The synergistic effect of borax and chlorinated paraffin as flame – retardants for epoxy and unsaturated polyester resins

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Abstract:

In this investigation , borax (B) (additive I) and chlorinated paraffin (CP.) (additive II) ,were used as flame retardants for each of epoxy and unsaturated polyester resins in the weight ratios of 2,4,6, & 8% by preparing films of (130×130×3) mm dimensions. Also films of these resins with a mixture of [50%(B.)+50%(CP.)] (additive III) in the same weight ratios were prepared in order to study the synergistic effect of these additives on the flammability of the two resins .

Three standard test methods were used to measure the flame retardation which are :

1-ASTM : D-2863
2-ASTM : D-635
3-ASTM : D-3014

The results obtained from these tests indicated that the additives (B),(CP.) and their mixture , gave a good effect as flame retardants for each epoxy and unsaturated polyester resins , but their synergistic effect was more effective than each of them alone .

Finally , the compatibility between the additives and resins (which showed a clear effect on retardation) was also studied .

Introduction:

The history of all polymer materials were traced by the success of their applications in replacing tradition materials like wood , leather and metals . The rapidly expansion of combustion incourage many researches to use many additives to retard flammability of the polymers [1] .

The chlorinated paraffins (CP) are group of chemicals manufactured by chlorination of liquid – paraffin or paraffin wax , containing from 30-70% chlorine , they are largely inert , almost insoluble in water and have extremely low vapor pressure . The most commercialy chlorinated paraffin products are liquids ranged from low to extremely high viscosity . Other types are solids which have longer carbon chains and usually contain 70-72% chlorine [2]. Boric acid and it's hydrated salts , in contrast to the anhydrous borates , have low melting point and to a glass at 600 K^o but only above 775 K^o they become sufficiently fluid to flow . Borax when heated in air dissolves in its own water of hydration and swells to a forty mass , it then loses water[3] . Boric acid and borax are frequently used together , and in the system H_3BO-$NaB_4O_7.10H_2O$, there is a sharp solubility maximum at a temperature depends on the boric acid : borax ratio[4] . The flame–retardation is essentially an interruption of the burning process [5] . There are two distinct types of flame-retardant must be recognized :

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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 of flame – retardants are incorporated into polymers by physically mixing with the polymer , normally after the polymerization complete [7,8] .

Experimentals:

1- Materials :

a. Polymers :

1- Epoxy resin , type (CY223), hardener type (HY 956), imported from Ciba-Geigy Co.

2- Unsaturated polyester resin , hardener type (MEKP) , imported from United Arab Emirate (U.A.E) .

b. Flame-retardants : Borax (B) in powder form , with purity of 99.5% , imported from MERCK Co. and chlorinated paraffin (CP.) containing 70% chlorine, from Oil research and development center- Ministry of Oil .

2- Equipments :

a. ASTM : D-2863 : The measurement of limiting oxygen Index (LOI) , is widely used for measuring flammability of polymers , The (LOI) is the minimum concentration of oxygen and nitrogen , that supports a candle-like combustion of specimen[9,10].

b. ASTM D-635 : The measurement of rate of burning (R.B) , Extent of burning (E.B) and time of burning (T.B) for self-supporting plastic in a horizontal position[11] .

c. ASTM D-3014 : The measurement of maximum flame height (H) [12] .

3- Preparation of samples :

The samples were prepared in the dimensions of (130×130×3)mm, Three sheets of each epoxy and unsatmated polyester resins were prepared for each percentage weight 2,4,6 & 8% with the additives I,II and III .

[6]

4- Compatibility measurement :

Light microscope was used to illustrate the compatibility of polymer with the additives.

Result and Discussion:

1- Measurement of LOI using ASTM : D-2863 :

The limiting oxygen index (LOI) for epoxy resin without additives is (19.8)[13], and for unsaturated polyester resin is (20.6) .The results obtained from this test are listed in Tables (1& 2), Figs.(1& 2) represent them.

The oxygen concentration required to support a candle-like of epoxy resin and unsaturated polyester resin samples was increased with increasing the weight percentages of additives . The efficiency of I,II and III additives was in the following order : III > II > I

2- Measurement of rate of burning by using

ASTM : D-635 :

The results obtained from these tests showed that the rate of burning (R.B) of the epoxy and the unsaturated polyester resins with the additives has a continuous reduction with increasing the percentage weight of additives , as in (Tables 3 & 4) respectively . (Figs 3 and 4) showed the flame speed curves of flame-retardation for epoxy resin and unsaturated polyester resin .

