

Tetrachlorophthalic Anhydride-Based Flame-Retardant Chloropolyesters for Inhibition of Double-Base Propellants*

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Synopsis

Seven unsaturated chloropolyesters based on tetrachlorophthalic anhydride (TCPAn) maleic anhydride (MAN), and propylene glycol (PG) (designated as CP-1) and TCPAn, MAN, and polyethylene glycol molecular weight 200 (PEG-200) (designated as CP-2), and TCPAn, MAN, and mixed glycols (PG & PEG-200 in different molar proportions) and designated as CPM-2, CPM-4, CPM-6, etc. (depending upon molar proportions) have been synthesized. The flame-retardant characteristics have been assigned by measuring heat resistance (loss in weight) and flame retardance (burning rate), and it is found that in these chloropolyesters thermal stability increases as chlorine percentage increases. In addition, these chloropolyesters have been characterized for gel time, exotherm peak temperature, tensile strength, percentage elongation and bond strength, nitroglycerine absorption, and cross-link density. Based on these properties, CPM-9 with 30% styrene (designated as CPM-9s) has been selected for inhibition and static evaluation trials, after conditioning at ambient, cold (-40°C), and hot ($+50^{\circ}\text{C}$) temperatures. The nature of pressure-time profiles indicate the suitability of "CPM-9s" for the inhibition of double-base (containing 2-NDPA) propellants.

INTRODUCTION

A wide variety of techniques have been employed in order to impart flame-retardant characteristics to unsaturated polyesters.¹ These techniques have been classified as (i) incorporation of inorganic additives; (ii) incorporation of organic additives; (iii) incorporation of inorganic and organic additives, in combination; and (iv) flame-retardant elements which become part of the macromolecules.

The present study utilizes technique (iv), and tetrachlorophthalic anhydride (TCPAn) in place of phthalic anhydride (PAN) or isophthalic acid (IPA), has been selected for the synthesis of chloropolyesters.

The synthesis of unsaturated chloropolyesters based on TCPAn, MAN, and several glycols and unsaturated bromopolyesters based on tetrabromophthalic anhydride (TBPAn), MAN, and several glycols and comparison of their effectiveness as flame retardants/heat resistant has been a topic of discussion by a number of investigators in the field.²⁻⁸ In general, bromopolyesters are more effective than chloropolyesters as flame retardants/heat resistant, and compounds such as Et_3PO_4 , Sb_2O_3 , Ph_3Sb , and triallyl phosphate etc., have synergistic effects on both bromo- and chloropolyesters.

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Tranchant et al.⁹ suggested the application of chloropolyesters for inhibition of double-base propellant, but the nature of the chloropolyester was not disclosed. A survey of the literature reveals that no work on tetrabromo/chlorophthalic anhydride-based bromo/chloropolyesters for inhibition of double-base propellants has been done. Since tetrachlorophthalic anhydride is indigenously available, it was considered of interest to study chloropolyesters based on TCPAn for this purpose. It is only recently that a number of chloropolyesters based on TCPAn, MAn, and several glycols have been synthesized, characterized, and evaluated in this laboratory for inhibition of double-base propellants¹⁰ and effect of alumina trihydrate and antimony trioxide has also been studied.¹¹

The object of this paper is to synthesize chloropolyesters based on TCPAn, MAn, and mixed glycols (PG and PEG-200 in different molar proportions), to study their flame-retardant and heat-resistant characteristics and evaluate them in the light of their application for inhibition of double-base propellants.

MATERIALS AND METHODS

The materials used for the synthesis of chloropolyesters are: Tetrachlorophthalic anhydride, propylene glycol, BDH L.R., polyethylene glycol MW 200, BDH L.R., maleic anhydride, technical grade and styrene monomer were procured from trade and used as such.

SYNTHESIS OF CHLOROPOLYESTERS

Chloropolyesters based on TCPAn, MAn, and PG (designated as CP-1) and TCPAn, MAn, and PEG-200 (designated as CP-2) have been synthesized by a two-step process as described earlier.¹⁰ CPM-2 has also been synthesized by condensing TCPAn 0.5 mole, MAn 0.5 mole, and mixture of PG and PEG-200 (0.20 and 0.80 moles, respectively) by a two-step process, similar to an earlier method. The details of mole ratios of glycols, acid values for CPM-4, CPM-6, etc. along with their number average MW (M_n) are shown in Table I.

