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FORMULATION OF NEW MODIFIED ALKYD RESINS AND THEIR APPLICATION IN THE FIELD OF SURFACE COATINGS

M. M. ELSHAHAWI [*], A. ABOU SHEAISHAA[*], M. ELSAYED [*], AND F. ABD EL-HAI [**]

*Departments of Chemistry, Faculty of Science, *Ain Shams University, **Al-Azhar University, Cairo, Egypt*

ABSTRACT

Alkyd resins are considered modified polyester resins, which may be modified with many chemicals such as polybasic acids, polyhydric alcohols and/or fatty acids to produce resins with different properties and give the final surface coating formulations wide performance range. In this research, the soya bean based N,N-bis(2-hydroxyethyl)thiophene-2-carboxamide (HETCA)-modified alkyd resins and N,N-bis(2-hydroxyethyl)furan-2-carboxamide (HEFCA)-modified alkyd resins are prepared by partial replacement of glycerol (G) with each (HETCA) (I) and (HEFCA) (III), respectively, which are reacted as source of polyhydric alcohols, with both phthalic anhydride (PA) and soya bean oil fatty acids (SOFA), as source of polyacids .

The new HETCA-modified alkyd resins and previously prepared HEFCA-modified alkyd resins enter in final coating formulations and their performance are evaluated and compared using the international standard test methods (ASTM) and involved the measurement of phyisco-mechanical properties such as viscosity, drying time, specular gloss, pencil hardness, adhesion, flexibility. In general, the results show that the modification enhances both phyisco-mechanical and chemical properties. The corrosion resistance of alkyd resins improved by such HETCA and HEFCA- modification

Additionally, expected corrosion inhibitors such as morpholino(thiophen-2-yl)methanone (II) and morpholino(furan-2-yl) methanone (IV) are prepared and their anticorrosion effect is investigated by two ways. First, as an additive with unmodified (commercial) alkyd resin in zinc phosphate primer formulations. Second, as an additive with previously prepared HETCA- and HEFCA-modified alkyd resins in the same primer formulations. Both of corrosion inhibitors (II) and (IV) improve the corrosion resistance at certain dosages.

Keywords– *anticorrosion coating, corrosion inhibitors, modified alkyd resin, N,N-bis(2-hydroxyethyl)thiophene-2-carboxamide (HETCA), N,N-bis(2-hydroxyethyl)furan-2-carboxamide (HEFCA), morpholino(thiophen-2-yl)methanone, morpholino(furan-2-yl)methanone*

INTRODUCTION

In the ongoing shift from solvent- to water-based coatings, alkyds have stubbornly resisted the change, and for valid reasons. Solvent-based alkyds are cost efficient and versatile, with a long history of proven performance in architectural, industrial and specialty applications. They offer excellent adhesion, hardness, gloss and corrosion resistance. These resins are also highly viscous: they originate as solids, making it very difficult to formulate shelf-stable coatings without the addition of solvent. Despite numerous options, including water-reducible alkyds, modified alkyd dispersions and alkyd emulsions, only 10% of alkyd-based coatings are currently waterborne[(1)]. Challenges to widespread adoption include delayed hardness development, lower gloss and reduced corrosion protection.

N,N-bis(2-hydroxyethyl)furan-2-carboxamide (HEFCA)-modified alkyd resins are previously prepared by partial replacement of glycerol with N,N-bis(2-hydroxyethyl)furan-2-carboxamide (HEFCA) which was reacted with Linseed oil fatty acids (LOFA) and phthalic anhydride (PA) without affecting the resin constant. The biological effect of HEFCA-modified alkyd resins are investigated and showed promising results[(2)].

The modification of short and medium alkyd resins using perfluorinated urethane toluene isocyanate (PFUTI), and incorporates the modified resins in a set of paint formulations containing different ratios of zinc phosphate as an inhibitive pigment, achieves promising results and illustrates corrosion protective properties in various paint formulations and also in the paint formulation free of the inhibitive pigment, s
qhows enhancement of the corrosion protection efficiencies by the improvement in the hydrophobicity of alkyd resin modified with PFUTI. In view of these results, minimizes or neglects the most expensive inhibitive pigments from an economical stand point[(3)].

The usage of maleic anhydride as a partial replacement of phthalic anhydride in long oil modified alkyd resins is investigated. The usages of maleic anhydride as a partial replacement of phthalic anhydride at these resins as well as at the vegetable oils improve the characteristics of the film of paint, such as its hardness and its resistance against atmospheric and corrosive agents. Maleic anhydride influences also in the condensation time of alkyd resins. Usually, the maleic anhydride is added before the phthalic anhydride, because it links with the double bonds of the radicals of vegetable oils, raising the stereo chemical structure and helps to achieve, in a short time, the proper viscosity of the resin. Experiments have shown that the optimal quantity of maleic anhydride for achieving the desirable results is 2%[4].

Alkyd resins are recently prepared by using recycled poly (ethylene terephthalate), PET, and different vegetable oils. Glycolysis of PET waste using pentaerytheritol (PEr) was used to produce suitable hydroxyl oligomers, GPEr, for alkyd resin. The glycolysis was carried out in the presence of manganese acetate as a catalyst and m-cresol as a solvent at 220 °C. Alkyd resins were prepared using phthalic anhydride, PET waste, glycerin, sunflower oil or linseed oil and ethylene glycol to produce PET-based alkyd resin. GPEr was used instead of PET waste to produce the second type of alkyd resin based on GPEr. The reactions were carried out in the presence of butylhydroxytin oxide as a catalyst to prepare alkyd resins. The curing characteristics of the resins produced were investigated. Corrosion resistivity based on salt spray and cathodic disbondment were evaluated for the cured alkyd as organic coating for carbon steel[5].

Recently microbial activity of N,N Di-hydroxyethyl-2-thiophenamide (HETCA) have been discussed and the studies showed promising results as biocidal coatings. Preparation of modified polyesteramides were also considered and found also improved the film performance and durability and lead to substantial antimicrobial growth control[6,7] .

Experimental Materials

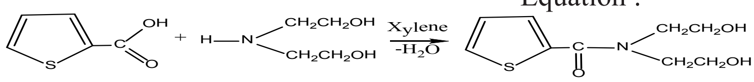
The Soya bean fatty acid (SOFA) used is supplied by Guangrao Welfare Resin Factory, China, the phthalic anhydride (PA) and the diethanolamine (DEA) are obtained from Sdfine Indian. The Glycerin are obtained from El Gomhouria Co., Egypt. Thiophene -2-carboxylic acid is obtained from SIGMA Chemical Co., USA. Furan-2-carboxylic acid is obtained from SIGMA-ALDRICH Co., United Kingdom.

METHODS AND TECHNIQUES

1. Preparation of N,N-bis(2-hydroxyethyl) thiophene-2-carboxamide (HETCA) I [6,7]

A mixture of thiophene -2-carboxylic acid (0.1 mole = 12.815 gm), freshly distilled diethanolamine (0.1mole=10.5 gm), and 21 ml xylene as a solvent were placed in 250 ml round-bottomed flask fitted with Dean and Stark apparatus, The reaction was allowed to reflux until the theoretical amount of water (0.1 mole =1.8 gm or 1.8 ml)was collected. The mixture was allowed to cool where a clear pale yellow viscous material was obtained.

Equation :



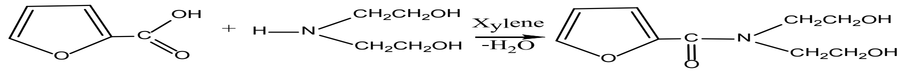
I

N,N-bis(2-hydroxyethyl)thiophene-2-carboxamide
HETCA

2- Preparation of N,N-bis(2-hydroxyethyl) furan-2-carboxamide (HEFCA) III [2]

A mixture of furan-2-carboxylic acid (0.1 mole = 11.208 gm), freshly distilled diethanolamine (0.1 mole=10.5 gm), and 21 ml xylene as a solvent were placed in 250 ml round-bottomed flask fitted with Dean and Stark apparatus, The reaction was allowed to reflux until the theoretical amount of water (0.1 mole =1.8 gm or 1.8 ml) was collected. The mixture was allowed to cool where a brown viscous material was obtained.

