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Optimization of a Waterborne Epoxy Coatings Formulation via Experimental Design

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ABSTRACT

Waterborne Epoxy based coatings were prepared by using a water-borne epoxy resin and a suitable hardener. The formulation and optimization procedure were carried out on the bases of experimental designs by the mixture design technique in which the important paint properties are modeled by using special cubic model. The corrosion behavior of these coatings was investigated using electrochemical impedance spectroscopy (AC impedance spectroscopy) for a period of 21 day exposure to a solution of 3.5 wt% NaCl in distilled water. Coating parameters such as the pore resistance and the coating capacitance were measured by ac impedance technique and considered as the response in the experimental design. Prog. Color Colorants Coat. 2(2009), 23-33.

1. Introduction

One of the mechanisms by which protection against corrosion of steel surfaces is offered, involves the formation of a barrier coating against the diffusion and the penetration of corrosive agents such as water vapor, oxygen, and ions [1].

Conventional solvent borne epoxy primers with excellent adhesion and water resistance properties have odecades. The volatile organic contents (VOCs) of current solvent borne epoxy primers are high enough to prevent to be considered environmentally safe. Low VOC waterborne epoxy primers were introduced to the market in the 1980s. Since then, the performance gap between the solvent borne and the waterborne primers has since been reduced considerably. Waterborne epoxy resins offer reduced organic volatiles, easy cleaning, and compatibility with widely used waterborne topcoats such as acrylic latex and urethanes.

In anti-corrosion coating markets, epoxy resin-based products dominate over other synthetic resins due to their superior strength, low shrinkage, better bonding with different substrates, good dimensional stability and long term corrosion and chemical resistance [2-3].

Waterborne coatings have been modified to be

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effective in corrosion protection, in which they are passed through several stages [4]. In the first stage, single-pack anti-corrosive coatings are developed, based on styrene-butadiene and vinyl acrylic terpolymers and alkyd emulsions [5]. In the following stages, two-pack epoxy anti-corrosive coatings, which are largely dependent on the synthesis of new binders, are developed [6]. Special attention is currently being paid to other binders such as fluorpolymers [7] and polyurethane dispersions [8], and also to additives and to special rheological aspects of waterborne coatings [9].

In summary, waterborne coatings have been experiencing technological unsteady growth for the past 20 years, but this has not been a steady growth. During the last years, considerable developments in new technologies became available to formulators. if appropriate pigments are available, the growth in waterborne coatings will continue in coming years, [10]. At present, it can be stated that new raw materials and both reticulating or curing agents will enable the relatively recent waterborne technologies to be improved and acceptable to the end-users. However, their higher price is the main obstacle in their way to play a major role in anti-corrosion paint marketing. This reason can be another incentive for further developments. As a complement to new waterborne formulations, there is a battery of tests used to demonstrate the protection conferred by coatings. The first test performed on a developing maintenance finish is usually the salt spray test. it has been a good measure of film quality as tight films are important in substrate protection. If films are not scored in a salt spray test, corrosion failure, they will largely reflect the presence of channels or pores in the coating. However, it has proved that salt spray is not the only or the best of way of measuring corrosion resistance. Nysteen and others refer to prohesion as a convenient test for evaluating new paint formulations [5]. Also other authors confirm that this is a better accelerated test for selecting waterborne coatings than salt spray test [11]. Funke noted that electrochemical testing, which requires charge transport through coatings, has gained considerable attention during the past decade and consequently, it is highly recommended for characterizing the protective qualities of organic coatings[12].

The above mentioned properties are of prime importance in constructions and building applications. The epoxy ambient curing systems generally consist of two components (a base component and a curing agent or hardener). The base component is an epoxy resin, which is normally a standard liquid epoxy resin DGEBA, diglycidyl ether of bisphenol-A (a condensation product of bisphenol-A and epichlorohydrin). The room temperature curing agents that are generally used along with epoxy resin to initiate the cross linking are polyamines, polyamides or their adducts [13-14].

