THE STUDY ON MILD STEEL CORROSION BY ADDING CARBON BLACK AND GRAPHITE TO EPOXY PAINT

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Abstract

This study affords to clear corrosion prevention properties of epoxy paint with graphite and carbon black pigments. To approach this goal, 7 different paint formulas were designed by experimental design and applied to mild steel plate. Raw material quality tests (XRD, Particle size and Ash content tests) general tests of paints (Abrasion resistance, MEK RUB resistance, Hardness, Gloss, Impact resistance, Cross Cut) and two special corrosion tests (Salt spray and EIS) were done to evaluate paints properties. All results analysed by DX7 software, a specific software for experimental design. Graphite ad carbon black final evaluation shows the best zone of graphite and carbon black quantity to use in epoxy resin as corrosion resistance pigments.

1-Introduction

Coating is the first selection for corrosion prevention of metals. Coating acts as a barrier and don't allowed to ions and electrons to transfer. Perfect coating can protect metals against corrosion [1]. But because of some defects in coating, cathodic protection is inevitable. Two important factor affect on coating properties; resin and pigments. Resin is a vehicle and is interface of coating and substrate. Proper selection of resin aids to proper properties of coating [2].

Epoxy resin has desirable properties to prevention of steel corrosion. Many pigments add to epoxy resin to improve special properties such as hardness, chemical resistance, corrosion prevention etc. There are many pigments to progress corrosion inhibition of epoxy resin. In this field, a few studies indicate on corrosion inhibition properties of graphite and carbon black pigments. Carbon black is a famous black pigment for paint and graphite has particular properties such as hydrophobic property because of its laminar structure. Laminar structure of graphite converts this material to a special material. The properties of graphite change in different direction of structure. [3]. Graphite fiber and epoxy can contribute to form a composite with excellent mechanical properties. Another important property of graphite is its electrical conductivity [4] . Conducting coatings were progressed by using of this graphite property. Darowicki used of this property to produce a conducting coat as anode in cathodic protection. [5]. Conductivity isn't proper specification for corrosion prevention because it facilitates electron transferring [1]. To evaluation properties of epoxy paint with carbon black and graphite, experimental design is used to analysis final data statistically. Single , dual and triple effects of materials can distinguish by this method. [6]

2-Experimental

Table 1 shows materials and their weight percent. This table was designed according to mixture experimental design. Three factors were selected as object of design. These factors are resin, graphite and carbon black. These three factors changes as table 1 and their effects on results will analysis.

Table 1. Weight percent of materials

components / No. of Paints	Resin	Graphite	Carbon Black
1	45	10	4
2	35	20	4
3	35	10	8
4	40	15	4
5	40	10	6
6	35	15	6
7	38.3	13.3	5.3

For evaluation the quality of raw materials, XRD, particle size and ash content were done on carbon black and graphite.

Epoxy resin 1001 Shell and its hardener mixed in three percent to achieve best hardener percent for mixing. MEK rub and Konig hardness tests were done on samples.

Adding of carbon black, graphite and TiO_2 to resin and mixing together was done simultaneously and gradually by using of mixture in 400 rpm for 1-1.5 hours. In first step Soyalestin had selected as dispersing agent but result in high viscosity of paint, then the dispersing agent changed to BYK 180.

Then mixture was milled by using of roller mill for 4 pulses and with maximum pressure between drums. Rolling was continuing till particle size reached below 20 μm.

Surface prepared according to SSPC-SP1,2 standards and then paint was applied to steel plate by spray. Samples were rested in room temperature for 7 days to drying completely. Special corrosion tests (salt spray & EIS) and general tests of paint (Abrasion resistance, MEK RUB resistance, Hardness, Gloss, Impact resistance, Cross Cut) were done on samples.

3- Results and Discussion

Fig1-1 and 1-2 show XRD graphs of Graphite and Carbon Black, respectively. Results show that graphite is crystalline but Carbon Black has amorphous structure similar a glass graph. XRD graph of graphite demonstrates only 1 peak that expresses no extra phase other than graphite.

