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Evaluation of Some Chromene Derivatives as Additives in Fire Retardant and Anticorrosive Coating Composition

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Abstract:
Epoxy coating was modified by physically mixing with 2,7-diamino-4-(4-chlorophenyl)-4H-chromene -3- carbonitrile (I), 2,7-diamino-4-(4-nitrophenyl)-4H-chromene-3- carbonitrile (II) and E7-amino-2-oxo-4-styryl-2H-chromene-3-carbonitrile (III) by the ratio of 0.3, 0.5 and 1.0% by weight. In order to achieve a proper ratio of chromene derivatives to produce a green epoxy formulation for surface organic coating application. A corrosion performance of mild steel coated specimens was investigated employing salt spray test. The coating modified with 1.0% of and E7-amino-2-oxo-4-styryl-2H-chromene-3-carbonitrile (III) possessed the best corrosion performances, among the coated specimens- Also the fire retardant of the modified epoxy varnishes was investigated by using limited oxygen index (LOI) chamber, and the result was 1.0 % of 2,7-diamino-4-(4-nitrophenyl)-4H-chromene-3- carbonitrile (II) gives the highest flame retardant outcome.

1. Introduction

Annual costs related to corrosion and corrosion prevention constitutes a substantial part of the gross national product in the world. Although the value of these numbers is always debatable, since the corrosion has great importance in modern societies in addition to economic costs and technological delay, corrosion can lead to failure of metal structures which have serious consequences for humans and the environment (F. Fragata et al 2006; J. Shah; G.B. Bhagchandani 2013). Thus, the study of mild steel corrosion and the inhibition of mild steel corrosion of have invited the attention of scientists and technocrats to devise ways to control the corrosion. Between the various corrosion control measures, the use of corrosion inhibitors is a familiar method. It is known that corrosion inhibitors act by adsorbing on the metal surface (J. Gopal et al 2013; L.C. Kamal, Sethuraman, M.G. Opuntiol 2014). Over the last decades, both organic and inorganic coatings have been widely applied for the protection of metals against corrosion. In many areas of coatings technology, anticorrosive paint gave great attention.

Recently several chemical compounds have been tested as a corrosion inhibition of metals and alloys, most of the reported corrosion inhibitors are organic compounds containing heterocyclic atoms (nitrogen, oxygen, sulfur and phosphorous), *incorporated in an aromatic system or triple bond* are commonly used to reduced the corrosion. The inhibition effect of organic compounds arises from the adsorption on the metal surface (A. A. Al-Amiery et al 2015). The use of environmental friendly corrosion inhibitors is nowadays very common because they are eco-friendly. To this end, the use of organic compounds containing nitrogen, oxygen, and/or sulfur in a conjugated system as inhibitors to reduce corrosion attack has received great concerns (S.P. Tambe et al 2016; M. Abd allah 2014; E. Sato, S. Nagai, A.Matsumoto 2013; İ. Kaya˙ , E. Bora, A. Aydın 2014; L. M. Vracar, D.M. Drazic 2002) .

Epoxy coatings are extensively utilized in the protective coatings to their generally high level of corrosion inhibitors, good chemical stability, adhesion, hardness, flexibility, toughness low water vapor permeability and good antibacterial proper. It is generally believed that most organic coatings adhere to metals via hydrogen bonds or secondary bonds, therefore, hydrogen bonds develop when an organic coating and a metallic surface are brought closely together and subsequently binders with polar groups display excellent adhesion characteristics. The bond strength of epoxy resins on steel is strongly dependent on the hydroxyl group content (M. Nakazawa1194). It was found that the epoxy compounds were dissociated between the phenoxy oxygen and the aliphatic carbon. The surface interactions were believed to be via the phenoxy and hydroxyl oxygen atoms, as illustrated in Fig (1).

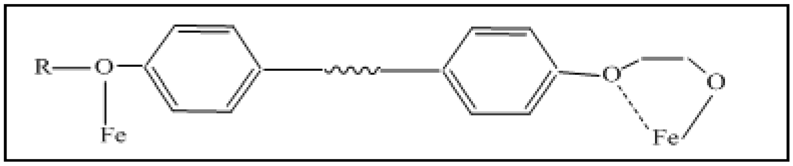


Figure 1: Adhesion of epoxy to steel by interacfacial bonds

The Scientists suggested that the adhesion strength dependent on the content of hydroxyl groups of epoxy resin was inevitably oriented on the surface of water in such a way that the hydrophilic part of the molecule pointed down to the interface while the hydrophobic part turned away from the interface.