The main goal of this study was to find an optimum formula for production of water-borne two-component epoxy paint with a good corrosion resistance. To aquire this task, numerous costly time-consuming trials were needed. Therefore, selecting a correct method to perform multi-parametric tests at several levels is essential. In this study statistical experimental design helped us to investigate the effects of several variables, like resin, pigment, filler and other additives at several levels. Here a model is presented to determine the optimum paint formula, using analysis of variance on the results of paint property tests. This research represents a new method to formulate and optimize coatings. In this method it is possible to obtain valuable results by doing the least experiments [15-16].

The present work involves the anticorrosive behavior evaluation of ten epoxy waterborne coatings using experimental design methodology. These include the salt spray and adhesion methods as the accelerated tests and the electrochemical impedance spectroscopy results as the references. Complementary measurements of the cross-cut adhesion test were also carried out.

2. Experimental

In order to attain an optimum formula, numerous experiments are needed. Each experiment involves a series of tests. Simultaneous alteration in system variables and their consequences have to be taken under close examination. an experimental design is an efficient procedure among methods with statistical analytical basis.

The aim of the above method is to determine system sensitivity to each parameter. This method is quite beneficial, because the behavior of the system can be easily verified depending on the factors incorporated [17].

Each experiment has two sides, experimental design and statistical analysis of the acquired data. To analyze the data, the experiment has to be organized in a way that right and credible data can be collected and eligibly computed. The general algorithm of the experimental design is proceeding by following steps:

(1) Recognition and expression of the problem;

(2) Choosing system variables and the range of variation for each one;
(3) Choosing objective function, this comprises all useful information about the system;
(4) Choosing one of the experimental design methods;
(5) Performing the experiments and getting the response;
(6) Analyzing the data to investigate the effects of the parameters on the objective function;
(7) Conclusion about the system.

The only way to attain an optimum paint formula is to perform several experiments. In the laboratory, after running the initial experiments and solving some problems occurred in formulation, a primary formula is obtained and selected as the basis for the experimental design. Now the main components of the water-borne paint (i.e. resin, pigment, filler) were selected as the input variables of the system [17]. The range of variation for each component are considered about 15% more or less than its basic value in the original formulation. Since a favorable quality control is depending on several paint properties,

Only one objective function alone is not sufficient to be considered for the formulation. Therefore, a few important end-use properties of the anticorrosion paint comprising impedance and salt spray resistances of the samples are considered as objective functions of the statistical analysis. Finally, at the optimization step, a weight coefficient allocated for each test result, has contributions in showing the degree of the importance of each property in the product.

Previous works have applied fractional factorial method, which is not efficient for multi-level experiments, and is mostly applied for two levels of variables. On the other hand, when the variables of experiments are only the components of the product, sum of the weight fractions resulted by this method is not exactly 100% because two equal experiments may be repeated in designing tables and this causes equal responses in the analysis [16]. So in this study, instead of using fractional factorial we took the advantage of a more advanced technique named mixture design which has not the problem of factorial method. In 1979, Robert Snee [16] clarified the qualification of the mixture method when the sum of the values of variables attains 100%. The sum of three fractions has to be one in three-fractional designs. In this condition, experimental valid points are located on a triangular page across. Each head and its opposite side indicate the highest and the lowest values of a fraction in the formulation, respectively. After testing the produced samples, the responses appear on the triangular page like a map with contour curves. Each curve represents the same response with different formulations. With regard to the presented method in this research, 10 different samples have been developed according to Table 4.

Methods

To prepare samples, a waterborne epoxy resin, hardener, pigments and their additives were used. Their properties are indicated in Table 1 and 2.

Table 1: Resins properties.

