

Evaluation of Industrial Waste of Iron Fines as Pigment for Paints

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Abstract

The present study deals with evaluation of iron waste samples, that represent the fines generated from a steel plant in Egypt, as a potential to be reused as a pigment in paints making. The iron waste samples are composed mainly of iron oxide, calcium oxide, zinc oxide, lead oxide, and other alkali oxides. The waste samples have basic nature, which make their application as pigment materials in paints is suitable. The samples are subjected to a simple washing step with hot water before their classification with different techniques to remove the majority of harmful impurities. The treated samples were then finely ground to the required size before their application as pigments. The samples were characterized for basic properties of pigment with chemical analysis, X-ray diffraction, scanning electron microscope, size analysis and magnetic properties. Properties of the prepared paints film in term of ductility, adhesion, hardness, storage stability and corrosion resistance were evaluated. The results indicated that such treated waste samples can be used as pigment in corrosion protection of steel and in magnetic applications.

Introduction

The contact of steel⁽¹⁾ with water and oxygen leads to its corrosion, sooner or later, whatever paint is applied. Chloride ions from sea water or salt solution will speed up the process. Paints, therefore, can slow down the migration of oxygen, water and chloride to the surface and in turn minimize the rate of corrosion. Two mechanisms protection can be involved when organic or inorganic films are employed. Organic films play the role of barrier, which may hinder the transport of molecules like dissolved oxygen towards the metal or the removal of the corrosion products from it. They are also expected to strongly reduce the insertion of very corrosive anions, such as chloride, in the film. Inorganic films, in particular noble metals, are used as protective coatings to cover less noble metal. In this case, an anodic galvanic protection is provided, maintaining the native passivity on the metal.

Pigments⁽²⁾ play an important role in the anticorrosive properties of paints. Iron oxides is widely used in anticorrosive paints. Iron oxides, except black iron oxide, Fe_2O_3 , do not react with the acid component of the vehicle to form soaps. Even soaps formed by Fe_3O_4 do not have anticorrosive properties and iron black is not found suitable as an antirust pigment. Iron oxides used in anticorrosive paints mainly consist of ferric oxide. The anticorrosive properties of natural oxide was attributes to the broader particle size distribution of both the coarse and fine particles, which gives a closer packing of the pigment in the paint films, and thus increase its barrier action against the penetration of moisture.

On the other hand, a lot of fine particles are generated as waste materials during steel making in one of the Egyptian plant. Such wastes are composed mainly of iron oxide in addition to ZnO, and CaO. Treatment of such iron oxide wastes to minimize their impurities might encourage their applications as pigments in paint industry. This can also help in solving a serious environmental problem due to the high degree of fineness of such wastes and the limitation of landfill areas available at the site of the plant.

An attempt has been made in the present study to utilize such industrial wastes of iron oxide in paints as pigments.

Experimental

Materials

The following materials are used in this study:

1. Allopren R 20 is chlorinated rubber with viscosity 15-25 cps, supplied by Imperial Chemical Industries Ltd., England.
2. Cereclor 42% Cl. Represents chlorinated paraffin obtained from Hoechst Chemicals Company, Germany.
3. Medium Oil Modified Alkyd Resin supplied by Heliobilis Company, Cairo, Egypt.
4. Two samples of industrial wastes of iron oxide pigments coded as sample I and sample II. These samples represents wastes generated two steel plants in Ain Sokhna and Sadat factories, Egypt.

Techniques

1- Processing of pigments

The received samples of industrial iron oxide wastes were first washed with hot water and then subjected to multi-classification process before their fine grinding to the required degree of fineness using a ball mill. Evaluation of different size fractions of the samples as pigment was performed on the ground product after their classification with a cyclosizer "Worman" unit. Preliminary tested showed that the finest size fractions below about 11 micron had the best performance as pigment than its respective coarse fractions. For this reason, the sample were ground 100 wt % to about 10 micron using a laboratory ball mill.

2- Chemical analysis

Chemical analysis of the pigment samples were carried out using "Philips" XRF. Determination of oil absorption and soluble matter in water were performed according to the standards methods DIN EN ISO787-5 95-10 and DIN EN ISO 787-8 79 respectively. Determination of hydrogen ion concentration "pH" was determined according to DIN EN ISO 787-9 95-04.

3-X-ray diffraction-analysis

X-ray powder diffraction analysis were performed at ambient temperature using a Philips XRD apparatus type 1390, Co-target and Fe-filter ($\lambda = 1.542 \text{ \AA}$). The

X-ray tube operated at 30 KV and 20 mA. The diffraction angle 2θ was scanned at a rate of one degree per minute.

4-Scanning Electron Microscope Analysis (SEM)

Scanning electron microscope (SEM) analysis of the powder was carried out on a dispersed sample, scanning electron micrograph was obtained using a JSM-T20 scanning microscope, supplied by JEOL, Japan.

5- Size analysis of samples

Particle size distribution of powders were determined using a “Fritsch type 22 Class 1” Laser particle size analyzer.