The basic resin was blended with 25% styrene monomer and 0.02% hydroquinone was added to stabilize the resin.

Gel time and exotherm peak temperature,¹² tensile strength and % elongation,¹³ bond strength,¹⁴ nitroglycerine absorption,¹⁴ and heat resistance¹⁵ (measured by "loss in weight" at 150°C) have been determined by the methods reported earlier. Flame retardance has been determined in terms of burning rate, by ASTM method D-635-63 with minor modifications reported elsewhere.¹¹

*Cross link densities*²⁰ for these chloropolyesters have been determined by Dupont 943 Thermomechanical Analyser (TMA) provided with a penetration probe. The experimental operation has been carried out according to manufacturer's instructions. A uniform sheet of cured chloropolyester (thickness 2.0 to 3.0 mm) was placed on the sample holder below the plunger, and the extent of penetration obtained by applying different forces was recorded. Figure 1 shows a plot of $\Delta l/l$ (where l is the initial thickness and Δl is the decrease in the thickness of the sample) vs. force (in grams). Ve/V was calculated as follows

TABLE I
Composition of Mixed Glycols and Tetrachlorophthalic Anhydride-Based Chloropolyesters

Designation	Molar ratios of ingredients			Acid values		\bar{M}_n
	PEG-200	PG	Tetrachlorophthalic anhydride (TCPAn)	Maleic anhydride (MAn)	Before MAn addition	
CP-2	1.2 ^a	0.00	0.5	0.5	35	35
CPM-2	0.80	0.20	0.5	0.5	40	40
CPM-4	0.60	0.40	0.5	0.5	45	45
CPM-6	0.40	0.60	0.5	0.5	50	50
CPM-8	0.20	0.80	0.5	0.5	55	55
CPM-9	0.10	0.90	0.5	0.5	57	57
CP-1	0.00	1.50 ^b	0.5	0.5	60	60

^a 20% Glycol (PEG-200) was taken extra to compensate loss.

^b 50% Glycol (PG) was taken extra to compensate loss and get the resin in liquid state.

