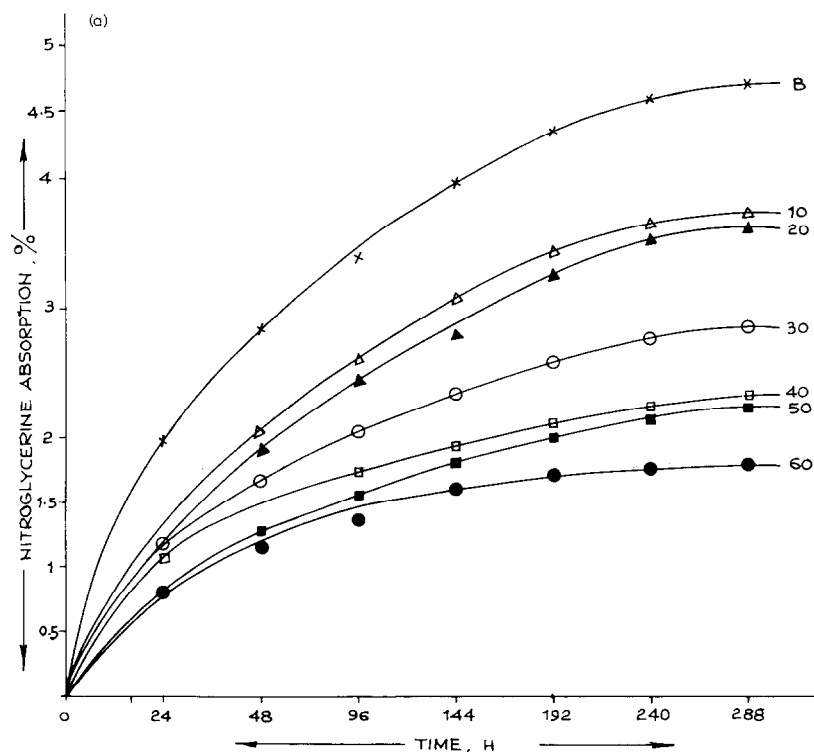
Fig. 2a. Nitroglycerine absorption of CPB 4 with different percentages of alumina trihydrate. B: no alumina trihydrate added; numbers refer to the percentage alumina trihydrate in the system.
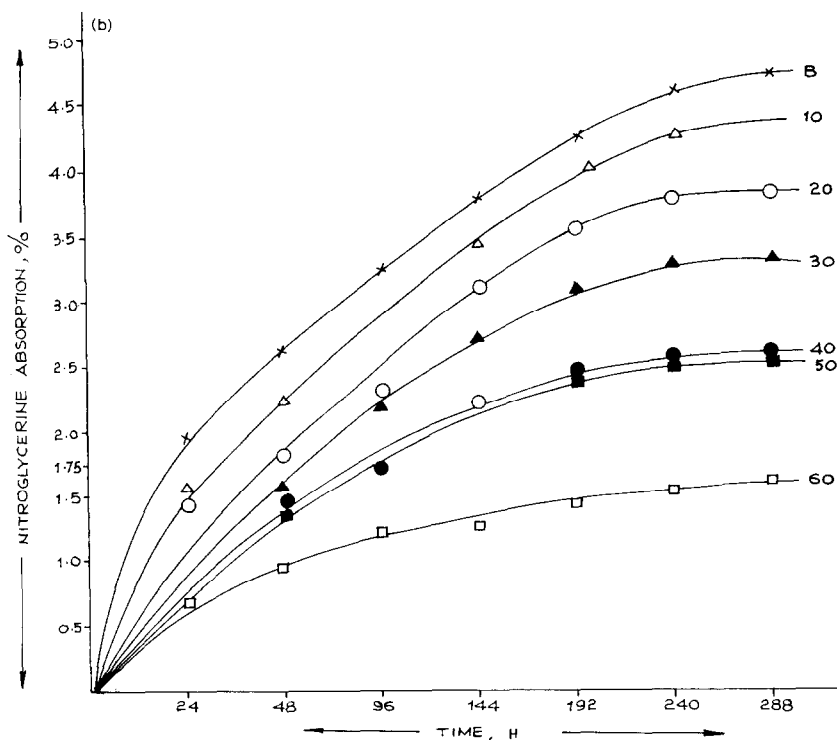
Fig. 2b. Nitroglycerine absorption of CPB 4 with different percentages of antimony trioxide. B: no antimony trioxide added; numbers refer to the percentage antimony trioxide in the system.