6-Magnetic properties

Magnetic properties of samples were examined using an LDJ vibrating sample magnetometer model 9600.

7- Preparation of paint formulations

A comparative study was carried out on nine formulations of paint having the same percentage of industrial iron oxide wastes, as pigment powder, with binder ratio (Pigment/Binder = P/B = 2:1). The process involves mixing all ingredients and adding appropriate quantity of solvent to the mill base to reach the desired consistency prior to form a smooth paint paste. The mill base was then ground in a ball mill until the desired degree of fineness was achieved (ASTM D 1210-1988).

8- Characterization of paint films

The formulated primers were tested and evaluated according to the following well known standard methods:

- Preparation of steel panels: ASTM-D-609-95.
- Ductility: ISO 1520-1973 (E).
- Adhesion: ASTM-D-3359-95a.
- Hardness using Konij Pendulum Hardness Tester: ASTM-D4366-95.
- Corrosion scratch test: Egyptian standard specification ES-823-66.
- Degree of blistering: ASTM-714-87; re-approved, 1994.
- Degree of rusting: ASTM-D610-95.

Results and Discussion

Evaluation of Industrial Iron Waste Samples

Chemical Analysis of Samples

Table 1 shows the chemical analysis of the industrial waste samples before (as received) and after (feed as pigments) their washing and classification. Sample I (as received) has ~ 47.3 % Fe_2O_3 , 16.6 % ZnO , 11.5 % CaO , 2.8 % PbO , and 5.4 % LOI in comparison to 32.5 % Fe_2O_3 , 17.7 % ZnO , 18.9 % CaO , 3.0 % PbO , and 8.23 % LOI for sample II. It is clear that after treatment of these sample through washing and classification, their contents of ZnO are increased to 22.1 % and 26.0 % respectively

while their contents of CaO and LOI are significantly decreased to 5.5 % and 1.5 % respectively for sample I and 12.8 % and 3.6 % respectively for sample II. The content of Fe_2O_3 is higher in sample I (47.3 %) in comparison to sample II (32.5 %) probably due to its higher contents of CaO and LOI.

The water-soluble salts of both samples before and after their treatment are also determined, the results of which are shown in Table (2). The untreated samples had higher contents of Na_2O (~ 1.8 %) and K_2O (0.43 – 0.58 %). The solubility of these salts (Na_2O 0.07 – 0.08 % and K_2O 0.016 – 0.02 %) in distilled water are significantly decreased after washing the samples in hot water followed by their classification. This indicates that the washing step is essential to get rid of the harmful impurities of soluble salts present in such wastes sample.

The treated samples were, also, tested for the following pigment properties: Hydrogen ion concentration (pH) and Oil absorption and matter soluble in water. The results are given in Table (3). It is clear that the oil absorption values of the industrial iron pigments are nearly the same 12 and 11.6 g/100g. Such lower values of oil absorption⁽³⁾ for these samples indicates their economical viability as pigment materials due to their expected lower consumption of binder without compromising aesthetic properties like gloss, dispersion and interfacial bonding of the paint. Oil absorption of an extender also gives an idea of theoretical critical pigment volume concentration (CPVC), which shows maximum percentage of pigment in paint over which air starts to occupy the place between pigment particles.

Iron pigments have a basic nature (Table 3) and gave a higher pH values (pH=10). The corrosion may be reduced or stopped by alkaline conditions⁽⁴⁾, due to the effective passivation via hydroxyl group.

X-ray Diffraction of Samples

Figures 1 and 2 illustrate the x-ray diffraction patterns of samples I and II respectively. The x-ray diffraction patterns of both samples indicated the presence of zinc ferrite pigment (ZnFe_2O_4) and ZnO as a major compounds in both samples in decreasing order. Unknown peaks (X) were, also, recorded and attributed to the formation of calcium complex.

Scanning Electron Microscope (SEM)

It is noteworthy to mention that the particle shape, size and distribution influence the rheological properties, shade of matting effect, gloss, weathering characteristics, ease of dispersion and durability of paint films⁽⁵⁾. For this reason the treated samples (I and II) are investigated scanning electron microscope as shown in Figures 3 and 4. It could be seen that the two pigments have spherical-like particles with different particle sizes. The coarse and fine⁽²⁾ particles, which give a closer packing of the pigment in the paint films attributed to increase its barrier action against the penetration of moisture.

Particle Size Distribution

The size distribution of industrial iron pigments (I) and (II) are represented in Figure (5). It is clear that sample (I) has significantly fine distribution than sample II. For example, the finest fraction below 11 micron in sample (I) is about 87.12 wt % in

comparison to 54.3 wt % for sample (II). The pigment (II) has the higher percent of coarse particles.

Magnetic Properties

The magnetic behaviors of industrial iron pigments (I) and (II) are determined at ambient temperature using a vibrating sample magnetometer, the results of which are shown in Figures (6) and (7). These results illustrate the hysteresis loops of industrial iron pigments (I) and (II). It can be seen that the maximum magnetic fields (H_m) are 5.007 Oe and 4.992 Oe and the coercive fields (H_c) are 14.88 Oe and 44.02 Oe for the two pigments.