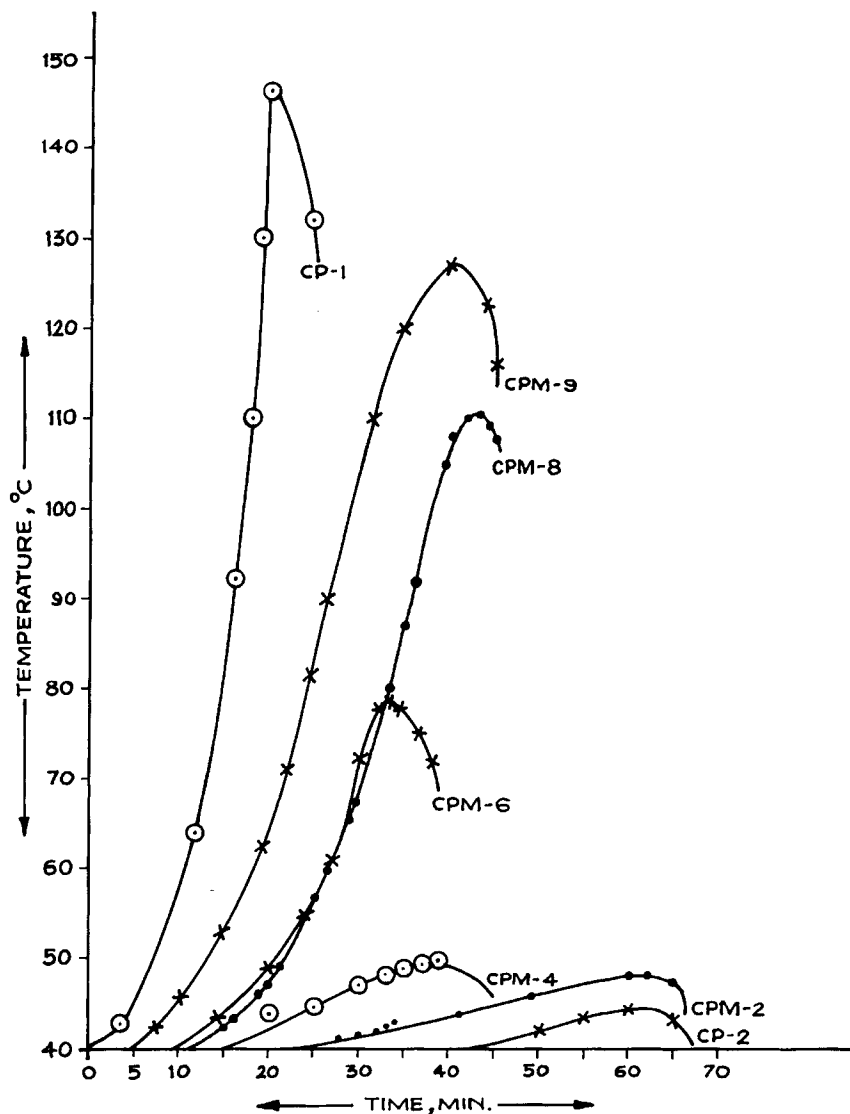


Fig. 1. Plot of penetration ratios ($\Delta l/l$) vs. force (F) for chloropolyesters.

$$Ve/V = \frac{F/A}{RT[\alpha - (1/\alpha^2)]} \quad (1)$$

Where F = force (dynes)

A = area of the probe (cm^2)

R = gas constant (J/K/mole)

and $\alpha = 1 + \epsilon$ (where ϵ penetration ratio = $\Delta l/l$) is calculated from the slope of the $\Delta l/l$ vs. F plot.

Number average molecular weight (\bar{M}_n) has been determined by vapor pressure osmometer (Wescan Model 233) as described in literature.¹⁶ Dou-

ble-distilled toluene was used as a solvent to prepare solution of different chloropolyesters and benzil was taken as standard.

Infrared (IR) spectra of plasticizers recovered from cured chloropolyesters have been recorded by smear method using Perkin-Elmer Model 457 spectrophotometer.

Inhibition and static evaluation trials. Three cast double-base propellant (containing 2-NDPA as stabilizer) sustainers were machined to the dimensions 108 mm diameter and 150–160 mm length and inhibited with CPM-9s by casting technique,¹⁴ X-rayed, and statically evaluated (one each) after conditioning at ambient, cold (-40°C), and hot ($+50^{\circ}\text{C}$) temperatures. The inhibition thickness was 2.5 to 3.0 mm.

RESULTS AND DISCUSSION

Gel Time, Bond Strength and Exotherm Peak Temperature

The data on gel time and exotherm peak temperature for chloropolyesters are given in Table II and its graphical presentation is in Figure 2. It is seen that the gel time increases from CPM-9 to CPM-2 as PG is replaced by PEG-200. This may be explained on the basis of number of chloropolyester chains in a specified weight of resin. It is evident from Table I that number average molecular weight (\bar{M}_n) of all chloropolyesters is the same. This means that as PG is gradually replaced by PEG-200, the number of chloropolyester chains decreases and consequently the length of chloropolyester chains increases in order to maintain same \bar{M}_n . As long-chain molecules are less reactive than short-chain molecules, it is expected that CPM-9 will have less gel time which will increase as PG is replaced by PEG-200 and the observed order of gel time is



It is our practical experience that the bond strength (BS) is related with gel time and if gel time increases, BS decreases. It is due to the migration of nitro bodies (NG and 2-NDPA, which interfere with the polymerization)^{18,19} from the propellant to the chloropolyesters.

If the gel time increases, the quantum of interference due to migration of nitro bodies also increases and BS decreases. Since the gel time increases from CPM-9 to CPM-2, it is expected that BS will decrease in this order, which is confirmed experimentally.

The chloropolyester molecular chains are linked to one another through the conversion of carbon-carbon double ($\text{C}=\text{C}$) bond into carbon-carbon single ($\text{C}-\text{C}$) bond during polymerization/curing and as a result, 17.2 Kcal/mole energy is liberated.¹⁷ As discussed earlier, the number of chloropolyester chains decreases as PG is replaced by PEG-200, it is therefore expected that amount of heat liberated during gelling/polymerization/curing will decrease from CPM-9 to CPM-2 or in other words, exotherm peak temperature will decrease from CPM-9 to CPM-2.