Aliphatic polyamine adduct Cytec Surface Specialties	
Dynamic Viscosity, DIN EN ISO 3219[mPa.s]	23000 - 31000(100 1/s; 23 °C)
Amine Value, DIN 16945 / 5.6[mg KOH/g]	220 - 240
Iodine Colour Number, DIN 6162	<= 10
density [g/cm³] approx.(20 °C)	1,10
flash point[°C]	> 100
Solid epoxy resin, Cytec Surface Specialties	
Dynamic viscosity [mPa.s]	3000 - 6000(25 1/s; 23 °C)
Epoxy Equivalent DIN 53188	464 - 520 g/mol (solids)
Non-Volatile Matter DIN EN ISO 3251	73 - 77%
Density (Liquids) DIN EN ISO 2811-2	1,10 g/cm³

Table 2: Ingredients properties.

Ingredients	Company	Product Code
Micro Talc	Mondo Minerals OY	Micro-Talc AT Extra
Zinc phosphate	Heubach	ZP10
Iron oxide	Lanxess	Bayferrox 130M
Barium sulphate	Sachtleben	Micro Blanc fixe
Defoamer	EFKA	EFKA 2526
Leveling agent	BYK	BYK 380N
Dispersing agent	BYK	BYK 190

Table 3: Paint Formulations.

Mill base formulation:	
Components	Content (g)
Polyamine hardener	5-10
Distilled Water	6-15
Defoamer	.5% on total formulation
Dispersing Agent	25% on total pigments
Leveling and Anti cratering agent	.5% on total formulation
ZP10	5-20
Bayferrox 130M	5
Micro-Talc AT Extra	5-20
Blanc fixe	8
Let down formulation:	
Waterborne epoxy resin	22-45
Distilled Water	5-10

Paints were formulated using pigments like synthetic iron oxide, zinc phosphate, blanc fixe and talc along with additives and solvents. Epoxy resin with the aromatic polyamine adduct based hardener were used as the binder. The compositions of various paint formulations are given in Table 3.

The mill base was prepared in the hardener and different pigments, filler and additives were added. After grinding, the paste particles size was less than 10 microns, the letdown mixtures (epoxy resin and distilled water) were added and the films applied on mild steel plates. The laboratory tests were carried our after the films were fully cured. The ten formulations summarized in Table 4 were designed by DX6 software and prepared as described.

The coated panels were left in laboratory for 7 days to ensure full curing. The edges of the steel panels were sealed with wax to prevent the ingress of chemicals from the edges. At least three panels were prepared for each test.

All the films were exposed to AC impedance spectroscopic studies (in 3.5% NaCl solution in a frequency range of 0.1 to 30,000 Hz (Gill AC, ACM Instruments) at OCP with 10mV perturbation. The reference electrode and counter electrode were Ag/AgCl and platinum, respectively.

In AC impedance studies it is very common to suppose an equivalent circuit for the coating to clarify the processes which occur at different bulk and interfacial zones. The most common equivalent circuit for intact coatings is Mansfeld circuit. The resulting data were analyzed by means of a frequency response analyzer.

The salt spray test which was performed based on ASTM B117 (Biazma Instruments Co.) and the evaluation of the results was based on ASTM-D 1654 and ASTM-D 714 tests. Adhesion of the coatings was qualitatively measured by cross-cut test (ISO2409:1992).

3. Results and discussion

An equivalent electrical circuit was fitted to the AC impedance spectroscopy measurement data using a frequency-response analysis software (Figure 1). It was found that the circuit in [30] shows the best fitting results. Then the numerical values of the electrical elements of the coated mild steel panels were extracted.

Coating resistance, coating capacitance, OCP (open circuit potential) after 20 and 500 hr exposure, the salt spray-induced corrosion (after 500 hr exposure) and cross-cut results were all considered as the inputs of the DX6 software.

Table 5 shows the electrical parameters and cross/cut measurements results.

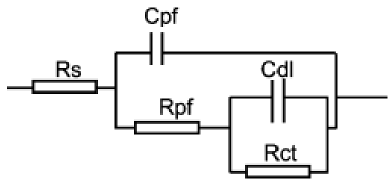

Figure 1: Electrical model of EIS results (Mansfeld).

Table 4: Formulation of the different samples proposed by Design Expert (DX6) software.