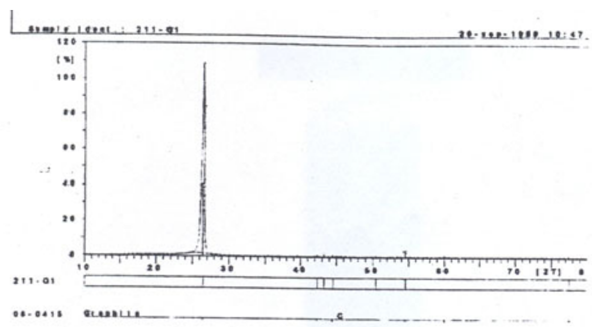


Figure 1-1. XRD graph of Graphite sample

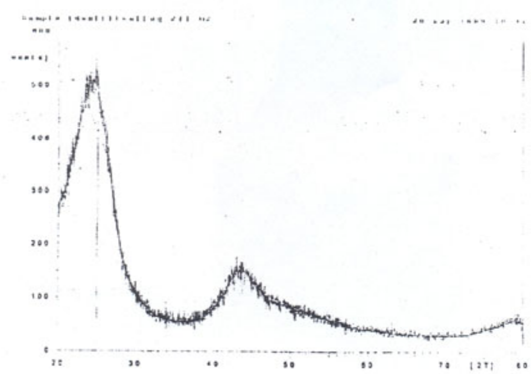


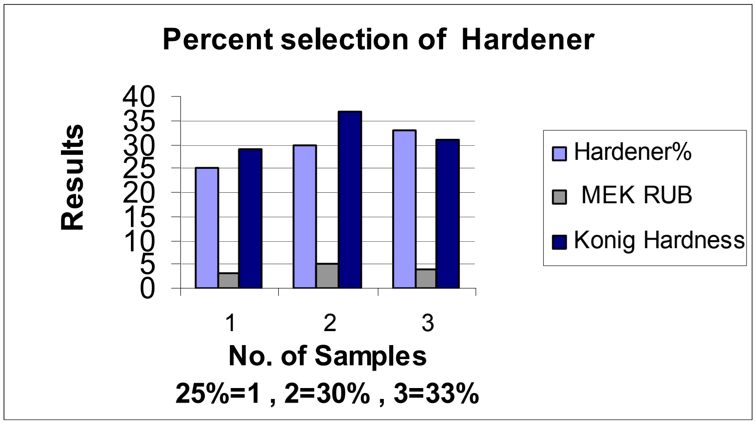
Figure 1-2. XRD graph of Carbon Black sample

Table 2 shows results of Particle size and Ash Content of Graphite and Carbon Black. ash content of these material is lower than 1% that show their purity aren't excellent but they are in standard range (below 1 %). This tables determined that particle size of graphite and carbon black is in normal range(10-20 μm) to produce paint but graphite is finer than Carbon black , then it was expected some problems in Carbon Black dispersing and wetting by resin .This results confirmed in mixing step that results in changing of dispersing agent and time of mixing.

Table 2. Results of particle size and ash content

	ASH CONTENT TEST	PARTICLE SIZE TEST	
Materials	Ash content (%)	Distribution range(µm)	Mostly Distribution range(µm)
Graphite	1	0.95-158.5	12-22
Carbon Black	0.5	0.955-478.63	15-23

Graph.1 represents results of MEK RUB and Konig Hardness tests on three percent of hardener. Results distinguished that best percent of hardener is 30% weight of resin that show excellent interaction and networking between resin and hardener in 30 % weight of resin.



Graph 1. Results of MEK RUB And Konig Hardness on three percent of Hardener

Eight tests applied to evaluate properties of 7 formulas. One of most important test is adhesion test. Adhesion test (cross cut) fulfilled on samples according to ASTM-D3924. There isn't difference between results of cross cut test and all results show the best adhesion (5B in ASTM -D3924) of paints without any damage. It was supposed that by adding pigments to resin, adhesion must be decreased, but proper selection of resin and suitable dispersion of pigments in resin obstacle adhesion decreasing. [7] Fig. 2 clears the effects of 3 factors (resin, graphite and carbon black) on results of abrasion test. This test was done according to ASTM D4060-01. As showing Fig.2, it's clear that adding of pigments increase resistance of paint against wear. Graph 2 indicates that between two pigments, graphite is more effective than carbon black in wear resistance increasing. Graphite has a compact crystalline structure and this adds to increase wear resistance. On the other hand, graphite particles size is less than carbon black particles size that result in compact graphite/resin composite and increasing wear resistance of paints.

