# Waterborne Methylamine Adduct as Corrosion Inhibitor for Surface Coatings

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**ABSTRACT:** Soybean oil was epoxidized using peracetic acid prepared *in situ* from acetic acid and hydrogen peroxide with Dowex 50 W-8X as a catalyst. The epoxidized soybean oil was allowed to react with methylamine. The resulting adduct was identified and emulsified. The emulsified methylamine adduct was added at different concentrations to an emulsion (styrene/acrylic)-based paint (blank). The effect of the methylamine adduct concentration on the physical, chemical, and mechanical properties of the paint was studied. Various tests such as metal substrate weight loss, corrosion, blister, and scratch resistance were performed to evaluate the efficiency of the prepared adduct. It was found that there is an optimum concentration at which the methylamine adduct is very effective as a corrosion inhibitor. This concentration is about 0.5% by weight. In comparison with chromate anticorrosive pigment, it was found that the methylamine adduct is superior with more economical and environmental advantages. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 286–296, 2001

**Key words:** environmentally friendly paint; waterborne paint; corrosion; methylamine adduct

# **INTRODUCTION**

Volatile organic compounds (VOCs), which include solvents such as acetone, methyl ethyl ketone, and toluene, are released into the atmosphere from various industrial, agricultural, and transportation sources. The negative environmental impact of VOCs includes the destruction of the ozone layer in the upper atmosphere, global warming, and the production of toxic gases due to their reaction with other air pollutants. This can cause damage to crops and pose health hazards to human and animals. According to Gleaves,<sup>1</sup> about 25% of the emitted

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VOCs come from the use of organic solvents and about one-third of this percentage comes from the industrial application of paints. Thus, the use of VOCs as well as anti-corrosive pigments in surface coatings represents a serious environmental concern. In some paint systems, VOCs exist at a minimum of 20% by volume. In addition, anticorrosive pigments, which contain unfriendly heavy metals, can exist at about 25% by volume. Recently, much research has focused on replacing solvent-based paints with water-based paints. The advantages of waterborne paints include being nonpolluting, easy to handle, quick drying, economic, and environmentally friendly.<sup>2</sup> Emulsified corrosion inhibitors can also be used to replace toxic anticorrosive inorganic pigments, to obtain waterborne anticorrosive paints, which further reduce the toxicity of the paints.

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Ingredient	Description/Properties	Source
Soybean oil Hydrogen peroxide Dowex 50W-8X	<ul> <li>I.V. 140, flash point &gt; 310°C</li> <li>30% strength</li> <li>Sulfonated poly(styrene/ divinylbenzene) copolymer, dark yellow, 17% sulfur</li> </ul>	Bakeen Co. (Cairo, Egypt)
Methylamine	Purified by distillation	

Table I Reactants

Amines are effective corrosion inhibitors because of their ability to form protective layers or films on the metallic surfaces. The role of the adsorbed inhibitors is to block the corrosive medium from the metal and/or to alter the electrode reactions that dissolve the metal. Many of them are held to the surface of the metal by electrostatic or van der Waal's forces. In addition, organic amines are held to the metal by chemisorption. Matsen et al.<sup>3</sup> suggested that chemisorption takes place by the formation of a charge-transfer complex. The ground state of the complex is described by a linear combination of the wave functions for a no-bond state and a dative state. In the dative state, an electron has been transferred from an orbital of the inhibitor to the metal. All organic inhibitors can bond to the metal surface in this manner.

Corrosion inhibitors for iron from the reaction of cuba-wax sugar production with mono- and diamines to obtain nitrogen-containing compounds were developed by Ledovskikh et al.<sup>4</sup> They stated that the efficiency of monoamides is better than that of diamides. Fokin et al.<sup>5</sup> investigated the corrosion inhibition of N,N-diethyloctadecaamine, N-ethyloctadecaamine, and N-2,2,2-trifluoroethyl-octadecaamine for steel in synthetic sea water. The compound containing the n-alkyl group of C<sub>18</sub> was found to be a better inhibitor than were the others. They ranked the efficiencies of the corrosion inhibition of the studied compounds in the following order: N-ethyloctadecaamine > N,N-diethyloctadecaamine.