Equation :



III

N,N-bis(2-hydroxyethyl)furan-2-carboxamide
HEFCA

3- Preparation Of Alkyd Resins via solvent process[8]:

The preparation of various modified alkyd resins carried out as shown in the following equations:

By partial replacement of Glycerol (G) with each of following compounds:

N,N-bis(2-hydroxyethyl)thiophene-2-carboxamide (HETCA) **I**

N,N-bis(2-hydroxyethyl)furan-2-carboxamide (HEFCA) **III**

As the ingredient source of the polyol, while Phthalic anhydride (PA) and Soya bean oil fatty acid (SOFA) is the source of the polybasic acid, in the presence of 10% xylene of their volume, the whole ingredient was placed in 250 ml round-bottomed flask fitted with Dean Stark apparatus.

It should be noted that within each set of formulation, the total number of acid and hydroxyl equivalents for various runs were kept constant and the partial replacement of Glycerol with each compound " I" and " III" is listed in table (1).

Table (1): List of hydroxyl equivalent of different runs

Resin	G	HETCA or HEFCA
B_X	1.00	0.00
T_{X1} or F_{X1}	0.95	0.05
T_{X2} or F_{X2}	0.90	0.10
T_{X3} or F_{X3}	0.80	0.20
T_{X4} or F_{X4}	0.70	0.30

X= 0, 1, 2 or 3 at 0%, 10%, 20% or 30% excess-OH respectively

B: Unmodified Alkyd Resin (Blank)

T: HETCA-modified Alkyd Resin

F: HEFCA-modified Alkyd Resin

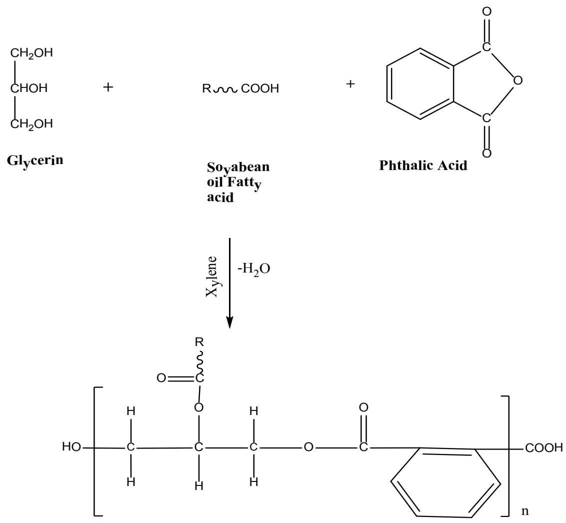
The following tables (2 –3) illustrate the resin characteristic constants for various modified alkyd resin formulations.

These formulations cover a wide range of various excess hydroxyl contents (0%, 10%, 20%, and 30% excess-OH).It is important to mention that in each series of resins there are:

1- Blank formulation containing no modifier compound and is introduced for comparison purpose. This formulation will be B0, B1, B2 or B3 to indicate excess-OH of 0%, 10%, 20% or 30% respectively.

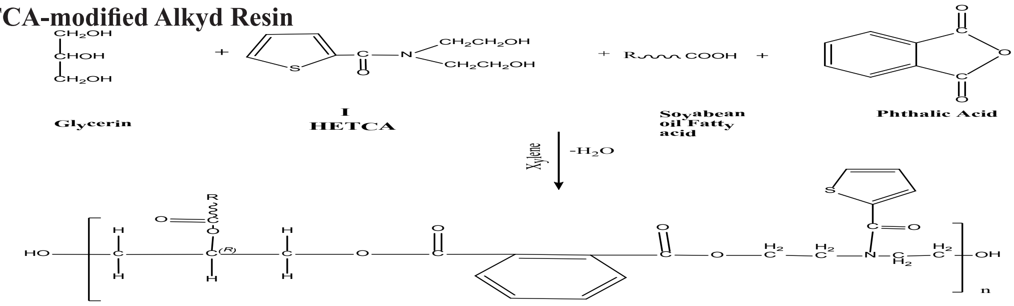
2- Gradual increase in the percentage of the modifier. The modifier is partially replaces the hydroxyl equivalent of Glycerol used in formulation. Such replacement is based on the hydroxyl equivalent constant and the second subscript numbers 1, 2, 3 and 4 are given after the formulation numbers to indicate 5%, 10%, 20% and 30% modification partial replacement, respectively.

3.1. Preparation of Unmodified Alkyd Resins[8]



Alkyd Resin

3.2.Preparation Of HETCA-Modified Alkyd Resins Based On Soyabean Oil Fatty Acid



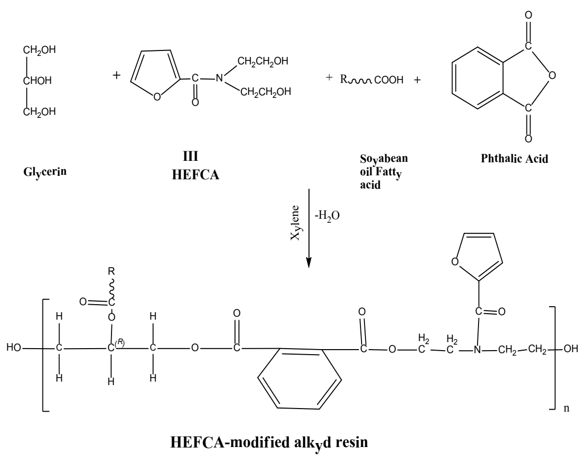
HETCA-modified alkyd resin

Table (2): Resin constants for HETCA -modified alkyd resins

Resin No.	Excess – OH (%)	Ingredients	E	F	e_0	e_A	e_B	R	H_2O off (ml)
$T_{01\text{-}04}$	0	G	30.7	3	0.520		0.520	1.00	6.7
		HETCA	107.6	2					
		FA	280	1	0.222	0.519			
		PA	74.1	2	0.297				
$T_{11\text{-}14}$	10	G	30.7	3	0.600		0.600	1.10	6.7
		HETCA	107.6	2					
		FA	280	1	0.200	0.546			
		PA	74.1	2	0.346				
$T_{21\text{-}24}$	20	G	30.7	3	0.716		0.716	1.20	6.8
		HETCA	107.6	2					
		FA	280	1	0.164	0.596			
		PA	74.1	2	0.432				
$T_{31\text{-}34}$	30	G	30.7	3	0.879		0.879	1.30	7.1
		HETCA	107.6	2					
		FA	280	1	0.111	0.679			
		PA	74.1	2	0.568				

G:glycerol; HETCA:N,N-bis(2-hydroxyethyl)thiophene-2-carboxamide; PA: Phthalic Anhydride; FA: Soya bean fatty acid E: Equivalent Weight; e_A: Number of acid equivalent ; e_B: Number of hydroxyl equivalent; e_0: Total equivalent present at the start of the reaction; F: Functionality ; R:Ratio of total-OH groups to total-COOH groups (= e_B/e_A) ; H2O off (ml): Number of water millimeters at which the reaction will be Completed (= $e_{acid}\times18 + e_{anhydride}\times9$)

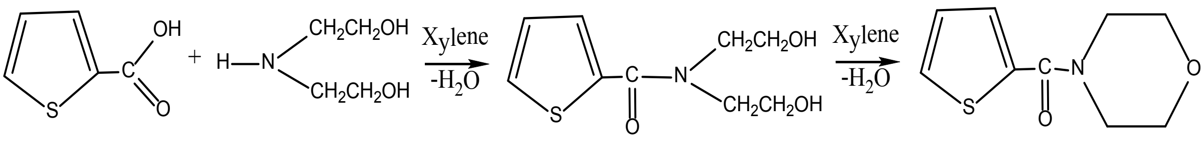
3.2. Preparation Of HEFCA-Modified Alkyd Resins Based On Soyabean Oil Fatty Acid[2]



4-Preparation of morpholino(thiophen-2-yl)methanone II

A mixture of thiophene-2-carboxylic acid (0.1 mole = 12.815 gm), freshly distilled diethanolamine (0.1 mole=10.5 gm), and 21 ml xylene as a solvent were placed in 250 ml round-bottomed flask fitted with Dean and Stark apparatus, The reaction was allowed to reflux until the theoretical amount of water (0.2 mole =3.6gm or 3.6 ml)was collected. The mixture was allowed to cool where a brown viscous material was obtained.