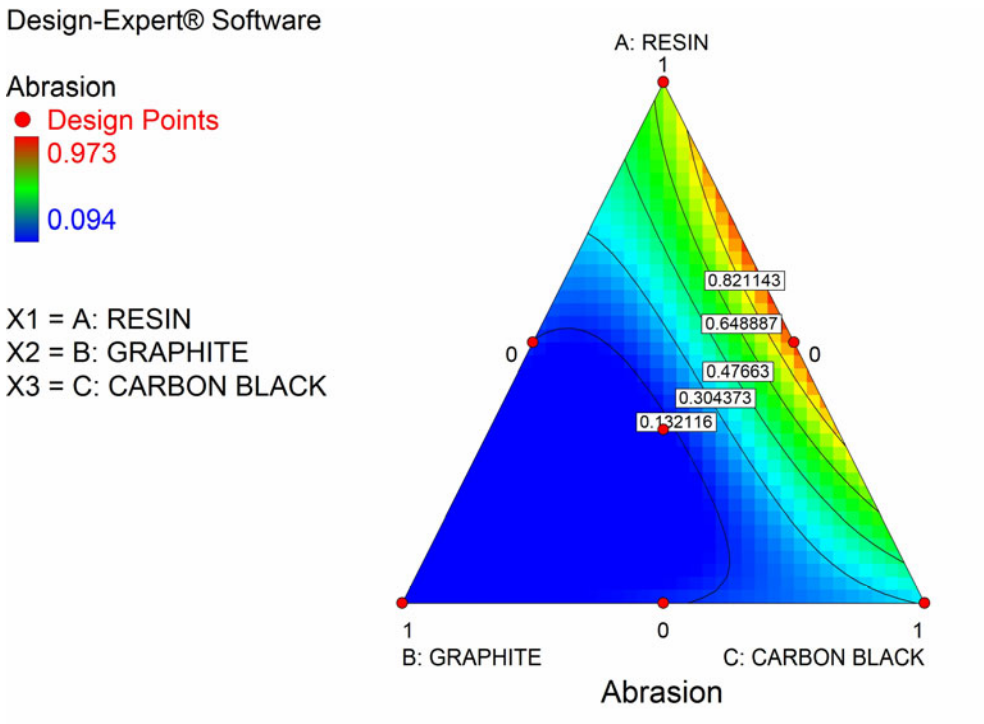
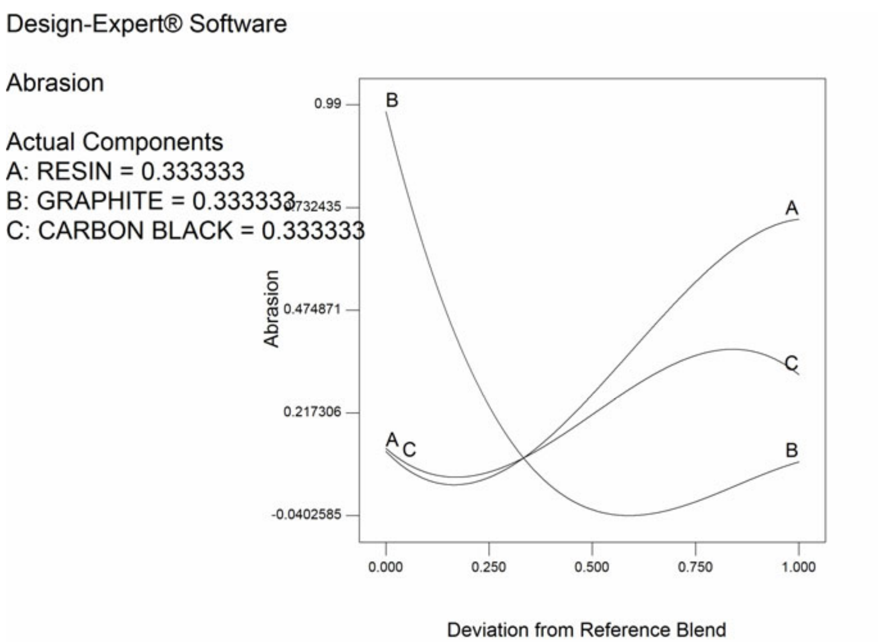


Figure 2. Final effects of 3 factors on wear resistance of paint



Graph 2. Individually effect of each factor on wear resistance of paints

In some application, it needs impact resistance of a paint. Then according to ASTM D6905 impact test applied to samples and Fig.3 clears the final effects of factors on direct impact results and fig.4 shows the effect of factors in indirect method. Two procedures exist to evaluate of impact resistance; direct impact and indirect impact. Direct impact exposed the surface paint directly but indirect impact applied to back of plate (without paint). [7]

Results of impact test indicate that adding pigment to resin lead to decrease the toughness of paint. Proper reaction between hardener and resin result in high elasticity but adding a brittle pigment such as graphite can reduce the elasticity of composite. This phenomenon terminates to low direct impact of paints. But in indirect method, increasing of pigments quantity, somewhat causes increasing toughness.

