The use of Some Aliphatic Halorgano antimony Compounds as combustion Retarding agents of Unsaturated Polyester and Epoxy Resins

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Abstract:

Four antimony compounds were used in this inves as additives to retard combustion of unsaturated polyester and epoxy resins, namely:

1. Tetraethyl ammonium tribromoethylantimonates (additive I).
2. Tetraethyl ammonium chlorodibromoethylantimonates (additive II).
3. Tetraethyl ammonium trichloroethylantimonates (additive III).
4. Tetraethyl ammonium bromodichloroethylantimonates (additive IV).

The effects of these additives on flammability of unsaturated polyester and epoxy resins have been studied by using sheets of the resins with weight percentages of (0.5,1.0,1.5,2.0,2.5&3.0%) of the additives in dimensions of (150 X150X3)mm .Three standard test methods were used to measure the flame retardation which are: (ASTM:D -2863), (ASTM:D-635)and (ASTM:D-3014).

The results obtained from these tests indicated that, additive I has a high efficiency as flame retardant causing , self – extinguishing (S.E.) at the percentage of (2.0%) for unsaturated polyester resin and the percentage (2.5%) for epoxy resin.
Self – extinguishing (S.E.) of additives II and IV were at the percentage of (2.5%) for unsaturated polyester resin and (3.0%) in the case of epoxy resin. Additive III showed low effect on flammability in both resins.

Key words: Flame retardant, additives, Aliphatic Halorgano antimony Compounds, unsaturated polyester and epoxy resins.

Introduction:

The history of all polymer materials were traced by the success of their applications in replacing traditional materials like wood, leather and metals. The rapid expansion of combustion gave motives to many researchers to use many additives to retard flammability of the polymers [1].

Flame retardation is essentially an interruption of the burning process [2]. There are two distinct types of flame retardants must be recognized:
a – Reactive flame retardants are compounds usually containing heteroelements which can also be chemically incorporated in smaller proportions, usually during the polymerization process.
b – Additives flame retardants are incorporated into polymers by physically mixing with the polymer, normally after complete polymerization [3, 4].

Halogen compounds [5] and antimony complex compounds [6] were widely used as commercial flame retardants. Rhys and Cleaver [7], studied the combustion of polyester laminates containing

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pentabromotoluene , they observed that the optimum atomic ratio of (Sb:Br) for flame retardancy is (1:3).

In (1993) Ugal [8], prepared some organo halogenated compounds (mixed types haloantimonates) in which antimony was the central element, such as $Et_4N[PhSbCl_2Br]$. In (1999) Ahmed [9] , prepared some aliphatic and aromatic mixed haloantimonates compounds and used them as flame retardants with polyethylene and polystyrene such as $Et_4N[EtSbCl_2Br]$. In (2005) Al –Baiati [10], prepared the compound $Et_4N[PhPCl_2Br]$ and used it as flame retardant with unsaturated polyester and epoxy resins . These compounds contain in their structure atoms such as bromine , chlorine , phosphorous , nitrogen , antimony and phenyl ring , the ratio between halogen atoms and antimony or phosphorous atoms is (3:1) , this ratio represents the ideal ratio for high efficiency in flame retardant ability and non- burning properties for the polymeric materials [9,10] .

Materials and Methods:

A. Polymers:

1. Unsaturated polyester resin, hardener type (MEKP), imported from Industrial Chemical and Resins Co. Ltd, Kingdom of Sudia Arabia.
2. Epoxy resin, type (CY223), hardener type (HY956), imported from Ciba – Geigy Co.

B. Flame – retardants materials :

1. Additive I**:** Tetraethylammonium tribromoethyl antimonates $Et_4N[(Et)SbBr_3]$.
2. AdditiveII**:**Tetraethylammoniumchlorodibromoethylantimonates $Et_4N[(Et)SbBr_2Cl]$.
3. Additive III**:** Tetraethylammonium trichloroethyl antimonates $Et_4N[(Et)SbCl_3]$.
4. Additive IV**:** Tetraethylammonium bromodichloroethyl antimonates $Et_4N[(C_2H_5)SbCl_2Br]$.