Equation :



I **II**

Morpholino(thiophen-2-yl)methanone

Table (3): Resin constants for HEFCA -modified alkyd resins

Resin No.	Excess –OH (%)	Ingredients	E	F	e_0	e_A	e_B	R	H_2O off (ml)
T_{01-04}	0	G	30.7	3	0.520		0.520	1.00	6.7
		HEFCA	99.5	2					
		FA	280	1	0.222	0.519			
		PA	74.1	2	0.297				
T_{11-14}	10	G	30.7	3	0.600		0.600	1.10	6.7
		HEFCA	99.5	2					
		FA	280	1	0.200	0.546			
		PA	74.1	2	0.346				
T_{21-24}	20	G	30.7	3	0.716		0.716	1.20	6.8
		HEFCA	99.5	2					
		FA	280	1	0.164	0.596			
		PA	74.1	2	0.432				
T_{31-34}	30	G	30.7	3	0.879		0.879	1.30	7.1
		HEFCA	99.5	2					
		FA	280	1	0.111	0.679			
		PA	74.1	2	0.568				

G:glycerol; HEFCA:N,N-bis(2-hydroxyethyl)furan-2-carboxamide; PA: Phthalic Anhydride; FA: Soya bean fatty acid E: Equivalent Weight; e_A: Number of acid equivalent ; e_B: Number of hydroxyl equivalent; e_0: Total equivalent present at the start of the reaction; F: Functionality ; R:Ratio of total-OH groups to total-COOH groups (= e_B/e_A) ; H2O off (ml): Number of water millimeters at which the reaction will be Completed (= $e_{acid}\times18 + e_{anhydride}\times9$)

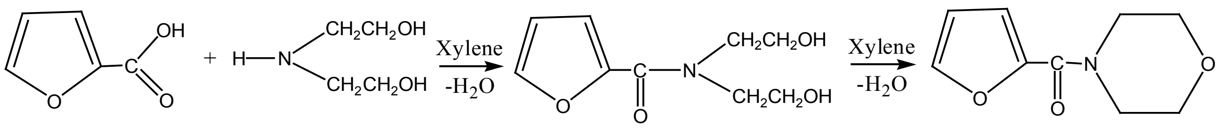
5-Preparation of furan-2-yl(morpholino) methanone IV

A mixture of furan-2-carboxylic acid (0.1 mole = 11.208 gm), freshly distilled diethanolamine (0.1 mole=10.5 gm), and 21 ml xylene as a solvent were placed in 250 ml round-bottomed flask fitted with Dean and Stark apparatus, The reaction was allowed to reflux until the theoretical amount of water (0.2 mole =3.6 gm or 3.6 ml) was collected. The mixture was allowed to cool where a brown viscous material was obtained.

Equation :

Furan-2-yl(morpholino)methanone

Spectral analysis of prepared compounds:



III **IV**

Structural features of each of the previous compounds is confirmed by IR spectroscopy which tabulated in table (4, 5, 6 and 7) and Figures (1, 2, 3 and 4) respectively

Table (4): FTIR spectra of N,N-bis (2-hydroxyethyl) thiophene-2-carboxamide (HETCAI

Functional group	IR peak (cm^{-1})
OH	3363 (Broad band)
CH aromatic	3099
CH aliphatic	2955
CO amide	1705

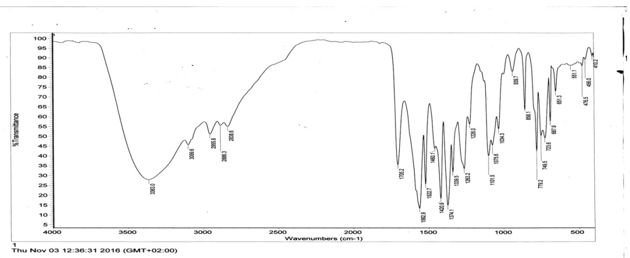


Figure (1) FTIR spectra of N,N-bis(2-hydroxyethyl) thiophene-2-carboxamide (HETCA) I

Table (5): Spectral analysis of morpholino (thiophen-2-yl) methanone II

Functional group	IR peak (cm^{-1})
OH	diminished
CH aromatic	3097
CH aliphatic	2943
CO amide	1708

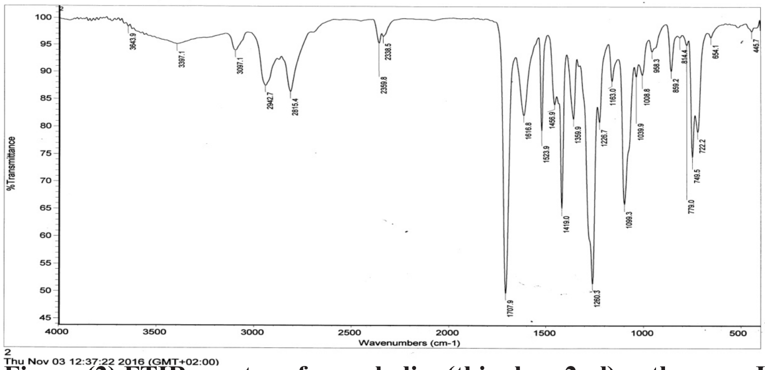


Figure (2) FTIR spectra of morpholino(thiophen-2-yl)methanone II

Table (6): Spectral analysis of N,N-bis(2-hydroxyethyl)furan-2-carboxamide (HEFCA) III

Functional group	IR peak (cm^{-1})
OH	3391(Broad band)
CH aromatic	3050
CH aliphatic	2957
CO amide	1719

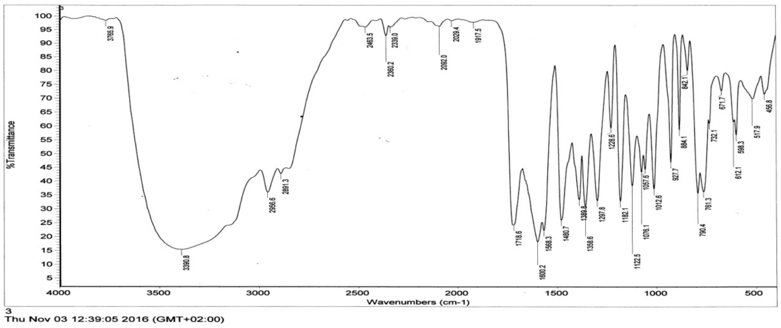


Figure (3) I.R. Spectrum of N,N-bis(2-hydroxyethyl)furan-2-carboxamide (HEFCA) III

Table (7): Spectral analysis of furan-2-yl(morpholino)methanone IV

Functional group	IR peak (cm^{-1})
OH	diminished
CH aromatic	3024
CH aliphatic	2955
CO amide	1734