Because increasing amount of pigments, exhibit high grains boundaries. Grain boundaries act as a dam against crack growth that is the major parameter in indirect method. By adding more amount of pigments, results show decreasing because of exceeding of CPVC. [2]

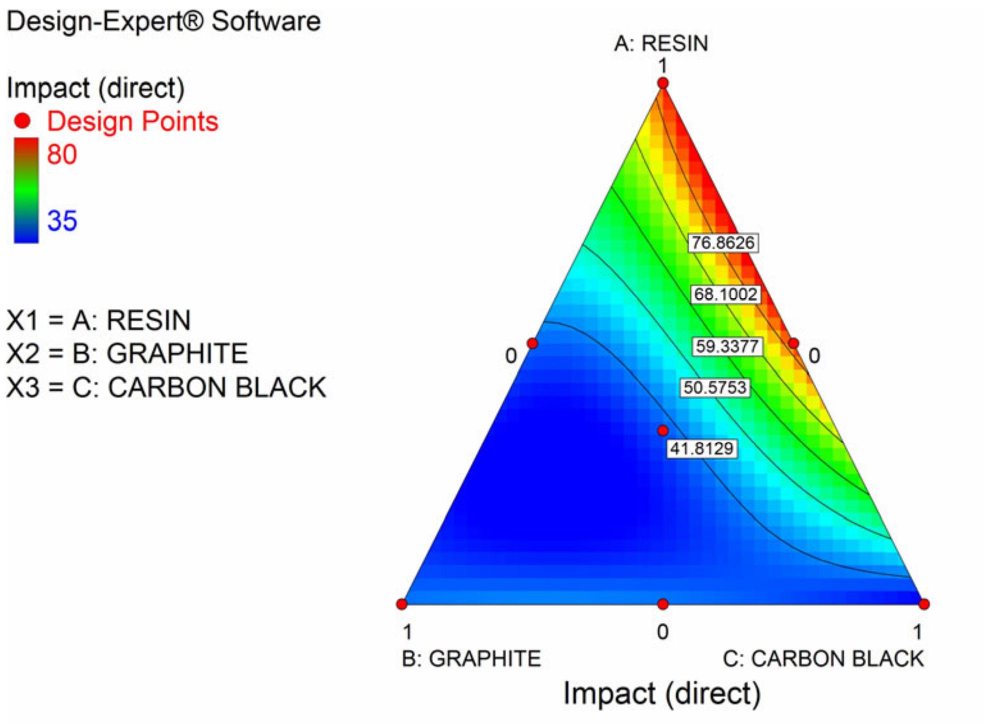


Figure 3. Final effects of 3 factors on direct impact resistance of paint

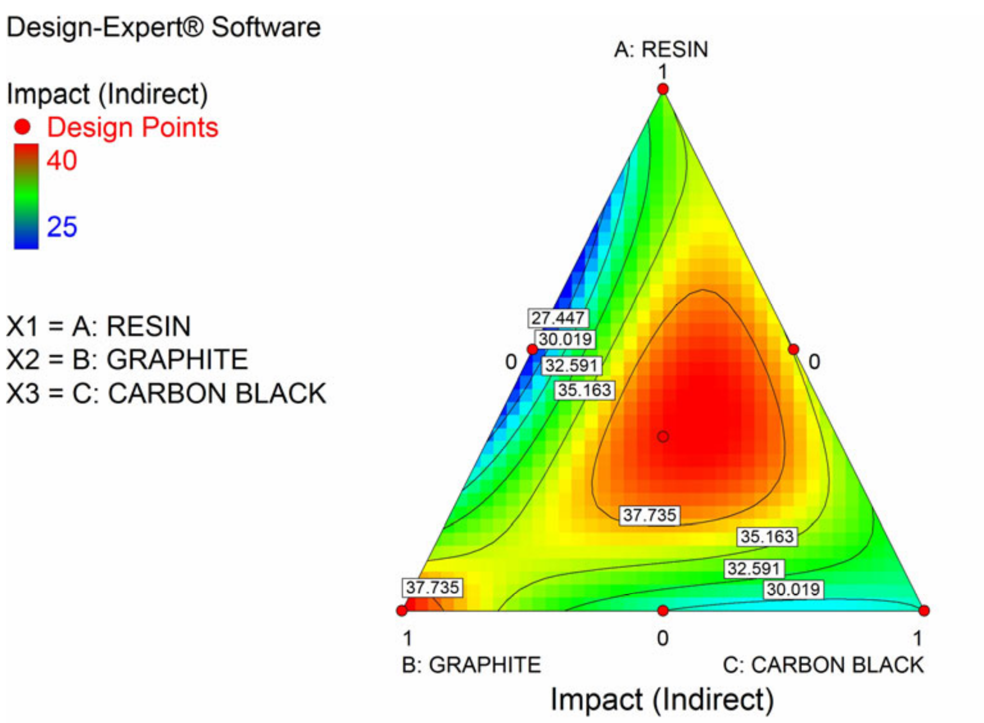
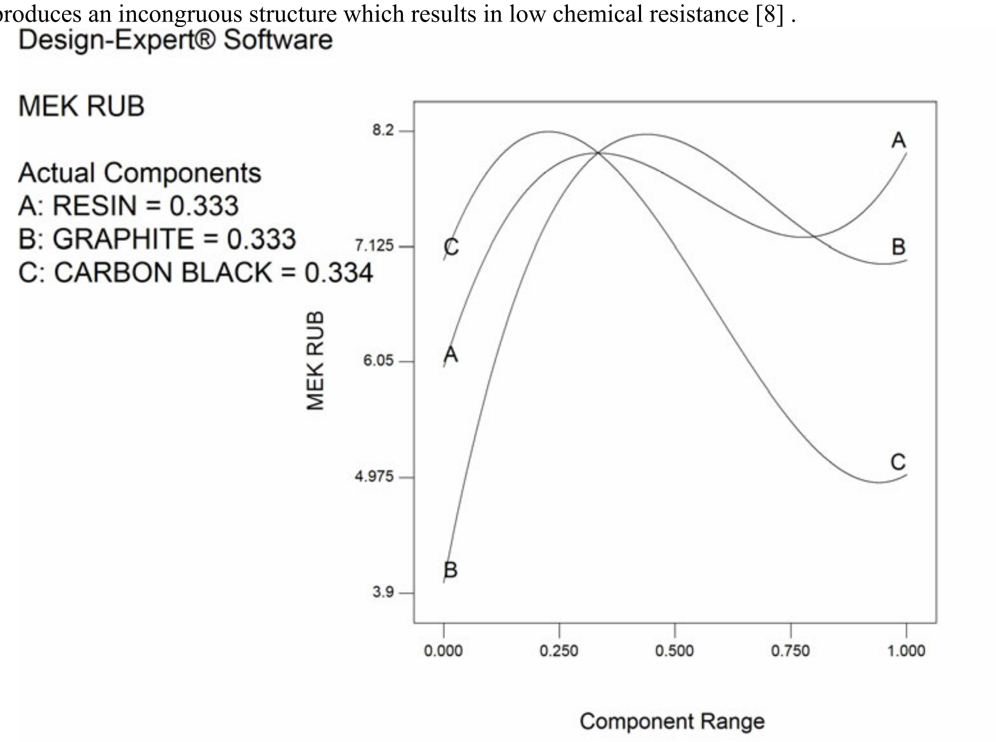


