# Aromatic Amine-Epoxidized Sunflower Free-Fatty-Acid Adducts as Corrosion Inhibitors in Epoxy-Curable Varnishes

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**ABSTRACT:** With strict regulation of environmental pollution, sunflower fatty acids were used to prepare high-molecular-weight aromatic amine adducts by reaction of their epoxidized form [epoxidized sunflower free fatty acid (ESFA)] with five aromatic amines [o-toluidine (o-T), m-toluidine (m-T), p-toluidine (p-T), p-anizidine (p-A), and p-chloroaniline (p-ClA)] under severe conditions of an inert atmosphere and high temperature. The produced adducts were characterized physically, chemically, and by IR spectroscopy. The acid values and oxirane contents of the prepared adducts were determined to confirm the participation of carboxylic groups and epoxy groups, respectively, in the reaction of ESFA with aromatic amines. Also, to avoid volatile organic compounds, the prepared adducts of ESFA (o-T–ESFA, m-T–ESFA, p-T–ESFA, p-A–ESFA, and p-ClA–ESFA) were evaluated as corrosion inhibitors of mild steel in electron-beam-curable epoxy acrylate oligomer formulations. Physical and mechanical measurements were carried out, in addition to corrosion-resistance tests and weight loss measurements of the coated steel panels. The optimum concentration of each adduct was determined for the prepared formulations. The corrosion-inhibition efficiency of the adducts in varnish formulations were determined. It was found that varnish formulations containing the prepared aromatic amine adducts could protect steel from corrosion. The corrosion-inhibition efficiencies of the prepared aromatic amines in epoxy acrylate oligomer varnishes were arranged as follows: p-A–ESFA > p-T–ESFA > m-T–ESFA > o-T–ESFA > p-ClA–ESFA. Superior corrosion-inhibition efficiency was obtained in the varnish formula containing 0.6% p-A–ESFA adduct. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2007–2015, 2012

**Key words:** Infrared spectroscopy, electron beam curing, adsorption, coatings, oligomers

## INTRODUCTION

The restriction of the use of volatile organic compounds has brought about the development of solvent-free coating technologies, such as powder coatings, electrocoatings, radiation-curable coatings, and waterborne systems. Radiation-curable coatings have gained increasing importance for many applications. Electron beam (EB)/UV curing coating systems are, in general, formulated from a reactive resin and, optionally, a low-viscous reactive diluent.[1] A photoinitiator is added to guarantee immediate curing upon exposure to UV light. Additionally, nonreactive additives are also introduced into formulations to meet specific application requirements.[2,3]

The phenomenon of corrosion in mild steel represents a fundamental problem both in basic research and in industry. Corrosion protection strategies have always played a vital role in industrial and economic development.[4] Corrosion protection in conventional coatings has generally been achieved with the use of inhibitors, such as metallic pigments, metal oxides, and salts, at relatively high volume concentrations;[5] these inhibitors include chromates, nitrites, phosphonates, silicates, zinc salts, cadmium salts, arsenic salts, and other cautions,[6–14] but a major disadvantage is their toxicity, and as such, their use has come under severe criticism.[15,16] The investigation of more environmentally acceptable corrosion inhibitors is of great practical interest. Recently, many attempts have been made to replace environmentally unfavorable inorganic compounds with more ecologically attractive alternatives. Among alternative corrosion inhibitors, organic compounds containing polar functions with nitrogen, oxygen, or sulfur atoms and heterocyclic compounds containing conjugated double bonds have been reported as effective inhibitors of mild steel corrosion.[17–27] Amines are another type of corrosion inhibitor that have played an important role in mild steel protection at very small concentrations.[28,29]

The aim of this work was to prepare some new organic corrosion inhibitors by the reaction of epoxidized sunflower free fatty acid (ESFA) with different aromatic amines. The produced adducts were added and evaluated in different EB-curable varnish formulations based on epoxy acrylate oligomer. The prepared adducts could be adsorbed at the metal surface to form a very thin uniform film through the lone pair of electrons of the nitrogen atom. Thus, they could act as corrosion inhibitors and were able to protect mild steel.

## EXPERIMENTAL

### Materials

Primary aromatic amines [o-toluidine (o-T), m-toluidine (m-T), p-toluidine (p-T), p-anizidine (p-A), and p-chloroaniline (p-ClA)] were used. They were supplied from Sigma-Aldrich Chemie Gmbh Munich, Germany. Sunflower free fatty acid is a pure fatty acid having an iodine value of 130–150; castor oil was used as plasticizer for the curable varnish formulations, and they were delivered from Paint and Chemical Industry (Egypt). Hydrogen peroxide (30% strength) was supplied by El Naser Pharmaceutical Chemical Co. (Egypt). Sulfonated poly(styrene/divinyl benzene) copolymer was delivered from Dow Chemicals, Ltd. (England) under the trade name Dowex 50W-8X. Epoxy acrylate oligomer consisting of 80% bisphenol A epoxy diacrylate diluted with 20% 1,6-hexanediol diacrylate was obtained from Cytec Surface Specialties (Drogenbos, Belgium) under the trade name EBECRYL 604.