In the last few decades epoxy coatings have evolved from high Volatile Organic Compounds (VOC) systems to more environmentally friendly systems e.g. high solids, solvent-free, powder and waterborne coatings (A. A. Al-Amiery et al 2015; S. Waśkiewicz et al 2013; M.Rufo et al 2007; S.D. Jagtap et al 2014; A. H. Navarchian, M. Joulazadeh, F. Karimi 2014; Z. Zhang et al 2015; *J. Zhao, G. Chen 2012).*

Polymeric materials have replaced many materials in our everyday lives. Although there are numerous advantages associated with polymeric materials there are serious drawbacks, such as poor resistance to fire. Deaths due to fire account for 10 to 20 deaths per million inhabitants in industrialized countries, and the number of people injured is ten times higher. Over time, different strategies have been developed in order to enhance the reaction to fire of these materials. These include the use of inherently flame retardant polymers, modification of the polymer backbone or incorporation of flame retardants into the polymers (C. Gerard, G. Fontaine, S. Bourbigot 2010; S. Bourbigot, X. Flambard 2002; D.Q. Chen 2005; J. Choi, A.F. Yee, R.M. Laine 2003).

As inherently flame retardant polymers can lead to high production costs, the modification of already existing systems is still valued by industry. The modification of the polymer backbone by the inclusion of P, Si, Br or N elements often provides good fire retardancy properties to the newly synthesized polymer (S.Y. Lu, I. Hamerton 2002). Unfortunately, epoxy resins tend to burn easily with releasing a high quantity of smoke and gas, and one of the traditional solutions is the incorporation of flame retardants containing halogen (S.V. Levchik, E.D. Weil 2004). Therefore, the efforts to promote the reactions of the fire on epoxy resins have been developed by adding flame retardants containing nitrogen, such as Schiff base monomer, and cyclodiphosph (V) azanederivatives (H. Abd El-Wahab 2015; H. Abd El-Wahab, M. Abd El-Fattah, M.Y. Gabr 2010; H. Abd El-Wahab, M. Abd El-Fattah, N. Abd El-Khalik 2010; Z. Liu, M. Dai, Y. Zhang, Q. Zhang 2016).

In this work a new green corrosion inhibitor as well as flame retardant additives from amino chromiene (I – III) derivatives are successfully synthesized and fully characterized by infra-red (IR), nuclear magnetic resonance (H^1NMR) spectroscopic studies and in addition to micro elemental analysis for C, H and N.

2. Experimental

2.1. Materials

Epoxy resin was obtained from Pachin Pints Company – Egypt, all other chemicals used are pure grade quality get from Sigma-Aldrich Chemical Co. All the melting points were determined by open capillary method and are uncorrected. Chemical structure of the prepared chromene derivatives were confirmed performed using a Perkin-Elmer 240 micro-analyzer at the Micro-Analytical Center of Cairo University, IR spectra were determined as K Br pellets on a Jasco FT/IR 460 plus spectrophotometer, in conjunction with ^{1}H NMR spectra were recorded using a BRUKER AV 300 MHz spectrometer using DMSO as an internal standard. The MS were measured on a Shimadzu GC/MS-QP5 spectrometer.

2.2. General procedure for synthesis of 2,7-Dimino-4-aryl-4H-chromene-3-carbonitrile (I, II) and (E) 7-amino-2-oxo-4-styryl-2H-chromene-3-carbonitrile(III)

A reaction mixture of 3-aminophenol (1) with 4-chlorobenzaldehyde, 4-nirtobenzaldehyde (2a, b) orcinnamaldehyde(2c), malononitrile (3) and piperidine (0.5 mL) in ethanol (30 mL) was heated under reflux for 2 h. After completion of the reaction, the reaction mixture was cooled to room temperature and the precipitated solid was filtered off, washed with Me OH and recrystallized from ethanol or ethanol and benzene. The physical and spectral data of compounds I-III are as follows:

2.2.1. 2,7-Dimino-4-(4-chlorophenyl-4H-chromene-3-carbonitrile (I)

This compound [m. p. 226-227 °C] was prepared by literature procedure (A. S .Abd-El- Aziz et al 2004)

2.2.2. 2,7-Dimino-4-(4-nitrophenyl-4H-chromene-3-carbonitrile (II)

This compound [m. p. 207-208 °C] was prepared by literature procedure (A. M. El-Agrody et al 2014).