From the previous results, iron pigment (II) possess the high magnetic properties ($H_c = 44.02$ Oe) which may be attributed to complete formation of zinc ferrite phase. Formation of the latter phase could be facilitated in presence of the higher percentage of zinc oxide as can be seen from its excess amount shown in Table 1 and XRD shown in Figure (2). Typical values of physical properties of iron pigments (I) and (II) can be used in coating layer in magnetic applications.

Preparation of Paint Formulations

Many attempts were done to mix the industrial iron pigments with different binders at pigment/binder ratio = 2:1 to study the physical, mechanical and corrosion properties. The results of these trials are discussed below.

a-Medium alkyd resin

Good results were obtained with respect to physical properties and corrosion test. Unfortunately, bad storage stability was noticed where the instability occurred after one week from preparation. This could be attributed probably to the high alkalinity of pigments which leads to the hydrolysis of alkyd resin.

b- Chlorinated rubber resin

Chlorinated rubber resin and chlorinated paraffin as a plasticizer were used in these formulations with ratio 5:1. The pigment/binder ratio was chosen as 2:1. Good results were obtained in corrosion tests and physical properties except the worst of bad adhesion. Storage stability of such formulations is very good.

c- Chlorinated rubber and alkyd resins

Chlorinated rubber resin and chlorinated paraffin as a plasticizer were mixed with ratio 2:1. Medium alkyd resin was added to the chlorinated rubber resin with different percent range from 5-50 % based on the weight of chlorinated rubber resin to improve the adhesion properties of the painted films on the substrate. All the formulations have the same pigment/binder ratios (P/B) equal to 1.3 :1. Each primer compositions based on industrial iron pigments (I) and (II) are listed in Table (4).

Characterization of Paint Films

Table 5 illustrates the effect of paint ingredients on film properties while Table 6 and Figures 8-10 illustrate the corrosion resistance of the films after immersion for 28 days in artificial sea water.

The performance of paint films in term of ductility, adhesion and hardness is sufficiently excellent. Formulation No.3 using pigment (II) had lowest ductility and adhesion. Storage stability are excellent for formulations No. 2 and 4 due to the low percentage of medium alkyd resin. By increasing the percent of medium alkyd resin more than 10 % the storage stability start to decrease due to the alkyd percent as indicated in formulations No. 1, 3, 8 and 9. The bad storage stability is attributed to the reaction of the acidic part in the alkyd resin with the basic pigment which hydrolyses the alkyd resin and form soaps which make gel in the paints.

All the nine formulations were exposed to artificial 3.5 % salt solution. All formulations were completely free from corrosion while formulations 1, 3, 5, 6, 7, 8 and 9 had shown very slight blistering. However, the metal surface remained free from corrosion. The best formulations are No. 2 and 4. The facts of the good corrosion protection are attributed to:

a- The alkalinity^(6,7,8,9) of the industrial iron pigments block the cathodic reaction and then reduces the OH^- ions which in turn decreases the saponification of the binder (saponify only free acids). From this point of view, the passivation^(10,11,12,13) effect was limited the corrosion spots to spread over the plates.

b- The resin type is the critical factor in determining the barrier properties of a paint system. Polymers with a high concentration of hydrophilic substituents or which are based on monomers which give rise to a high concentration of ester links are generally quite permeable to water. Hence oil and alkyd systems, which have backbone ester groups, do not make good barrier paints. On the other hand, polymers with a skeletal chain of carbon atoms and non-polar substituents will be much less permeable. Thus, chlorinated polymers such as chlorinated rubber provide good barrier to both water vapor and oxygen.

c- The closer packing of the coarse and fine particles of the pigments increase the barrier action against the penetration of moisture which was attributed the anticorrosive properties of the pigment.

Thus, it can be concluded that excellent corrosion protection was obtained from chlorinated rubber resin which is responsible for the barrier effect and alkyd resin which for passivation of the substrate.

Conclusions

The conducted measurements allow the following conclusions:

- Industrial iron powder tailing wastes have zinc ferrite spherical structure and can reuse as pigments in paints.
- The high magnetic properties of the industrial iron powder tailing wastes attributed to be used in magnetic applications
- Particle size distribution of both the coarse and fine spherical shape particles give a closer packing structure of the industrial iron powder tailing wastes in the paint films which increases the barrier penetration of moisture.
- The basic nature of the industrial iron powder tailing waste pigments react with the acidic binder and produce soaps which can also passivate the substrate and protect from corrosion.
- High performance corrosion protection of steel was achieved by using chlorinated rubber with the medium alkyd resin to reduce the water vapor transmission.