obtained by us in the case of the semiflexible unsaturated system consisting of polyester resin 4—alumina trihydrate [11]. Chloropolyesters are macromolecules, and an idealised structure of a crosslinked chloropolyester based on TCPAn is shown in Fig. 4 [12]. Nitroglycerine and water molecules, being small in size, can easily seep into the structure of chloropolyester. The migration of nitroglycerine and water is prevented by physically blocking the pores as a result of addition of alumina trihydrate or antimony trioxide. Both nitroglycerine and water absorption are almost directly proportional to the quantity of CPB 4 and go on decreasing with an increase in the concentration of filler.

Heat resistance
Heat resistances of the filled systems CPB 4—alumina trihydrate and CPB 4—antimony trioxide were measured in terms of loss in weight at 150°C, and are shown in Tables 5a and 5b. The graphical presentation of loss in weight versus time is shown in Figs. 5a and 5b, respectively. In case of the CPB 4—$Al_2O_3 \cdot 3H_2O$ system loss in weight increases as the concentration of filler increases up to 30% and then slowly decreases from 40 to 60%. These observations are contrary to those made in the case of the semiflexible
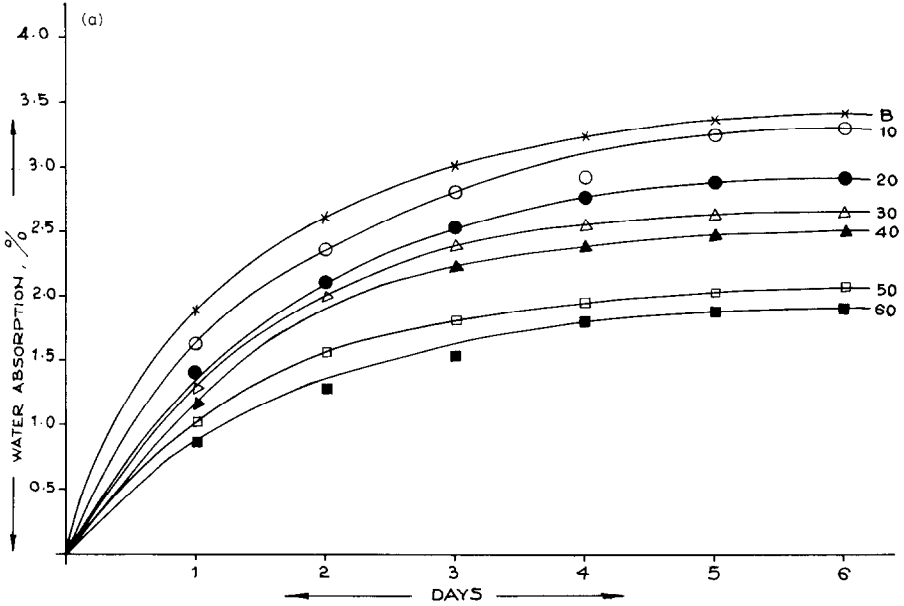
Fig. 3a. Water absorption of CPB 4 with different percentages of alumina trihydrate filler.
B: no filler added; numbers refer to the percentage alumina trihydrate in the system.
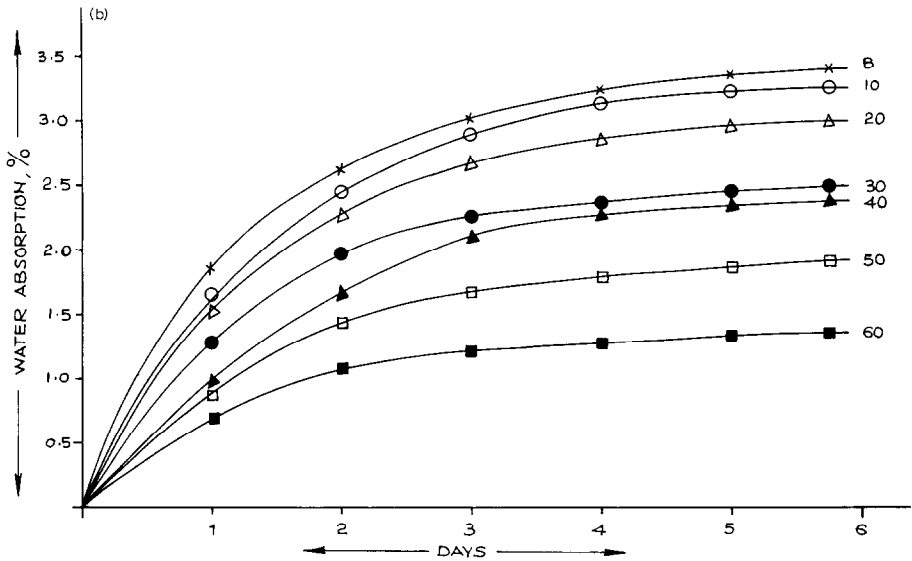