2.2.3. Synthesis of (E) 7-amino-2-oxo-4-styryl-2H-chromene-3-carbonitrile (III)

Yellow needles from ethanol; m. p. 129-131°C; yield 82 %; IR (K Br) υ (cm^{-1}): 3464, 3310 (NH_2), 3082, 3028, 2928, 2855 (CH), 2222 (CN), 1708 (CO) (δ- lactone); ^{1}H NMR δ: 8.31-7.23 (m, 8H, aromatic), 6.78 (d, 1H, =CH, J = 16 Hz,), 6.70 (d, 1H, =CH, J = 16. Hz,) 6.58 (bs, 2H, NH_2); MS m/z (%): 288 (M^+, 3.97) with a base peak at 180 (100); Anal. calculated for $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72. Found: C, 75.29; H, 4.43; N, 9.97 %.

2.3. Preparation of Epoxy Paint Films Containing- Chromene Derivatives (I-IV) Surface Paint

The epoxy paint compositions were prepared by physically incorporate chromene derivatives, in the ratio of 0.3, 0.5 and 1.0% by weight into epoxy paint. The samples of different molar ratio were then applied to both steel, glass and wood panels by means of a brush. All efforts were made to maintain a uniform film thickness of 50± 5 µm. for evaluating the physical and mechanical properties and the solid content was 60%.

2.4. Film Casting and Testing

Glass plates (100 x 150 mm) coated with the individual resins were utilized to measure the drying schedule, in terms of time of set-to-touch and dry - through times (ASTM D1640-03). In addition, the same coated glass plates were also used to measure the degree of gloss for individual resin coatings (ASTM 523- 08). The measurements were undertaken using a gloss meter set at a 20^{o} angle, also this plates were utilized to measure the coating film thickness (ASTM D 1005- 07), with this being undertaken using a Model 2100 Minitest microprocessor coating thickness gauge, manufactured by Electro – Physic, West Germany. The coated steel strips used to measure the mechanical resistance of the coated resin films, with testing undertaken on adhesion strength, by means of the cross-cut method (ASTM D 3359-02), flexibility (ASTM D 522-93), and scratch hardness (ASTM D5178-98(2008)) and resistance to mechanical damage (impact resistance) (ASTM D 2794-04).

2.5. Flame Retardant Testing Method

The epoxy paint compositions were prepared by means of incorporating 2,7-Diamino-4-ARYL -4-*H*-Chromene -3-Carbonitrile (I, II) or(E) 7-Amino-2-Oxo-4*H*-Styryl-2*H*-Chromene-3-Carbonitrile (III) derivatives by the ratio of 0.3, 0.5 and 1.0% (A - C) by weight into epoxy paint were evaluated in a limited oxygen index (LOI) chamber. LOI values were determined by standardized tests such as ISO 4589-1: 1996 and ASTM D: 2863-97. Test panels were prepared using a combustible material (wood specimen). It was important that the panels were free of any surface contamination, or imperfections, prior to the coating application. Hand tool cleaning (sand paper) was carefully used to treat the faces and edges of the panels. Final dry film thickness (DFT) was 50 ± 5µm. In all cases, the film application was applied by means of brushing. Following 10 days of air drying, the panels under study were oven heated at 50–60 ◦C for 2 h to eliminate any remaining solvent.

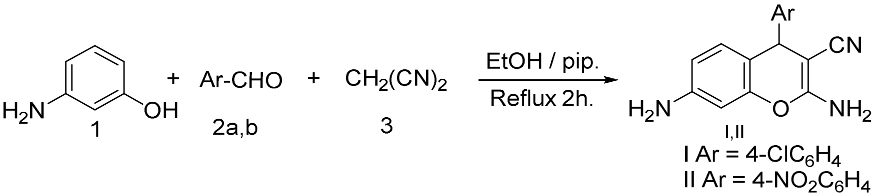
2.6. Anti-corrosive Performance Evaluation of Primer Formulations through Accelerated Testing

The test pieces were 20 x 20 x 3 mm. The samples were first mechanically polished with a fine grade emery paper in order to obtain a smooth surface, followed by degreasing with acetone and then rinsed with distilled water, dried between two filter papers. A salt fog chamber was utilized for each of the resin formulations; with a set of three coated panels being placed in the salt spray chamber according to ASTM B117-03. The corrosion resistance was evaluated in terms of blistering, scribe failure and degree of rusting, in relation to ASTM standards, i.e. ASTM D714-02, D1654- 00 and D610-01 respectively.