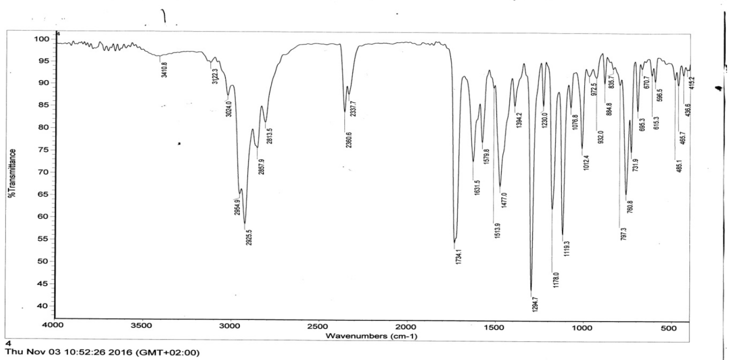


Figure (4) I.R. Spectrum of furan-2-yl(morpholino)methanone IV

Method of testing and evaluation:

The structure of the prepared N,N-bis(2-hydroxyethyl)thiophene-2-carboxamide (HETCA) **I**, morpholino(thiophen-2-yl)methanone **II**, N,N-bis(2-hydroxyethyl)furan-2-carboxamide (HEFCA) **III** and furan-2-yl(morpholino)methanone **IV** was confirmed by FTIR and showed in Figure 1, 2 3 and 4 respectively.

All resins are adjusted to solid content = 60 % (according to ASTM Method, D1644 - 01 (Reapproved 2012) and the following tests were carried out according to international standards:

Test method for color of transparent liquid, ASTM method, D1544 - 04 (Reapproved 2010).

Test method of viscosity, ASTM method, D4287 - 00 (Reapproved 2014).

Preparation of glass panels, ASTM method, D3891 - 96

Water resistance of dried films, ASTM method, D870 – 15

Alkali resistance of dried films, Indian Standard Specification, 158(1950)

Acid resistance of dried films, Indian Standard Specification, 159(1950)

Solvent resistance of dried films, ASTM method, D2792-69 (Reapproved 2015)

Flexibility by conical mandrel bending tester, ASTM method, D522/D522M - 13

Pencil Hardness measurements, ASTM method, D3363 – 05 (Reapproved 2011) e2

Adhesion by cross-cut adhesion, ASTM method, 3359 - 09e2

Specular gloss, ASTM method, D523 – 14

Impact test, ASTM method, D2794 – 93 (Reapproved 2010)

Measurement of film thickness, ASTM method, D1005 – 95 (Reapproved 2013)

Preparation of steel panels for testing purpose, ASTM method, D609 – 00 (Reapproved 2012)

Corrosion Resistance test, ASTM method, D2803 – 09 (Reapproved 2015), Procedure B (ISO 4623)

Determination of degree of blistering, ASTM method, D714 – 02 (Reapproved 2009)

RESULTS AND DISCUSSION

During the course of the preparation, it was felt of interest to determine the reaction time, the reaction completion. This is indicated by watching the amount of water collected in the trap and compared its amount by that calculated. The data obtained are given in the following tables (8 and 9) and Figures (5 and 6)

Table (8) The reaction time of formation of HETCA-modified alkyd resins

Resin Code	Excess-OH%	HETCA replacement (%)	Reaction Time (minutes)
B0	0%	0	720
T01		5	600
T02		10	300
T03		20	90
T04		30	240
B1	10%	0	360
T11		5	300
T12		10	120
T13		20	70
T14		30	180
B2	20%	0	480
T21		5	70
T22		10	90
T23		20	50
T24		30	60
B3	30%	0	300
T31		5	90
T32		10	70
T33		20	60
T34		30	60

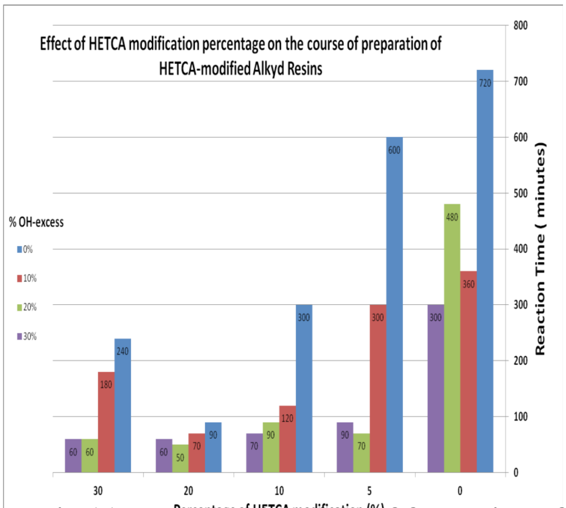


Fig (5): The reaction time of formation of HETCA-modified alkyd resins

Table (9) The reaction time of formation of HEFCA-modified alkyd resins

Resin Code	Excess-OH%	HEFCA replacement (%)	Reaction Time (hours)
B0	0%	0	720
F01		5	240
F02		10	105
F03		20	50
F04		30	220
B1	10%	0	360
F11		5	210
F12		10	220
F13		20	210
F14		30	210
B2	20%	0	480
F21		5	55
F22		10	120
F23		20	140
F24		30	60
B3	30%	0	300
F31		5	100
F32		10	60
F33		20	55
F34		30	45

The reaction rate for various resins increases by the increasing of the percentage of modifier and also increases with the increase of excess-OH percentage.

Evaluation Studies

Following the preparation of two series of

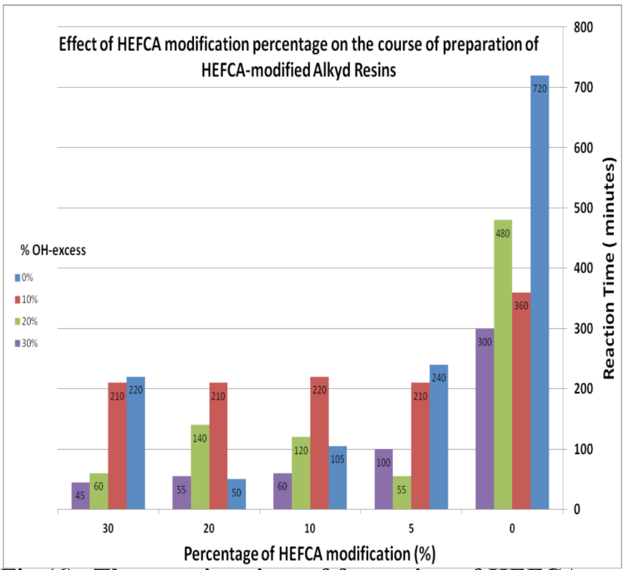


Fig (6): The reaction time of formation of HEFCA-modified alkyd resins

modified alkyd resins, the solid content of all formulations are adjusted to 60% solids. The drier combinations are added as mixed combinations by 3 % from the weight of resin. The mixed driers consist of the following components:

Table (10)

Component	%
Cobalt Octoate 10%	20
Calcium Octoate 10%	45
Zirconium Octoate 12%	29
Anti skinning agent	6
Total	100

And, Varnish formula will be,

Table (11)

Component	%
Alkyd resin or Modified alkyd resin (Solid content=100%)	60
Xylene	37
Mixed Drier	3
Total	**100**

Table (12): Viscosity, Color, Drying time Characteristics of various HETCA-Modified Alkyd Resins