### Techniques

Preparation of the aromatic amine–ESFA adducts

Sunflower free fatty acid was epoxidized by hydrogen peroxide and acetic acid with sulfonated poly(styrene/divinyl benzene) copolymer as a catalyst.[29] The reactions of epoxidized fatty materials and amines were carried out in sealed ampules under an inert atmosphere at 130°C for 3 h.

The amounts of amine added to the epoxidized fatty acid were calculated on the basis that 1 mol of amine would react with each epoxy group and 1 mol of amine would react with each carboxylic group.

### Characterization of the prepared adducts

The oxirane oxygen contents[30–32] were measured for both ESFA and the prepared adducts. The sample was titrated against 0.1N HBr in a glacial acetic acid solution in the presence of crystal violet indicator until a bluish green end point. The oxirane oxygen content was determined with eq. (1):

$$\text{Oxirane oxygen content } (\%) = LN \times 1.6/W \quad (1)$$

where $L$ is the volume of HBr solution, $N$ is the normality of the HBr solution, and $W$ is the weight of the sample.

The acid value was determined for both ESFA and the prepared adducts according to ASTM D 1639-90. It was calculated mathematically according to eq. (2):

$$\text{Acid value} = (NV \times 56.1)/W \quad (2)$$

where $N$ is the normality of KOH, $V$ is the volume of KOH, and $W$ is the weight of the sample.

Fourier transform infrared spectrometry was used for scanning and measuring the transmittance spectra of the prepared adducts at a resolution of $4 \text{ cm}^{-1}$.

### Preparation and curing of varnishes by EB irradiation

Twenty-six varnish formulations based on epoxy acrylate oligomer (V1–V26) were prepared, and castor oil was added as a plasticizer. V1 was blank and free from any prepared adducts. The formulations V2–V26 were prepared with the incorporation of different concentrations of the prepared aromatic amine–ESFA adducts.

The formulations were applied as a thin films on different substrates, such as glass, tin, and carbon steel metal, with a film applicator (100 μm thick) according to ASTM D 823-07.

The curing of the varnishes was carried out by irradiation with the EB accelerator facility of the National Center for Radiation Research and Technology (NCRRT), Atomic Energy Authority (AEA), Naser City, Cairo, Egypt (energy = 1.5 MeV, power = 37.5 kW, beam current = 25 mA, and variable scan widths up to 90 cm). The required doses were obtained by adjustment of the EB parameters and conveyor speed. The radiation dose was 10 kGy for all formulations.

### Evaluation of the prepared adducts in epoxy acrylate varnish formulations

The formulated varnishes were tested and evaluated according to well-known standard methods. The measurement of film hardness was carried out with a Wolff–Wilborn pencil hardness tester according to ASTM D 3363 (2000). Bending tests were done according to ASTM D 522-93$_a$ with 2-mm diameter mandrels. The adhesion of the cured films was measured according to ASTM D 3359-97. Alkali- and acid-resistance tests were carried out according to ASTM D 1647-89 and ASTM B 287-74, respectively. Corrosion scratch tests were carried out according to
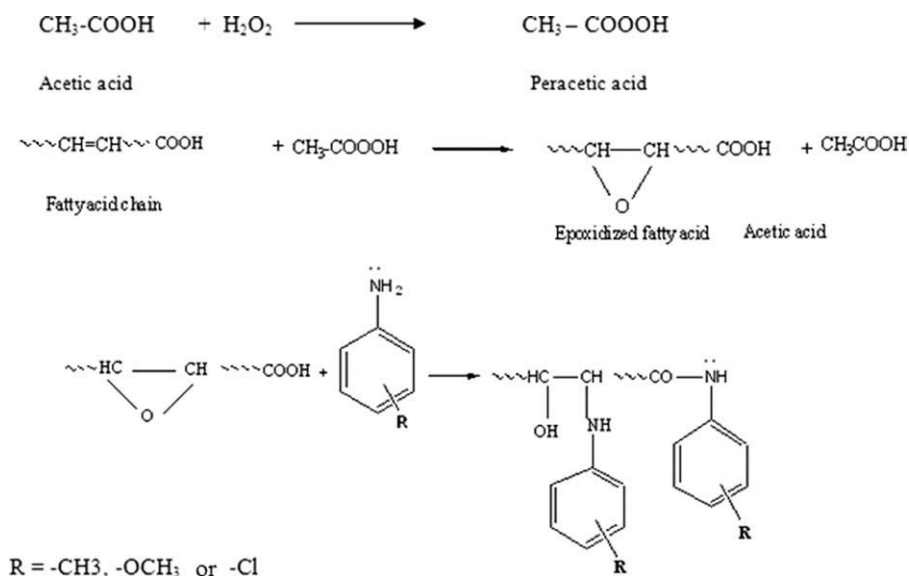
**Figure 1** Reaction equations.

ASTM D 1654-92 (2000). Blister-resistance tests were carried out according to ASTM D 714-87 (2000). Rusting was determined according to ASTM D 610-01. The weight loss of coated steel was measured according to ASTM D 2688-94 (1999).