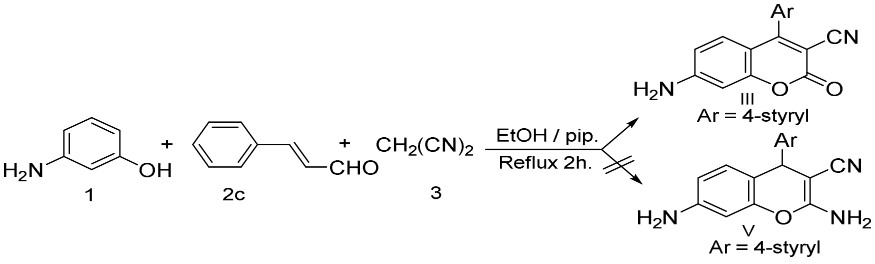
3. Result and Discussion

In the present investigation, chromene derivatives were synthesized in the hope that they might demonstrate enhanced flame retardancy and anticorrosive properties.

2,7-Dimino-4-aryl-4*H*-chromene-3-carbonitrile (I,II) was prepared via three-component condensation of 3-aminophenol (1) with 4-chlorobenzaldehyde or 4-nirtobenzaldehyde (2a,b) and malononitrile (3) in ethanolic piperidine solution under reflux for 2 h. as shown in (Scheme 1), while reaction of 3-aminophenol (1) with cinnamaldehyde (2c) and malononitrile (3) gave (E) 7-amino-2-oxo-4-styryl-2*H*-chromene-3-carbonitrile(III) instead of 2,7-dimino-4-styryl -4*H*-chromene-3-carbonitrile (IV) as shown in (Scheme 2).



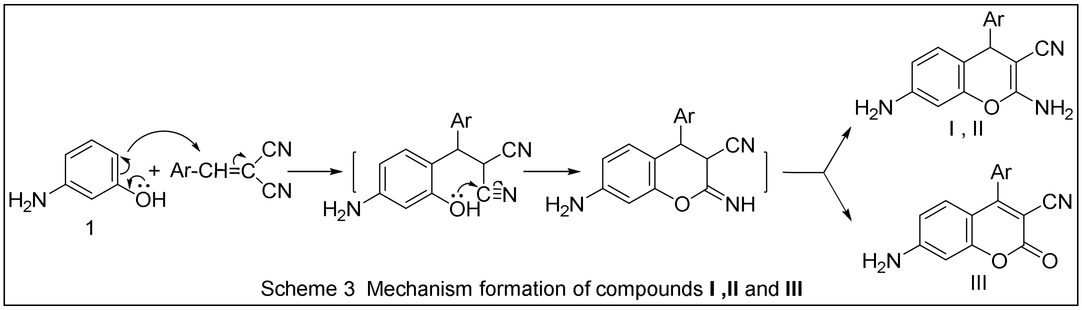
Scheme 1. Synthesis of 2,7-diamino-4*H*-chromene derivatives (I,II)



Scheme 2. Synthesis of 7-amino-2-oxo-4-styryl-2*H*-chromene-3-carbonitrile (**III**)

Figure 2

The formation of I, II and III indicates that the phenolate anion (C-6) of 1 attacks at the *β*-carbon of*α*-cyano-4-substitutedcinnamonitriles to yield an acyclic Michael adduct, which underwent cyclization to give I , II or cyclized, hydrolysis of the imino group into carbonyl group and loss hydrogen to give III as shown in (Scheme 3).



Scheme 3 Mechanism formation of compounds **I** ,**II** and **III**

Figure 3

The relative *(E)* configuration of compounds (III) was established from the coupling constant values (J = 16 Hz) for (III).

3.1. Coating Properties

Modified epoxy resins were evaluated for some physical and mechanical properties and their anticorrosive and fire retarded properties. Evaluation of the physical and mechanical properties of modified epoxy varnish. The effects of adding modifiers chromenes derivatives to epoxy resin formulation, were evaluated using a variety of standard test methods. This was done to ascertain any negative aspects that might arise due to the presence of the additives. The drying time, gloss, scratch hardness, adhesion, flexibility and impact were all measured. The resulting data is shown in Table (1). All films of epoxy paint compositions gave a very clear, transparent and homogeneous appearance.