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Table 1: Chemical Analysis of Industrial Iron Wastes Samples

%	Original wastes samples (as received)		Treated samples (Feed as pigments)	
	Sample I	Sample II	Sample I	Sample II
Fe₂O₃	47.32	32.52	46.89	35.99
ZnO	16.58	17.72	22.07	26.01
PbO	2.79	3.02	3.07	3.02
SiO₂	5.34	5.71	3.56	4.02
CaO	11.48	18.86	5.47	12.83
MgO	2.47	1.77	2.48	2.43
LOI	5.38	8.23	1.53	3.63

Table 2: Matter soluble in water (DIN EN ISO 787-8 79)

Sample	Wt%	Wt%	Before washing		After washing	
	Solid	Lost	Na ₂ O%	K ₂ O%	Na ₂ O%	K ₂ O%
I	90.99	9.01	1.827	0.427	0.073	0.016
II	87.91	12.09	1.824	0.579	0.085	0.02

Table 3: Pigment characterization

pigment	oil absorption (g/100g)	pH
Iron pigment (I)	12	10.08
Iron pigment (II)	11.6	10.16

Table 4: Percent Composition of the anticorrosive primer formulations

Composition	Formulation No.								
	1	2	3	4	5	6	7	8	9
Pigments I & II	57.2	57.2	57.2	57.2	57.2	57.2	57.2	57.2	57.2
Chlorinated rubber resin (C.R)	-	28.5	19	27.2	25.7	22.9	20	17.1	14.3
Chlorinated paraffin 42% Cl (C.P)	14.3	14.3	9.5	14.3	14.3	14.3	14.3	14.3	14.3
Medium alkyd resin	28.5	-	14.3	1.4	2.8	5.7	8.6	11.4	14.3
C.R/C.P	2/1	2/1	2/1	2/1	2/1	2/1	2/1	2/1	2/1
P/B	1.3/1	1.3/1	1.3/1	1.3/1	1.3/1	1.3/1	1.3/1	1.3/1	1.3/1

Table 5: Film Characteristics of the various coatings

Test	Type of pigment	Formulation No.								
		1	2	3	4	5	6	7	8	9
Ductility (mm)	I	8.6	8.5	8.7	8.6	8.4	8.3	8.3	8.2	8.4
	II	8.7	8.3	3	8.3	8.5	8.2	8.3	8.2	8.2
Adhesion	I	5B	5B	5B	5B	5B	5B	5B	5B	5B
	II	5B	5B	1	5B	5B	3B	5B	5B	5B
Hardness (Sec)	I	100	100	100	100	100	100	100	100	100
	II	100	100	100	100	100	100	100	100	100
Storage stability	I	Gel	Excel lent	Gel	Excel lent	Good	Good	Good	Gel	Gel
	II	Gel	Excel lent	Gel	Excel lent	Good	Good	Good	Gel	Gel

Table 6: Evaluation of immersed panels in artificial sea water

Test	Type of pigments	Formulation No.								
		1	2	3	4	5	6	7	8	9
Blistering	I	2M	10	2M	10	2F	2M	2F	2F	2F
	II	10	10	2M	10	10	2M	2M	2F	2M
Degree of rusting	I	10	10	10	10	10	10	10	10	10
	II	10	10	10	10	10	10	10	10	10

● ZnFe₂O₄

▲ ZnO

X unknown calcium complex

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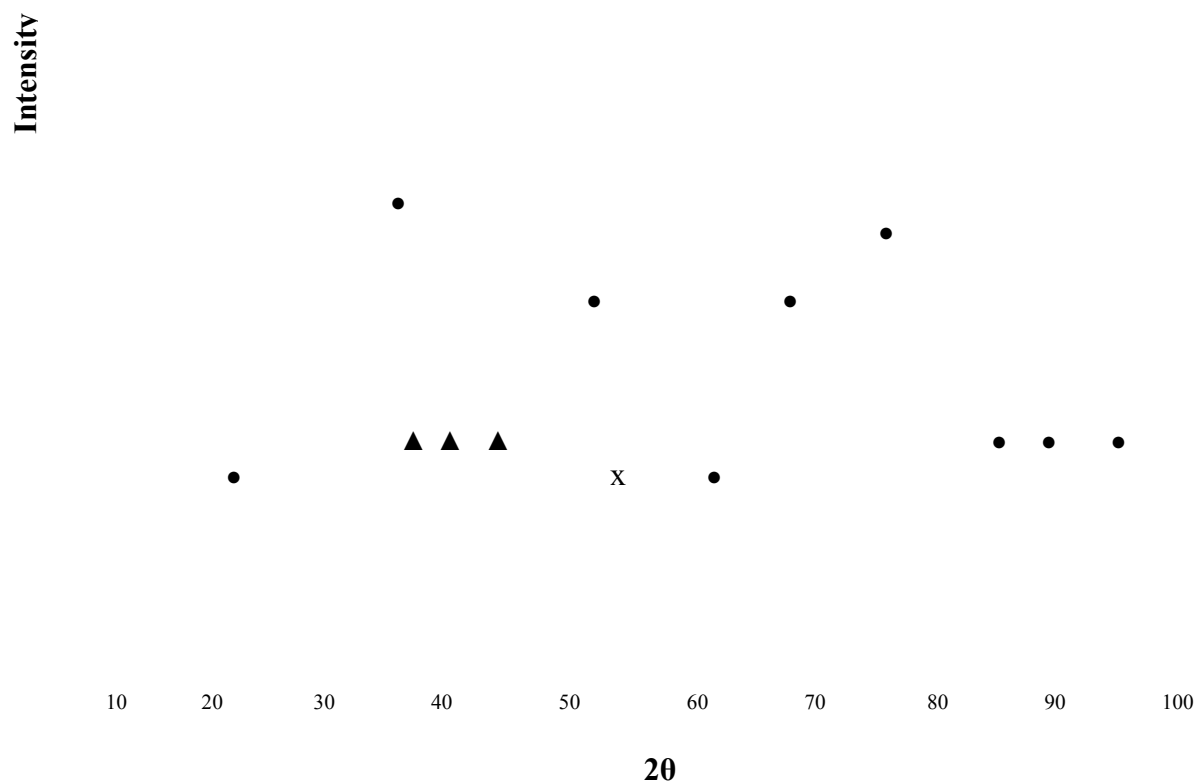