## RESULTS AND DISCUSSION

### Preparation and characterization of the prepared aromatic adducts

The prepared ESFAs and their reaction with the aromatic amines (o-T, m-T, p-T, p-A, and p-ClA) was confirmed by IR spectroscopy and estimation of the oxirane content and acid value. The oxirane oxygen content of the prepared ESFA was measured volumetrically, and it was found to be 5%. Figure 1 shows the reaction equations of the prepared adducts.

The IR spectrum of epoxidized free fatty acid showed a very characteristic band of the epoxy group, which appeared at 824 cm$^{-1}$, and a characteristic band of the C—O group appeared at 1160 cm$^{-1}$, as shown in Figure 2. The carboxylic acid group exhibited two bands, a strong band at 1740 cm$^{-1}$ due to C=O groups and a broad band at 3475 cm$^{-1}$ due to O—H groups. Also, there was a strong band at 2940 cm$^{-1}$ due to aliphatic C—H attached to the carboxylic group.

IR chart spectra of all of the aromatic amine adducts, which are shown in Figures 2 and 3, proved that all epoxy groups of the ESFAs were consumed during the reaction with the primary amines, where the bands of the epoxy group, which appeared at 824 cm$^{-1}$, had completely diminished. Moreover, new characteristic bands of secondary amino groups (one band) and hydroxyl groups

appeared; they appeared as an overlapped broad peak at 3200–3500 cm$^{-1}$. In addition, another a bending band near 1560 cm$^{-1}$ due to secondary N—H and a characteristic band of C—N appeared at 1400 cm$^{-1}$ as a result of the addition reaction of amino groups to the epoxy ring. These observations
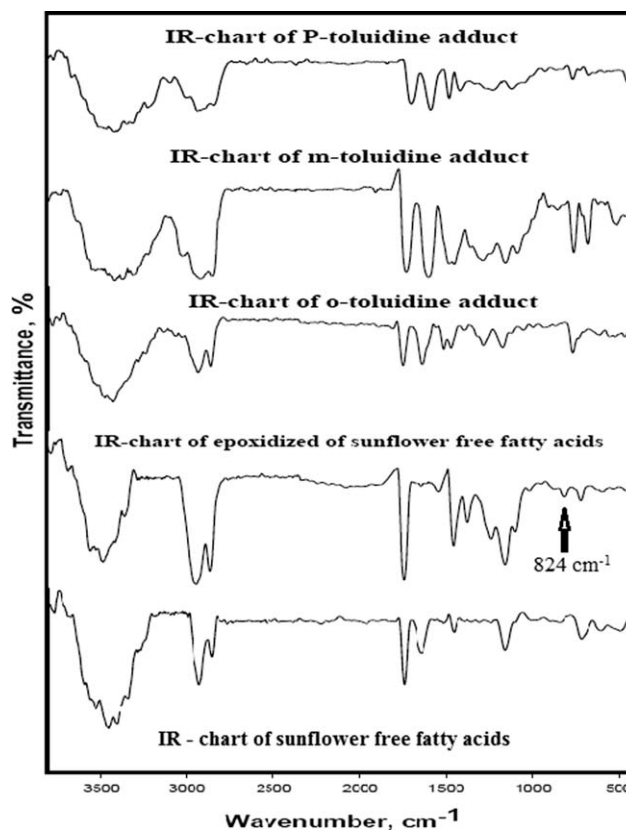


**Figure 2** IR spectra of sunflower free fatty acid, ESFA, and the o-T, m-T, and p-T adducts.
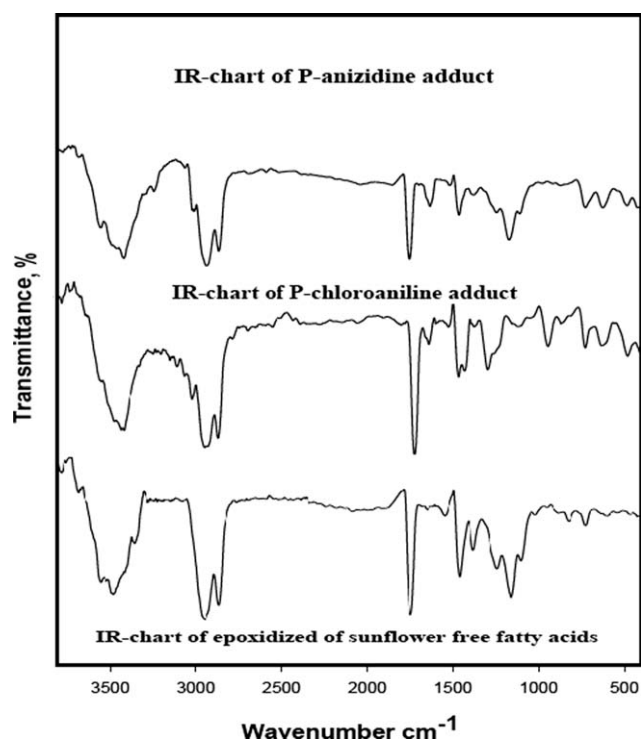
**Figure 3** IR spectra of ESFA and its adducts with *p*-A and *p*-ClA.

indicated that the epoxy/amine reactions took place successfully.