3- Measurement of flame height (H) using ASTM: D-3014:

(Figs. 5&6) showed that the flame height(H)was inversly proportional with increasing the percentage weight of the

additives as mentioned in Tables (5&6) respectively.

4- The compatibility :

The compatibility between polymer and additives is one of the most important factors which effects the flame-retardation and means a homogeneous fabric of polymer with additives. Figs. (7 & 8) illustrate the distribution of additives particles and their percentages .

Conclusion:

1- The flame-retardancy efficiency of the additives I,II and III appeared to follow the order :

III > II > I

2- Borax (B) and chlorinated paraffin (CP.) together have a good effect to retard the flammability and combustion of both epoxy and unsaturated polyester resins . Their synergistic effect is better in action . .

3- The (LOI) increased with increasing the weight percentages of the additives .

4- The (R.B) decreased with increasing the weight percentages of the additives .

5- The flame height (H) decreased with increasing weight percentages of the additives .

6- The good results of limiting oxygen index (LOI), rate of burning (R.B) and flame height (H) mean that the compatibility was of a significant effect on the burning of the two polymers which mean that a good compatibility has taken place during the preparation of the samples .

Finally, the combustion products like; free radicals , (Ċl, OH, chare, ...etc.) will form a layer to prevent burning and oxygen that help continuous burning of polymers to reach the burning front.

Table-1: (LOI) for Epoxy resin with additives

% / Additives	(LOI)				
	Non	2	4	6	8
I	19.7	21.07	21.80	22.51	23.34
II	19.7	21.34	22.30	23.10	23.78
III	19.7	21.76	22.67	23.52	24.67

Table-2: (LOI) for unsaturated polyester resin with additives.

% / Additives	(LOI)				
	Non	2	4	6	8
I	20.4	21.82	22.60	23.32	24.10
II	20.4	22.14	23.11	23.79	24.41
III	20.4	22.57	23.45	24.31	25.27

Table-3: Rate of burning of epoxy resin with additives

% / Test	Non	2	4	6	8	Additives
AEB (cm)	10 10 10	10 10 10	10 10 10	10 10 7.4	7.4 6.8 2.85	I II III
ATB (min)	5.12 5.12 5.12	5.73 6.30 6.83	6.52 7.43 8.34	6.80 8.71 8.5	5.5 6.5 3.69	I II III
R.B (cm/min)	1.95 1.95 1.95	1.74 1.58 1.46	1.53 1.34 1.19	1.47 1.14 0.87	1.34 1.04 0.77	I II III
S.E	… … …	… … …	… … …	… … yes	… … yes	I II III
N.B	… …	… …	… …	… …	… …	I II III

Table-4: Rate of burning (R.B) of unsaturated polyester resin with additives.

% / Test	Non	2	4	6	8	Additives
AEB (cm)	10 10 10	10 10 10	10 10 10	10 10 7.50	7.8 6.1 3.4	I II III
ATB (min)	6.92 6.92 6.92	7.52 8.02 8.63	8.29 9.25 10.10	9.34 10.89 10.69	8.1 7.53 8.09	I II III
R.B (cm/min)	1.44 1.44 1.44	1.32 1.24 1.15	1.20 1.08 0.99	1.07 0.91 0.70	0.96 0.81 0.42	I II III
S.E	… … …	… … …	… … …	… … yes	yes … yes	I II III
N.B	… …	… …	… …	… …	… …	I II III

Table-5: Flame height (H) of epoxy resin with additives

% / Test	Non	2	4	6	8	Additives
W1	4.52 4.52 4.52	5.03 4.81 5.06	5.11 5.08 5.14	5.19 5.15 5.23	5.26 5.25 5.29	I II III
W2	1.43 1.43 1.43	1.35 1.15 1.28	1.42 1.26 1.38	1.50 1.35 1.48	1.59 1.14 1.55	I II III
PWR	68.36 68.36 68.36	73.16 76.09 74.70	72.21 75.19 73.34	71.09 73.78 71.70	69.77 72.00 70.69	I II III
H	12.00 12.00 12.00	11.00 10.50 10.00	9.50 9.00 7.50	8.00 7.00 6.50	7.50 6.60 5.00	I II III