Fig. 3b. Water absorption of CPB 4 with different percentages of antimony trioxide filler.
B: no filler added; numbers refer to the percentage antimony trioxide in the system.

Fig. 4. Idealized structure of a polyester resin containing tetrachlorophthalic anhydride.

Fig. 5a. Volatile losses for CPB 4 with different percentages of alumina trihydrate. B: no filler added; numbers refer to the percentage of alumina trihydrate in the system.
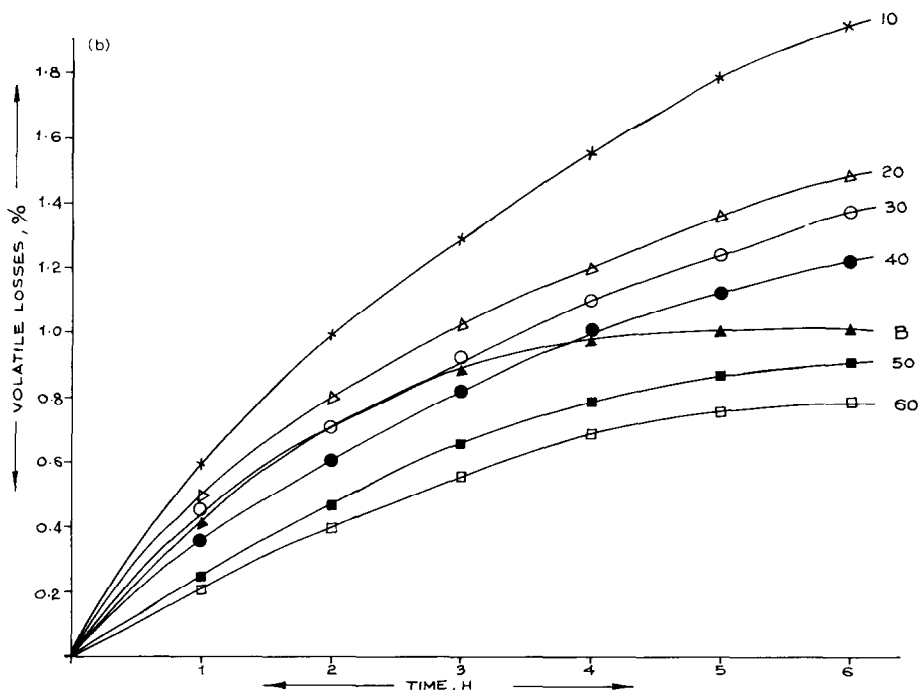
Fig. 5b. Volatile losses for CPB 4 with different percentages of antimony trioxide. B: no filler added; numbers refer to the percentage of antimony trioxide in the system.

system polyester resin $4-Al_2O_3 \cdot 3H_2O$ [11]. In case of the CPB $4-Sb_2O_3$ system also, the increase in loss in weight is up to 20% and subsequently decreases. This is considered to be because of the formation of some complex chlorospecies which are more susceptible to heat; however, it is not supported by infrared spectra of both systems (shown in Figs. 6a and 6b), where no additional peaks are observed.