On the other hand, the acid values and oxirane oxygen contents of the ESFAs and their reaction products with aromatic amines were followed, and the obtained results are given in Table I. More than 86% of the carboxylic groups of the ESFAs reacted with the added primary aromatic amines except the adducts containing chloroaniline because not more than 18% of the carboxylic groups were reacted and about 82% of the carboxylic groups were still free.

With respect to the oxirane oxygen content, as shown in Table I, the oxirane oxygen content in the aromatic amine adducts had a very low value compared to the 5%/mol found in the starting material (ESFA). This means that almost all of the oxirane oxygen (>98%) participated in the reaction.

### Evaluation of the prepared aromatic amine–ESFA adducts as corrosion inhibitors in curable varnishes

All of the formulations (26 formulations) were based on 70% epoxy acrylate oligomer and castor oil as a plasticizer. A constant radiation dose (10 kGy) was applied for all formulations. The aim of this application was to study the efficiency of the prepared aromatic amine adducts (*o*-T, *m*-T, *p*-T, *p*-A, and *p*-ClA adducts) as corrosion inhibitors for carbon steel and to select the optimum concentration of the prepared

aromatic amine adducts with the best performance as a corrosion inhibitor.

### Group 1: Evaluation of *o*-T–ESFA, *m*-T–ESFA, and *p*-T–ESFA as corrosion inhibitors

It was interesting to assess the corrosion-inhibition performances of the *o*-T–ESFA, *m*-T–ESFA, and *p*-T–ESFA adducts when they were incorporated in curable varnish formulations. There were sixteen varnish formulations, in which formula V1 was selected as a blank. Group 1 was divided into three subgroups, 1A, 1B, and 1C, containing *o*-T, *m*-T, and *p*-T adducts. All of the subgroups, A, B, and C, involved five varnish formulations and contained different concentrations of toluidine adducts (0.2–1.0 g in increments of 0.2 g). The varnish formulations of group 1 are listed in Table II.

There were no marked changes in the physicomechanical properties of the cured films of this group as a result of the *o*-T–ESFA, *m*-T–ESFA, or *p*-T–ESFA adduct addition in comparison with the addition of the blank. It was noted that all of the cured films of the investigated formulations showed excellent adhesion (4B) to the steel panels. The results of the other mechanical properties, such as bending, were acceptable. Narrow decreases in the hardness (from 4H to 3H) of the cured films were observed with increasing concentration of *o*-T–ESFA, *m*-T–ESFA, and *p*-T–ESFA compared to the blank (4H). In addition, all of the coated glass panels had good chemical resistance in acid, alkali, and water for 24 h without considerable defects.

The corrosion-resistance tests of the coated steel panels of the group 1 formulations after immersion in artificial seawater for 28 days were studied extensively, and the results are listed in Table III for the different concentrations of toluidine adducts.

Table III shows that the addition of 0.4 g of *o*-T–ESFA in V3 and *m*-T–ESFA in V8 to the formulations protected the metal surface under the varnish films against corrosion, where no sign of blisters (rating 10) but a slight degree of corrosion were observed

### TABLE I
### Acid Values and Oxirane Oxygen Contents (mol %) of the Prepared Aromatic Amine Adducts

| Amine adduct | Index | Acid value | Oxirane oxygen content (mol %) |
|---|---|---|---|
| ESFA | ESFA | 205.0 | 5 |
| *o*-T adduct | *m*-T–ESFA | 27.7 | 0.065 |
| *m*-T adduct | *m*-T–ESFA | 24.3 | 0.073 |
| *p*-T adduct | *p*-T–ESFA | 20.0 | 0.045 |
| *p*-A adduct | *p*-A–ESFA | 18.5 | 0.085 |
| *p*-C adduct | *p*-ClA–ESFA | 168.7 | 0.088 |

## TABLE II
### Varnishes Formulations of Group 1

| | Formula | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Blank | Group 1A | | | | | Group 1B | | | | | Group 1C | | | | |
| Test | V1 | V2 | V3 | V4 | V5 | V6 | V7 | V8 | V9 | V10 | V11 | V12 | V13 | V14 | V15 | V16 |
| Epoxy acrylate (%) | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 |
| 1,6-Hexanediol diacrylate (%) | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| Castor oil (%) | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| $o$-T–ESFA (g) | — | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | — | — | — | — | — | — | — | — | — | — |
| $m$-T–ESFA (g) | — | — | — | — | — | — | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | — | — | — | — | — |
| $p$-T–ESFA (g) | — | — | — | — | — | — | — | — | — | — | — | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |

(rating 8), and very little delamination around the scribe was recorded (rating 9) for each mentioned adduct. Beyond this concentration, corrosion appeared again with some loss of adhesion of the cured films around the scribe. With respect to varnish formulations that included the $p$-T–ESFA adduct, it was found that the best corrosion protection for carbon steel was obtained by the formula V14, which contained 0.6% inhibitor, and in which no sign of blisters on the cured films (rating 10) was observed and a bright metal surface with a little degree of rusting (rating 9) was noticed, and the adhesion of the cured film around the scribe was unaffected (rating 10).