All of them were prepared as reported in literature[11].

C.* Tests*:

1. ASTM: D-2863: The measurements of limiting oxygen Index (LOI) is widely used for measuring flammability of polymers [12].

2. ASTM: D-635: This deals with the measurement of rate of burning (R.B), Average time of burning (ATB), Non – burning (N.B), Self- extinguishing (S.E) and Average extent of burning (AEB) for self Supporting plastic in a horizontal position [13].

3. ASTM: D-3014: This method was used to measure the maximum flame height (H), and the ratio of loss of weight of polymeric materials [14].

D. Preparation of Samples:

Samples were prepared tow in dimensions of (150X150X3) mm, three sheets of each unsaturated polyester and epoxy resins were prepared having the percentage weight (0.5, 1.0, 1.5, 2.0, 2.5 &3.0%) of the additives. These sheets cut as samples according to ASTM standard used in this work.

Results and Discussion:

1. Measurement of limiting oxygen index (LOI) according to ASTM: D - 2863:

The limiting oxygen index (LOI) for unsaturated polyester resin without additives is (20.4) [15] and for epoxy resin without additives is (19.7) [16]. , (Tables – 1 and 2) and (Figs.-1 and 2) indicated that , oxygen concentration required to support a candle – like in unsaturated polyester and epoxy resins samples increased with increasing the weight percentage of additives .The efficiency of additives under study were in the following order :

I > II > IV > III

2. Measurement of rate of burning (R.B) according to ASTM: D-635:

Results obtained from these tests showed that the rate of burning (R.B) of the resins with additives are inversely proportional with the percentage weight of additives, as indicated in (Tables -3 and 4) and (Fig.- 3 and 4) which show the flame speed curves of flame retardation for the resins.

3. Measurement of flame height (H) according to ASTM: D-3014:

Figs.-5 and 6 showed that, the maximum flame height (H) was decreased with increasing the percentage weight of additives (inversely proportional), as indicated in Tables – 5 and 6 respectively. The results obtained from this test indicated that, the same efficiency of additives are in a good agreement with the measurements of LOI and rate of burning respectively.

The action of these additives was due to the formation of chare as aresult of removing the hydrogen atoms from the polymer chains with the liberation of the hydrochloric acid HCL which acts in the gas phase .The combustion products like; free radicals (˙Cl, ˙OH), chare,…etc., will form a layer to prevent burning and prevent oxygen to help contineous burning of polymers.

Results obtained from these tests showed that, the bromine atom was more effective from chlorine atoms to retard combustion for both resins.

Table 1: Limiting Oxygen Index (LOI) for unsaturated polyester resin with additives

Additives % / Additives	Non	0.5	1.0	1.5	2.0	2.5	3.0
I	20.4	21.50	21.95	22.47	23.0	23.45	23.77
II	20.4	21.31	21.80	22.30	22.85	23.34	23.52
III	20.4	20.85	21.32	21.71	22.28	22.85	23.11
IV	20.4	21.02	21.55	22.07	22.63	23.19	23.43

Table 2: Limiting Oxygen Index (LOI) for epoxy resin with additives.

Additives% / Additives	Non	0.5	1.0	1.5	2.0	2.5	3.0
I	19.7	20.73	21.35	21.98	22.48	22.89	23. 3
II	19.7	20.54	21.11	21.77	22.30	22.75	23.08
III	19.7	20.23	20.82	21.41	21.88	22.36	22.84
IV	19.7	20.35	20.94	21.49	22.01	22.47	22.93

Table 3: Rate of burning (RB) for unsaturated polyester resin with additives.

