

SOME FIRE-RESISTANT COMPOUNDS FROM DIGLYCERYL BORATE-TRICHLOROACETATE

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SUMMARY : Diglyceryl borate trichloroacetate ester was prepared from a mixture of diglycerylborate, and trichloroacetic acid in mole ratio 1 : 2 in presence of titanium dioxide as a catalyst under stream of nitrogen at high temperature. Samples of fire-resistant compounds from a polymer (poly vinyl chloride), plasticizers (dioctylphthalate and triisopropylphenylphosphate), variable proportions of (diglycerylborate trichloroacetate or diglycerylborate) as fire-resistance modifier, a heat stabilizer (dibutyltindilaurate), a fire-retardant (anti-mony trioxide), beside a filler and pigment (titanium dioxide) were formulated. Several formulations from the prepared samples were experimented for their fire-resistancy.

Key Words: Fire-resistant, diglycerylborate trichloroacetate.

INTRODUCTION

Flame retardation is essentially an interruption of the burning process which requires a heat source causing degradation and decomposition with subsequent ignition and combustion. The products of burning (10) depend on polymer structure and on burning conditions. Products such as CO, CO₂, HCl, NO₂ organic acids, and NH₃ would be typical.

Flammability can be reduced by several techniques (1,13,14): a) reduce fuel available by using a thermally stable resin or an inert filler (9,11), b) Produce a thermal barrier by charring or using glass formers such as phosphorus and boron compounds (3,4,7,15), c) Quench the chain reactions in the flame by adding free radicals, scavengers such as bromine and chlorine compounds (6), and d) Cool by introducing water or other endothermic materials such as Borax and hydrated alumina compounds.

The halogenated materials by themselves do not greatly improve flame-retardance they require metal oxides (12) to facilitate decomposition.

Flame-retardant polymers are used extensively for various industrial purposes such as coating, casting, fiber laminates, and laboratory furniture (10).

MATERIALS AND METHODS

Preparation of diglycerylborate

Diglycerylborate (5) was prepared by the reaction of glycerol with boric acid in mole ratio 2:1.

The reaction took place at 100-110°C, an inert solvent may be used to form an azeotrope with water found from the reaction. The reaction was considered complete when the evolution of water ceased. Thus, 184 g of glycerol and 61.8 g of boric acid were refluxed in 500 g dioxane, the reaction took place at 100°C during four hours, the dioxane-water azeotrope was removed during two hours. Residual dioxane was removed by heating to 120°C under vacuum (Water pump), leaving diglycerylborate product.

The obtained diglyceryl borate was characterized in Table 1.

Preparation of diglycerylborate trichloroacetate

The denoted compound was synthesized by reacting 9.6 g (0.05 mole) of diglycerylborate with excess of trichloroacetic acid,

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Table 1: Characteristics of diglycerylborate.

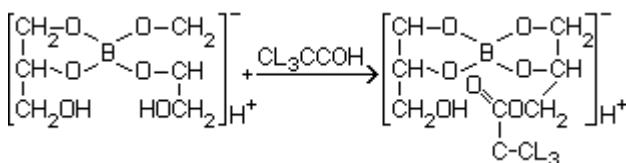
	Appearance	Average M.Wt	Viscosity 30°C. Pa. S.	Specific gravity 25/25°C	n ²⁵ _D
Diglycerylborate	Viscous, Sirup, colourless	192	2.3029	1.3113	1.6983

25 g (0.1 mole) in presence of 0.025 g of titanium dioxide as a catalyst. The reaction mixture was then refluxed for 8-12 hours at 160-170°C under stream of nitrogen.

The prepared diglycerylborate trichloroacetate was characterized and their characteristics are given in Table 2.

Table 2: Characteristics of diglycerylborate trichloroacetate.

	Average M.Wt	n ¹⁷ _D	Density 17°C	CL%	Yield %	Appearance
Diglycerylborate tri-chloroacetate	333.30	1.4984	1.5894	31.95	83.29	Viscous, transparent, paleyellow.



Formulation of the samples

Through the present work, several formulations were experimented, the best samples were obtained by mixing the components in the proportions, shown in Table 3.

Table 3: Formulations of fire-resistant samples.

	F	F ₁	F ₂	F ₃	F ₄	F ₅	F ₆	F ₇	F ₈
Poly (vinyl chloride)	5	5	5	5	5	5	5	5	5
Diocetylphthalate*	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
*Triisopropylyphenylphosphate	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
*.Diglycerylborate	-	0.5	1	1.5	2	-	-	-	-
*.Diglycerylborate tricholoacetate	-	-	-	-	-	0.5	1	1.5	2
Dibutyltindilaurate	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Titanium dioxide	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Antimony trioxide	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Fire-resistance content, %	0	14.28	25	33.33	40	14.28	25	33.33	40

Where, Fire-resistance content, % = $\frac{\text{fire - resistance modifier, g.} \times 100}{\text{Plasticizer (total) g.}}$

*Plasticizer (total) g.

The general procedure for formulation was as follows: Homogenous samples were prepared by adding variable proportion of the prepared diglycerylborate trichloroacetate (D.G.B.T. cl.A.) or diglycerylborate (D.G.B) as fire resistancy modifier portion wise at room temperature to a composition containing a poly (vinyl chloride) (K value 70, Apparent bulk density g/ml 25°C 0.30), a dioctylphthalate, a triisopropylyphenylphosphate plasticizers under stirring. The whole mixture was then mixing with dibutyltindilaurate (as a heat stabilizer), antimony trioxide as a fire-retardancy beside a titanium dioxide which acts as a pigment as well as a filler to give the required samples which represented termed as F, F₁, F₂,.....to F₈ respectively.