Also, similar behavior was observed when the concentration of the prepared $p$-T adducts increased over 0.6%, as seen in the $o$-T and $m$-T adducts.

The weight loss results of the coated carbon steel as a function of immersion time in artificial seawater for 60 days were determined and are plotted in Figure 4. The determined results were parallel with the obtained corrosion resistant results, where minimum weight loss values were evidenced in the panel coated with varnish formulations V3 (0.344 mg/cm$^2$),V8 (0.333 mg/cm$^2$), and V14 (0.300 mg/cm$^2$), which corresponded to 0.4 g of $o$-T–ESFA, 0.4 g of $m$-T–ESFA, and 0.6 g of $p$-T–ESFA adducts, respectively. Also, the obtained results prove the superior performance of the $p$-T–ESFA adduct as a corrosion

inhibitor for steel panels over both those of the $o$-T–ESFA and $m$-T–ESFA adducts. The superior performance of the $p$-T adduct may have been due to the methyl group in the para position, which donated electrons to the nitrogen atom of the amino group through hyperconjugation and because the positive inductive effect through the benzene ring was easier than in the other toluidine isomers.

## Group 2: Evaluation of $p$-A–ESFA as a corrosion inhibitor

This group contained six varnish formulations, in which formula V1 was selected as a blank. The prepared $p$-A adduct was added in different concentrations to optimize its proper concentration, as shown in Table IV.

The physicomechanical and chemical properties were not affected significantly with the addition of the prepared $p$-A adduct. All cured films showed high adhesion and excellent flexibility (bending). Moreover, the hardness of the cured films decreased very slightly with increasing concentration of the $p$-A adduct (from 4H to 3H). Also, all of the prepared cured films passed the acid-, alkali-, and water-resistance tests.

The corrosion-resistance tests results of the immersed films for cured 28 days are given in Table V. The results show a significantly superior

## TABLE III
### Corrosion Resistance Tests of the Coated Steel Panels of Group 1

| | Formula | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Blank | Group 1A | | | | | Group 1B | | | | | Group 1C | | | | |
| Test | V1 | V2 | V3 | V4 | V5 | V6 | V7 | V8 | V9 | V10 | V11 | V12 | V13 | V14 | V15 | V16 |
| Degree of rusting[a] | 4 | 8 | 8 | 9 | 4 | 3 | 8 | 8 | 8 | 6 | 3 | 7 | 8 | 9 | 7 | 6 |
| Degree of blistering[b] | 2F | 10 | 10 | 10 | 10 | 2F | 10 | 10 | 10 | 10 | 2F | 10 | 10 | 10 | 10 | 10 |
| Failure at scribe[c] | 7 | 6 | 9 | 5 | 7 | 7 | 5 | 9 | 9 | 7 | 2 | 9 | 9 | 10 | 9 | 9 |

[a] Rating of rust as area percentage; it is graded on a scale from 10 to 0, where $10 < 0.01\%$ and $0 > 50\%$.
[b] Graded on a scale from 10 to 0, where 10 is no blistering and 0 indicates the largest blisters. The frequency is denoted by F, M, MD, and D (few, medium, medium dense, and dense, respectively).
[c] Rating of corrosion or loss of paint extending from the scribe; it is graded on a scale from 10 (no creepage) to 0 ($>16$ mm).
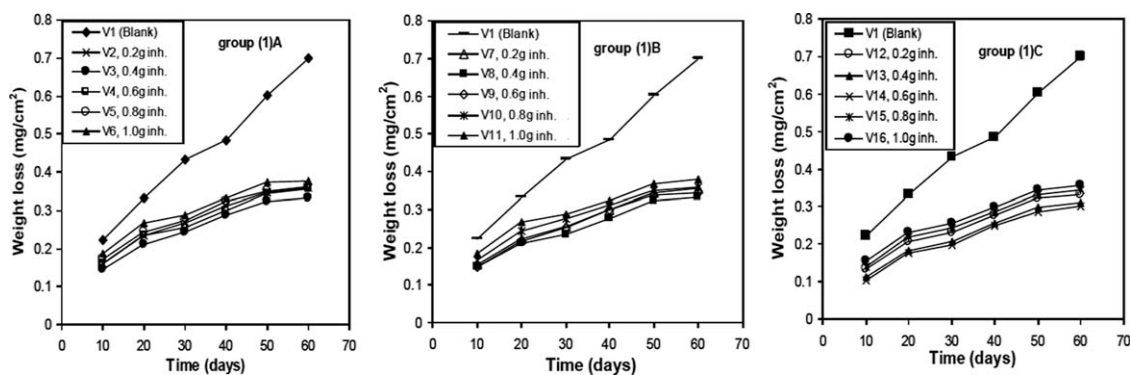
**Figure 4** Weight loss measurements of the coated metal plates of group 1 during immersion in artificial seawater.

performance of formula V19, which contained 0.6 g of the p-A–ESFA adduct and in which no signs of apparent corrosion of the unscribed face (rating 9) and excellent adhesion were observed (rating 10). It was noticed that the scribed face exhibited good anticorrosive performance of the cured film, as proven by the absence of blistering (rating 10) and disappearing delamination at the scribe. It should be noted that all of the cured films of different concentrations did not show any signs of blister formation (rating 10).