Figure 4. Final effects of 3 factors on indirect impact resistance of paint

To evaluate chemical resistance of paints, MEK RUB test was done on samples according to ASTM D5402-93. The times that paints can resist till to reach substrate is the criterion. Graph 3 demonstrates results of this test that shows effective role of graphite in increasing solvent resistance of paints. But carbon black has negative effects on solvent resistance of paints. Main reason of this difference is in wetting of pigments. Graphite has finer particle size than carbon black. Then it can wet by resin easily and it causes to raise chemical resistance. But incompletely wetting of carbon black produces an incongruous structure which results in low chemical resistance [8] .



Graph 3. Individually effect of each factor on MEK RUB test

Two important corrosion tests (salt spray and EIS) help us to complete our viewpoint about these formulas. In salt spray test, samples with a X cut on their surface, exposed to 5% NaCl solution according to ASTM -D1654. Samples removed of cabin after 400 hours and inspected in two procedures. [7]

In first step, they inspected visually and in second step their damaged surface percent was defined to compare together statistically. Second step was done by a special instrument that gives us video images (VIEEW) of samples with specified damaged zone according to ASTM D1654- PROCEDURE A. Fig. 5 shows the surface of sample 2 image after 400 hours salt spray. By both methods, it's clear that sample 5 has the most damaged surface (52%) and some blisters were viewed in this sample. In sample 1, we can see a general corrosion on surface that damaged 41% of surface. Corrosion damage begins of X cut location and solution leaks to interface of paint and substrate in sample 4 by 35% damaged surface area. Sample 6 shows some blisters on its surface with damage in X cut. Image of this sample clears 29% damage in surface area. Performance of VIEEW will be clear in comparison between sample 2 and sample 3. There isn't any visual difference between them and they are incomparable statistically but images of them show that damaged surface of sample 2 is higher than sample 3.