Sample code	Resin	Hardener	Zinc phosphate	Iron oxide	Talc	Blanc fixe	DFT (microns)
1	22.5	5	12.5	5	12.5	8	75
2	22.5	5	20	5	10	8	70
3	33.75	7.5	7.5	5	20	8	78
4	45	10	20	5	5	8	70
5	45	10	5	5	20	8	77
6	22.5	5	10	5	20	8	76
7	22.5	5	15	5	15	8	50*
8	39.37	8.75	16.88	5	9.375	8	78
9	33.75	7.5	10.63	5	16.88	8	70
10	45	10	20	5	5	8	76

*Because of the lower DFT, the results of this sample has not been considered.

Table 5: Coatings resistance (Rc), coatings capacitance (Cc), open circuit potential (OCP) and cross cut results of the samples after 20 and 500 hours.

Sample code	Rc-20	Rc-500	Cc-20	Cc-500	OCP-20	OCP-500	Crosscut (ISO2409-1992)
1	1.20E+06	3.20E+04	1.10E-07	2.32E-04	-568.94	-625.02	5B
2	3.70E+06	1.25E-05	5.45E-06	5.22E-05	-563.05	-648.58	5B
3	8.32E+05	6.75E+04	3.33E-06	8.23E-04	-598.34	-565.42	5B
4	8.97E+08	8.25E+05	8.32E-07	9.33E-05	-592.37	-556.01	5B
5	3.22E+06	1.25E+04	6.23E-06	6.02E-05	-547.62	-650.49	5B
6	6.35E+06	5.25E+04	4.40E-07	6.24E-05	-446.72	-606.2	5B
7	Allied						
8	3.22E+08	2.54E+06	3.22E-08	5.22E-06	-636.38	-619.18	5B
9	1.23E+06	6.32E+04	4.21E-07	2.20E-05	-520.13	-617.72	5B
10	5.21E+08	2.24E+06	3.20E-08	1.25E-06	-519.14	-586.9	5B

The results (cross/cut) show that all samples have very good adhesion to the mild steel.

Table 6 shows the results of evaluation of salt spray tests after 500 hours.

The software proposes the best fit model for analizing the results. The suggested model for each response is shown in the Table 7.

Figure 2 shows Contour plot and 3-D view of coating resistance after 20 hour exposure. As it can be seen the higher coating resistance is obtained in lower amounts of talc and higher proportions of zinc phosphate pigment. This is reasonable because talc is a hydrophilic filler which is added to the formula to decrease the cost. It may increase the water absorption of the films and cause the resistance of the films to decrease and the relevant capacitance to increase. It has been stated that zinc phosphate hydrolyzes to form zinc hydroxide and secondary phosphate ions. Phosphate ions form basic iron (III) phosphate as a complex on the iron surface [18-21]. Anyhow, the inhibitive action of zinc phosphate pigment is not well understood. Many researches have been done on the aqueous extract of zinc phosphate and its dispersions in polymeric films and very different results were reported. Some authors believe that because of the low solubility of zinc phosphate it can not act as an inhibitor. Some authors have pointed out that zinc phosphate increases the barrier properties of organic coatings, while others have reported non- barrier effect of this pigment. Figures 3, 4 and 5 also confirm the results of Figure 2.

Because of selective permeability of the coating, accumulation of OH^- ions at the coating- substrate interface takes place. This leads to the interface passivation and higher charge transfer resistance. The cathodic/anodic area ratio also rises which in turn results in an increase in OCP The higher the zinc phosphate content of the film, the higher will be the OCP (Figure 6).

After 500 hour exposure in the salt spray chamber, the panels are evaluated based on number, shape and size of the blisters and also the creepage of the rust under the films in the scribe areas.

Results of the salt spray evaluation show that samples contain more resin and zinc phosphate have better resistance after 500 hour exposure in the salt spray chamber (Figure 7).

Table 8 shows the optimum amount of ingredients in the formulation for achieving optimum properties. The table is presented or proposed by DX6 software.

As the water solubility of zinc phosphate is low, it could retard the formation of the ions and act as the barrier pigment. This behavior results in higher electrical resistance of the coatings. Coatings containing more zinc phosphate have better protection for the metallic surfaces through passivating and barrier mechanisms.