The reaction products of an aliphatic diamine  $\rm RNH(\rm CH_2)_3\rm NH_2$ , where (R = C<sub>8-22</sub>), with 3–25% formaldehyde as a corrosion inhibitor for carbon steel in a 3% NaCl solution were studied by Dalewska et al.<sup>6</sup> The prepared materials were successful in protecting carbon steel up to 95–98% by weight. Ramaki<sup>7</sup> studied the branching and steric effect on corrosion inhibitors for iron in 6.1*M* HCl. They found that the steric effect of the

branched chain or of free amine is directly related to the degree of branching in the alkyl group. This, in turn, lowered the anodic inhibition efficiency, increasing the steric effect in the following order: monoalkylamine < N-ethylalkylamine < N-dimethylalkylamine. Akimov et al.<sup>8</sup> studied the surface charge on iron in a neutral solution containing diethylamine as the corrosion inhibitor. The diethylamine was found to inhibit the anodic dissolution of iron by enhancing the formation of the passive layer of iron oxide. Lar'kin and Behikh<sup>9</sup> studied the influence of the chain length of amine on the corrosion of iron. They found that the interchange of iron and nitrogen increased by increasing the chain length. Badran et al.<sup>10</sup> and El-Sawy et al.<sup>11</sup> replaced toxic organic anticorrosive pigments by the reaction product of the epoxydized linseed oil free fatty acids with four aliphatic amines (methylamine, ethylamine, *n*-propylamine, and butylamine) as corrosion inhibitors for carbon steel. They found that the optimum concentration range of the methyl adduct and butyl adducts as corrosion inhibitors are similar and equal to 0.4-0.7%.

In the present research, a waterborne methylamine corrosion inhibitor was prepared and its performance was evaluated in different emulsion paint formulations to produce environmentally friendly anticorrosive paints. The mechanism by which the methylamine adduct prevented or retarded the corrosion of steel surfaces was also investigated. Comparison between the formulated paints and commercially available anticorrosive paints was made.

#### **EXPERIMENTAL**

#### Materials

The materials used in this research are listed in Tables I–III.

Ingredient	Description/Properties	Source
Talc		General Co. for Trading and Chem. (Cairo, Egypt)
Titanium dioxide, R-902	$91\%~{\rm TiO_2},2\%~{\rm SO_2}$ and $4.5\%~{\rm AlO}$	DuPont Co. (Wilmington, DE, USA)
Disperse-Ayd W-30	Dispersing agent, aqueous	Daniel Products (Jersey City, NJ, USA)
Sodium polyphosphate	Wetting agent	Heliopolis Co. for Chemical Industries (Cairo, Egypt)
Ethylene glycol	Coalescing agent	Heliopolis Co. for Chemical Industries (Cairo, Egypt)
Torysol LAC	Leveling agent	Troy Chemical Co. (Burton, OH, USA)
Ethanolamine	PH stabilizer, pH 8-9	
Polyol DF 3163	Antifoaming agent	Daniel Products Co. (Jersey City, NJ, USA)
Urethane-based thickener	Thickener and rheology modifier for aqueous paints	Allied Colloids Co. (Cairo, Egypt)
Acticide SPX	Biocide	Thor Chemical Co. (Trumball, CT, USA)
Water	Distilled	
Lead chromate	Orange, density 4.1, oil absorption 15	Samoral Trading (Cairo, Egypt)

#### Table II Emulsion Paint Ingredients

#### Preparation of Adducts, Paints, and Test Samples

# Preparation of Epoxidized Soybean Oil and Methylamine Adduct

Soybean oil was epoxidized *in situ* by hydrogen peroxide and acetic acid using Dowex 50 W-8X as a catalyst.<sup>12</sup> The oxirane oxygen content of the epoxidized oil was measured by Durbetaki's<sup>13</sup> and Badran's<sup>14</sup> techniques. The reaction of the epoxidized soybean oil and methylamine was carried out in sealed ampules under an inert atmosphere at 130–140°C for 3–4 h. The amine was added to the epoxidized soybean oil by a molar ratio of 4:1 according to the oxirane oxygen content.

