

**EVALUATION OF SOME PREPARED FIRE-RETARDING
EPOXY RESINS COATING FROM EGYPTIAN RAW-MATERIALS**

BY

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ABSTRACT

Locally coal tar phenols and crude cresilic acid are used for preparing epoxy resins coatings and modified with fire-retarding modifier in different proportions in presence of some curing agents.

Low molecular weight homopolyepoxy resin was prepared from pure phenol by condensation of prepared epichlorohydrin with obtained bisphenol A. By the same manner copolyepoxy resins have been prepared from Egyptian coal tar phenols or crude cresilic acid.

Fire-retarding coating samples were prepared by mixing homo- and copolyepoxy resin with the curing agent 4, 4' -diaminodiphenyl-methane and modified by different ratios of hexachlorocyclopentadiene.

The effect of methyl substituent group present in the diphenyl derivative and the chlorine compound content were studied. Standard test method was used to evaluate those samples. Some of it were found to be efficient as fire-retarding coating.

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INTRODUCTION

The flame resistance of epoxy, phenolic, ureaformaldehyde and related resin systems appears to represent examples of polymers which are intermediate in their combustion behavior between most of the vinyl systems and the so-called non-flammable, heat resistant polymers [1].

Many ways to decrease the flammability of polymers and coatings have been discovered as results of research done on various mechanisms of flame retardation. Currently, the most effective flame-retardant materials contain halogen, phosphorus, various transition metal oxides, strong acids, or some amine and metal salts. These materials can be used to produce acceptable flame retardance in coatings when the substances are either chemically combined with the film forming polymer or used as additives [2,3].

Epoxy solution coatings are very important in the total epoxy resin production [4].

In order to produce a coating with suitable performance properties, many additives [5,6] are included in a coating formulations to achieve specific property modifications or improvements.

Halogens, occupy an important position today among the fire-extinguishing and flame-retardant agents [5], although this property is not inherent in conventional epoxy systems.

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Halogen-containing epoxides are used extensively for various industrial purposes such as adhesives, paints, casting, and fiber laminates [7]. They are also used in combination with other resins for various coating types [8-10], of metals and laboratory furniture.

EXPERIMENTAL AND RESULTS

Materials and methods:

1- Coal tar phenols (Tph) and crude cresilic acid (CA), are products of El-Nasr Co., for coke and Industrial chemicals, Egypt. Their characteristics after ordinary distillation are given in (Table 1)

(Table 1) : Characteristics of (T ph) and (CA) :

Materials	Boiling range, °C	Dry Yields, %	Water, %	Residue, %	Average molecular weight	Specific gravity	Refractive Index	Viscosity at 30°C, m.ps.	Elemental Analysis, %		
									C	H	O N
Tph	170-235	78.18	12.00	9.82	140	1.0630	1.4639	8.329	79.14	7.66	13.20-
CA	170-210	82.80	15.00	2.20	225	1.0690	1.5387	9.122	86.11	7.69	6. 20-

Gas liquid chromatographic (GLC) Analysis of (TPh) and (CA):-

Dry (TPh) and (CA) were run through a GLC (perkin Elmer, Model sigma 3-B, provided with flame ionization) column. The

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separation conditions are given [11]. Its chromatographic resolution percent are given in (Table 2):

(Table 2) Chromatographic Resolution, % of (TPh) and (CA):

Materials	Phenol	Cresols			Xylenols,
		o-	p-	m-	
Tph.	48.8340	1.2023	6.8760	31.9257	11.1620
CA.	1.0230	22.8010	6.3660	54.3680	15.4420