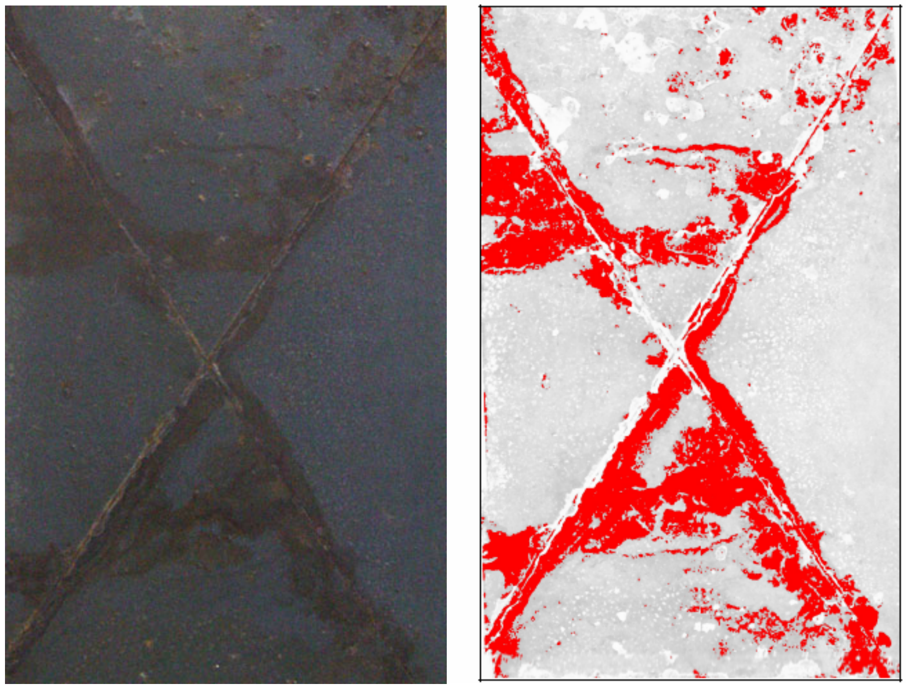
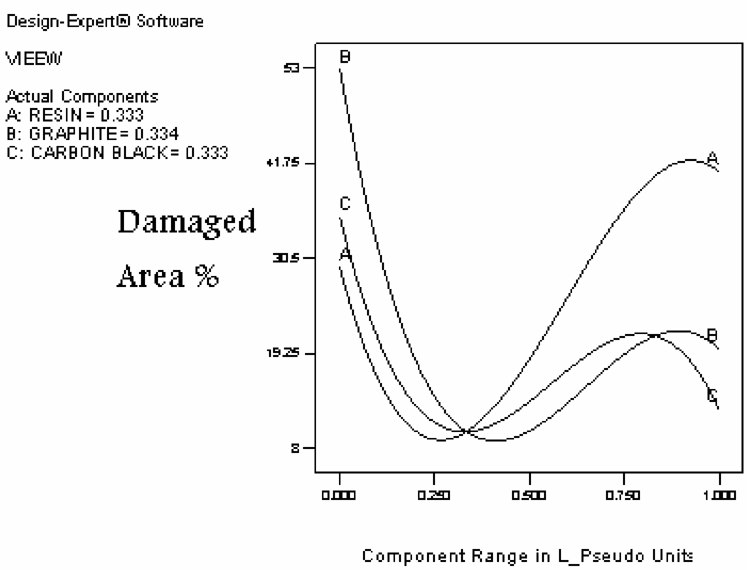


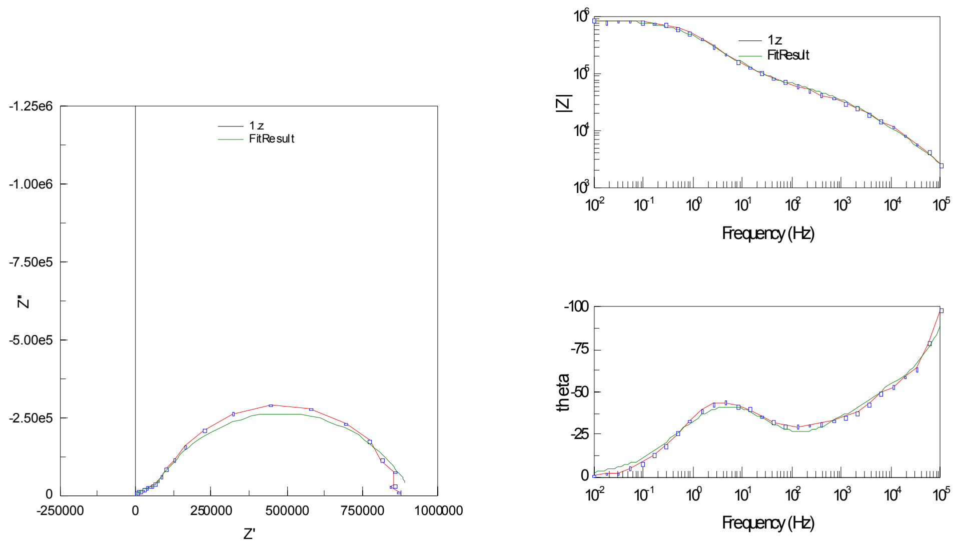
Figure 5. Surface of sample 2 after 400 hours salt spray and its video image