# **Preparation of Emulsion Paint Formulations**

Emulsion paint formulations were prepared in two stages: The first stage was high-speed stirring of the filler, pigment, dispersing agent, and water. The second stage was low-speed stirring of the emulsion polymer, water, leveling agent, antifoaming agent, thickener, and biocide with the mixture from the first stage. The emulsified inhibitor was added before the second stage. The pH of the medium was adjusted to 8-9 using ethanolamine.<sup>15</sup>

# Sample Preparation and Paint Application

Carbon steel with a nominal thickness of 1 mm was used as the substrate in the corrosion tests. Samples of dimensions of  $3 \times 3$  cm were machined for weight-loss tests and of  $5 \times 7$  cm were machined for the corrosion resistance, blister, and corrosion scratch tests. Tin plates were used as a substrate for the bending test, and glass plates were used for the adhesion and hardness tests.

Table III	Emulsion	<b>Polymers</b>	Used in	Emulsion	<b>Paint Formulations</b>	
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Ingredient	Description/Properties	Source
Styrene/acrylic copolymer Dibutylphthalate	Emulsion Plastisizer used with the styrene/acrylic copolymer,	DMS Resins (Netherlands) Daniel Products Co. (USA)

Property	Test Method	Property	Test Method		
Viscosity	ASTM 562	Synthetic sea water	Ref. 16		
Drying time	Ref. 17	Corrosion resistance	ASTM D 1653		
Dry film hardness	ASTM D3363	Corrosion scratch	Ref. 18		
Dry film thickness	Ref. 19	Blistering test	<b>ASTM 714</b>		
Surface preparation	ASTM D 1653	Alkali resistance	ASTM D 1647		
Ductility	DIN 50 101	Acid resistance	<b>ASTM B 287</b>		
Bending	ASTM 1737	Water uptake	Ref. 20		
Dry film adhesion	ASTM 3359	Weight loss	Ref. 21		

#### Table IV Test Methods

All the substrates were prepared according to ASTM D 1653. Paints were applied to the substrate and all tests were performed after 7 days to ensure that the paints were completely dry.

#### **Testing and Evaluation**

The formulated emulsion paints were tested and evaluated according to standards listed in Table IV.

#### **RESULTS AND DISCUSSION**

#### **Characterization of the Prepared Adduct**

Soybean oil was epoxidized using peracetic acid prepared *in situ* from acetic acid and hydrogen peroxide with Dowex 50 W-8X as a catalyst. This is explained in eqs. (1) and (2):

$$CH_3COOH + H_2O_2 \rightarrow CH_3COOOH + H_2O$$
 (1)

$$-CH = CH + CH_{3}COOOH \rightarrow$$
$$-HC - CH + CH_{3}COOH (2)$$
$$\swarrow$$

The oxirane oxygen content of the epoxidized materials was measured by titration against HBr in acetic acid and it was found to be 6.5%. Theoretically, the oxirane content falls in the range 9.6-10%, meaning that more than 65% of the ethylenic groups were converted to epoxy groups. The remaining 35% were either converted to acetoxy hydroxy compounds, due to the cleavage of some epoxy groups by acetic acid during the epoxidation reaction, or were still unreacted as described in eq. (3):

$$-HC--CH- + CH_{3}COOH \rightarrow$$

$$-HC--CH-$$

$$| | (3)$$

$$HO = OCOCH_{3}$$

The IR spectrum of epoxidized soybean oil is given in Figure 1. It shows a very characteristic band of the epoxy group, which appears at 750– 880 cm<sup>-1</sup>. The ester group exhibits two bands: a strong band at 1740 cm<sup>-1</sup> due to the C=O group and a broad band at 1100–1200 cm<sup>-1</sup> due to the C=O group. There also is a strong band at 2855 cm<sup>-1</sup> due to aliphatic C-H attached to the ester group.

