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## **UTILIZATION OF THE EGYPTIAN BENTONITE ORE BASED ON NEW MODIFIED ALKYDS IN ANTICORROSIVE COATING FORMULATIONS**

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### **Abstract**

New modified alkyd resin compositions containing Egyptian bentonite ore (high grades) are evaluated as anticorrosive coating compositions for steel protection. The results indicated substantial corrosion inhibiting properties.

### **Keywords:**

Bentonite ore, Steel protection, Alkyd resin, Corrosion inhibiting, Anticorrosive paint.

### **Introduction**

The main function of coating on metal surface is to protect it from corrosion. Many additives including pigments and binders are used as corrosion inhibitors in protective coatings (1). The effect of organic compounds containing nitrogen and sulphur on the corrosion behavior of iron and steel has been well documented and showed to be quite efficient to prevent corrosion(2,3). Polyaniline, polyaminophenol and polyaminothiophenol, polyesteramide and acrylic modified alkyd are also evaluated as corrosion inhibitors (4-6). The aim of the present work is to evaluate a new anticorrosive coating compositions based on modified alkyd and Egyptian bentonite ore. The characterization study included the oil absorption, density, color, mineralogical and chemical composition, crystal morphology, surface area and porosity. The effect of heat treatment and acid activation on the surface area were also studied (7). The anticorrosive modified alkyd resins were prepared by partial replacement of polyols used in manufacture of resin by N, bis 2-hydroxyethyl 4-aminobenzamide. This coating composition and the bentonite ore (high grades,) which replaced titanium dioxide pigments in the formulation would expect to have good anticorrosive properties.

### **Experimental**

All solvents and chemical used through the whole investigation were at least of chemically pure grade, except where mentioned. The bentonite ore (oil absorption 28, specific gravity 2.6gal/lb, refractive index 1.56, particle size 15  $\mu$ ) was obtained from Cairo-Ismailia desert road "Gabal Hamza area" Egypt.

**Methods of preparations:****A) Preparation of N,bis 2-hydroxyethyl 4-aminobenzamide ( HEABA).**

A mixture of 4-amino benzoic acid (0.1 mole) and of freshly distilled diethanolamine (0.1 mole) was refluxed in presence of xylene solvent using Dean and Stark trap until 1.8 ml of water (0.1 mole) was approximately collected, A clear pale brown viscous material was obtained.

**Table (1) resin characteristic constant of various HEABA-modified alkyd resins**

Resin No.	Ingredients	$e_o$	$e_A$	$e_B$	E	F	$w = E/e_o$	$m_o = e_o/F$	$R = e_B/e_A$	$K = m_o/e_A$	H <sub>2</sub> O off (ml)
I <sub>a</sub>	G	0.260	-	0.260	30.7	3	7.98	0.087	1	1.05	
	HEABA	-	-	-	-	-	-	-			
	LOFA	0.111	0.111	-	280	1	31.08	0.111			2
	PA	0.149	0.149	-	74.1	2	11.04	0.075			1.34
			0.260	0.260			50.1	0.273			3.34
I <sub>b</sub>	G(0.90)	0.234	-	0.234	30.7	3	7.18	0.078	1	1.065	
	HEABA(0.10)	0.026	-	0.026	112	2	2.91	0.013			
	LOFA	0.111	0.111		280	1	31.08	0.111			2
	PA	0.149	0.149		74.1	2	11.04	0.075			1.34
			0.260	0.260			52.21	0.277			3.34
I <sub>c</sub>	G(0.80)	0.208	-	0.208	30.7	3	6.39	0.069	1	1.081	
	HEABA(0.20)	0.052	-	0.052	112	2	5.82	0.026			
	LOFA	0.111	0.111	-	280	1	31.08	0.111			2
	PA	0.149	0.149	-	74.1	2	11.04	0.075			1.34
			0.260	0.260			54.33	0.281			3.34
I <sub>d</sub>	G(0.70)	0.182	-	0.182	30.7	3	5.59	0.061	1	1.10	
	HEABA(0.30)	0.078	-	0.078	112	2	8.73	0.039			
	LOFA	0.111	0.111	-	280	1	31.08	0.111			2
	PA	0.149	0.149	-	74.1	2	11.04	0.075			1.34
			0.260	0.260			56.44	0.286			3.34
I <sub>e</sub>	G(0.60)	0.156	-	0.156	30.7	3	4.79	0.052	1	1.115	
	HEABA(0.40)	0.104	-	0.104	112	2	11.64	0.052			
	LOFA	0.111	0.111		280	1	31.08	0.111			2
	PA	0.149	0.149		74.1	2	11.04	0.075			1.34
			0.260	0.260			58.55	0.290			3.34

$e_o$  :Total equivalents present at the start of the reaction,  $e_A$  : Number of acid equivalents,  $e_B$  :Number of hydroxyl equivalents, E : Equivalent weight, F : Functionality, W : Weight,  $m_o$ : Total moles present at the start of the reaction, R : Ratio of total -OH groups to total -COOH group and K :Alkyd constant ( $m_o/e_A$ ).