With regard to weight loss measurements, it was evident that the weight loss results were consistent with observations of the corrosion-resistance results of group 2, as illustrated in Figure 5. It can be seen from this figure that the coated steel panels with formulations V18 and V19, which contained 0.4 and 0.6 g of the p-A–ESFA adduct, showed the lowest weight losses, 0.30 and 0.29 mg/cm$^2$, respectively, after 60 days of immersion in artificial seawater. On the other hand, formulations V20 and V21 showed relatively higher weight losses with time.

Group 3: Evaluation of p-ClA–ESFA as a corrosion inhibitor

Different concentrations of the p-ClA–ESFA adduct were added in regular increments of 0.2 g to the blank, as shown in Table VI.

The physicomechanical and chemical properties of the cured films of group 3 showed good adhesion

(4B) and hardness values (4H–2H). Also, it appeared that all of cured films were able to pass the bending and acid- and alkali-resistance tests. It was evident that the addition of a small portion of the prepared p-ClA–ESFA adduct to the formulated varnishes caused a very slight decrease in the film hardness, from 4H in case of the V22 and V23 formulations to 3H for formulas V24 and V25 and, finally, to 2H in the case of formula V26.

The corrosion-resistance test results, after immersion of the coated panels of this group in artificial seawater for 28 days, are shown in Table VII and represented photographically in Figure 6. The results show a significantly superior performance of varnish formula V23, which contained 0.4 g of the p-ClA–ESFA adduct and n which no signs of blisters in the cured film (rating 10) but a very slight degree of rust on the metal surface (rating 8) and some delamination of the cured films around the scribe (rating 9) were observed. On the other hand, the worst corrosion resistance was evident in formulations V25 and V26, which showed high blisters (rating 2F) and rust ratings of 6 and 5, respectively. Also, the cured films showed high delamination around the scribe (rating 4) for formulations V25 and V26. The weigh loss measurements of the group 3 coated metal plates are given in Figure 7. The measurements went side by side with the aforementioned results. On the basis of this finding, we concluded that the lowest weight loss values were obtained with formula V23, which contained 0.4 g of the p-ClA adduct (0.588 mg/cm$^2$ after 60 days).

**TABLE IV**
**Varnish Formulations of Group 2**

| Composition | Blank | Group 2 | | | | |
|---|---|---|---|---|---|---|
| | V1 | V17 | V18 | V19 | V20 | V21 |
| Epoxy acrylate (%) | 70 | 70 | 70 | 70 | 70 | 70 |
| 1,6-Hexanediol diacrylate (%) | 20 | 20 | 20 | 20 | 20 | 20 |
| Castor oil (%) | 10 | 10 | 10 | 10 | 10 | 10 |
| p-A–ESFA (g) | — | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |

**TABLE V**
**Corrosion Resistance Tests of the Coated Steel Panels of Group 2**

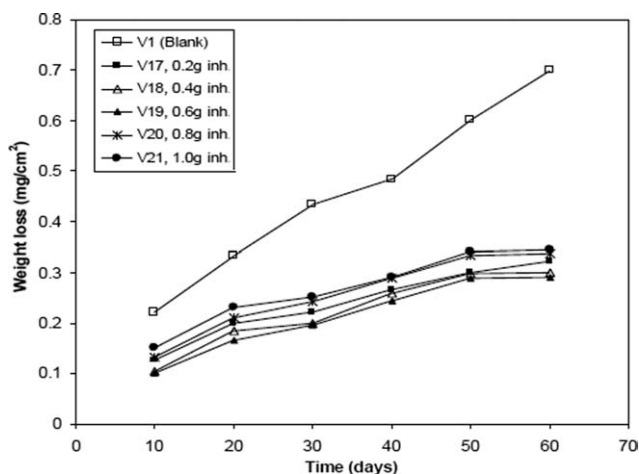| Test | Blank | Group 2 | | | | |
|---|---|---|---|---|---|---|
| | V1 | V17 | V18 | V19 | V20 | V21 |
| Degree of rusting | 4 | 8 | 8 | 9 | 8 | 7 |
| Degree of blistering | 2F | 10 | 10 | 10 | 10 | 10 |
| Failure at scribe | 7 | 7 | 9 | 10 | 9 | 9 |

**Figure 5** Weight loss values of the coated metal plates of group 2 with immersion time in artificial seawater.

On the other hand, the weight loss values started to increase with higher inhibitor concentration, especially in formula V26.

### Corrosion-inhibition efficiency of the prepared aromatic amine adducts

Photos were taken of the blank formula and other formulations with aromatic adduct concentrations of 0.4 and 0.6% after 28 days of immersion in artificial seawater, as shown in Figure 6. The photos showed that the coated steel panels with formulations containing the prepared aromatic amine–sunflower free fatty acid adduct resisted corrosion compared with the blank formula. Also, superior corrosion resistance was found in formula V19, which contained 0.6 g of *p*-A–ESFA per 100 g of coating.