Figure 1: X-ray diffraction pattern of the industrial pigment (I)

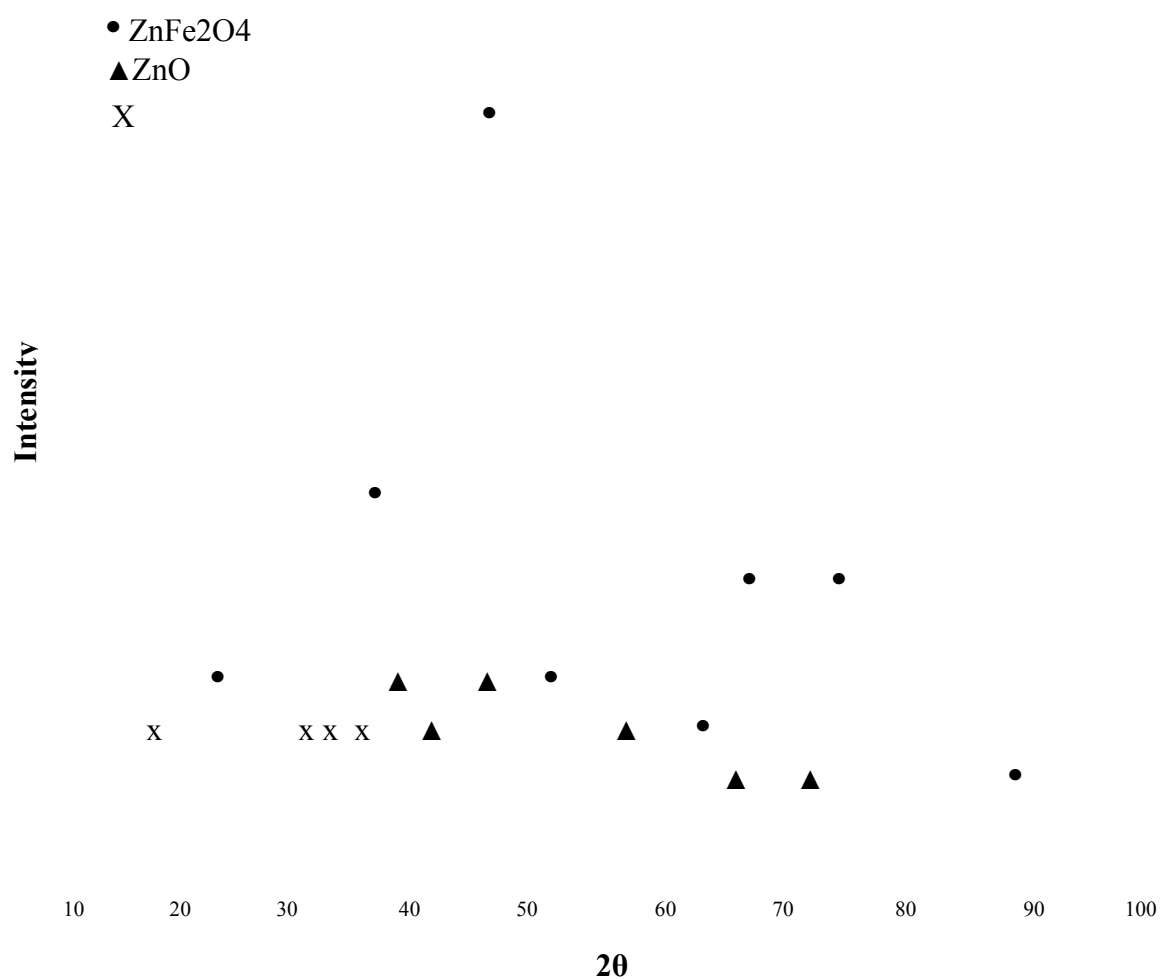


Figure 2: X-ray diffraction pattern of the industrial pigment (II)