TABLE II
Gel Time, Exotherm Peak Temperature, Tensile Strength, % Elongation, and Bond Strength of Chloropolyesters
Based on Mixed Glycols and TCPAn

Chloropolyester	Gel time ± 1 min	Exotherm peak temperature °C ± 5°C	Tensile strength kg/cm ²	% Elongation	Bond strength with propellant kg/cm ²
CP-2	40	44.5	5.40	17.00	5.00
CPM-2	34	48.5	5.99	18.50	8.50
CPM-4	20	50.0	14.50	24.17	13.25
CPM-6	14	79.0	25.57	35.83	16.25
CPM-8	12	111.0	35.17	40.00	19.50
CPM-9	10	127.0	53.20	42.50	28.50
CP-1	7	148.0	340.0	1.60	86.00

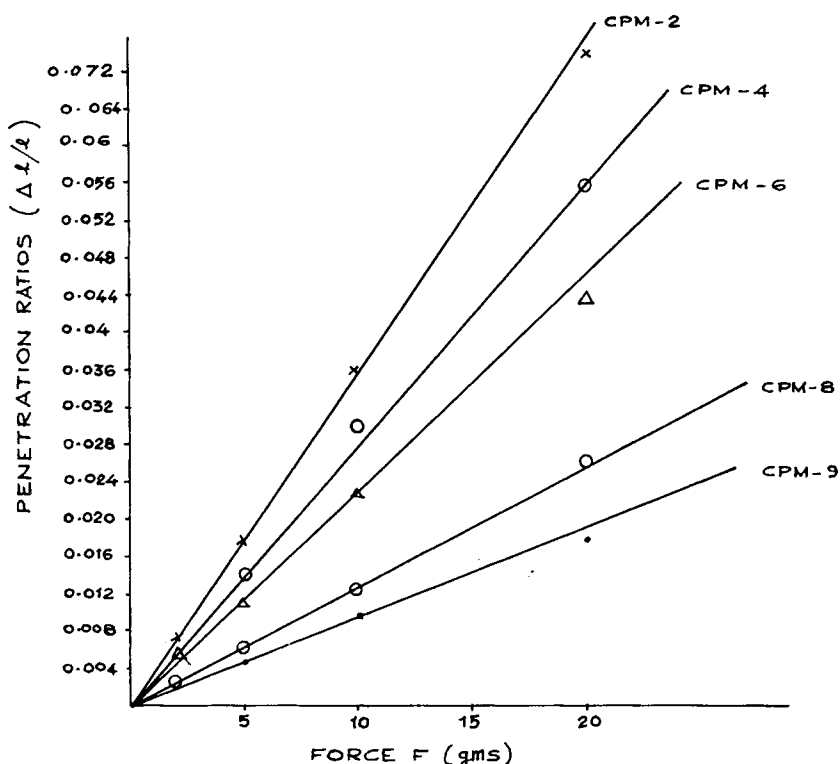


Fig. 2. Exotherm curves for chloropolyesters.

Tensile Strength and % Elongation

The data on tensile strength (TS) and % elongation (E) are given in Table II. It is seen that both tensile strength as well as % elongation increase as the PEG-200 is replaced by PG. This is contrary to the fact that both properties are closely related and if TS increases, % elongation decreases and vice versa in polyesters and most other cross-linked polymeric.¹⁷ The increase in TS as a result of replacement of PEG by PG is expected similar to semiflexible polyesters¹¹ and may be explained similarly. The increase in % E is due to the formation of increased amount of plasticizer (with the increase in molar proportion of PG as a result of reaction of TCPAn and PG which is present in excess and gives plasticization effect). In order to prove this point, cured chloropolyesters were refluxed with diethyl ether for 4 to 6 h and subsequently ether was removed from the extract on water bath. The "loss in weight" data (on reflux) is given in Table III. The data on loss in weight (indicative of loss as plasticizer Table III) shows that the formation of plasticizer increases as the proportion of PEG-200 is replaced by PG. This is further supported by the IR spectra of residue (obtained from the extract on reflux) which are comparable to that of plasticizers obtained by reacting TCPAn and PG and TCPAn and PEG-200 (Figs. 3 and 4).

TABLE III
Loss in Weight of Mixed Glycols Based
Chloropolyesters After Refluxing with
Diethyl Ether for 4-6 h

Chloropolyester	% Loss
CP-2	—
CPM-2	12.36
CPM-4	15.38
CPM-6	17.73
CPM-8	18.35
CPM-9	19.99
CP-1	—

Cross-Link Density, Nitroglycerine Absorption, and Heat Resistance

The cross-link density, nitroglycerine absorption, and heat resistance data are presented in Table IV. It is evident that as the PEG-200 is replaced by PG, the cross-link density increases.