It was stimulating to study the inhibition efficiency of the aromatic amine adducts as corrosion inhibitors at their optimum concentrations and correlated a suitable relation between them. As estimated from the weight loss measurements,[33,34] the corrosion-inhibition efficiencies (*I*'s) of the prepared anticorrosive formulations containing the prepared aromatic adducts were calculated from eq. (3), and the obtained results are represented graphically in Figure 8:

**TABLE VI**
**Varnish Formulations of Group 3**

| Composition | Blank | Group 3 | | | | |
|---|---|---|---|---|---|---|
| | V1 | V22 | V23 | V24 | V25 | V26 |
| Epoxy acrylate (%) | 70 | 70 | 70 | 70 | 70 | 70 |
| 1,6-Hexanediol diacrylate (%) | 20 | 20 | 20 | 20 | 20 | 20 |
| Castor oil (%) | 10 | 10 | 10 | 10 | 10 | 10 |
| *p*-ClA–ESFA (g) | — | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |

**TABLE VII**
**Corrosion Resistance Tests of the Coated Steel Panels of Group 3**

| Test | Blank | Group 3 | | | | |
|---|---|---|---|---|---|---|
| | V1 | V22 | V23 | V24 | V25 | V26 |
| Degree of rusting | 4 | 7 | 8 | 8 | 6 | 5 |
| Degree of blistering | 2F | 10 | 10 | 10 | 2F | 2F |
| Failure at scribe | 7 | 9 | 9 | 7 | 4 | 4 |

$$I(\%) = 100(W_o - W_i)/W_o \qquad (3)$$

where $W_o$ and $W_i$ are the weight loss values in the absence and presence of the prepared adducts, respectively.

The obtained results prove that the formulation containing 0.6 g of the *p*-A–ESFA adduct imparted superior corrosion-inhibition performance in comparison with the other aromatic amine adducts. On the other hand, the corrosion-inhibition efficiency of the prepared adducts obeyed the following descending order:

$$p - A - ESFA > p - T - ESFA > m - T - ESFA$$
$$> o - T - ESFA > p - ClA - ESFA$$

The corrosion inhibition of the coated steel panels with varnishes containing optimum concentrations (0.4–0.6 g per 100 g of varnish) of the prepared aromatic amine adducts was attributed to their polarity and their adsorption on the steel panels through a lone pair of electrons on the nitrogen atom of the amino group. The position and kind of substituted functional groups in the prepared adducts played important roles in the corrosion-inhibition efficiency, as follows:
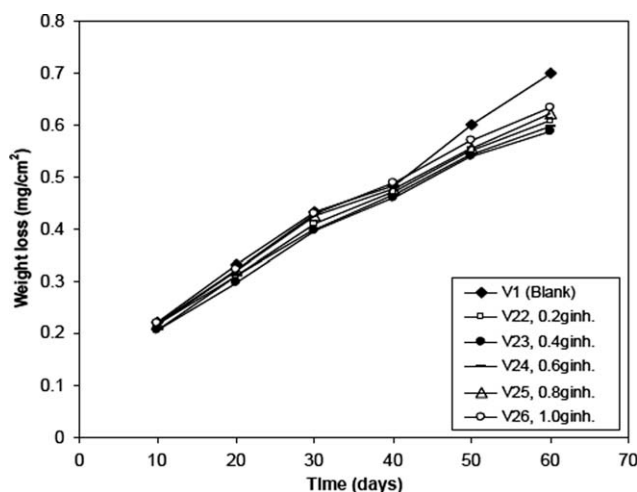