Additives% / TEST	Non	0.5	1.0	1.5	2.0	2.5	3.0	additives
AEB(cm)	10	10	9.8	9.2	8.5	7.1	6.4	I
	10	10	10	9.7	9.0	8.3	7.5	II
	10	10	10	10	9.6	9.1	8.4	III
	10	10	10	1.0	9.4	8.7	8.0	IV
ATB(min.)	6.92	8.47	8.67	8.52	8.50	7.97	8.31	I
	6.92	8.19	8.54	8.66	8.57	8.93	9.14	II
	6.92	7.75	8.06	8.40	8.42	8.45	8.75	III
	6.92	7.93	8.33	8.69	8.6	8.96	8.98	IV
R.B (Cm/min.)	1.44	1.18	1.13	1.08	1.0	0.89	0.77	I
	1.44	1.22	1.17	1.12	1.05	0.93	0.82	II
	1.44	1.29	1.24	1.19	1.14	1.07	0.96	III
	1.44	1.26	1.20	1.15	1.09	0.97	0.89	IV
S.E.	-	-	-	-	yes	yes	yes	I
	-	-	-	-	-	yes	yes	II
	-	-	-	-	-	-	yes	III
	-	-	-	-	-	yes	yes	IV
N.B	-	-	-	-	-	-	-	I
	-	-	-	-	-	-	-	II
	-	-	-	-	-	-	-	III
	-	-	-	-	-	-	-	IV

Table 4: Rate of burning (RB) for epoxy resin with additives.

additives% / TEST	Non	0.5	1.0	1.5	2.0	2.5	3.0	additives
AEB(cm)	10	10	10	10	9.5	8.3	7.2	I
	10	10	10	10	10	8.7	4.8	II
	10	10	10	10	10	9.7	9.1	III
	10	10	10	10	10	9.4	8.8	IV
ATB(min.)	5.12	8.0	4.8	9.0	8.8	8.7	8.3	I
	5.12	7.8	8.1	8.5	8.9	8.4	9.2	II
	5.12	7. 4	7.8	8.1	8.4	8. 8	9.0	III
	5.12	7.6	8.0	8.3	8.6	8.9	9.1	IV
R.B (Cm/min.)	1.95	1.25	1.19	1.11	1.07	0.95	0.86	I
	1.95	1.28	1.22	1.17	1.12	1.03	0.91	II
	1.95	1.34	1.27	1.23	1.18	1.09	1.01	III
	1.95	1.31	1.24	1.20	1.15	1.05	0.96	IV
S.E.	-	-	-	-	-	yes	yes	I
	-	-	-	-	-	-	yes	II
	-	-	-	-	-	-	-	III
	-	-	-	-	-	-	yes	IV
N.B	-	-	-	-	-	-	-	I
	-	-	-	-	-	-	-	II
	-	-	-	-	-	-	-	III
	-	-	-	-	-	-	-	IV

Table 5: Flame height (H) (cm) for unsaturated polyester resin with additives.

additives % / TEST	Non	0.5	1.0	1.5	2.0	2.5	3.0	additives
W1 (gm)	5.63	6.07	6.11	6.15	6.19	6.23	6.27	I
	5.63	6.04	6.09	6.12	6.16	6.20	6.24	II
	5.63	5.69	5.73	5.76	5.79	5.83	5.86	III
	5.63	5.82	5.86	5.89	5.93	5.97	6.01	IV
W2 (gm)	2.57	2.14	2.17	2.19	2.22	2.25	2.28	I
	2.57	2.09	2.11	2.14	2.17	2. 20	2.23	II
	2.57	1.94	1.97	2.00	2.03	2.06	2.09	III
	2.57	1.98	2.01	2.04	2.07	2.10	2.14	IV
PWR (%)	54.35	64.74	64.48	64.39	64.13	63.88	63.63	I
	54.35	65.39	65.35	65.03	64.77	64.51	64.26	II
	54.35	65.90	65.61	65.27	64.93	64.66	64.33	III
	54.35	65.97	65.69	65.36	65.09	64.82	64.39	IV
H (cm)	14.0	9.0	8.5	8.0	7.0	6.0	4.5	I
	14.0	9.5	9.0	8.5	7.5	6.5	5.0	II
	14.0	11.5	11.0	10.5	10.0	9.5	9.0	III
	14.0	11.0	10.5	10.0	9.5	9.0	8.5	IV

NOTE:
W1: weight of sample before burning (gm) .
W2: weight loss after burning (gm).
PWR: The percentage of Weight Ratio (%) .