The NG absorption increases as PG is replaced by PEG-200. This may be explained on the basis of cross-link density. As PG is replaced by PEG-200 the number of chloropolyester chains decreases resulting into decrease in cross-linking density (Table IV) and consequently increase in NG absorption. As PG is replaced by PEG-200, cross-link density decreases from CPM-9 to CPM-2 and therefore loss in weight increases from CPM-9 to CPM-2, which is confirmed experimentally. In other words, heat resistance decreases from CPM-9 to CPM-2.

Flame Retardance

This is expressed in terms of *burning rate*. The data of burning rate along with theoretically calculated chlorine percentage of chloropolyesters is given in Table V. The data indicate that the burning rate decreases as the chlorine percentage increases. This can be explained if we assume that the polymer degradation governs regression rate. As explained under exotherm peak temperature, the number of chloropolyester chains decreases as PG is replaced by PEG-200 and consequently the number of bonds also decreases from CP-1 to CP-2 through CPM- series. It means that the CP-1 has maximum number of bonds. Therefore CP-1 requires greater energy for breaking polymer chains as compared to CPM-2 and CP-2 to give degradation products responsible for flame reaction. Thus, burning rate of CP-1 is minimum and increases as the number of bonds decreases with the replacement of PG by PEG-200. This is similar to data reported in the literature²⁰ in cases of composite propellants and also reported by us in cases of semirigid polyesters.²¹

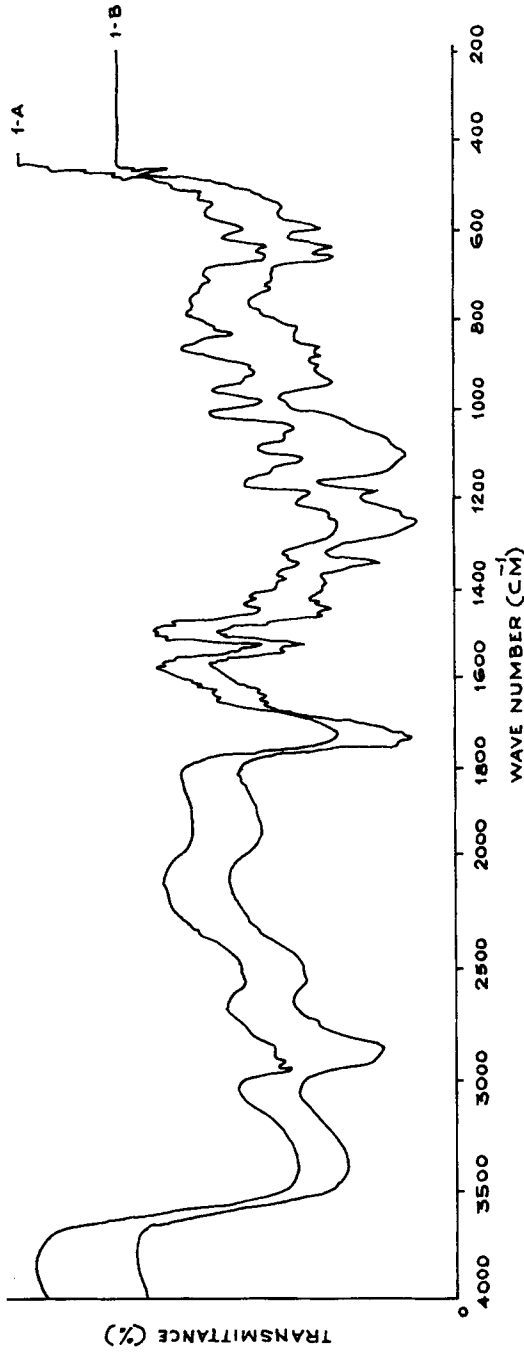


Fig. 3. Infrared spectra of plasticizers obtained by the reaction of 1-A—TCPAn + PG and 1-B—TCPAn + PEG-200.