3.1.1. Drying Time

This was conducted by placing the test panel in a horizontal position at the height such that when the thumb is placed on the film, the arm of the operator is in a vertical to the shoulder. Bear down on the film with the thumb, exerting the maximum pressure of the arm, at the same time turning the thumb through an angle of 90 ° on the plane of the film. The film is considered hard dry when there is no distortion of the film. It is clear that the addition of modifiers chromene was reduced drying times the probability of the presence of the amino-groups.

3.1.2. Gloss

This was measured using a Sheen UK glossmeter. On observing the films using a 60◦ angle, it could be seen that the modifiers chromene actually increased the gloss levels. This is obviously a positive result which may be attributed to the introduction of aromatic rings, present in the additive structure.

3.1.3. Cross-hatch Adhesion Test

This was measured by using a Sheen UK crosscut adhesion tester. For this test method a lattice with six cuts in each direction was made in the film (the cuts were spaced at 2 mm). Pressure-sensitive tape was then applied over the lattice and subsequently removed. All the coating film demonstrated good cross-hatch adhesion. The modifiers chromenes did not change the adhesion properties of the epoxy varnish.

3.1.4. Resistance to Mechanical Damage (Impact Resistance)

This was measured using a Sheen UK impact tester. The impact resistance of the coating on the steel panels was tested by means of dropping an 890 g steel ball from a height of 1 m. The impact strength was shown to increase in the presence of the flame modifiers chromene, which may be attributed to the incorporation of aromatic ring into the epoxy paint formulation.

3.1.5. Scratch Hardness Test

This was determined by using a Sheen UK hardness tester. The scratch hardness is observed to vary between 1500 and 2000 g and it is clear from the data that as we increase the flame modifiers chromene, the scratch hardness of the film increases.

3.1.6. Flexibility (bend) Test

Flexibility was determined by using a 1/4 in. Mandrel bend tester from Sheen UK, in such a way that the surface of the panel was directed outside. The films for all the coating compositions passed the 1/4 in. Mandrel bend test. The varnish was considered satisfactory if no cracking marks, or dislodging, are observed following the bending procedure. Based on this qualitative measurement, it can be stated that all the films showed reasonably good flexibility.

Sample	**Chromene %**	**Drying time (h)**	**Gloss at 60°**	**Adhesion**	**Impact (J)**	**Hardness (gm)**	**Flexibility**
Blank	-	7	59	5B	1.72	1500	Pass
Epoxy with comp. I A	0.3	6	58	5B	1.7	1500	Pass
B	0.5	6	60	5	1.73	1500	Pass
C	1.0	5	57	5B	1.74	1500	Pass
Epoxy with comp. II A	0.3	5.15	62	5B	1.84	1500	Pass
B	0.5	5	65	5B	1.90	1500	Pass
C	1.0	4	66	5B	2.00	1500	Pass
Epoxy with comp. III A	0.3	5	62	5B	1.92	1500	Pass
B	0.5	5	63	5B	1.98	1500	Pass
C	1.0	4.15	65	5B	2.05	1500	Pass

Table 1: Physical and mechanical properties of epoxy paint incarnated chromene derivatives

3.2. Evaluation of Chromene Derivatives as a Flame Retardant Additive Incorporated Physically into Epoxy Paint

The LOI is defined as the minimum concentration oxygen, expressed as a percentage that will support combustion of a polymer. It is measured by passing a mixture of oxygen and nitrogen over a burning specimen, and reducing the oxygen level until a critical level is reached. The LOI is expressed as:

$$\mathrm{LOI}=100\frac{[O2]}{[O2]-[N2]}$$

This method proved suitable as a semi-quantitative indicator of the effectiveness of the flame retardant during the research and development phase of the work. This was due to the fact that the equipment is relatively inexpensive and the size of the test sample that is required is reasonably small. It is clear that the incorporation of chromene derivatives into epoxy paint, in the ratio's mentioned in the experimental section, results in enhanced flame retardancy when compared with an epoxy control sample. The results obtained from the LOI test are shown in Table 2 and Figs. 2.