Table 6: Evaluation of creepage & rate of corrosion degree of blistering after 500 hours.

Sample code	Millimeters	Rate Number (ASTM D 1654)	Blister size No. (ASTM D 714)	Frequency (ASTM D 714)
1	3	6	2	M
2	4	5	4	MD
3	7	3	2	MD
4	4	5	4	M
5	5	5	2	MD
6	2	7	4	M
7	Allied			
8	2	7	2	M
9	7	3	2	M
10	4	5	2	M

MD=Medium Dense, M=Medium

Table 7: The best fitted model for each response, suggested by DX6.

Response	Suggested Model
Rc-20	Linear
Rc-500	Linear
Cc-20	Quadratic
Cc-500	Linear
OCP-20	Special Cubic
OCP-500	Quadratic
Salt spray	Quadratic
Cross cut	Linear

Table 8: Optimum formulation and properties suggested by DX6.

Resin	Zinc Phosphate	Talc	Rc-20	Rc-500	Cc-500	OCP-20	OCP-500	Salt spray ranking	Cross cut
55	18	7.3	4.7E+008	1.4E+006	0.00011	-5.7E+002	-6.0E+002	6.2	5.0

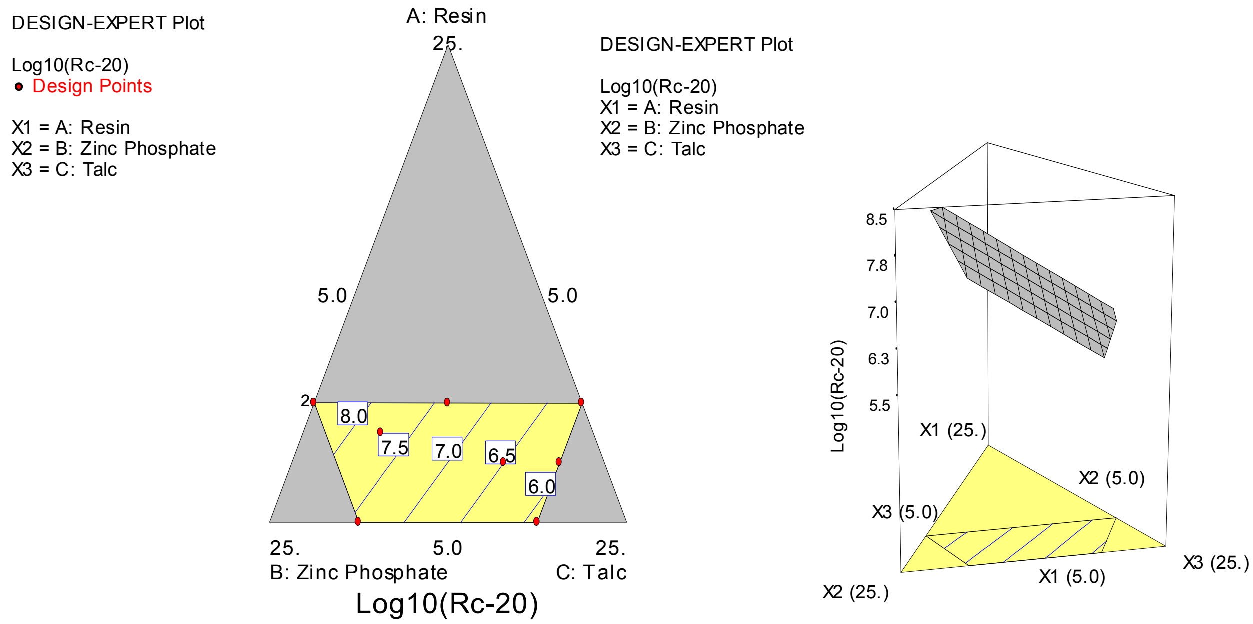

Figure 2: Contour plot and 3-D view of coating resistance after 20 hour exposure.