2-Preparation of bisphenol (Bis A) , (B Tph) and (B CA):-

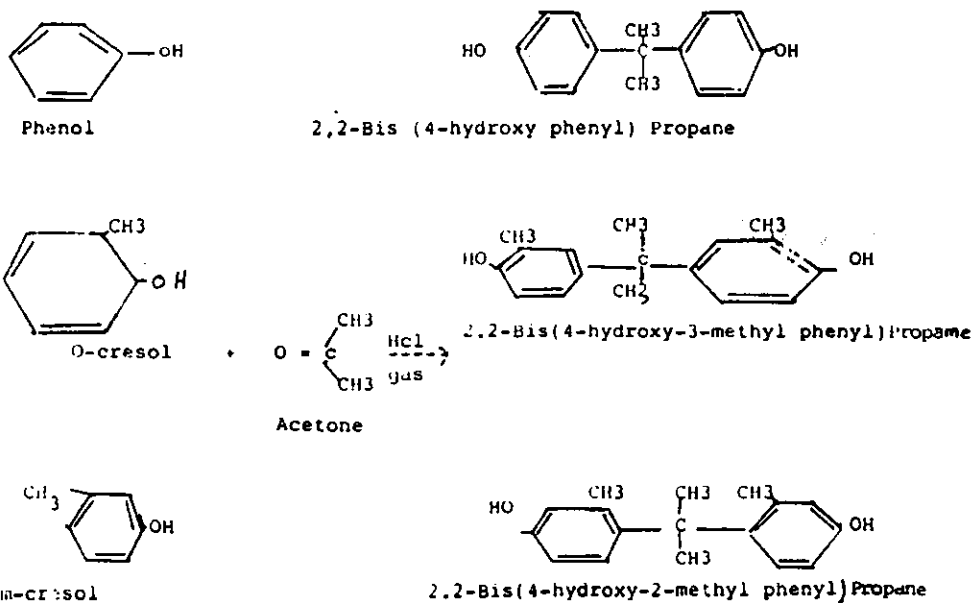
A mixture of phenol, (T ph) or (C A) (80 ml) reacts with acetone (15 ml) to give bisphenols (Bis A), (B TPh) or (BCA) according to the method described in [12,13], while, pure phenol gives with acetone the corresponding bisphenol 2,2- Bis(4- hydroxyphenyl) propane (Bis A).

On the other hand, (T ph) or (CA) reacts with acetone to give the corresponding bisphenols (B Tph) or (B CA) derivatives- which are composed of - mixtures of 2,2- Bis (4 -hydroxyphenol) propane (from phenol), 2,2-Bis (4-hydroxy-3-methyl phenyl) propane (from O-cresol), 2,2 -Bis(4-hydroxy-

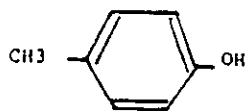
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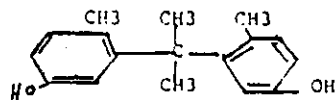
-2-methyl phenyl) propane (from m-cresol) and 2,2 Bis(5-hydroxy 2- methyl phenyl) propane (from p-cresol) in different ratios according to the equation:



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p-cresol



2,2-Bis(5-hydroxy-2-methyl phenyl) Propane

Beside these formulae of known bisphenols in the literature other formulas could be possible.

The characteristics of obtained bisphenols are given in (Table 3):

(Table 3) : The characteristics of Bisphenols

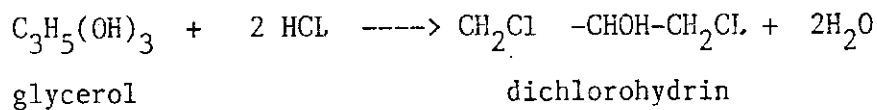
Prepared bisphenol	Used Phenols	Yield, gm.	Melting points, °c	Average molecular weight	Elemental Analysis,				
					c	H	O	N	
Bis A	Phenol	96	153	231	78.60	6.81	14.59	-	
B	Tph	T ph	70	103	241	71.22	7.11	21.67	-
B	CA	CA	80	90	260	79.27	8.20	12.53	-

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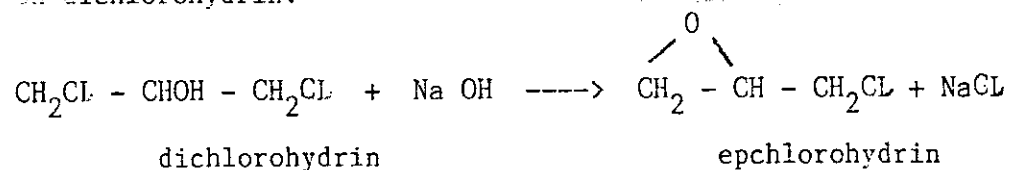
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3- Preparation of Epichlorohydrin

Dichlorohydrin was prepared from glycerol, a product of El-Nil company, for oils and detergents, Egypt (Mw = 93) according to the cited method [14].