**B) Preparation of HEABA- modified alkyd resins.**

A mixture of linseed oil fatty acid (LOFA), phthalic anhydride (PA), anhydrous glycerol (G), and / or N,bis 2-hydroxyethyl 4-aminobenzamide (modifier) were refluxed in presence of 10% xylene by using Dean and Stark apparatus. The course of the esterification was followed by observing the amount of water liberated versus the time of the reaction. The various resin characteristics are tabulated in table (1).

**Methods of evaluation:**

Methods of testing and evaluation were performed according to standard methods, including, acid value [8], hydroxyl value [9], solid content [10], preparation of test panels [11], drying time [12], viscosity [13], color [14], The pencil hardness [15], film thickness [16], adhesion [17], gloss [18], flexibility [19], chemical resistance [20-23], and corrosion resistance [24-28].

**Results and Discussion**

New modified alkyd resins were prepared through chemical modification with N, bis 2-hydroxyethyl 4-aminobenzamide, such modification showed better film performances and leads to the formation of corrosion inhibiting varnish. The modifier N, bis 2-hydroxyethyl 4-aminobenzamide, was prepared by the reaction of 4-amino benzoic acid (0.1 mole) and (0.1 mole) diethanolamine using Dean and Stark trap The structure of the modifier was elucidated on the following basis:

1- Acid Value: 8 mg. KOH/gm (Theo. Zero mg. KOH/gm)

2- Hydroxyl Value. 408 mg. KOH/gm (Theo. 412 mg. KOH/gm)

3- The IR spectrum (Fig.1) showed the following absorption bands:

3402  $\text{cm}^{-1}$  (OH), 3950  $\text{cm}^{-1}$  (C-H aromatic), 2250-2685  $\text{cm}^{-1}$  (CH aliphatic) and 1659, 1721  $\text{cm}^{-1}$  ( C=O) and 1586  $\text{cm}^{-1}$  ( C=N)

4- HNMR spectrum (Fig. 2) was measured in DMSO -d6 and showed signals at  $\delta =$  2.6 ppm (t, 4H, 2CH<sub>2</sub>-N), 3.5 (t, 4H, 2CH<sub>2</sub>-OH), 4.8(hump, 2H, 2OH), and 6.4-7.8 ppm (m, 3H,Ar H).