Resin Code	Excess-OH (%)	HETCA Replacement (%)	Viscosity (mPa.s) at solid content = 70%	Air Drying (HD Time) (hr)	Stoving dry					Color (Gardner)
					110 C		120 C			
					1 hr	2 hrs	1 hr	2 hrs	Extra Stoving Drying time (hrs)	
B0	**0%**	**0**	50	13	VST	HD	-	-	-	8
T01		**5**	80	10	VST	HD	-	-	-	>18
T02		**10**	85	> 24	ST	VST	HD	-	-	>18
T03		**20**	100	> 24	T	T	VST	VST	3	>18
T04		**30**	100	> 24	T	T	T	T	>12	>18
B1	**10%**	**0**	140	11	VST	HD	-	-	-	8
T11		**5**	100	8	VST	HD	-	-	-	>18
T12		**10**	150	9	VST	HD	-	-	-	>18
T13		**20**	250	> 24	T	T	T	T	12	>18
T14		**30**	750	> 24	T	T	T	T	>12	>18
B2	**20%**	**0**	450	7	VST	HD	-	-	-	9
T21		**5**	675	6	HD	-	-	-	-	>18
T22		**10**	1100	7	VST	HD	-	-	-	>18
T23		**20**	4000	9	T	ST	VST	VST	3	>18
T24		**30**	28500	> 24	T	T	ST	ST	>12	>18
B3	**30%**	**0**	40000	5	HD	-	-	-	-	9
T31		**5**	144000	3.5	HD	-	-	-	-	>18
T32		**10**	250000	4	VST	HD	-	-	-	>18
T33		**20**	160000	4.5	ST	VST	HD	-	-	>18
T34		**30**	280000	11	T	ST	VST	VST	3	>18

HD: Hard Dry VST: Very Slight Tacky ST: Slight Tacky T: Tacky

Table (13): Viscosity, Color, Drying time Characteristics of various HEFCA-Modified Alkyd Resins

Resin Code	Excess-OH (%)	HEFCA Replacement (%)	Viscosity (mPa.s) at solid content = 70%	Air Drying (HD Time) (hr)	Stoving Dry					Color (Gardner)
					110 C	120 C				
					1 hr	2 hrs	1 hr	2 hrs	Extra Stoving Drying time (hrs)	
B0	0%	0	50	13	VST	HD	-	-		8
F01		5	50	> 24	VST	HD	-	-		>18
F02		10	75	> 24	VST	HD	-	-		>18
F03		20	125	> 24	T	ST	VST	VST	>12	>18
F04		30	150	> 24	T	T	ST	ST	>12	>18
B1	10%	0	140	11	VST	HD	-	-		8
F11		5	100	3.5	HD	-	-	-		>18
F12		10	150	4.0	VST	HD	-	-		>18
F13		20	250	4.5	T	ST	VST	HD		>18
F14		30	325	> 24	T	T	ST	ST	>12	>18
B2	20%	0	450	7	VST	HD	-	-		9
F21		5	1250	4	HD	-	-	-		>18
F22		10	1550	4.5	HD	-	-	-		>18
F23		20	1850	5	T	T	ST	ST	>12	>18
F24		30	2250	> 24	T	T	ST	ST	>12	>18
B3	30%	0	40000	5	HD	-	-	-		9
F31		5	4400	4	HD	-	-	-		>18
F32		10	260000	4.5	HD	-	-	-		>18
F33		20	280000	5	ST	VST	VST	VST	3	>18
F34		30	25000(at solid content =50%)	5.5	ST	VST	VST	VST	3	>18

HD: Hard Dry VST: Very Slight Tacky ST: Slight Tacky T: Tacky

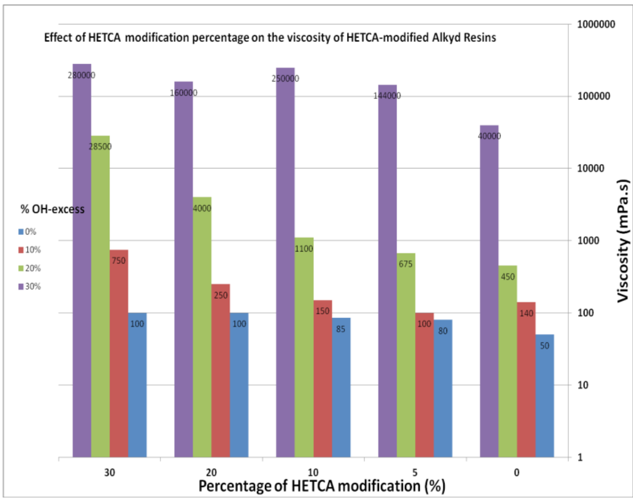


Figure: 7

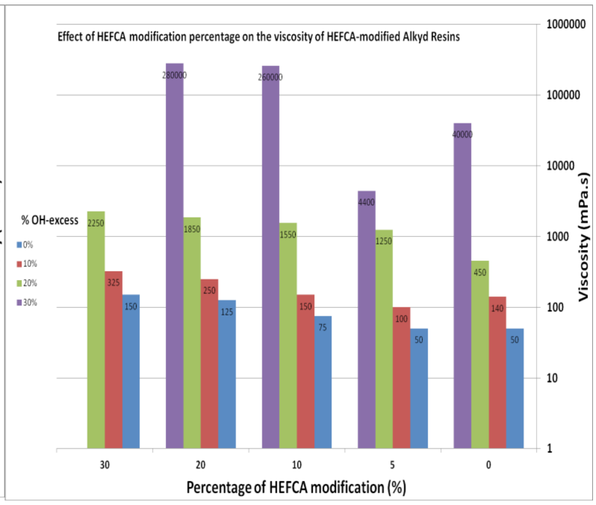


Figure: 8

The drying time increase by increasing the modifier percentage and by decreasing OH-excess of alkyd resins. The drying time of 20% and 30% modification samples at low OH-excess is very bad (e.g. T03, T04, F03, F04, T14, F14).

The best drying time is obtained at 30% OH-excess resins at 5% modification (e.g. T31 and F31).

-The viscosity for various resins at constant solid content increases slightly by the increasing of the percentage of modifier, but increases dramatically with the increase of excess-OH percentage as shown in Figure (7 and 8)

-The color of prepared varnishes was very dark due to the presence of nitrogen atom in the modified alkyd chain.

B- Water, Acid, Alkali and Solvent Resistance

Preliminary evaluation studies are carried out to show the air drying and stoving drying films of all formulations towards water, acid, alkali and solvent resistances. The evaluation tests are conducted according to standard methods. The data are collected in tables (14 - 15).

The main conclusion drown from the water, acid, alkali and solvent resistances data for the various HETCA and HEFCA-modified alkyd is tabulated in tables (10 - 11) indicate the following:

1. Except unmodified resins (B0, B01 and B03), all examined films show excellent water, acid and solvent resistance indicating no significant effect of the presence of the modifier within the employed experimental conditions.

2. The alkali resistance of the dried films is clearly improved upon the modification.

Table (14): Water, Acid, Alkali and solvent Resistance data for HETCA-modified Alkyd Resins

Resin Code	Excess-OH %	Water resistance		Acid resistance		Alkali Resistance		Solvent Resistance	
		A	S	A	S	A	S	A	S
B0	0%	Ex	Ex	Ex	Ex	F	P	Ex	Ex
T01		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
T02		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
T03		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
T04		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
B1	10%	Ex	Ex	Ex	Ex	Ex	F	Ex	Ex
T11		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
T12		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
T13		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
T14		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
B2	20%	Ex	Ex	Ex	Ex	Ex	G	Ex	Ex
T21		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
T22		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
T23		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
T24		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
B3	30%	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
T31		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
T32		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
T33		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
T34		Ex	Ex	G	Ex	Ex	Ex	Ex	Ex

Ex : Excellent (Almost no change) G : Good (Very slight change) F : Fair (Partially attacked) P : Poor (Complete film failure) S : Stoved drying film A: Air drying film

Table (15): Water, Acid, Alkali and solvent Resistance data for HEFCA-modified Alkyd Resins

Resin Code	Excess-OH %	Water resistance		Acid resistance		Alkali Resistance		Solvent Resistance	
		A	S	A	S	A	S	A	S
B0	0%	Ex	Ex	Ex	Ex	F	P	Ex	Ex
F01		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
F02		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
F03		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
F04		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
B1	10%	Ex	Ex	Ex	Ex	Ex	F	Ex	Ex
F11		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
F12		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
F13		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
F14		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
B2	20%	Ex	Ex	Ex	Ex	Ex	G	Ex	Ex
F21		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
F22		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
F23		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
F24		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
B3	30%	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
F31		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
F32		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
F33		Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
F34		Ex	Ex	G	Ex	Ex	Ex	Ex	Ex

Ex : Excellent (Almost no change) **G : Good (Very slight change)**
F : Fair (Partially attacked) **P : Poor (Complete film failure)**
A: Air drying film **S : Stoved drying film**

Extensive Evaluation Studies:

Attention the directed towards more extensive studies to indicate how much the films can withstand the various attacks in terms of immersion periods. The extensive evaluation studies for water resistance, acid resistance and solvent resistance are given in table (16). The tests are carried out on the actual coating films (air dried and stoving dry) for 30 days immersion period and the films are examined for any defects.