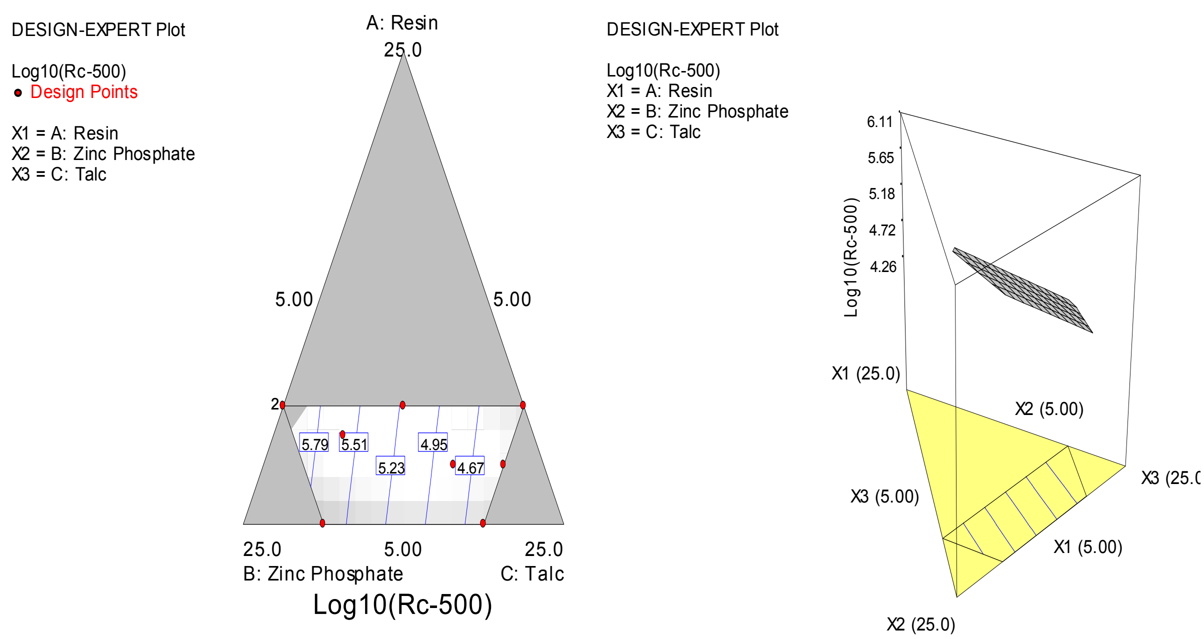

Figure 3: Contour plot and 3-D view of coating resistance after 500 hour exposure.

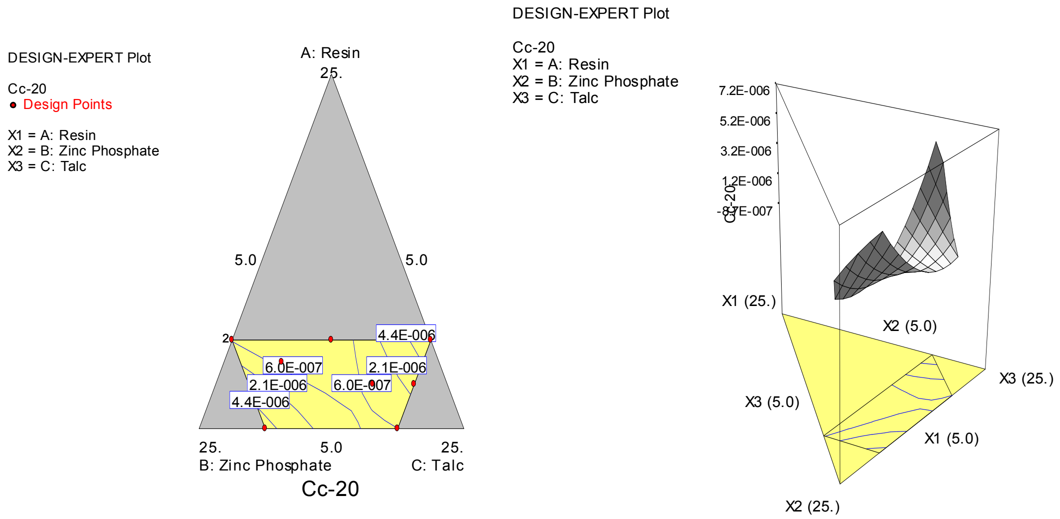

Figure 4: Contour plot and 3-D view of coating capacitance after 20 hour exposure.