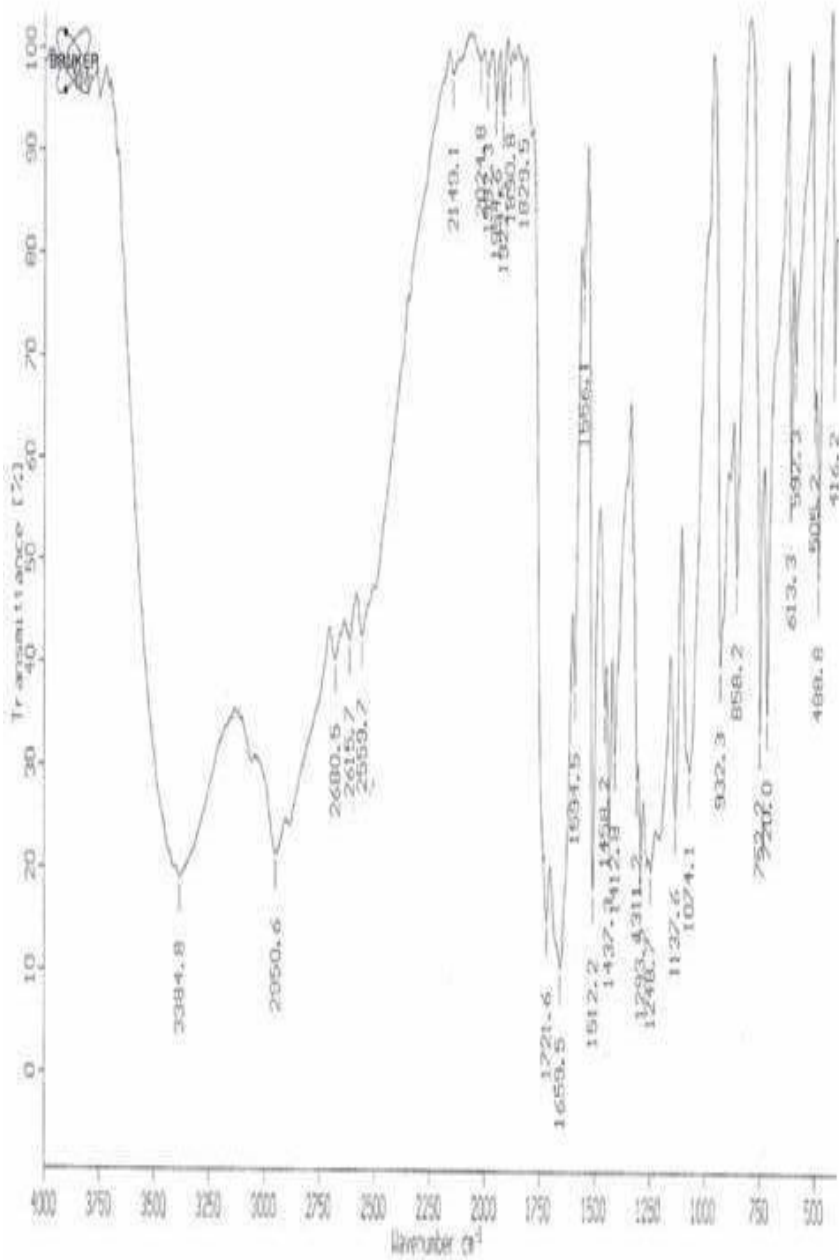


Fig (1): IR Spectra of N,bis(2-hydroxyethyl) 4-aminobenzamide(HEABA) .

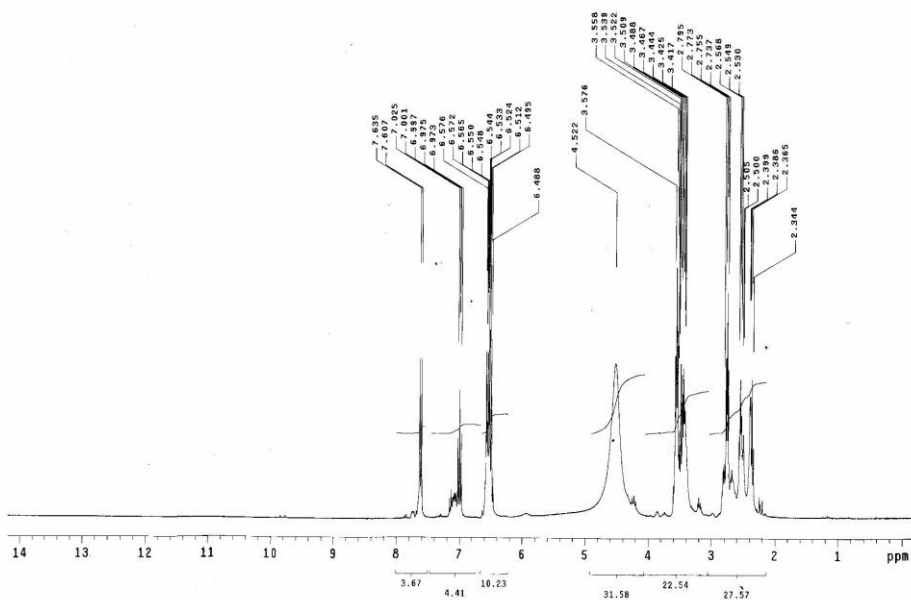


Fig.(2):<sup>1</sup>HNMRSpectraof . N,bis 2-hydroxyethyl 4,aminobenzamide(HEABA).

After the successful preparation of the modifier, various modified alkyds were prepared and evaluate as varnishes. The data obtained are given in table (2).

Table (2): Effect of modifier (HEABA) upon varnishes characteristic.

Resin No.	Excess-OH (%)	Replacement (%) Of HEABA	Viscosity (Gardner)	Color (Gardner)	Air drying time(h)	Stoving at 120 °C	Reaction time(h)
Ia	0	0	E	10	8	HD(90min)	7
Ib		10	F	15	6	HD(60min)	6.30
Ic		20	H	>18	5	HD(50min)	6
Id		30	J	>18	5	HD(40min)	5.30
Ie		40	K	>18	4	HD(30min)	5

From the data recorded in table (2), the following conclusions were drawn:

- 1- All modified and unmodified alkyd compositions showed very clear transparent and homogenous appearance
- 2- Viscosity of varnishes increases through modification
- 3- The color of the modified resins was darker (> 18 Gardner scale) than unmodified alkyd (10 Gardner scale) due to the presence of nitrogenous base
- 4- Increasing the percentage ratio of the modifiers leads to decreasing in the air and stove dry time
- 5- The reaction time decreases with increasing the amount of the modifier (HEABA)

The dry films mechanical and chemical characteristics of various modified resins were carried out according to standard methods and well- known techniques and the results are tabulated in Tables (3-4).