Additionally, the extensive evaluation studies for alkali resistance are shown in tables (17) which are carried out on the actual coating films (air dried and stoving dry) for 10 days immersion period and the films are examined for any defects.

In general, water, acid and solvent resistance for all resins are good after 30 days for both air and stoving films.

The alkali resistance of resins generally improved by increasing the modification and excess-OH% of the prepared alkyd resins.

Table (16):Water, Acid, Alkali and solvent Resistance data for modified Alkyd Resins after 30 days

Resin Code	Excess-OH %	Water resistance		Acid resistance		Solvent Resistance		Resin Code	Excess-OH %	Water resistance		Acid resistance		Solvent Resistance	
		A	S	A	S	A	S			A	S	A	S	A	S
B0	0%	Ex	Ex	Ex	Ex	Ex	Ex	B0	0%	Ex	Ex	Ex	Ex	Ex	Ex
T01		Ex	Ex	Ex	Ex	Ex	Ex	F01		Ex	Ex	Ex	Ex	Ex	Ex
T02		Ex	Ex	Ex	Ex	Ex	Ex	F02		Ex	Ex	Ex	Ex	Ex	Ex
T03		Ex	Ex	Ex	Ex	Ex	Ex	F03		Ex	Ex	Ex	Ex	Ex	Ex
T04		Ex	Ex	Ex	Ex	Ex	Ex	F04		Ex	Ex	Ex	Ex	Ex	Ex
B1	10%	Ex	Ex	Ex	Ex	Ex	Ex	B1	10%	Ex	Ex	Ex	Ex	Ex	Ex
T11		Ex	Ex	Ex	Ex	Ex	Ex	F11		Ex	Ex	Ex	Ex	Ex	Ex
T12		Ex	Ex	Ex	Ex	Ex	Ex	F12		Ex	Ex	Ex	Ex	Ex	Ex
T13		Ex	Ex	Ex	Ex	Ex	Ex	F13		Ex	Ex	Ex	Ex	Ex	Ex
T14		Ex	Ex	Ex	Ex	Ex	Ex	F14		Ex	Ex	Ex	Ex	Ex	Ex
B2	20%	Ex	Ex	Ex	Ex	Ex	Ex	B2	20%	Ex	Ex	Ex	Ex	Ex	Ex
T21		Ex	Ex	Ex	Ex	Ex	Ex	F21		Ex	Ex	Ex	Ex	Ex	Ex
T22		Ex	Ex	Ex	Ex	Ex	Ex	F22		Ex	Ex	Ex	Ex	Ex	Ex
T23		Ex	Ex	Ex	Ex	Ex	Ex	F23		Ex	Ex	Ex	Ex	Ex	Ex
T24		Ex	Ex	Ex	Ex	Ex	Ex	F24		Ex	Ex	Ex	Ex	Ex	Ex
B3	30%	Ex	Ex	Ex	Ex	Ex	Ex	B3	30%	Ex	Ex	Ex	Ex	Ex	Ex
T31		Ex	Ex	Ex	Ex	Ex	Ex	F31		Ex	Ex	Ex	Ex	Ex	Ex
T32		Ex	Ex	Ex	Ex	Ex	Ex	F32		Ex	Ex	Ex	Ex	Ex	Ex
T33		Ex	Ex	Ex	Ex	Ex	Ex	F33		Ex	Ex	Ex	Ex	Ex	Ex
T34		Ex	Ex	G	Ex	Ex	Ex	F34		Ex	Ex	G	Ex	Ex	Ex

Ex : Excellent (Almost no change) **G :** Good (Very slight change) **F :** Fair (Partially attacked) **P :** Poor (Complete film failure) **A:** Air drying film **S :** Stoved drying film

Table (17): Alkali and solvent Resistance data for modified Alkyd Resins after 10 days

Resin Code	Excess-OH %	Alkali resistance (after 10 days)		Resin Code	Excess-OH %	Alkali resistance (after 10 days)	
		A	S			A	S
B0	0%	P	P	B0	0%	P	P
T01		P	Ex	F01		P	Ex
T02		P	Ex	F02		P	Ex
T03		P	Ex	F03		P	P
T04		G	G	F04		P	P
B1	10%	P	P	B1	10%	P	P
T11		P	Ex	F11		F	Ex
T12		F	Ex	F12		G	Ex
T13		Ex	Ex	F13		Ex	Ex
T14		Ex	Ex	F14		Ex	F
B2	20%	F	P	B2	20%	F	P
T21		Ex	Ex	F21		Ex	Ex
T22		Ex	Ex	F22		Ex	Ex
T23		Ex	Ex	F23		Ex	G
T24		Ex	Ex	F24		Ex	P
B3	30%	Ex	G	B3	30%	Ex	G
T31		Ex	Ex	F31		Ex	Ex
T32		Ex	P	F32		Ex	Ex
T33		Ex	Ex	F33		Ex	F
T34		Ex	Ex	F34		Ex	P

Ex : Excellent (Almost no change) G : Good (Very slight change) F : Fair (Partially attacked) P : Poor (Complete film failure) A: Air drying film S : Stoved drying film

C- Mechanical properties of dried films:

The dry film characteristics of various modified resin films are carried out according to standard methods and well-known techniques and the results are tabulated in tables (19, 20, 21 and 22). These tables show some mechanical properties such as gloss, hardness, scratch resistance and adhesion of both varnishes and primers-containing modified alkyd resins. The formulation of primer will be as shown in the following table:

Table (18): Zinc Phosphate Primer formula

serial	Component	%
1	Resin/modified resin	30
2	Bentone38	1
3	Ethanol	0.3
4	Wetting & dispersing Agent	0.3
5	TiO_2	10
6	Zinc phosphate	5
7	$CaCO_3$	24
8	Talc	5
9	Xylene	22.21
10	Calcium Octoate (10%)	1
11	Cobalt octoate (10%)	0.43
12	Zirconium Octoate (12%)	0.63
13	Ex skin 2	0.13
Total		100