Graph 4. Individual effect of each factor on percent of damaged surface area

Sample 7 has the best situation in all samples because of no blistering in surface and its low damaged surface area (10%). Graph 4 determines the individually effects of 3 main factors as a result of VIEEW test. It was seen that graphite has the most important role between these 3 factors and increasing quantity of graphite helps to decrease corrosion on samples because of its laminar structure and hydrophobic property. Carbon black acts similar role but in low range. One of the most important tests in corrosion studies is Electrochemical Impedance Test (EIS). Results of this test help investigators to determine the properties of paints [9]. By using of EG&G model 1025 instrument and in three electrode method, EIS test was done on samples. Electrolyte is 3.5% NaCl solution and a standard paint cell takes into service.

Results are three plots; Nyquist plot, Bode magnitude plot and Bode phase plot. Equivalent circuit was applied to these plots to simulate electrochemical phenomena. Graph 5 shows these three types plots and the nearest fitted plot of sample 1. Fig. 6 is a equivalent circuit for sample 1. of three types plots, it was found that there are two or three time constant. One of them is for double layer and another is for coating. Third time constant is probably for diffusion of corrosion products [10]. Two important parameters were achieved to comparison between samples. Coating resistance and coating capacity were determined that they are representative of paint porosity and paint depolarization capability, respectively [11].



Graph 5. Nyquist and Bode plots and their fitted plot of sample 1

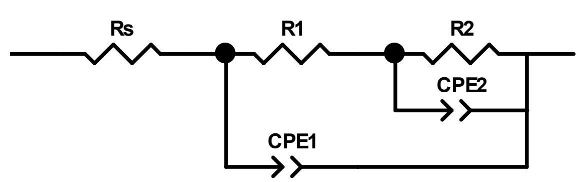
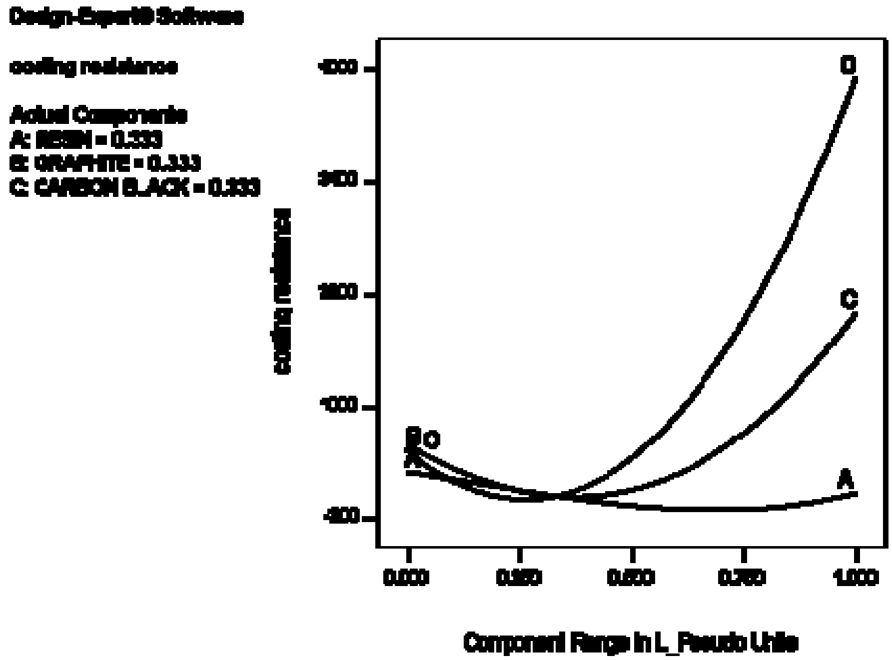
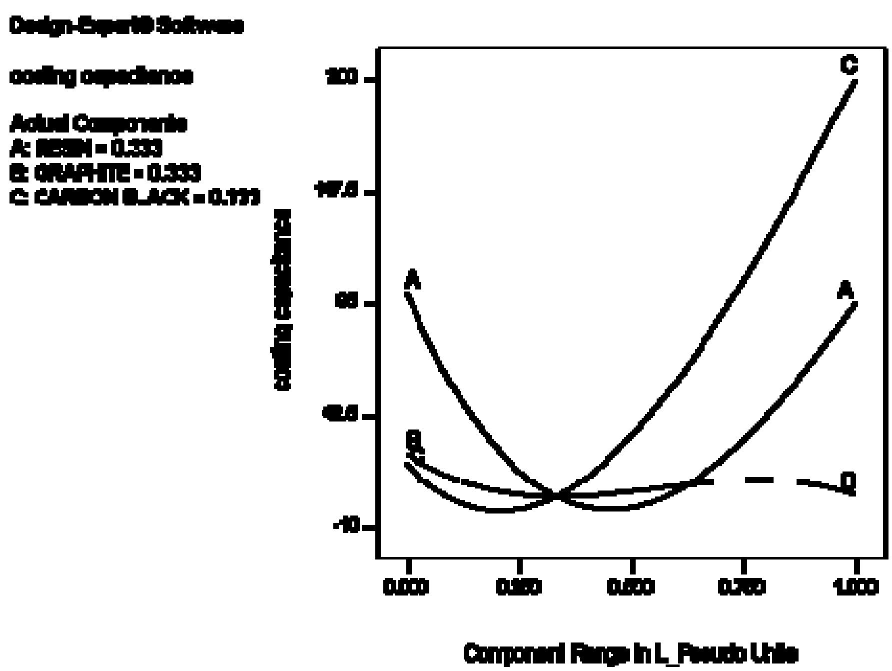