**Table (3): Mechanical Characteristics of Various Modified Alkyd Resins.**

Resin No.	DFT ( $\mu$ )		Gloss at 20 °C		Scratch Hardness(Kg)		Flexibility		Adhesion	
	A	S	A	S	A	S	A	S	A	S
<b>Ia</b>	40	35	90	92	< 1	< 1	Pass	Pass	5B	5B
<b>Ib</b>	43	38	90	94	>1	>1	Pass	Pass	5B	5B
<b>Ic</b>	45	40	93	94	>1	>1.2	Pass	Pass	5B	5B
<b>Id</b>	45	42	93	95	>1	>1.4	Pass	Pass	5B	5B
<b>Ie</b>	43	42	93	95	>1	>1.5	Pass	Pass	5B	5B

DFT: Dry Film Thickness

A: Air dried film

S: Stove dried film

**Table (4): Chemical Characteristics of Various Modified Alkyd Resins.**

Resin No.	Water Resistance (Day)		Acid Resistance * (Day)		Alkali Resistance ** (Day)		Solvent Resistance (Day)	
	A	S	A	S	A	S	A	S
<b>Ia</b>	24	25	15	12	1	1	>30	>30
<b>Ib</b>	26	30	18	20	1	3	>30	>30
<b>Ic</b>	30	30	20	22	3	4	>30	>30
<b>Id</b>	30	30	25	25	3	5	>30	>30
<b>Ie</b>	30	30	25	27	5	8	>30	>30

\* Acid concentration ( $H_2SO_4$ ) 10 % by weight

\*\* Alkali concentration ( $Na_2CO_3$ ) 5% by weight

The main conclusions drawn from the film characteristic data tables (3-4) indicate the following generalizations:

- 1- The modified films showed outstanding performance compared with unmodified films
- 2- Gloss and scratch hardness of varnishes increases through modification with HEABA
- 3- Stove dried films showed better gloss and scratch hardness than air dried films
- 4- All films passed successfully the flexibility and adhesion test
- 5- Stove dried films exhibit better water, acid and alkali resistance compared with air dried films
- 6- Increasing the percentage of the modifier leads to a substantial improvement in the film resistance towards water, acid and alkali
- 7-Modification with HEABA does not effect on solvent resistance since all examined films showed excellent performance within the experimental time (up to 30 days)

#### **Evaluation of HEABA – modified alkyd resin as corrosion inhibitor.**

The work was extended to include the utilization of modified alkyd resin as binder and Egyptian bentonite as an extender in primer formulations, these types of corrosion inhibitors work via decreasing the permeability of coating to water, oxygen and aggressive ions. Five primer formulations based on modified alkyd resin (0, 10, 20, 30 and 40% replacement), containing 20% Egyptian bentonite ore as filler, were prepared and represented in (table 5).

**Table (5) Percent Composition of the Anticorrosive Primer Formulations.**

Composition	Formulation No.				
	1	2	3	4	5
Type of alkyd	Unmodified	10 %HEABA	20 %HEABA	30 %HEABA	40 %HEABA
Alkyd Resin	30	30	30	30	30
TiO <sub>2</sub>	45	25	25	25	25
Bentonite	-	20	20	20	20
Talc	10	10	10	10	10
Solvent	11	11	11	11	11
Additives	4	4	4	4	4

The primers were evaluated on actual coated steel panels by subjecting it to salt spray cabinet for 400 hr. the corrosion was observed via three techniques.

- 1- Determination the degree of blistering (size and frequency).
- 2- Determination the degree of scribe failure.
- 3- Determination the degree of rusting.

The data obtained are listed in table (6) and can be clearly showed in figure (3).

**Table (6) Evaluation of corrosion resistance of painted films**

Formula No.	Modification %	Degree of Rusting *	Blistering **		Scribe *** Failure rating
			Size	Frequency	
1	Unmodified Alkyd Without Bentonite	5	4	MD	5
2	10% Replacement 20% Egyptian Bentonite	6	4	M	7
3	20% Replacement 20% Egyptian Bentonite	7	6	M	8
4	30% Replacement 20% Egyptian Bentonite	9	8	M	8
5	40% Replacement 20% Egyptian Bentonite	9	8	F	9

\* Rusting is rated on scale 10 to 0, where 10 being no rusting and 0 being sever rusting

\*\* Blistering size is graded also from 10 to 0, in which 10 represents no blistering and 0 represents the largest blister. Blistering frequency is denoted by F, M, MD and D (Few, Medium, Medium Dense and Dense)

\*\*\* Scribe failure is also rating on scale from 10 to 0, where 10 being zero (mm) from the scribe mark and 0 is 16 (mm) from the scribe mark.

The main conclusions derived from these data are that, the presence of modifier (HEABA) And Bentonite ore substantially increase the corrosion resistance (formulations 2-5)



**Fig. (3) Salt spay cabinet and samples**



Salt Spray Cabinet



Unmodified



10 % Replacement



20 % Replacement



30 % Replacement



40 % Replacement

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