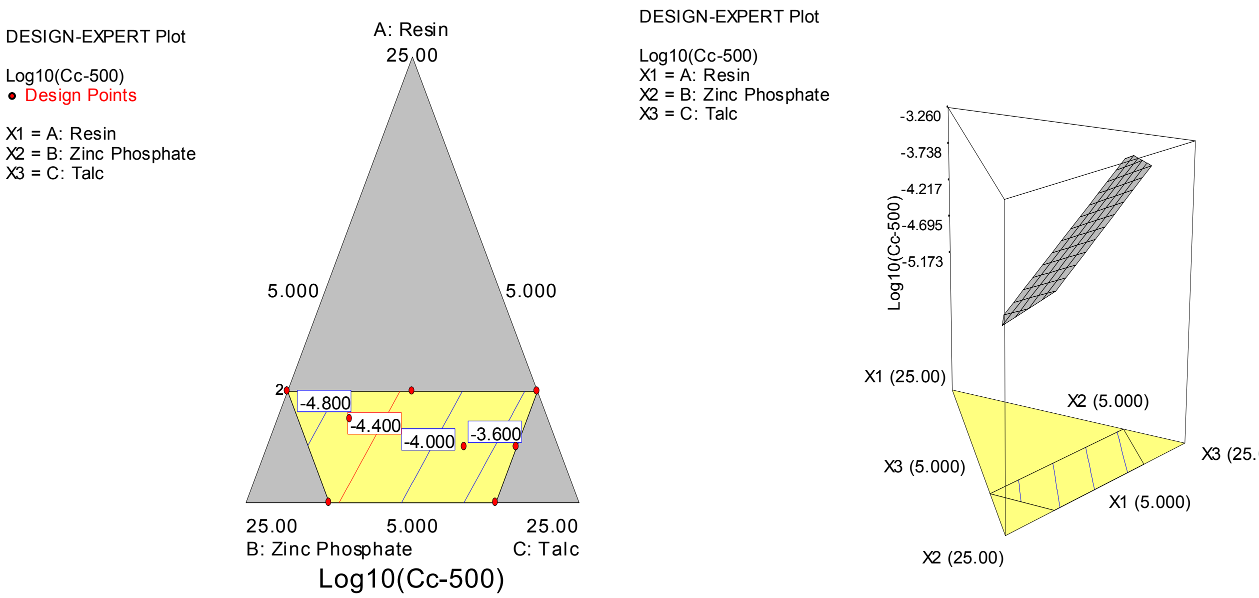

Figure 5: Contour plot and 3-D view of coating capacitance after 500 hour exposure.