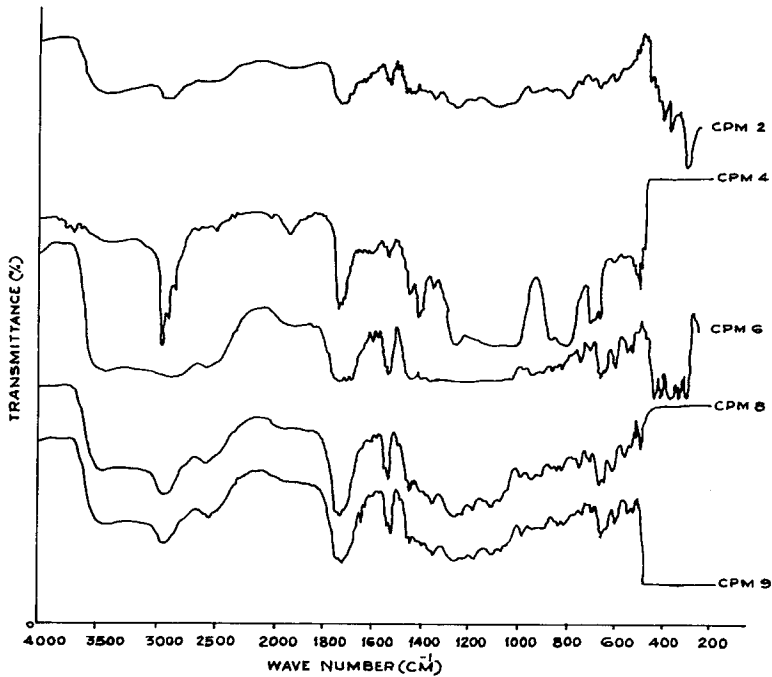


Fig. 4. Infrared spectra of residue received after refluxing chloropolyesters with diethyl-ether.

TABLE IV
Cross-Link Density, Nitroglycerine Absorption, and Heat Resistance for Chloropolyesters

Chloropolyester	Cross-link density, V_e/V moles/cm ³	Nitroglycerine absorption % (wt/wt) (after 14 days)	Heat resistance % (wt/wt) after 6 h
CP-2	—	<i>Specimen shattered into pieces</i>	1.68
CPM-2	2.6×10^4	6.70	1.69
CPM-4	3.2×10^4	5.36	1.52
CPM-6	3.4×10^4	3.13	1.15
CPM-8	7.7×10^4	2.46	1.12
CPM-9	9.6×10^4	1.98	1.06
CP-1	—	0.88	0.40

Static Evaluation (Functional Test)

Based on various characteristics, CPM-9s has been selected for inhibition and static evaluation trials. The pressure–time profiles of inhibited double-base propellants at different temperatures are shown in Figure 5. The pressure level is constant in all profiles throughout the combustion duration. Since the pressure is constant, the burning surface is also constant as expressed by the Eq. (2).

TABLE V
Flame Retardance of Mixed Glycols and TCPAn-Based
Chloropolyesters Along with Theoretical Chlorine
Percentage

Chloropolyester	Burning rate mm/s	Theoretical chlorine %
CP-2	0.5824	12.86
CPM-2	0.4917	13.66
CPM-4	0.4508	14.58
CPM-6	0.3859	15.78
CPM-8	0.3368	16.66
CPM-9	0.3206	17.75
CP-1	0.3132	18.50

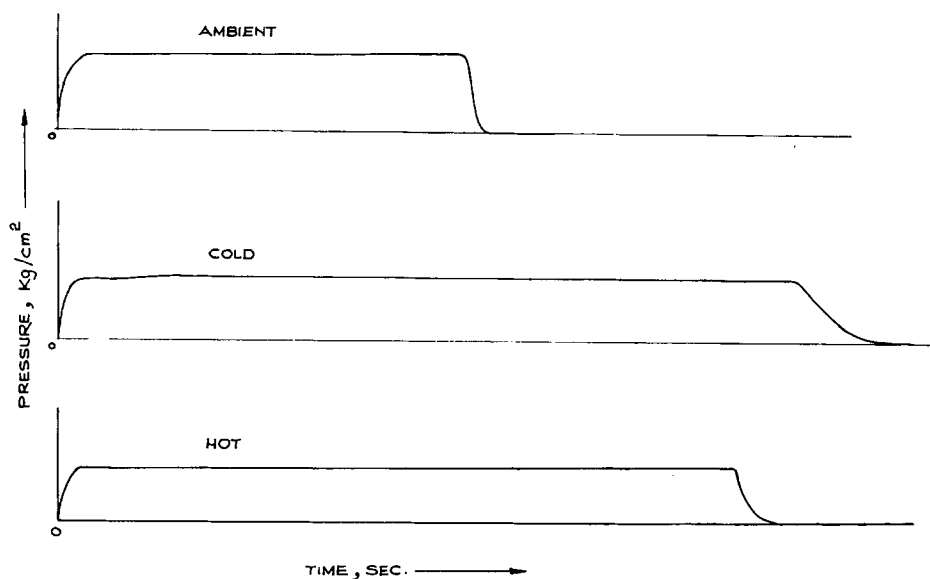


Fig. 5. Pressure-time profiles for double-base propellant sustainers inhibited with CPM-9s at ambient, cold, and hot temperatures.