Epichlorohydrin can be obtained by the action of alkalies on dichlorohydrin:



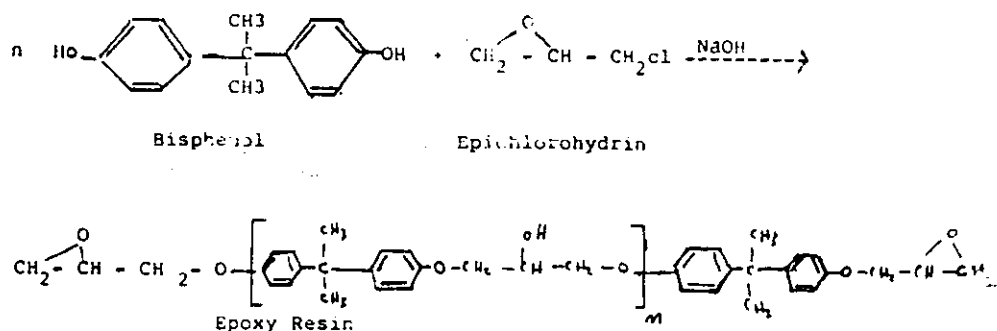
Its characteristics are given in (Table 4)

(Table 4) The characteristics of prepared Epichlorohydrin:

Average Molecular weight	Specific gravity at 20°C, gm/cm ³	Refractive index at 20°C	Boiling point. °C	Viscosity at 30°C m.p.s.	Elemental Analysis, %				
					C	H	Cl	O	
92.5	1.18	1.4381	117	1.7637	Calculated	38.92	5.41	38.38	17.29
					found	35.82	5.31	37.01	21.1

4- Preparation of low Molecular weight homo- and copolyepoxy resins

Low molecular weight homopolyepoxy resins (E Bis A) and copolyepoxy resins (E Tph) or (E CA) were prepared according to the procedures described in [15,16], by condensation of bisphenol (230 g) with epichlorohydrin (280 g) in presence of sodium hydroxide:



by the same manner copoly epoxy resins were prepared.
 The characteristics of epoxy resins are given in (Table 5)

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(Table 5) The characteristics of Epoxy Resins :

Prepared Epoxy Resin	Parent Bis-Phenol	Yield, gm.	Average molecular weight	Drop falling temp, °c	Viscosity, at 50°C m.p.s.	Epoxy group content, %	Hydroxy group content, %	Elemental Analysis, %			
								C	H	O	N
E Bis A	Bis A	416	350	61	390	24.34	12.88	69.70	6.55	23.75	-
E Tph	B Tph	336	360	50	340	27.18	24.18	70.78	7.19	22.03	-
E CA	B CA	297	410	45	220	25.66	30.53	71.45	7.88	20.67	-

5-4,4' -diamino diphenylmethane (Di-Am)

Curing agent, a product of protective Materials limited, Ford Air field Estate, England.

6- preparation of coated samples :

Through the present work, several formulations of coatings were tried. The best samples were obtained by mixing the components in the proportions shown in (Table 6). The general procedure for formulation of coating samples prepared by (dissolving homopolyepoxy resin (E Bis A) or copolyepoxy resins (E Tph) or (E CA) and 4,4' -diaminodiphenyl methane (Di - Am) (30 % of the weight of resin) as curing agent in acetone, followed by addition of hexachloro-cyclopentadiene

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(H.Cl.c.p.D) in different ratios (0-30%) of the weight of mixture) with mixing at room temperature to give the required solutions of coatings.

The solution samples were poured on metallic panels and dried at room temperature for variable times to form the required samples of coatings.

The results of drying rate and fire retarding test (17) for the prepared coated samples are given in (Table 7,8) respectively.