It can be observed, that the LOI value of the control epoxy resin is19 and the maximum LOI with 1.0% of 2,7-diamino-4-(4-nitrophenyl)-4-*H*-chromenes -3- carbonitrile (**II**) is 53. Normal atmospheric air contains approximately 21% oxygen, so a material with an LOI of less than 21% would burn easily in air. In comparison, a material with a LOI value greater than 21%, but less than 27%, would be considered to be ‘slow-burning’. However, a self-extinguishing material is one that has a LOI greater than 27% and this would stop burning after the removal of the fire, or the ignition source**.**

Sample	**Chromene %**	**Limiting Oxygen Index (LOI)**
Blank	-	19
Epoxy with comp. I A	0.3	20
B	0.5	22
C	1.0	23
Epoxy with comp. II A	0.3	30
B	0.5	42
C	1.0	53
Epoxy with comp. III A	0.3	39
B	0.5	43
C	1.0	48

Table 2: Flame retardant characteristics of epoxy varnish incorporated chromene derivatives as flame retardant additives

An interesting point associated with the results is that the LOI curves for the chromene derivatives are more or less linear. This is as result of the fact that they are a high molecular weight nitrogen and oxygen compounds, and therefore provide superior flame retardant properties compared to low molecular weight flame retardants. A further interesting point is that the LOI values of (2,7-diamino-4-(4-nitrophenyl)-4*H*- chromene-3- carbonitrile is the highest, this may be attributed to that the nitro group contain a duple bond between nitrogen and oxygen atoms.

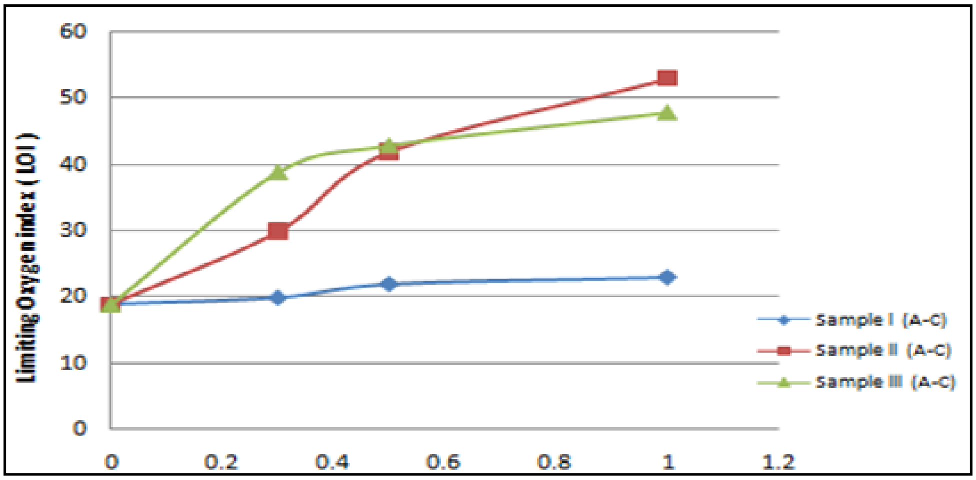


Figure 4: Limited Oxygen Index (LOI) Characteristics of Reactive Flame Retardant Modified Epoxy Resins

3.3. Corrosion Resistance

The epoxy paint compositions were prepared by means of incorporating chromene derivatives by the ratio of 0.3, 0.5 and 1.0% by weight into epoxy paint and film thickness 50 ±5µm. were evaluated as the anti-corrosive. The paint formulations were evaluated on coated steel panels. To ensure that the steel panels were free of all surface contamination before the coating application, pre-treatment involved wire brushing and sand paper cleaning of the surface. The coated steel panels were exposed to salt spray tests according to CSN ISO 9227for 500 h. Photographic reference standards were used to evaluate the degree of blistering. The reference standards highlight the various degrees of blistering that can potentially develop when paint systems are subjected to these specific test conditions. The blistering size is graded from 10 to 0, where 10 represents of no blistering and 0 representative of the largest blister. Blistering frequency is denoted by F, M, MD and D (few, medium, medium dense and dense). Painted, or coated, specimens subjected to a corrosive environment are also evaluated by recording the average (mean) maximum and minimum creep age from the scribe mark. Scribe failure is also rated on a scale from 10 to 0, with 10 being zero (mm) from the scribe mark and 0 is 16 (mm) from the scribe mark. Finally, visual comparison of the surface with photographic reference standards, to determine the percentage of the area that has been rusted, is also used. These visual standards were developed in cooperation with the Steel Structure Painting Council (SSPC) to further standardization of test methods. The amount of rusting beneath, or through, a paint film is a significant factor in determining whether a coating system should be repaired, or replaced. The rust grade is rated on scale from 10 to 0, where10 is no rusting and 0 is severe rusting. The results of corrosion resistance of the painted films of prepared samples are given in Table 3 and Fig.3 explains the photo of the painted films after salt test spray (3.5% of Na Cl). The results show that all chromene derivatives have an excellent effect as a corrosion inhibitor, and the increasing modifier percentage lead to slightly improvement anticorrosive properties especially compound III [(E) 7-amino-2-oxo-4-styryl-2*H*-chromene-3-carbonitrile]. The improvement in corrosion resistance may be attributed to the introduction of a compound that contains amino, carbonyl and nitrile linkages. Also the high molecular weight of the modifier decreases the permeability of coating to water, oxygen and the aggressive ions such as chloride. The corrosion resistance increase is also due to the absorption of resin onto the metal through its hydroxyl function.