$$P_c \propto S^{\left(\frac{1}{1-n}\right)} \quad (2)$$

Where P_c = chamber pressure
 S = burning surface
 n = pressure exponent or index

which means that the CPM-9s is a potential inhibitor for inhibition of double-base propellant.

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References

1. R. C. Nametz, *Ind. Engng. Chem.*, **39**, 99 (1967).
2. Chemische Werke Witten G.M.b.H. (by Edith Behnke and Helmut Wulff) Ger. 1,109, 886; *Chem. Abstr.*, **56**, 1600h (1962).
3. Chemische Werke Witten G.M.b.H. Brit. 960, 556 June 10, 1964; *Chem. Abstr.*, **61**, 7195a (1964).
4. C. S. Shull, E. P. Benzing, R. A. Cass, and R. J. Rohrbacker, *Proc. Ann. Tech. Conf.*, SP I (Soc. Plast. Ind.) Reinf. Plast. Div., 22nd, Washington, D.C., 1967, 6-B/10.
5. Y. C. Chae, W. M. Rinehart, C. S. Shull, R. A. Cass, and R. J. Rohrbacker, *Proc. Ann. Tech. Conf.*, SP I (Soc. Plast. Ind.) Reinf. Plast. Div., 22nd, Washington, D.C., 1967, 6-E/8.
6. R. C. Nametz, J. Di Pietro, I. N. Einhorn, *Am. Chem. Soc. Div. Org. Coatings Plast. Chem.*, **28**(1), 204-224 (1968).
7. J. A. Schneider, R. G. Pews, and J. D. Herring, *Am. Chem. Soc. Div. Org. Coatings Plast. Chem.*, **29**(9), 382-392 (1969).
8. P. G. Pape, *Poliplasti Plast. Reinf.*, **19**(162), 24-31 (1971).
9. M. Caire-Maurisier and J. Tranchant, Fr. Damande, 2,337,117 (to Societe Nationale des Poudres et Explosifs) 29 July, 1977; *Chem. Abstr.*, **89**, 27030 (1978).
10. J. P. Agrawal and K. S. Kulkarni, Paper presented at the 34th Congress of the International Astronautical Federation, held in Budapest, Oct. 1983.
11. J. P. Agrawal, K. S. Kulkarni, and S. S. Deo, *J. Hazardous Materials (Netherlands)*, **10**, 43 (1985).
12. J. P. Agrawal, M. P. Chouk, and R. S. Satpute, *Br. Polym. J.*, **14**, 29 (1982).
13. *1975 Annual Book of ASTM Standards*, part 35, D 638-72, American Society for Testing Materials, Philadelphia.
14. J. P. Agrawal and R. D. Pokharkar, *J. Sci. Ind. Res.*, **39**, 633 (1980).
15. P. E. Robitschek and B. C. Thomas, *Ind. Eng. Chem.*, **46**(8), 1629 (1954).
16. J. F. Rabek, *Experimental Methods in Polymer Chemistry (Physical Principles and Applications)*, John Wiley and Sons, New York, 0000.
17. H. V. Boenig, *Unsaturated Polyesters; Structure & Properties*, Elsevier Publishing Co., New York, 1964.
18. T. Urbanski, *Chemistry & Technology of Explosives*, Pergamon Press, New York, 1964, Vol. 1, p. 214.
19. S. G. Foord, *J. Chem. Soc.*, **48** (1940).
20. K. Kishore and R. S. Yadav, *Ind. J. Technol.*, **8**(11), 429 (1970).
21. J. P. Agrawal, M. P. Chouk, A. K. Singhal, K. S. Kulkarni, and P. S. Vasudevan, *Proceedings of Indian National Science Academy, Part A, Physical Sciences*, 1985 (in press).

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