The epoxidized soybean oil was allowed to react with methylamine in sealed ampules under an inert atmosphere at 130–140°C for 3–4 h:

$$\begin{array}{c|c} -HC-CH-+RNH_2 \rightarrow -HC-CH-\\ & & | & |\\ O & HO & NH \\ & & |\\ R \end{array}$$
(4)

where  $R = -CH_3$ .

The prepared methylamine adduct was dark yellow and freely soluble in benzene, toluene, xylene, and acetone, that is, it was not crosslinked. IR spectroscopy was used on the reaction products to determine the results of the reaction [Fig. (2)].

It was found that the characteristic bands of the starting compounds [i.e., the epoxy band at  $750-880 \text{ cm}^{-1}$  and the primary amine bands at  $3300-3500 \text{ cm}^{-1}$  (two bands)] disappeared, and a broad band at  $3600 \text{ cm}^{-1}$  due to the free O—H group and secondary amine band at 3300-3500



Figure 1 IR chart of epoxidized soybean oil.

 $\rm cm^{-1}$  (one band) appeared. These bands are very characteristic of the methylamine adduct which was formed. Thus, all the epoxy groups were consumed and the reaction stopped at the secondary amine formation. The reaction products of epoxidized soybean oil with methylamine were emulsified and added to different emulsion paint formulations to study their effect as a corrosion inhibitor for carbon steel.

#### Performance of the Adduct in Water-based Paints

The basic ingredients given in Table V form the base paint or the blank. It does not contain any of the prepared inhibitors or any type of anticorrosive pigments. Titanium dioxide and talc were used as an inert pigment and extender, respectively. The binder used was a styrene/acrylic emulsion copolymer. The pigment/binder ratio was 1.31. The solid content of the blank was 57.9%. For comparison, one formulation utilizing lead chromate instead of titanium dioxide was tested.

# Effect of Methylamine Adduct Concentrations on the Corrosion Inhibition

A series of experiments was carried out using different concentrations of the emulsified methyl-

amine adduct in paint formulations based on a styrene/acrylic emulsion copolymer to determine the optimum concentration. A fixed weight of paint (100 g) was used and the weight of the methylamine adduct was varied from 0.1 to 1 g at 0.1-g increments. Thus, the concentration is defined as the weight of adduct per 100 g of paint.

The results related to the effect of adduct concentration are discussed through three main performance-related criteria. The first criteria deals with qualitative and quantitative physical, chemical, mechanical, and corrosion properties. The second and third criteria are related to the water uptake of the paint film and the weight loss of the steel-coated samples during synthetic sea water immersion.

# *Physical, Chemical, Mechanical, and Corrosion Tests Results*

The physical, chemical, and mechanical properties and corrosion tests of the emulsion paints are given in Table VI. It can be seen from Table VI that the viscosity of the emulsion paint formulations decreases slightly with increase in the concentration of the methylamine adduct. This also caused a slight decrease in the hardness of the paint films and led to a slight increase in ductil-



Figure 2 IR chart of methylamine adduct.

ity. All paint formulations possessed high adhesion. All emulsion paint formulations were able to pass the tests of bending over a small-diameter (0.9 mm) mandrel. The prepared films passed acid- and alkali-resistance tests. Also, it was clear that the metal surfaces coated by the blank paint were highly tarnished, while the others with the methylamine adduct between 0.4 and 0.7 g/100 g kept their bright appearances. At the same concentrations, corrosion was found only in the scratch with good adhesion. Some loss of adhesion of the paint films to the metal surface was noticed at higher (more than 0.7 g/100 g) methylamine adduct concentration. Thus, the obtained results