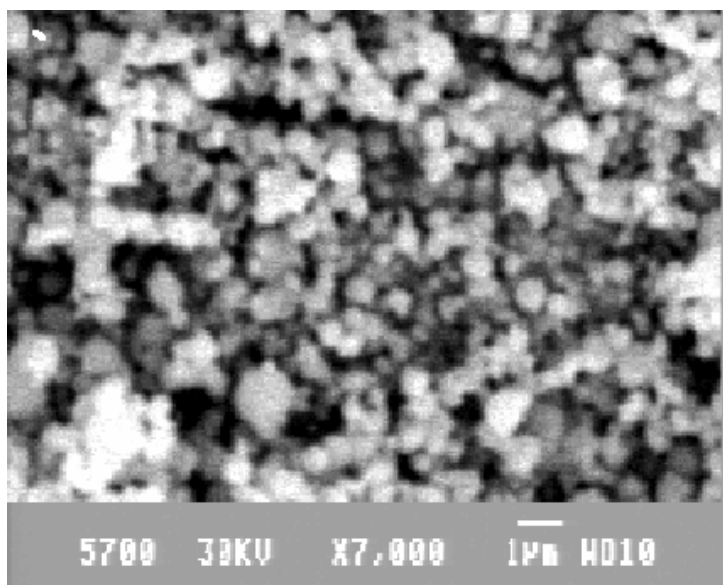


Figure 3: Scanning electron microscopy of industrial pigment (I)

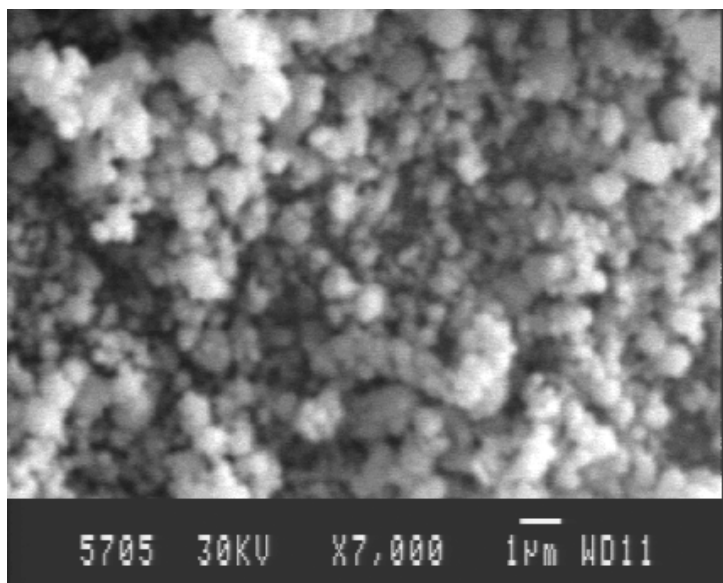


Figure 4: Scanning electron microscopy of industrial pigment (II)