(Table 6) Formulation of the components used in preparing fire retarding coating samples

Components, t	Group I				Group II				---Group III			
	E ₁	E ₂	E ₃	E ₄	E ₅	E ₆	E ₇	E ₈	E ₉	E ₁₀	E ₁₁	E ₁₂
E Bis A	70	70	70	70	-	-	-	-	-	-	-	-
E Tph	-	-	-	-	70	70	70	70	-	-	-	-
E CA	-	-	-	-	-	-	-	-	70	70	70	70
Di-Am	30	30	30	30	30	30	30	30	30	30	30	30
H.cl.c.p.D	0	10	20	30	0	10	20	30	0	10	20	30

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(Table 7) Drying Rate of prepared coated samples:

Drying time, hrs	Group I				Group II				Group III			
	E ₁	E ₂	E ₃	E ₄	E ₅	E ₆	E ₇	E ₈	E ₉	E ₁₀	E ₁₁	E ₁₂
12	D	S	S	S	D	S	N	N	N	N	N	N
24		D	D	D			S	S	D	S	N	N
36							D	D		D	S	S
72											D	D

N = non-drying

S = semidrying

D = drying

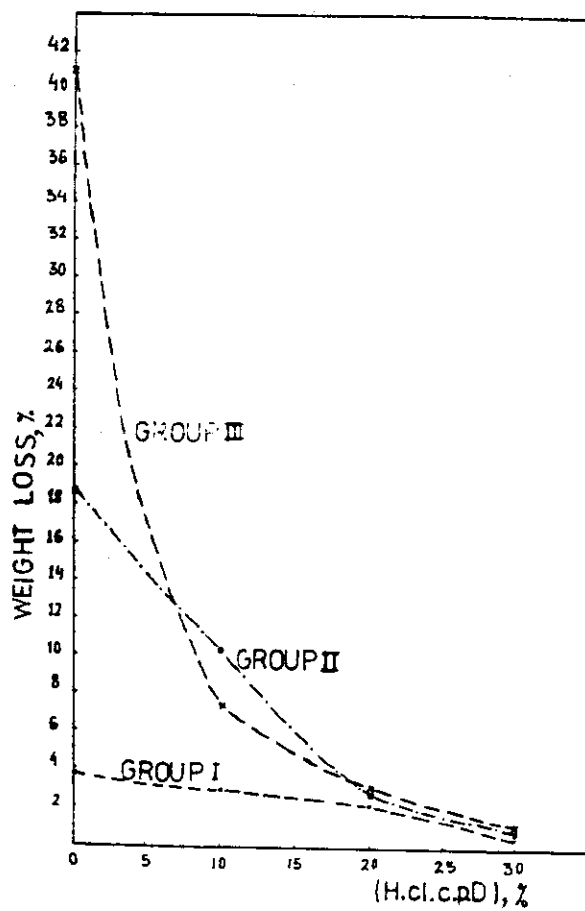
(Table 8) fire retarding test for prepared coated samples:

Property	Group I				Group II				Group III			
	E ₁	E ₂	E ₃	E ₄	E ₅	E ₆	E ₇	E ₈	E ₉	E ₁₀	E ₁₁	E ₁₂
Weight loss, %	3.67	3.01	2.26	0.53	18.84	10.21	2.66	0.66	41.9	7.4	2.96	1.22
Flammability	B	B	NB	NB	B	B	NB, C	N	B	B	NB	NB

B = burning

NB = Non-burning

C = charring



VARIATION OF WEIGHT LOSS % OF
SAMPLES WITH PERCENT OF (H.cl.c.p.D)

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DISCUSSION

During our research work on fire-retarding epoxy resin coating from Egyptian raw-materials (phenols, coal tar phenols T ph, and crude cresilic acid CA), several experiments and formulations for the prepared samples were carried out. Homopolyepoxy resins (E Bis A) or copolyepoxy resins (E T ph or E CA), (H.Cl.c.p.D.) and 4,4' diaminodiphenylmethane were formulated together to form fire-retarding epoxy resins coating samples.

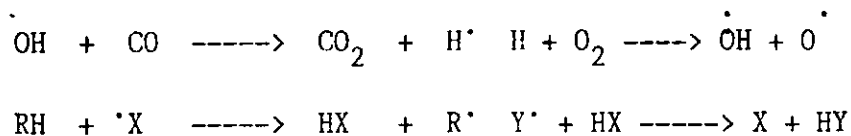
Epoxy resins by itself may be considered as flammable, but when it modified with a wide variety of (H.Cl.c.p.D)- as fire-retarding modifier-prior to curing, this flammability is depressed, (C.f. tables 6,8).