High-speed I	Mixing	Low-speed mixing			
Composition	Weight (g)	Composition	Weight (g)		
Water	10.0	Styrene/acrylic	22.09		
Wetting agent	0.2	Plasticizer (DBP)	1.0		
Dispersing agent	0.3	Turpentine	1.2		
Etylene glycol	2.0	Leveling agent	0.6		
TiO <sub>2</sub>	16.0	Methyl inhibitor (g)	_		
Lead chromate	_	Ethanolamine	1.0		
Talc	13.0	Water	31.11		
Total pigment	29.0	Defoamer	0.5		
Defoamer	0.2	Thickener	0.5		
Pigment: binder	1.31	Biocide	0.3		

Table V Blank Formulation Based on Styrene/Acrylic Emulsion Copolymer

 $^{\rm a}$  The actual added weight of styrene/acrylic was 47 g, where its solid content was 47%, while 22.09 represents the 100% solid mass of styrene/acrylic copolymer.

	Adduct Weight (g/100 g paint)										
Test	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Viscosity											
KU	83.1	83.1	83.0	82.6	82.3	82.2	81.1	81.0	80.5	80.0	79.0
cP	820	820	819	815	812	811	801	800	792	791	780
Adhesion <sup>a</sup>	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness <sup>b</sup>	$2\mathrm{H}$	2H	2H	2H	2H	Н	Η	Н	Н	Н	HB
Ductility	6.5	6.6	6.6	6.7	6.8	6.9	6.9	6.9	7.0	7.0	7.1
Bending (0.9 mm)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Alkali/acid resistance	V.g.	V.g.	V.g.	V.g.	V.g.	V.g.	V.g.	V.g.	V.g.	V.g.	V.g.
Corrosion resistance <sup>c</sup>	h.t.	s.t.	v.s.t	v.s.t	b.	b.	b.	b.	v.s.t	s.t.	m.t.
Degree of blistering <sup>d</sup>	4D	6F	8F	10	10	10	10	10	8F	8F	6F
Corrosion scratch tests <sup>e</sup>	F	С	В	В	А	А	А	А	В	D	$\mathbf{E}$
Water uptake all over the immersion period											
(35 days)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table VIEffect of Methylamine Adduct Concentration on the Physical, Chemical, and MechanicalProperties and Corrosion Resistance of Styrene/Acrylic Emulsion Paint

<sup>a</sup> The adhesion of dry film decreases in descending order: Gt0 > Gt1 > Gt2 > Gt3 > Gt4.

<sup>b</sup> Lead pencils supplied with the unit, softest to hardest, are as follows: 6B, 5B, 4B, 3B, 2B,B, HB, H, 2H, 3H, 4H, 5H, 6H.

<sup>c</sup> b.: Bright surface; v.s.t.: very slight tarnishing; s.t: slight tarnishing; m.t.: medium tarnishing; h.t.: high tarnishing; h.t.p.: high tarnishing and pitting.

<sup>d</sup> It is graded on a scale from 10 to 0, where 10 is no blistering and 0 is the largest blister and the frequency is denoted by F, M, MD, and D (few, medium, medium dense, and dense).

 $^{\rm e}$  A–E: corrosion just in the scratch but differ in the adhesion of the film around the scratch; A: the best adhesion; F: bad adhesion; and F<sup>0</sup>: bad adhesion with pitting corrosion.

reveal that 0.4-0.7 g of the methylamine adduct/ 100 g paint gave the best corrosion protection to carbon steel based on the qualitative tests performed. It can also be seen from Table VI that the water uptake of all formulations was zero for up to 35 days immersion in distilled water.

#### Weight Loss Results

The weight loss of carbon steel panels, up to 60 days, coated with the laboratory-prepared emulsion paints are shown in Figure 3 for different methylamine concentrations. An interesting trend emerges in Figure 3. All curves, except the 10 days' immersion, exhibit a minimum weight loss at about 0.5 g of the methylamine adduct concentration. The effectiveness of methylamine is pronounced at higher immersion times. At shorter immersion times, however, the concentration of methylamine has little effect on the weight loss.