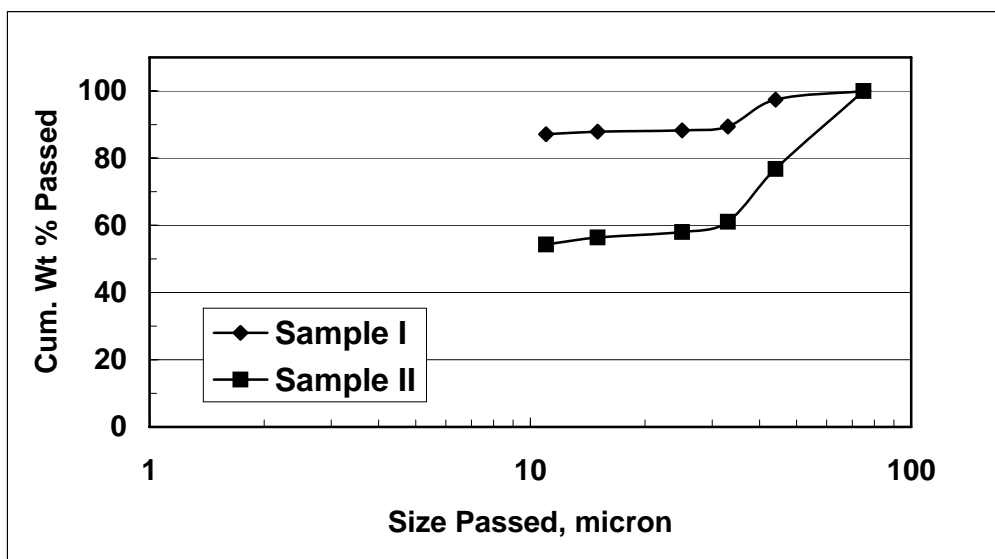


Figure 5: Size distribution of pigment samples

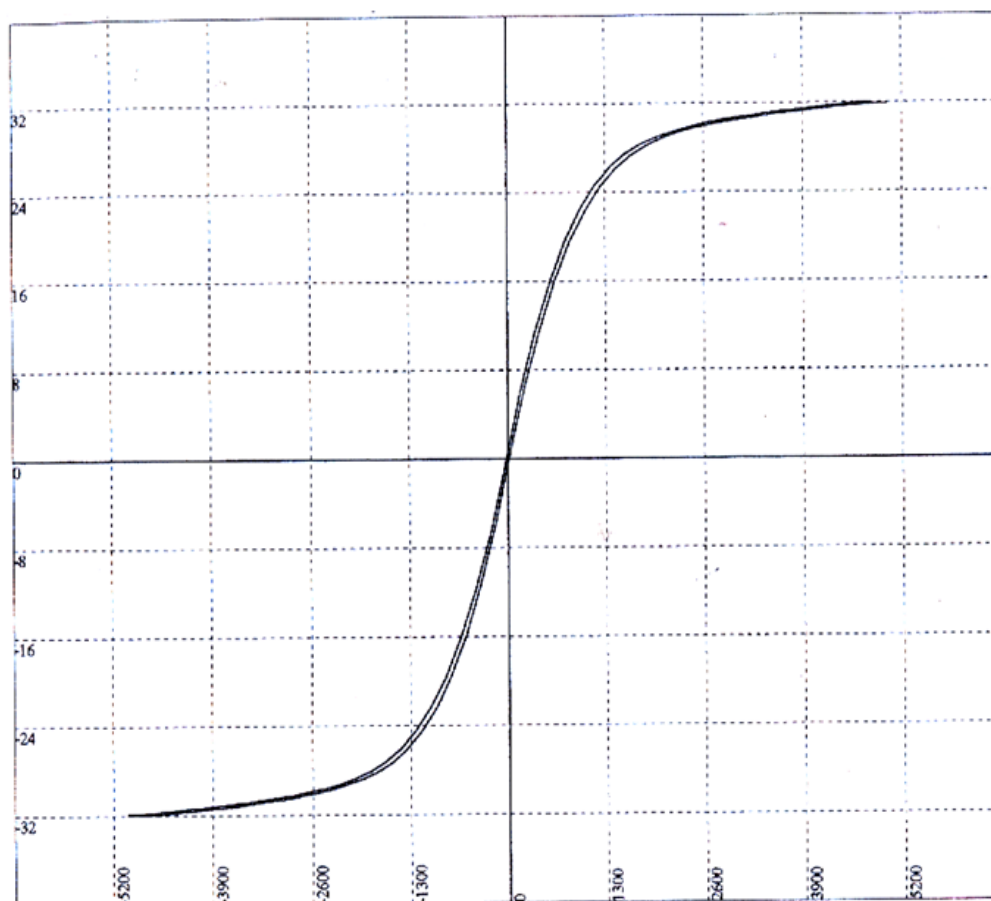


Figure 6: Hysteresis loops of industrial pigment (I)