TABLE 5a

Volatile losses of chloropolyester blend CPB 4 with different percentages of alumina trihydrate

Alumina trihydrate (%)	Volatile losses (%) in time (h)					
	1	2	3	4	5	6
0	0.42	0.76	0.90	0.97	1.03	1.06
10	0.93	1.12	1.47	1.80	1.91	1.92
20	0.84	1.08	1.32	1.62	1.80	1.93
30	0.76	0.91	1.10	1.33	1.51	1.61
40	0.41	0.51	0.60	0.77	0.91	1.00
50	0.37	0.46	C.52	0.66	0.76	0.83
60	0.34	0.39	0.40	0.53	0.61	0.68

TABLE 5b

Volatile losses of chloropolyester blend CPB 4 with different percentages of antimony trioxide

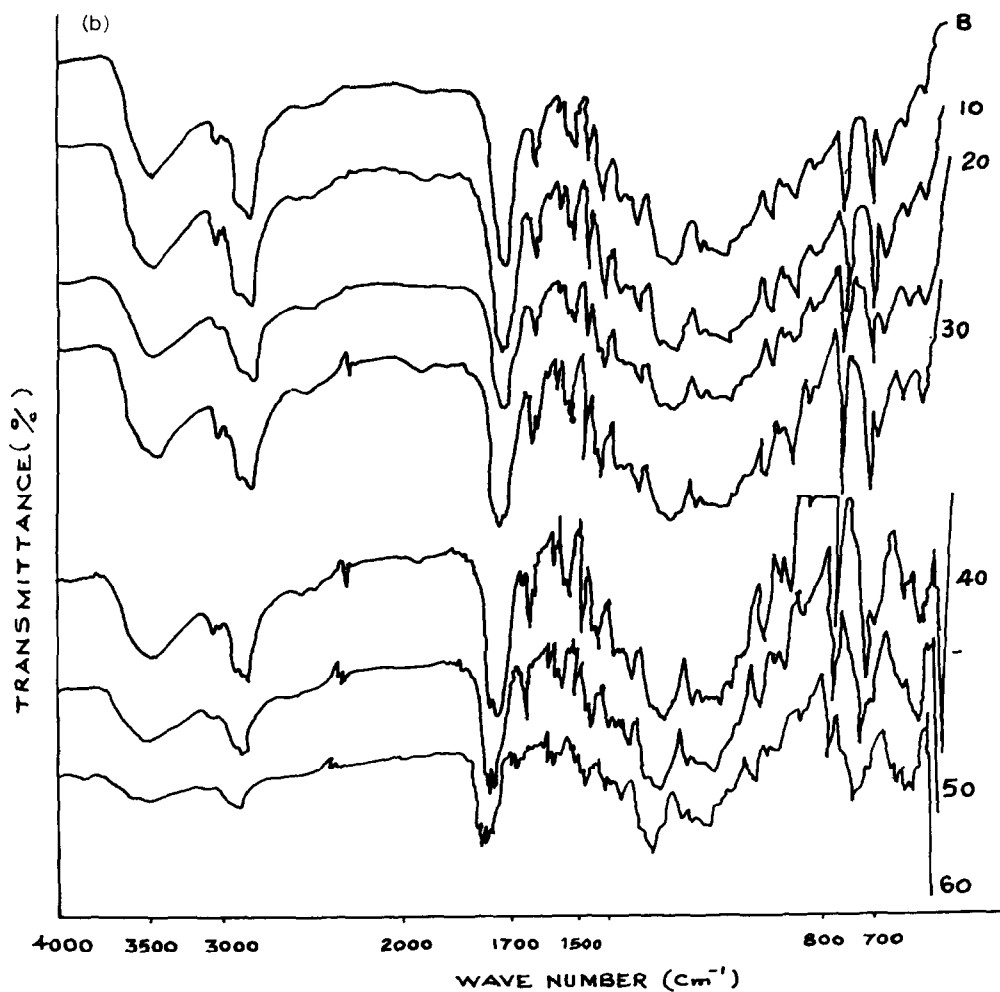| Antimony trioxide (%)	Volatile losses (%) in time (h)					
	1	2	3	4	5	6