**Figure 6** Photos of some formulations after 28 days of immersion time.
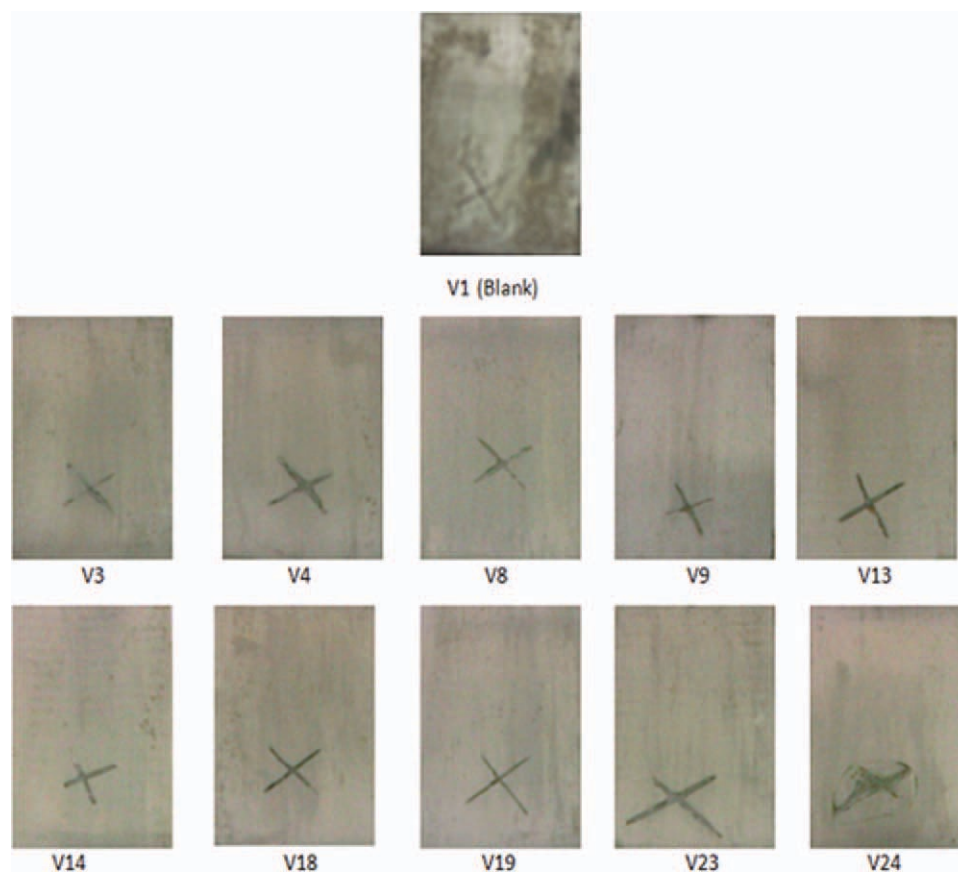
**Figure 7** Weight loss values of the coated metal plates of group 3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1. In the toluidine adducts, the presence of an electron-donating methyl group increased the electron density of the nitrogen atom. The superior performance of the *p*-T adduct may have been due to the methyl group in the para position donating electrons to the nitrogen atom of the amino group through hyperconjugation and by the easier positive inductive effect through the benzene ring compared to the other toluidine isomers. This may, in turn, have increased the electron density at the nitrogen atom of that amine and, consequently, increased the coordinate bond strength through chemisorptions between the aromatic amine and the metal surface.[26] With respect to the *o*-T adduct, it was clear that the corrosion-inhibition efficiency of the ortho isomer was lower than those of the para and meta isomers. This finding was attributed to steric hindrance arising from the proximity of the methyl group in the ortho position to the amino group, which rendered it less adsorptive to the metallic surface.

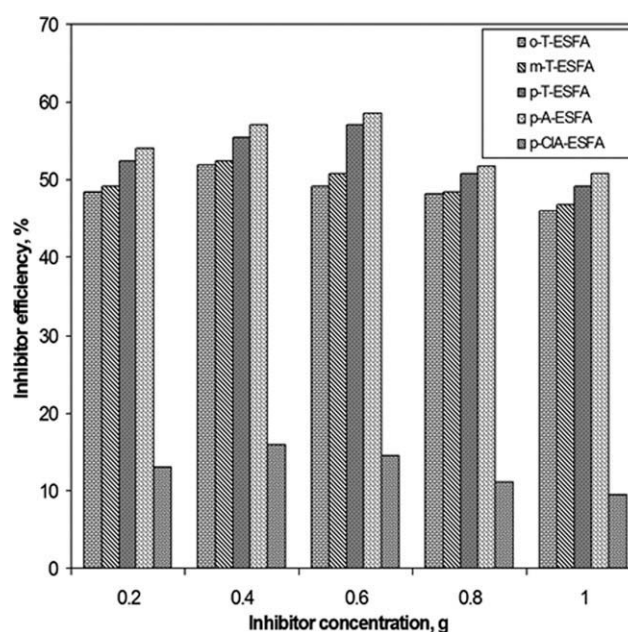2. In case of the *p*-A adduct, the substituted methoxy group (—OCH$_3$) was more electron-



**Figure 8** Efficiency of the prepared aromatic amine adducts depending on their concentrations in curable formulations.

repelling than the methyl group (—CH$_3$) in the *p*-T adduct; consequently, the electron pair on the nitrogen atom was more available compared with that of the *p*-T adduct. Accordingly, the *p*-A adduct had superior adsorption on the metallic surface in the monolayer and superior corrosion-inhibition efficiency.

3. In *p*-ClA, the substituted chlorine atom was electron-attracting (had a negative inductive effect); this led to more deficiency in the electron density on the nitrogen atom, which may have, in turn, decreased the inhibition efficiency of the *p*-ClA adduct.

4. On the other hand, at high concentrations of the prepared adduct (0.8–1.0 g per 100 g of varnish), the corrosion inhibition decreased because of the random distribution of the prepared adducts, which may have bloomed to the surface and attracted water molecules to the cured film through its hydrophilic groups, and also because of the increasing acid value content, as shown in Table I.

## CONCLUSIONS

The prepared aromatic amine—sunflower free fatty acid adducts to epoxy coating formulations induced by EB irradiation were able to give extra protection to mild steel without remarkable changes in the physicomechanical and chemical properties of the cured films. The optimum concentrations of the prepared adducts as corrosion inhibitors were found to be 0.4–0.6 g per 100 g of solid coating. This amount was enough to form a thin film over the steel surface through chemisorption action. The superior corrosion-inhibition performance of the *p*-A–ESFA adduct with only 0.6 g per 100 g of coating, compared with those of the other prepared adducts, was proven by both qualitative and quantitative corrosion-resistance tests.

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