Samples were screened as fire-resistant samples according to standard method (2). The results were given in Table 4.

DISCUSSION OF THE RESULTS

The purpose of the present work is; a) to prepare fire-resistant compounds, using diglycerylborate trichloroacetate or diglycerylborate as a fire-resistancy modifier with poly (vinyl chloride as a polymer. Dioctylphthalate and triiso propylphenylphosphate were subsequently used as

Table 4: Fire - resistant test for the prepared samples.

	F	F ₁	F ₂	F ₃	F ₄	F ₅	F ₆	F ₇	F ₈
Weight loss, %	3.82	1.83	1.58	0.89	0.83	1.18	1.03	0.85	0.02
Flam-ability	B	NB	NB	NB	C,NB	NB	NB	NB	NB

B: Burning, NB: Non-burning, C: Charring

plasticizers with other additives; b) and to evaluate these compounds for their fire-resistancy.

The infrared spectrum of the synthesized diglycerylborate trichloroacetate ester shows frequency at 1700-1800 cm^{-1} (Figure 1), for -COO group (ester), frequency at 1200-1300 cm^{-1} for C-O group (ester), and frequency at 600-700 cm^{-1} for chlorine group (C-Cl) [measured by spectrophotometer Perkin-Elimer Model (598)]. The characterizations of this compound are shown in Table 2.

Poly (vinyl chloride may be considered-itself as non-flammable, but when it plasticized with dioctylphthalate, this property is depressed, but when it modified with a wide variety of diglycerylborate trichloroacetate (D.G.B.T. cl. A.) or diglycerylborate (D.G.B.), this flammability is depressed (Tables 3 and 4).

The results in Figure 2 and Tables 3 and 4 show that the weight loss %, of the sample F_8 (containing 40% D.G.B.T. cl. A.) is 0.02%, of the sample F_7 (containing 33.33% D.G.B.T. cl. A.) is 0.85%, of the sample F_6 (containing 25% D.G.B.T. cl. A.) is 1.03%, of the sample F_5 (containing 14.28% D.G.B.T. cl. A.) is 1.18%, and of the sample F (unmodified) is 3.82%.

This means that the fire resistance of these samples is in the order $F_8 > F_7 > F_6 > F_5 > F$ since F_8 has the lowest value of weight loss %.

This indicates that the fire-resistance property improves gradually with increasing the amount of diglycerylborate trichloroacetate from (0-40%). This is due to the fact that the halogenated compounds produce HCl which is a non combustible gas as well as a flame-propagation inhibitor. HCl is known to inhibit flame-propagation by a free radical mechanism (8).

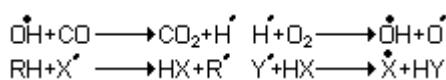


Figure1: Infrared spectrum of diglycerylborate trichloroacetate.

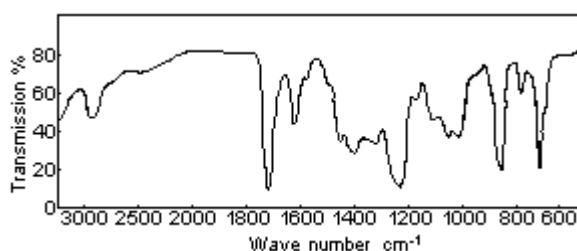
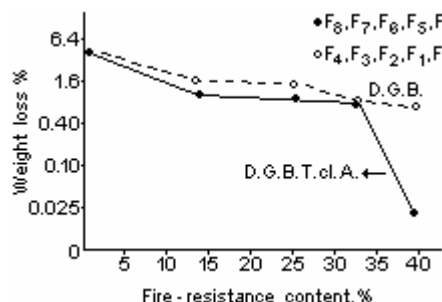


Figure 2: Weight loss (%) versus fire-resistance modifier content (%) for prepared samples.



RH denotes the fuel, X denotes the halogen, and Y refers to active radicals such as H, OH, and CH_3 .

Moreover, the presence of boron compound can improve the fire-resistance property. i.e. produce a thermal barrier by charring or using glass formers (4).

Also, the weight loss %, of the sample F_4 (containing 40%, D.G.B.) is 0.83%, of the sample F_3 (containing 33.33%, D.G.B.) is 0.89%, of the sample F_2 (containing 25%, D.G.B.) is 1.58%, of the sample F_1 (containing 14.28% D.G.B.) is 1.83%, and of the sample F (unmodified) is 3.82%.

This means that the fire resistance of these samples is in the order $F_4 > F_3 > F_2 > F_1 > F$ since F_4 has the lowest value of weight loss %.

This indicates that the fire-resistance property improves gradually with increasing the amount of diglycerylborate from (0-40%). This is due to the fact that the presence of boron compounds as diglycerylborate produce a thermal barrier by charring or using glass formers (it is structure function by a glass forming mechanism) (13).

It is clear that the results in Tables 3 and 4 and Figure 2 show that the prepared diglycerylborate trichloroacetate, impart to (F₈, F₇, F₆ and F₅) samples, exhibit higher fire-resistance (lowest weight loss%, non-burning) than those imparted by incorporation of diglycerylborate (F₄, F₃, F₂ and F₁) samples respectively.

Generally the presence of both boron and chlorine compounds in the same structure of diglycerylborate trichloroacetate, beside small amounts of metal oxides (Sb₂O₃) improves the fire-resistancy, due to antimony trioxide acts synergistically with halogens to improve their ability to scavenge.

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