Table 6: Flame height (H) (cm) for epoxy resin with additives .

additives % / TEST	Non	0.5	1.0	1.5	2.0	2.5	3.0	additives
W1 (gm)	4.52	5.02	5.05	5.08	5.11	5.14	5.18	I
	4.52	5.00	5.03	5.06	5.09	5.12	5.16	II
	4.52	4.61	4.64	4.67	4.70	4.73	4.76	III
	4.52	4.68	4.71	4.74	4.77	4.80	4.83	IV
W2 (gm)	1.43	1.04	1.06	1.08	1.10	1.12	1.14	I
	1.43	1.07	1.09	1.11	1.13	1.15	1.17	II
	1.43	1.09	1.11	1.14	1.17	1.20	1.23	III
	1.43	1.10	1.12	1.15	1.18	1.21	1.25	IV
PWR (%)	68.36	79.28	79.01	78.74	78.47	78.21	77.99	I
	68.36	78.60	78.33	78.06	77.79	77.53	77.32	II
	68.36	76.35	76.07	75.58	75.10	74.63	74.15	III
	68.36	76.49	76.22	75.73	75.26	74.79	74.12	IV
H (cm)	12.0	8.0	7.5	6.5	6.0	5.5	5.0	I
	12.0	8.5	8.0	7.5	7.0	6.5	6.0	II
	12.0	11.0	10.5	10.0	9.5	9.0	8.3	III
	12.0	10.5	10.0	9.5	9.0	8.5	8.0	IV

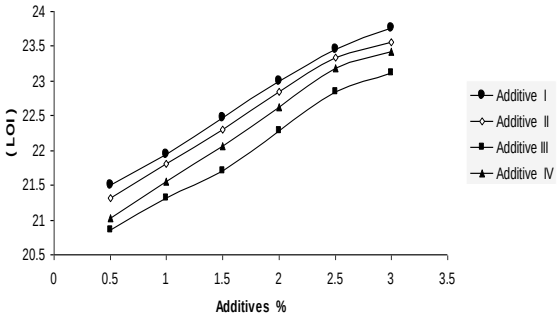

Fig. (1): (LOI) for unsaturated polyester resin with additives.

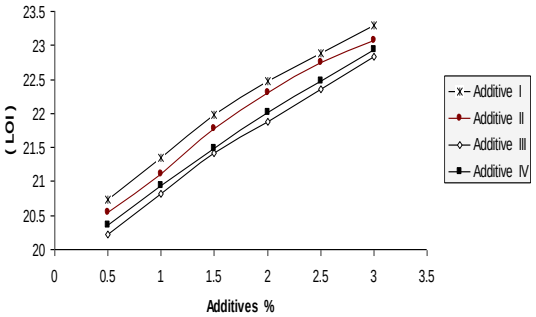

Fig. (2): (LOI) for epoxy resin with additives.

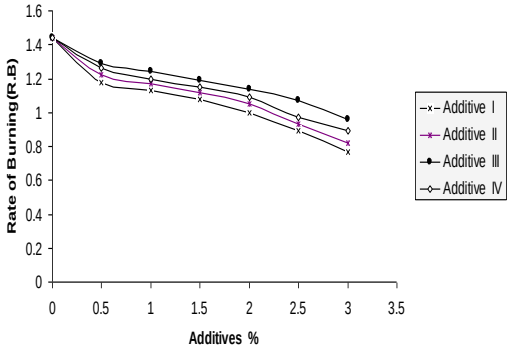

Fig. (3): Rate of burning (R.B.) for unsaturated polyester resin with additives.