0	0.42	0.76	0.90	0.97	1.03	1.06
10	0.81	1.00	1.21	1.53	1.78	1.96
20	0.68	0.82	0.97	1.19	1.37	1.49
30	0.58	0.71	0.88	1.08	1.24	1.37
40	0.48	0.61	0.82	0.98	1.12	1.33
50	0.45	0.46	0.70	0.85	0.87	0.91
60	0.31	0.39	0.49	0.60	0.77	0.79
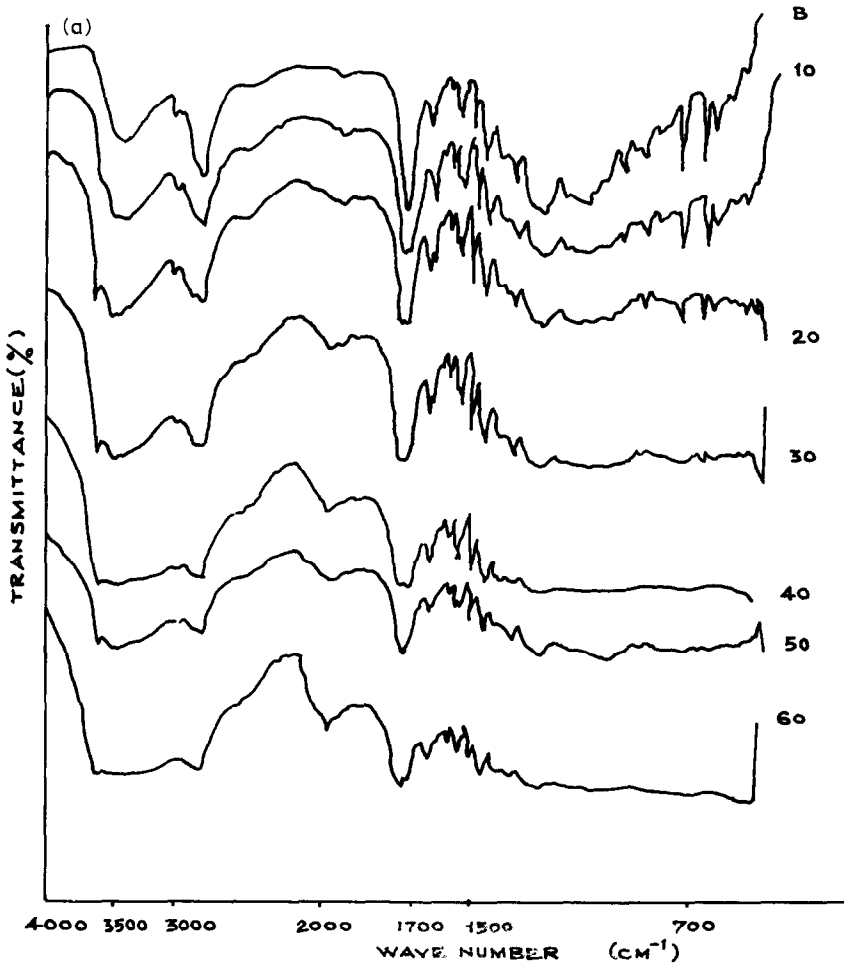
Fig. 6a. Infrared spectra of CPB 4 with different percentages of alumina trihydrate. B: no filler added; numbers refer to the percentage of alumina trihydrate in the system.

Fig. 6b. Infrared spectra of CPB 4 with different percentages of antimony trioxide. B: no filler added; numbers refer to the percentage of antimony trioxide in the system.