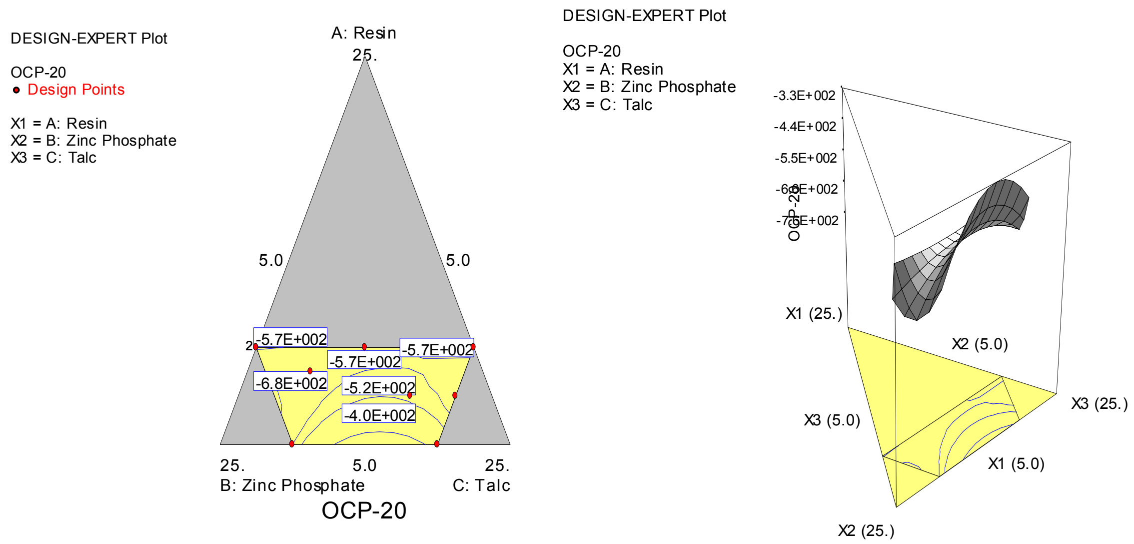

Figure 6: Contour plot and 3-D view of OCP after 20 hour exposure.

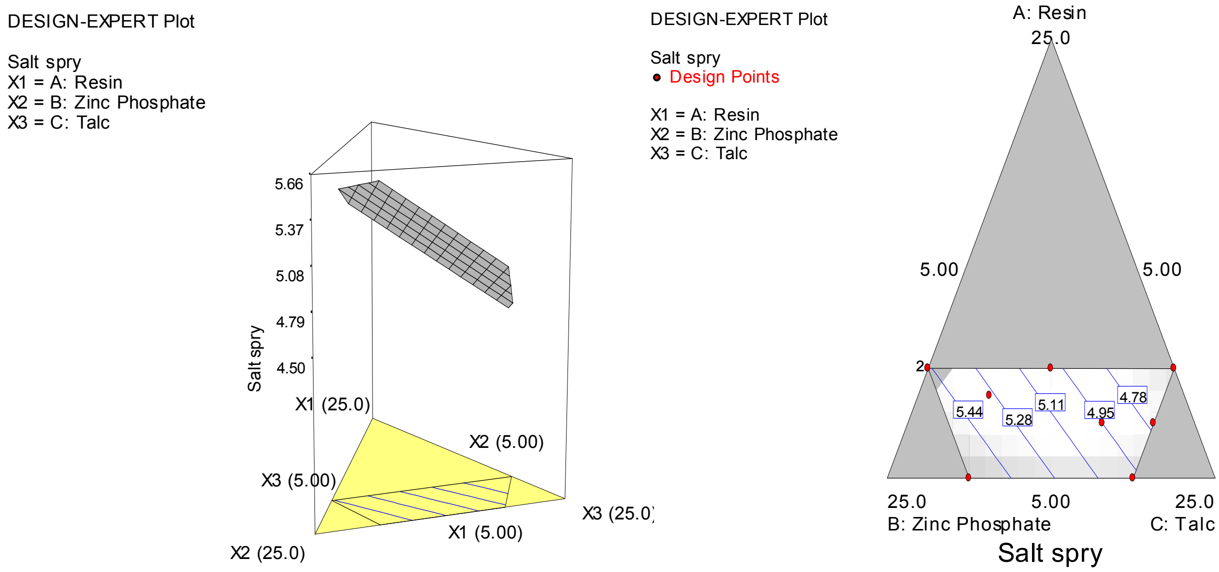

Figure 7: Contour plot and 3-D view of salt spray after 500 hour exposure.

4. Conclusions

The amount of resin, pigment and filler are selected as variable parameters in a waterborne anticorrosion paint and 10 formulations were designed by DX6 software.

Anticorrosion properties of the samples were studied by AC impedance spectroscopy and salt spray. The data analysis showed that the sample 4 (repeated as samples 8 and 10) shows the best results compared to the others. These samples contain higher zinc phosphate and resin. A higher resin content results in a more intact film and a stronger adhesion to the mild steel.

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