Resin Code	Excess-OH %	Film Thickness (μ)			Gloss at 20^0			Flexibility at 3 mm			Adhesion		
		A	S	P	A	S	P	A	S	P	A	S	P
B0	**0%**	42	27	75	76	100	4	Ex	Ex	Ex	5B	5B	5B
T01		25	20	37	81	93	4	Ex	Ex	Ex	5B	5B	5B
T02		25	25	57	82	85	5	Ex	Ex	Ex	5B	5B	5B
T03		35	20	45	85	93	11	Ex	Ex	Ex	5B	5B	5B
T04		30	25	36	90	95	7	Ex	Ex	Ex	5B	5B	5B
B1	**10%**	25	25	42	77	96	10	Ex	Ex	Ex	5B	5B	4B
T11		40	25	43	79	90	5	Ex	Ex	Ex	4B	5B	5B
T12		40	25	75	81	88	7	Ex	Ex	Ex	5B	5B	5B
T13		25	25	48	82	84	21	Ex	Ex	Ex	5B	5B	4B
T14		25	30	75	90	70	42	Ex	Ex	Ex	5B	5B	5B
B2	**20%**	35	30	61	83	98	4	Ex	Ex	Ex at 5 mm	5B	5B	5B
T21		50	50	60	79	95	6	Ex	Ex	Ex	2B	5B	5B
T22		70	50	65	83	67	24	Ex	Ex	Ex	5B	5B	5B
T23		55	50	50	81	89	10	Ex	Ex	Ex	2B	5B	5B
T24		60	40	50	93	89	25	Ex	Ex	Ex	5B	5B	4B
B3	**30%**	35	20	56	96	99	11	Ex	Ex	Ex	0B	5B	5B
T31		40	45	63	89	97	9	Ex	Ex	Ex	0B	5B	5B
T32		45	30	70	92	89	35	Ex	Ex	Ex at 10 mm	0B	5B	4B
T33		35	25	60	84	76	27	Ex	Ex	Ex	0B	5B	4B
T34		30	21	70	84	92	15	Ex	Ex	Ex	0B	5B	2B

Ex: Excellent

0B : Removed area is greater than 65% , 1B : 35 – 65% removed area, 2B : 15 – 35% removed area, 3B : 5 - 15% removed area, 4B : Less than 5%, 5B: 0% removed area

Table (19): Primer and Varnish Characteristic of Various HETCA-modified Alkyd Resins

Resin Code	Excess-OH %	Impact (1 Kg) Excellent at (cm)			Scratch Hardness (Pencil Hardness)		
		A	S	P	A	S	P
B0	**0%**	100	100	100	2B	8H	9H
T01		100	100	100	B	6H	9H
T02		100	100	100	5B	3H	9H
T03		100	100	100	6B	4H	8H
T04		100	100	100	6B	6H	3B
B1	**10%**	100	100	100	2B	6H	4H
T11		100	100	100	2B	8H	9H
T12		100	100	100	2B	6H	6H
T13		100	100	100	2B	6H	5H
T14		100	100	100	5B	6H	4H
B2	**20%**	100	100	100	3B	7H	9H
T21		90	100	100	2B	HB	9H
T22		60	100	100	2B	HB	3B
T23		100	100	100	2B	HB	5H
T24		90	100	100	2B	HB	4H
B3	**30%**	90	100	100	7H	9H	7H
T31		55	100	100	7H	2H	6H
T32		90	100	100	5H	2H	6H
T33		80	100	100	H	F	3H
T34		75	100	100	H	F	3H

6B<5B<4B<3B<2B<B<HB<F<H<2H<3H<4H<5H<6H<7H<8H<9H

Softer → Harder

Table (20) Impact and Pencil hardness of HETCA-modified alkyd resin

Resin Code	Excess-OH %	Film Thickness (μ)			Gloss at 60°			Flexibility at 3 mm			Adhesion		
		A	S	P	A	S	P	A	S	P	A	S	P
B0	**0%**	42	27	75	76	100	4	Ex	Ex	Ex	5B	5B	5B
F01		35	25	66	79	80	14	Ex	Ex	Ex	5B	5B	5B
F02		40	30	40	79	92	9	Ex	Ex	Ex	5B	5B	5B
F03		35	25	39	75	91	14	Ex	Ex	Ex	5B	5B	4B
F04		30	20	50	79	80	6	Ex	Ex	Ex	5B	5B	4B
B1	**10%**	25	25	77	77	96	10	Ex	Ex	Ex	5B	5B	4B
F11		45	35	40	77	73	13	Ex	Ex	Ex	5B	5B	5B
F12		50	40	34	77	75	6	Ex	Ex	Ex	5B	5B	4B
F13		40	35	66	79	84	7	Ex	Ex	Ex	5B	5B	5B
F14		40	45	60	76	91	9	Ex	Ex	Ex	5B	5B	4B
B2	**20%**	35	30	61	83	98	4	Ex	Ex	Ex	5B	5B	5B
F21		65	50	44	82	72	12	Ex	Ex	Ex	0B	5B	5B
F22		45	62	60	77	87	7	Ex	Ex	Ex	0B	5B	5B
F23		30	50	90	80	71	10	Ex	Ex	Ex	2B	5B	5B
F24		70	26	70	82	79	11	Ex	Ex	Ex	0B	5B	5B
B3	**30%**	35	20	56	96	99	11	Ex	Ex	Ex	0B	5B	5B
F31		30	20	75	91	66	6	Ex	Ex	Ex	0B	5B	5B
F32		43	30	70	86	66	7	Ex	Ex	Ex	0B	5B	5B
F33		25	27	100	84	36	6	Ex	Ex	Ex	0B	5B	4B
F34		15	13	56	77	77	3	Ex	Ex	Ex	2B	5B	5B

Ex: Excellent 0B : Removed area is greater than 65% , 1B : 35 – 65% removed area, 2B : 15 – 35% removed area, 3B : 5 - 15% removed area, 4B : Less than 5%, 5B: 0% removed area

Table (21): Primer and Varnish Characteristic of Various HEFCA-modified Alkyd Resins

Resin Code	Excess-OH %	Impact (1 Kg) Excellent at (cm)			Scratch Hardness (Pencil Hardness)		
		A	S	P	A	S	P
B0	**0%**	100	100	100	2B	8H	9H
F01		100	100	100	B	6H	9H
F02		100	100	100	2B	7H	4H
F03		100	100	100	4B	7H	2B
F04		100	100	100	5B	7H	F
B1	**10%**	100	100	100	2B	6H	4H
F11		100	100	100	F	7H	6H
F12		100	100	100	B	3H	4H
F13		100	100	100	B	3H	9H
F14		100	100	100	4B	2H	6H
B2	**20%**	100	100	100	3B	7H	9H
F21		100	100	100	HB	6H	3H
F22		100	100	100	HB	6H	2H
F23		100	100	100	H	6H	2H
F24		100	100	100	H	5H	9H
B3	**30%**	90	100	100	7H	9H	7H
F31		35	100	100	6H	6H	6H
F32		40	100	100	6H	4H	6H
F33		70	100	100	6H	3H	7H
F34		80	100	100	H	3H	5H

6B<5B<4B<3B<2B<B<HB<F<H<2H<3H<4H<5H<6H<7H<8H<9H

Softer ⟶ Harder

Table (22) Impact and Pencil hardness of HEFCA-modified alkyd resins

The evaluation the corrosion resistance of prepared modified alkyd resins and corrosion inhibitors are carried out by dipping in 5% NaCL solution for 240 hours. The results are shown in the following tables:

Table (23)
Evaluation the corrosion resistance of modified alkyd resins

Resin Code	Blistering		Resin Code	Blistering	
	Size	Frequency		Size	Frequency
B0	10	F	**B0**	10	F
T01	10	F	**F01**	10	F
T02	10	F	**F02**	10	F
T03	10	F	**F03**	10	F
T04	10	F	**F04**	10	F
B1	10	F	**B1**	10	F
T11	10	F	**F11**	10	F
T12	10	F	**F12**	10	F
T13	10	F	**F13**	10	F
T14	10	F	**F14**	10	F
B2	10	F	**B2**	10	F
T21	10	F	**F21**	10	F
T22	10	F	**F22**	10	F
T23	10	F	**F23**	10	F
T24	10	F	**F24**	9	F
B3	10	F	**B3**	10	F
T31	10	F	**F31**	10	F
T32	10	F	**F32**	10	F
T33	10	F	**F33**	10	F
T34	10	F	**F34**	10	F