The relationship between the weight loss and time for the formulation with optimum concentration (0.5 g/100 g) together with the blank formulation is shown in Figure 4. It can be seen from Figure 4 that the rate of weight loss of the steel

panels coated with the methylamine adduct paint is about half that of the blank paint. After 60 days' immersion in synthetic sea water, the rate



**Figure 3** Effect of methylamine adduct concentration on the weight loss of steel panels coated with styrene/ acrylic emulsion paint.



**Figure 4** Comparison between the weight-loss rate of coated steel panel for the blank and the methylamine adduct paint.

of weight loss of steel panels coated with the blank paint is about twice higher than that of the methylamine adduct paint.

As seen in Figure 3, the weight loss decreases gradually by adding the methylamine adduct in small increments up to 0.5 g of per 100 g of the emulsion paint. Above that concentration, the weight loss starts to increase again. At the optimum concentration of 0.5/100 g, the adduct appears to have formed an adsorbed monolayer film on the metal surface. The adduct molecules can be adsorbed on the metal surface via the lone pair of electrons of the nitrogen atom of the amino groups and the oxygen atom of the hydroxyl groups. This can lead to the improvement of the adhesion of the paint films. Moreover, the hydrocarbon tails of the oil, which is originally hydrophobic in nature, could orient themselves away from the metal interface toward the bulk of the paint film.<sup>22,23</sup> Thus, further protection is provided by the formation of an originally hydrophobic network, which excludes water and aggressive ions from the metal surface. The proposed mechanism of the corrosion inhibitor is illustrated in Figure 5.

The addition of the prepared adduct in concentrations higher than the optimum amount may lead to random distribution of the excess amount in the bulk of the emulsion paint film. The unarranged polar molecules may act to drive more water molecules from the surrounding medium through the hydrophilic groups; consequently, they may oppose the action of protection and produce emulsion paint films of less protective properties under prolonged exposure, Figure 6 provides an explanation of this phenomenon.

# Comparison between Methylamine Adduct and Lead Chromate

It is interesting to compare the efficiency of the prepared methylamine adduct with a standard anticorrosive pigment such as lead chromate. Trials have been made to compare paint containing lead chromate, which is used at a concentration of at least 25% of the total weight of paint, with 0.5 g of the methylamine adduct per 100 g paint. The 25% lead chromate anticorrosive emulsion paint was formulated with 25 g of lead chromate to replace 16 g of TiO<sub>2</sub> and 9 g of talc.

# *Physical, Chemical, Mechanical, and Corrosion Test Results*

Table VII represents the physical, chemical, and mechanical properties of the blank paint, the



**Figure 5** Mechanism of corrosion inhibition at the optimum inhibitor concentration.



**Figure 6** Mechanism of corrosion inhibition using higher than the optimum inhibitor concentration.

emulsion paint containing the optimum concentration of the methylamine adduct (0.5 g per 100 g paint), and the emulsion paint formulation which contains 25% lead chromate. The results in Table VII show that the difference in the viscosity of these formulations is small and can be neglected. Also, the paint films of the above formulations passed bending (0.9 mm) tests successfully. With respect to chemical resistance, the paint films of the above formulations passed the water-resistance tests. In the case of acid and alkali resistance, the paint films of formula containing lead chromate pigment showed fading in its yellow color without any damage to the matrix of the film on exposure to acid and alkali solutions for 72 h. This may be due to the sensitivity of chromate pigments toward chemicals. Paint films of the blank and the formula containing the methylamine adduct showed very good chemical resistance. With respect to the corrosion tests, the blank paint showed dense blistering on the paint film surface at the end of the corrosion test period