Sample	**Blistering**		**Scribe failure (mm)**	**Rust grade**
	Size	**Frequency**		
Blank	2	D	13	2
Epoxy with comp. I A	4	MD	9	3
B	4	MD	8	5
C	6	M	6	5
Epoxy with comp. II A	4	M	9	4
B	6	M	6	6
C	8	F	5	7
Epoxy with comp. III A	6	M	6	5
B	6	F	4	6
C	8	F	2	8

Table 3: Evaluation the corrosion resistance of the painted films

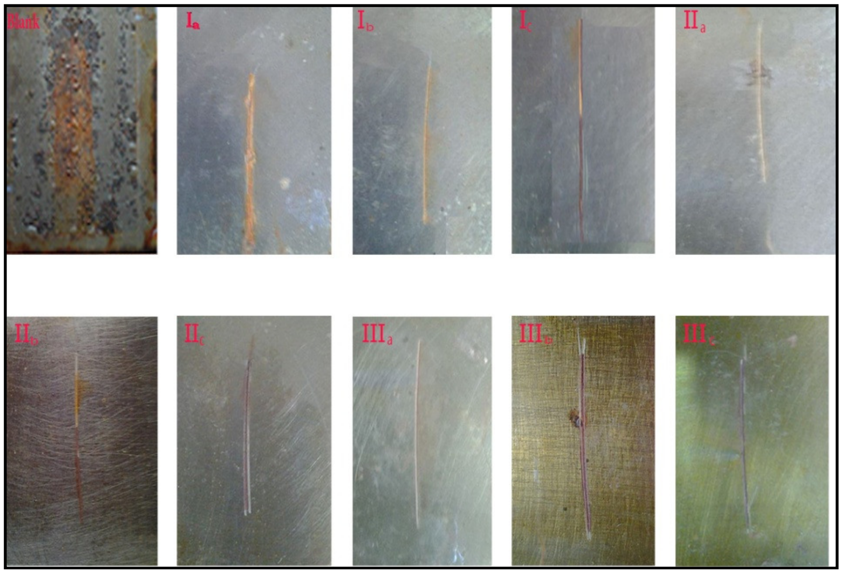


Figure 5: The photo of the painted samples after exposed to sea water test ((3.5% of Na Cl)

From the experimental test of anticorrosive protection was found, that the both coatings resist 24 hours with damage of cut that is 4 months short-time anticorrosive protection in real environment C5. Anticorrosive coating without damage resist 120 hours, that is 20 months' anticorrosive protection in real environment C5(J. Podjuklova 2010).

Corrosive resistance in corrosive chamber	
Simulated time in corrosive chamber	**Reality- approximately**
720 hours	10 years
72 hours	1 year
6 hours	1 month

Table 4: Corrosive resistance in corrosive chamber

4. Conclusions

The results of the study revealed that the incorporate chromene derivatives have improved some of physical properties as resistance to mechanical damage and drying time of epoxy varnishes, and increasing the modifier percentage decrease drying times.

Adding of (II and III) to the epoxy resin show impressive results as fire retardants, and as the percentage of modifier increase the fire retardance increase. The compound (II) has the highest fire retardant property. All compounds (I, II and III) behave as a good steel anticorrosive and as the percentage of modifier increase the anticorrosive increase. The compound (III) was the highest the anticorrosion one.

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