Table-6: Flam height (H) of unsaturated polester resin with additives

Test \ %	Non	2	4	6	8	Additives
W1	5.63	6.14	6.22	6.30	6.36	I
	5.63	6.10	6.19	6.24	6.33	II
	5.63	6.18	6.26	6.35	6.43	III
W2	2.57	2.49	2.56	2.64	2.70	I
	2.57	2.27	2.38	2.51	2.60	II
	2.57	2.41	2.55	2.69	2.77	III
PWR	54.35	59.44	58.84	58.09	57.54	I
	54.35	62.27	61.55	59.77	58.92	II
	54.35	61.00	59.26	57.63	56.92	III
H	14.00	12.50	11.60	9.70	8.50	I
	14.00	12.30	11.00	9.00	8.00	II
	14.00	11.00	9.00	8.00	6.00	III

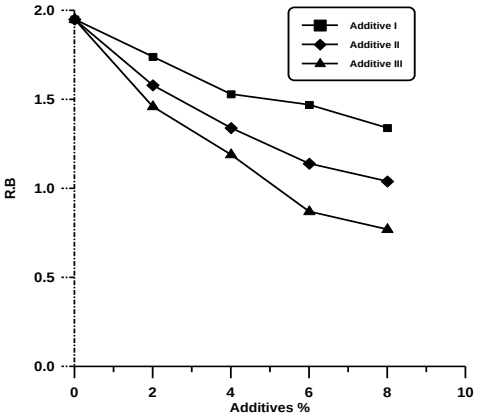

Fig. (3) Rate of burning (R.B) for the epoxy resin with additives.

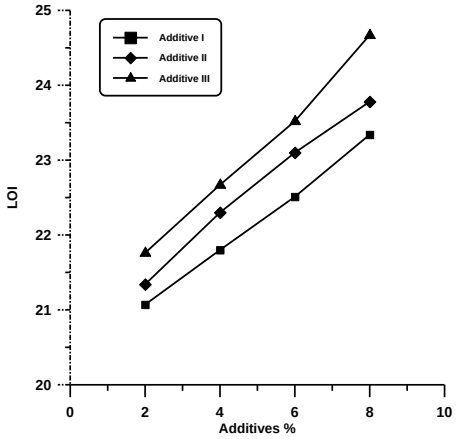

Fig.(1)LOI of the epoxy resin with additive.

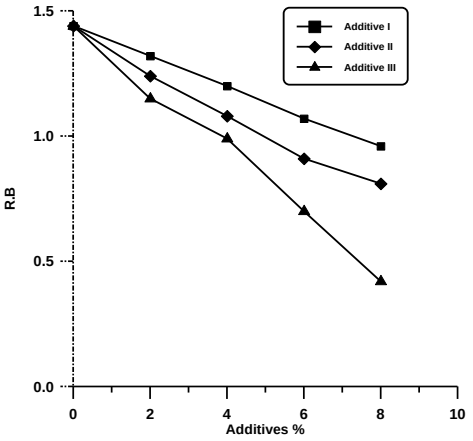

Fig-4 Rate of burning (R.B) for the unsaturated polyester resin with additives

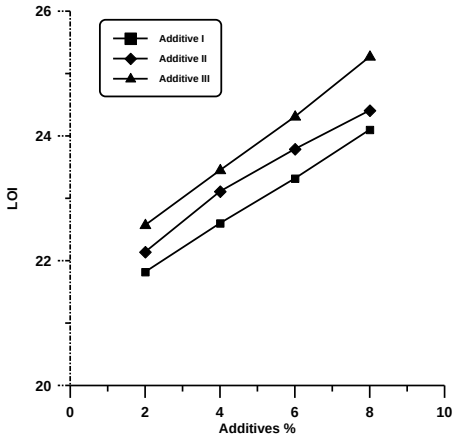

Fig. (2) LOI of the unsaturated polyester resin with additives

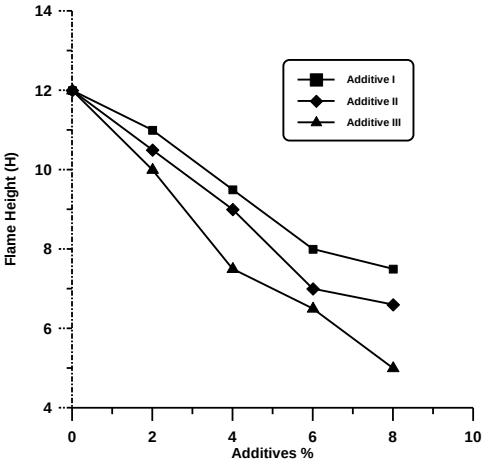

Fig.(5) Flame height (H) for the epoxy resin with additives.