Flame retardance

Flame retardance data are depicted in terms of burning rate in Tables 6a and 6b. It is seen that the resin becomes self-extinguishing in nature at 30% alumina trihydrate and 20% antimony trioxide concentrations. The most important correlation between the flame retardance and heat resistance characteristics is that loss in weight increases up to 30% in case of the CPB 4—$Al_2O_3 \cdot 3H_2O$ system, and the system becomes self-extinguishing at

30% filler. Similarly, in case of the CPB 4—Sb_2O_3 system, loss in weight increases up to 20%, and the system becomes self-extinguishing at a level of 20% filler. This would require a detailed investigation in order to find out the chemistry involved, which is not important from our angle.

TABLE 6a

Burning rate of chloropolyester blend CPB 4 with different percentages of alumina trihydrate

Alumina trihydrate (%)	Burning rate (mm/sec)	
	corresponding to 1-inch length	corresponding to 3-inch length
0	0.41	0.39
10	0.32	0.40
20	0.11	0.14
30	†	†
40	††	††
50	††	††
60	††	††

†Self-extinguishing, ††non-burning.

TABLE 6b

Burning rate of chloropolyester blend CPB 4 with different percentages of antimony trioxide

Antimony trioxide (%)	Burning rate (mm/sec)	
	corresponding to 1-inch length	corresponding to 3-inch length
0	0.41	0.39
10	0.007	0.007
20	†	†
30	††	††
40	††	††
50	††	††
60	††	††

†Self-extinguishing, ††non-burning.

Inhibition and static evaluation trials

Based on flame retardant characteristics and other data such as gel time, exotherm peak temperature, tensile strength, per cent elongation, water absorption, nitroglycerine absorption and heat resistance, 30% $Al_2O_3 \cdot 3H_2O$ and 20% Sb_2O_3 with CPB 4 were considered suitable for inhibition and static

evaluation of double-base propellants. The static evaluation of double base propellants with both these inhibition systems was carried out separately:

(a) at ambient temperature,

(b) at −30°C after conditioning for 18 hours, and

(c) number at +50°C after conditioning for 18 hours.

The pressure—time profiles for both systems are shown in Figs. 7 and 8, respectively. The expected pressure level theoretically calculated on the basis of eqn. (1) matches with the pressure level obtained experimentally in both the systems.

$$P_c = \left[\frac{a\rho k_N}{C_D} \right]^{\left(\frac{1}{1-n} \right)} \tag{1}$$

where P_c = chamber pressure; a = a constant; ρ = density of propellant; k_N = A_b/A_t, the ratio of burning area to throat area; C_D = discharge coefficient; and n = pressure index.
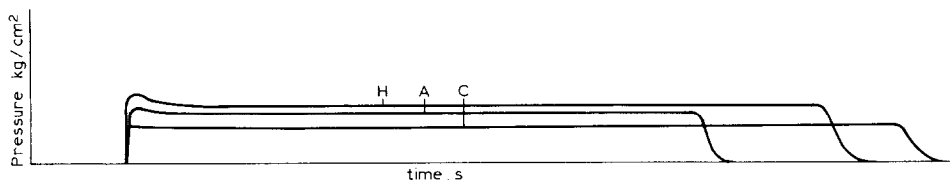

Fig. 7. Pressure—time profiles for propellant inhibited with CPB 4 + 30% alumina tri-hydrate filler. H — +50°C, A — ambient, C — −40°C.
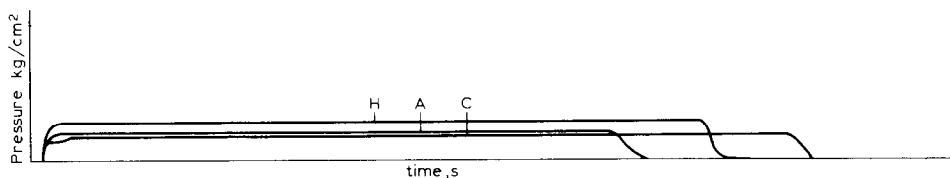

Fig. 8. Pressure—time profiles for propellant inhibited with CPB 4 + 20% antimony tri-oxide filler. H — +50°C, A — ambient, C — −40°C.

Acknowledgements

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