Table (24): Evaluation of prepared corrosion inhibitors morpholino(thiophen-2-yl)methanone II and morpholino(furan-2-yl)methanone IV with standard commercial alkyd resin

Resin Code	Blistering		Resin Code	Blistering	
	Size	Frequency		Size	Frequency
ST	10	F	**ST**	10	F
ST+ 0.5% II	10	F	**ST+ 0.5% IV**	10	F
ST+ 1% II	10	F	**ST+ 1% IV**	10	F
ST+ 3% II	10	F	**ST+ 2% IV**	10	F
ST+ 5% II	10	F	**ST+ 3% IV**	10	F

Table (25): Evaluation of prepared corrosion inhibitors morpholino(thiophen-2-yl)methanone " II " and morpholino(furan-2-yl)methanone " IV " with some prepared modified alkyd resin (synergism)

Resin Code	Blistering		Resin Code	Blistering	
	Size	Frequency		Size	Frequency
T32	10	F	**F32**	10	F
T32+ 0.5% II	10	F	**F32+ 0.5% IV**	10	F
T32+ 1% II	10	F	**F32+ 1% IV**	7	M
T32+ 3% II	10	F	**F32+ 2% IV**	10	F
T32+ 5% II	10	F	**F32+ 3% IV**	5	MD

10 : means no blistering (the best) 0: the worst blistering degree
F: few M: medium MD: medium dense

The following photos of tested films after 240 hours in 5% NaCL solution are shown below:

Fig. (9): ZnPO4 primer with HETCA-modified alkyd resins resins

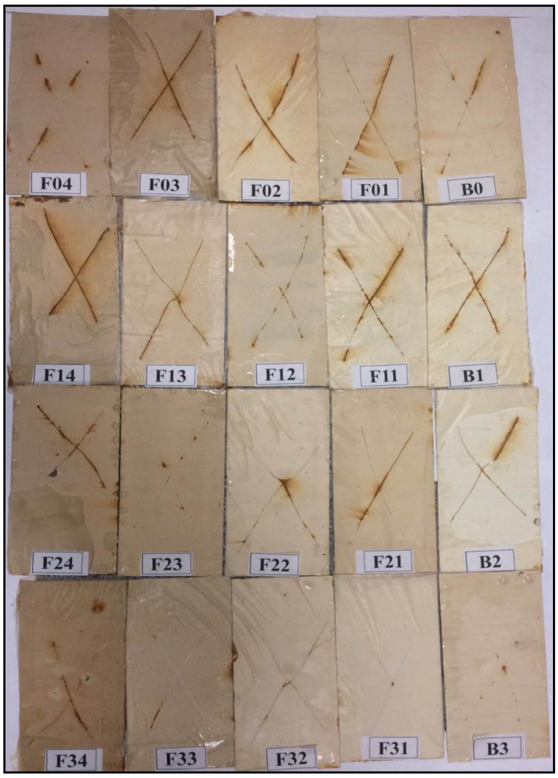


Fig. (10): ZnPO4 primer with HEFCA-modified alkyd

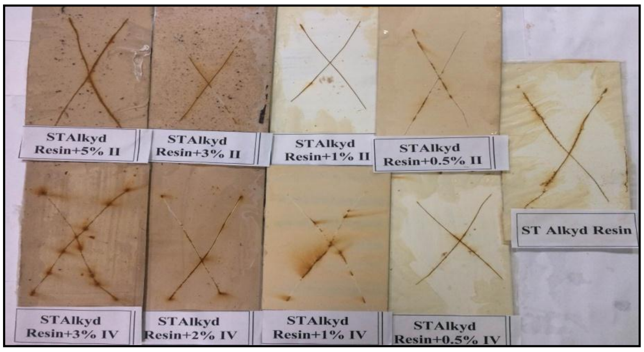


Fig. (11): ZnPO4 primer with standard commercial alkyd resins with prepared corrosion inhibitors II & IV.

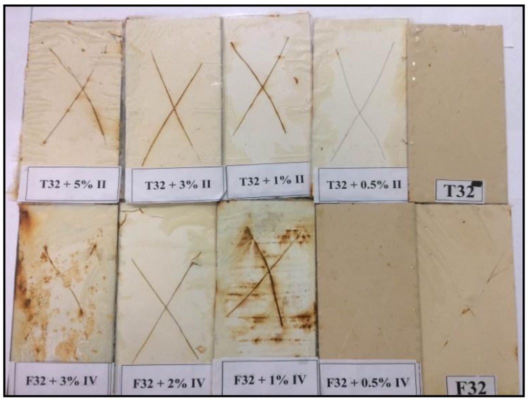


Fig. (12): ZnPO4 primer with T32 and F32 alkyd resins and prepared corrosion inhibitors II and IV.

0B : Removed area is greater than 65% , 1B : 35 – 65% removed area, 2B : 15 – 35% removed area, 3B : 5 - 15% removed area,

The corrosion resistance increases by the increase of excess-OH percent of both modified and unmodified alkyd resins.

There is a certain modification percent of alkyd resins at which such alkyd resin achieves maximum corrosion resistance, and this optimum modification decreases by increasing excess-OH % of alkyd resin.

For example:

At 0% excess-OH alkyd resins (their Blank sample is B0) the maximum corrosion resistance achieves at 20- 30% modification (i.e. T03 and F04)

At 10% excess-OH alkyd resins (their Blank sample is B01) the maximum corrosion resistance achieves at 5- 20% modification (i.e. T11 and F12)

At 20% excess-OH alkyd resins (their Blank sample is B02) the maximum corrosion resistance achieves at 5- 20% modification (i.e. T23 and F23)

At 10% excess-OH alkyd resins (their Blank sample is B01) the maximum corrosion resistance achieves at 5- 10% modification (i.e. T32 and F31)

In other words, for achieving the maximum corrosion resistance of alkyd resins, the need for modification will decrease by increasing excess-OH percent.

The addition of prepared compounds II and IV achieves corrosion resistance effect and the optimum dosage of the addition will be as follow:

1- Morpholino(thiophen-2-yl)methanone II is 1% on total formula weight

2- Morpholino(furan-2-yl)methanone IV is 0.5% on total formula weight

The addition of prepared corrosion inhibitors II and IV on some modified alkyd resins such as T32 and F32, respectively, improves their corrosion resistance and gives additional protection (SYNERGISM) for the metal substrate at a certain dosage 0.5% on total formula weight .

Conclusions

The following observations were noticed during the investigation:

1- All resins prepared are very clear and transparent and homogenous

2- The color of modified alkyd resins is very dark due to the entering of nitrogen atom in their chains.

3- The reaction rate for various resins increases by the increasing of the percentage of modifier and also increases with the increase of excess-OH percentage.

4- The viscosity for various resins at constant solid content increases slightly by the increasing of the percentage of modifier, but increases dramatically with the increase of excess-OH percentage.

5- The drying time increases by increasing the modifier percentage and by decreasing excess-OH percent of alkyd resins. There are some difficulties in the drying of lower excess-OH % alkyd resins , and also, in higher modified alkyd resins due to the presence of Soya bean fatty acids in their structure.

6- All dried films are excellent water, acid, solvent resistance

7- Only the higher excess-OH percent alkyd resins are good alkali resistant.

8- The HETCA- and HEFCA-modification increases the alkali resistance of alkyd resins.

9- All films passed the adhesion and flexibility test except the higher modified alkyd resins in adhesion tests.

10-The HETCA and HEFCA modification increases the corrosion resistance performance of alkyd resins at certain optimum values.

11- The prepared Morpholino(thiophen-2-yl) methanone II and Morpholino(furan-2-yl)methanone IV are corrosion inhibitors additives and they can improve the corrosion resistance of HETCA- and HEFCA- modified alkyd resins.

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