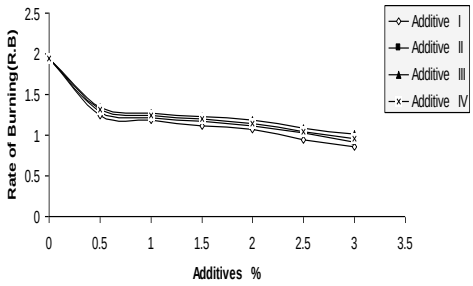

Fig.(4) : Rate of burning (R.B.) for epoxy resin with additives .

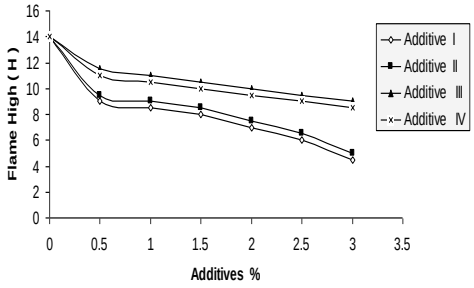

Fig. (5): Flam height (H) for unsaturated polyester resin with additives

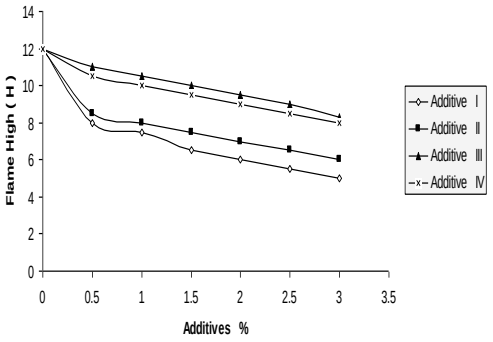

Fig . (6): Flam height (H) for epoxy resin with additives.

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دراسة تأثير بعض مركبات الانتيمون العضوية الهالوجينية الاليفاتية في تثبيط لهوبية راتنجي البولي استر غير المشبع والايبوكسي

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الخلاصة :

استخدمت في هذا البحث أربعة معقدات بوصفها مضافات لتثبيط لهوبية راتنجي البولي استر غير المشبع و الايبوكسي ، وهي :

1. رباعي اثيل امونيوم ثلاثي برومو أثيل انتيمونات (المضاف I) .
2. رباعي اثيل امونيوم كلوروثنائي برومو أثيل انتيمونات (المضاف II).
3. رباعي اثيل امونيوم ثلاثي كلورو أثيل انتيمونات (المضافIII).
4. رباعي اثيل امونيوم بروموثنائي كلورو أثيل انتيمونات (المضافIV).

لقد تمت دراسة تأثير هذه المضافات في تثبيط لهوبية راتنجي البولي استر غير المشبع والايبوكسي. وذلك بأستخدام ألواح من الراتنجين مع نسب مئوية وزنيه من المضافات **(0.5 ,1.0 ,1.5 ,2.0 ,2.5 3.0%)** وبقياسات (150x150x3) ملم. استخدمت ثلاث طرائق قياسية لقياس تثبيط اللهوبية هي (ASTM:D-3014) (ASTM:D-635), (ASTM:D-2863) .

إن النتائج التي تم الحصول عليها من هذه القياسات تشير الى ان المضاف I يمتلك كفاءة عالية في تثبيط اللهوبية ، اذ حدث اطفاء ذاتي عند النسبة(2.0%) لراتنج البولي استر غير المشبع والنسبة (2.5%) لراتنج الايبوكسي، كذلك حدوث إطفاء ذاتي بأستخدام المضافين II و IV عند النسبة(2.5%) لراتنج البولي استر غير المشبع و النسبة (3.0 %) مع راتنج الايبوكسي. بينما أظهر المضاف III تأثيراً قليلاً في تثبيط اللهوبية لكلا الراتنجين .