	Inhibitor						
Test	Blank	0.5 g/100 g Methylamine Adduct	25% Lead Chromate				
Viscosity							
KU	83.1	82.2	81.8				
cP	820	811	808				
Adhesion <sup>a</sup>	Gt0	Gt0	Gt0				
Hardness <sup>b</sup>	$2\mathrm{H}$	Н	Н				
Ductility	6.5	6.9	6.9				
Bending (0.9 mm)	Pass	Pass	Pass				
Alkali/acid resistance	V.g.	V.g.	F.c. <sup>c</sup>				
Corrosion resistance <sup>d</sup>	h.t.	b.	b.				
Degree of blistering <sup>e</sup>	4D	10	6F				
Corrosion scratch tests <sup>f</sup> Water uptake immersion period	$\mathbf{F}$	А	А				
(35 days)	0.0	0.0	0.0				

Table VIIEffect of Methylamine Adduct and Lead Chromate on thePhysical, Chemical, Mechanical, and Corrosion Properties ofStyrene/Acrylic Emulsion Paint

 $^{\rm a}$  The adhesion of the dry films decreases in the following descending order: Gt0 > Gt1 > Gt2 > Gt3 > Gt4.

<sup>b</sup> Lead pencils supplied with the unit, softest to hardest, are as follows: 6B, 5B, 4B, 3B, 2B,B, HB, H, 2H, 3H, 4H, 5H, 6H.

<sup>c</sup> F.c.: Fading of color without damage of the paint film.

<sup>d</sup> b.: Bright surface; v.s.t.: very slight tarnishing; s.t.: slight tarnishing; m.t.: medium tarnishing; h.t.: high tarnishing; h.t.p.: high tarnishing and pitting.

<sup>e</sup> It is graded on a scale from 10 to 0, where 10 is no blistering and 0 is the largest blister and the frequency denoted by F, M, MD, and D (few, medium, medium dense, and dense).

<sup>&</sup>lt;sup>f</sup> A–E: Corrosion just in the scratch but differ in the adhesion of the film around the scratch; A: the best adhesion, F: bad adhesion, and F<sup>0</sup>: bad adhesion with pitting corrosion.



**Figure 7** Effect of methylamine adduct and lead chromate on weight loss of the coated carbon steel plates.

(28 days). Corrosion was found in the scratch with a high loss of adhesion and high tarnishing under the paint film. The formula containing the methylamine adduct showed a bright metal surface under the paint film and no blistering was found. Corrosion was found only in the scratch and the adhesion between the metal substrate and the paint films was not affected. The formula containing lead chromate showed a few small blisters and a bright metal surface under the paint film. The scratch tests showed similar results as those for the methylamine adduct paint, meaning that both the methylamine adduct and lead chromate can protect carbon steel against corrosion.

Water uptake measurements up to 35 days of the paint films of the present formulations show that there is no change in the weight of the emulsion paint films and, consequently, water uptake was found to be nil. This can be attributed to the effectiveness of the styrene/acrylic binder used.

#### Weight-loss Results

The relationship between the weight loss from the carbon steel, under the emulsion paint films of these formulations, and immersion time in synthetic sea water is shown in Figure 7. It is clear from Figure 7 that the paint films which contain the methylamine adduct protect carbon steel against corrosion better than does the paint containing the 25% lead chromate pigment (which is considered as one of the powerful anticorrosive pigments) over the entire 60-day period of immersion in synthetic sea water. Thus, the methylamine adduct provides an economically effective

inhibiting coating with low or no hazardous nature.<sup>24–26</sup> In addition to being environmentally friendly, the methylamine adduct paint is much cheaper, since only 0.5 g/100 g was used instead of 25 g/100 g of lead chromate.

# CONCLUSIONS

The methylamine adduct was prepared, emulsified, and successfully used in styrene/acrylicbased paint formulations to develop an environmentally friendly waterborne anticorrosive paint. It can be concluded that 0.5 g of the methylamine adduct per 100 g paint was the optimum concentration which provided the most protective corrosion inhibition. Below this concentration, the corrosion inhibition was not enough, and above it, the corrosion inhibitor produced an adverse effect.

It was also found that paint containing the optimum concentration of 0.5% of the methylamine adduct provided better protection to carbon steel than did paint containing 25% lead chromate. This gives economical and environmental advantages to the formulated paint, using the methylamine adduct as a corrosion inhibitor.

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