The results given in the figure and table 6,8 show that the weight loss % of the sample E_4 (Containing 30% H.Cl.c.p, D.) is 0.53%, of the sample E_3 (containing 20% H.Cl.c.p.D.) and is 2.26%, of the sample E_2 (containing 10% H,Cl,c,p,D,) and is 3.01 %, of the sample E_1 (unmodified, 0% H.Cl.c.p.D.) of the value 3.67 %. This means that the fire-retarding of these four samples is in the order $E_4 > E_3 > E_2 > E_1$ since E_4 has the lowest value of weight loss, %.

This indicates that, the fire-retarding property improves gradually with increasing the amount of (H.Cl.c.P.D.) from (0-30%). 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

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by a free radical mechanism (1):



RH denotes the fuel, X denotes the halogen, and Y refers to active radicals such as H, OH and CH₃.

At the same time the fire retardency decreases from E₃ to E₅ samples and also from E₁₂ to E₉ samples.

It is clear that from the figure and tables 2,5,6,8 the samples of group I (containing hydroxyl group 12.88%, and free methyl group) have fire retardance better than samples of group II (containing hydroxyl group 24,18 % and rich in methyl group). These samples are also better than samples of group III (containing hydroxyl group 30.53% and more rich in methyl group) respectively. This indicates that the presence of hydroxyl and methyl groups in a fire-retarding epoxy coating samples increases flammability, i.e. flammability decreases by lowering hydroxyl and methyl groups content according to Rosser [18]. the halide active species is the hydrogen halide, which reduces the concentration of the free radicals OH,CH₃ and H considered responsible for the propagation of the flame.

On the other hand, the results of chromatographic resolution (Table 2) show that the drying rate of the prepared

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samples was improved by decreasing the content of methyl group in epoxy resin.

From the experimental data, it can be concluded that:

1- The samples can be arranged according to the best of fire-retarding (lowest weight loss, %, non-burning) as follows:

a- $E_4 > E_8 > E_{12} > E_7 > E_{11}$

b- group I > group II > group III

2- The rate of weight loss, % indicates the flammability or rapidity of burning.

3- The prepared fire-retarding epoxy resins coating samples improve gradually with increasing the amount of hexachlorocyclopentadiene from (0- 30%).

4- The presence of hydroxyl and methyl groups in a fire-retarding epoxy coating sample increases flammability.

5- The drying rate of the prepared epoxy coating samples improved by decreasing the percentage of methyl groups content in epoxy resins.

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تقييم بعض طلاءات راتنجيات الايبوكسى المقاومه للحريق المحضرة من الخامات المحلية

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حضرت طلاءات من راتنجيات الايبوكسى المحضرة من قطران الفحم وكذلك
حامض الكريزليك المحلى. وتم تحسين هذه الطلاءات باضافة مواد مقاومه للحريق فى
وجود مواد مصلدة.

حضرت راتنج الايبوكسى المتشابه ذو الوزن الجزيئى المنخفض من الفينول
النقى عن طريق تكثيف ثنائى الفينول بروبان الناتج مع الايبيركلورهيدرين
المحضر من الجليسرول. وبنفس الطريقة تم تحضير راتنج الايبوكسى
المختلط من قطران الفحم الحجرى او حامض الكريزليك الخام المصرى.

حضرت عينات من الطلاءات المقاومة للحريق من راتنجيات الايبوكسى
المطورة بنسب مختلفة من سداسى كلوروبنتادين الحلقى فى وجود ٤و٤ -
ثنائى امين ثنائى الفينيل ميثان كعامل تصلد.

تم دراسة تأثير مجموعة الميثيل فى مشتقات ثنائى الفينيل وكذلك محتوى
الكلور على خواص الطلاءات.

تم تقييم هذه الطلاءات بواسطة الطرق القياسية لمعرفة مدى مناسبتها
لمقاومة الحريق.