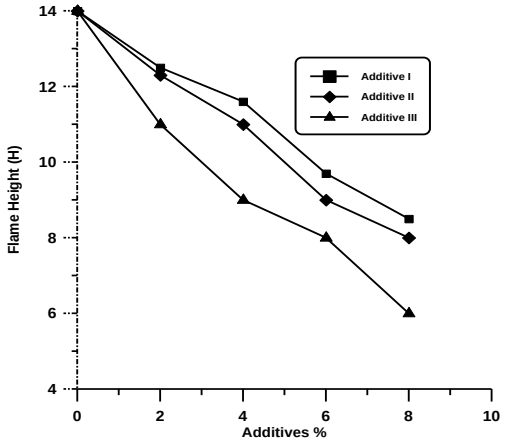

Fig- 6 flame height (H) for the unsaturated polyester resin with additives

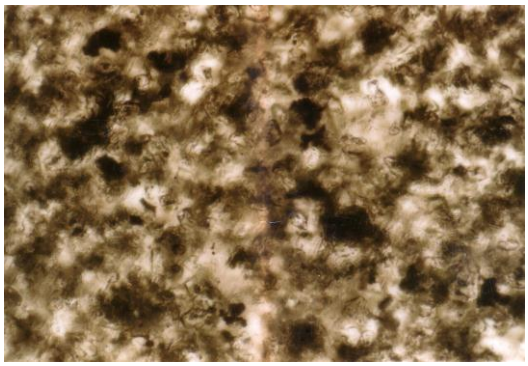

Fig. 7: 8% borax and epoxy resin

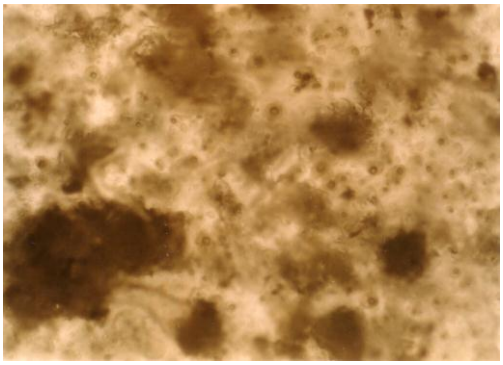

Fig. 8: 6% borax, chlorinated paraffin and unsaturated polyester resin

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التأثير التأزري للبوراكس والبارافين المكلور كمثبطات للهب لراتنجي الايبوكسي والبولي استر غير المشبع

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الخلاصة :

تم في هذا البحث استخدام البوراكس (B.) المضاف I والبارافين المكلور (C.P) المضاف II كمثبطات لهب لكل من راتنجي الايبوكسي والبولي استر غير المشبع وبنسب مئوية وزنية (2 , 4 , 6 و 8 %) من خلال تحضير شرائح ذات ابعاد (3 × 130 × 130) ملم . كذلك تم تحضير شرائح بنفس القياسات لخليط مكون من (50% من البوراكس + 50% .CP) المضاف III وبنفس النسب الوزنية اعلاه حيث استخدم هذا الخليط لدراسة تأثير التآزر بين هاتين المادتين على تثبيط اللهوبية للراتنجين .

تم استخدام ثلاث طرق قياسية لقياس تثبيط اللهوبية وهي :

1- الطريقة القياسية ASTM : D-2863
2- الطريقة القياسية ASTM : D-635
3- الطريقة القياسية ASTM : D-3014

تشير النتائج المستحصل عليها من هذه القياسات الى أن المضافات I ، II و III أعطت تأثيراً جيداً على تثبيط لهوبية واشتعال راتنجي الايبوكسي والبولي استر غير المشبع لكن تأثير المضاف III (التآزري) كان اكثر فعالية وبشكل واضح كلما ازدادت نسبة المضاف .

كذلك فقد تمت دراسة عملية التوافق بين المضافات والراتنجات على تثبيط اللهوبية حيث كان تأثيرها واضحاً على التثبيط .