Figure 6. Equivalent circuit for sample 1

Graph 6 that distinguishes coating resistance and effects of 3 main factors, indicates that resistance increases by adding graphite to epoxy resin. Reason of this result is two important specifications of graphite; hydrophobic property and laminar structure. Hydrophobic property helps to lower contact between solution and coating surface that result in low diffusion of corrosive ions. Laminar structure of graphite is a excellent barrier to reach solution to substrate. This means that there is a difficult way to ion transfer between solution and substrate.



Graph 6. Individually effect of each factor on coating resistance



Graph 7. Individual effect of each factor on coating capacitance

Results study of coating capacitance is summarized in graph 7.In spite of coating resistance, graphite effect on coating capacitance is negligible. Conductivity of graphite can't keep electrons to show capacitance specifications. But carbon black can rise coating capacitance more than resin. According to $C=ee.A/d$ equation , e is dielectric constant that returns to natural properties of materials and their conductivity. For epoxy resin **e=3.8**. By adding amorphous carbon black to coating , the conductivity of composite decreases that results in increasing coating capacitance.

4-Conclusion

Graphite has properties that can affect on coating properties as a pigment. Mechanical properties of graphite and carbon black progress the mechanical properties of coating such as wear resistance of coating. This way isn't in similar approach and has distortion in some tests. Advantages of graphite are hydrophobic property and its laminar structure. These two properties improve corrosion prevention capability of coating such as salt spray resistance and rising coating resistance. Graphite has one big disadvantage; its conductivity. This property helps to electron transferring between substrate and solution and affects on coating capacitance. But by optimization between advantages and disadvantages of graphite , there are some zone in triangle of experimental design that exhibit excellent properties of coating.

References

1- Chals G. Munger ، *Corrosion Prevention by Protective Coating* ، NACE ، pages 35-43 ،1993 .

2- Zeno W. Wicks ، Frank N. Jones، S. Peter Pappas ، *Organic Coatings Science and Technology* ، second edition ، Wiley Intersciencen publication ، 1999 .

3- I. Spain، *In Chemistry and Physics of Carbon* ،Marcel Dekker pub. ، Vol.16 ، page 119 ، 1981.

4- B. M. Kavlicoglu ، *"Analysis and Testing of Graphite/ Epoxy Concrete Bridge Girders under Static Loading"* ، Proceeding on Repair of Bridges ، London ، July 2001.

5- K. Darowicki ، *"Conducting coating as Anodes In Cathodic Protection"* ، Progress in Organic Coatings ، vol.46 ، pages 191-196، 2003.

6- J. Sward ، *Basics of Experimental Design* ، Elsevier pub. ، pages 31-44، 1998.

7- Joseph V. Kloeske ، *Paint and Coating Testing Manual* ، 14th edition، ASTM ، 1995.

8- Temple C. Patton ، *Pigment handbook* ، Vol. 2 ، Wiley pub. ، pages 36-48 ، 1996.

9- B. Lengyel ، *"Electrochemical Methods to Determine the Corrosion Rate of a Metal Protected by a Paint Film"* ، Progress in Organic Coatings ، vol. 36، pages 11-14 ، 1999.

10- D. Ramirez ، *"Evaluation of Protecting Properties of Epoxy Coating on Navy Steel by EIS* "، Jo. Of Chilean Cemical Scociety ، vlo. 50 ، 2005.

11- G. Grundmeier ، *"Corrosion Protection by Organic Coatings : Electrochemical Mechanism and Novel Methods of Investigation"* ، Electrochemical Acta ، vol. 45 ، pages 2515-2533، 2000.