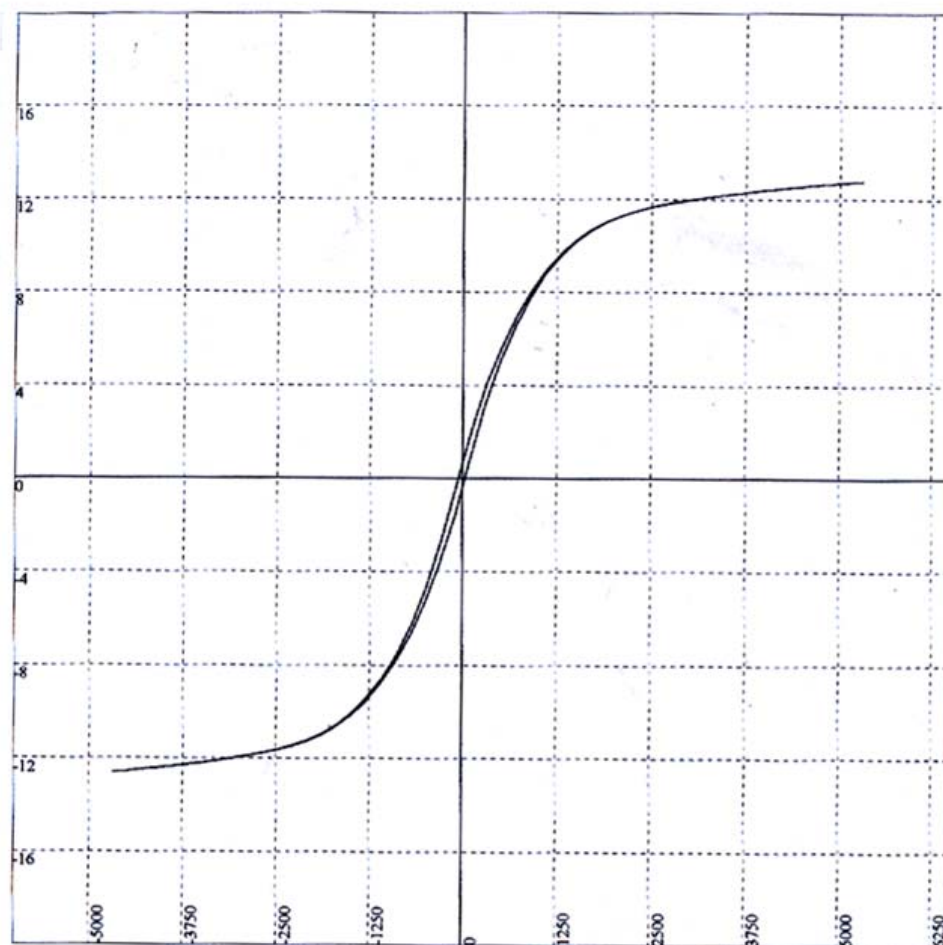


Figure 7: Hysteresis loops of industrial pigment (II)

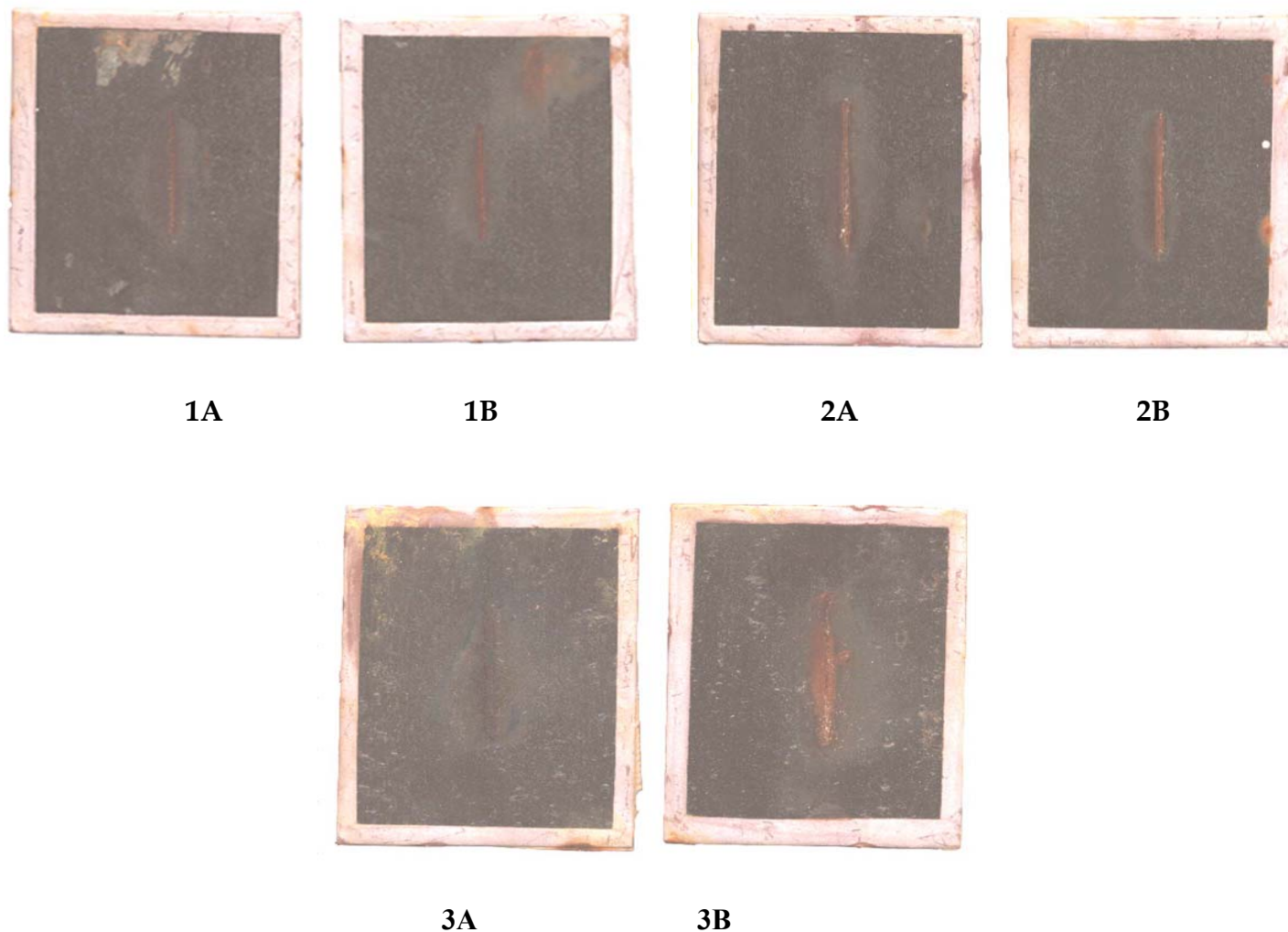


Figure 8: Pictures of coated panels for formulations no. 1, 2 & 3 after 28 days immersion in 3.5% salt solution

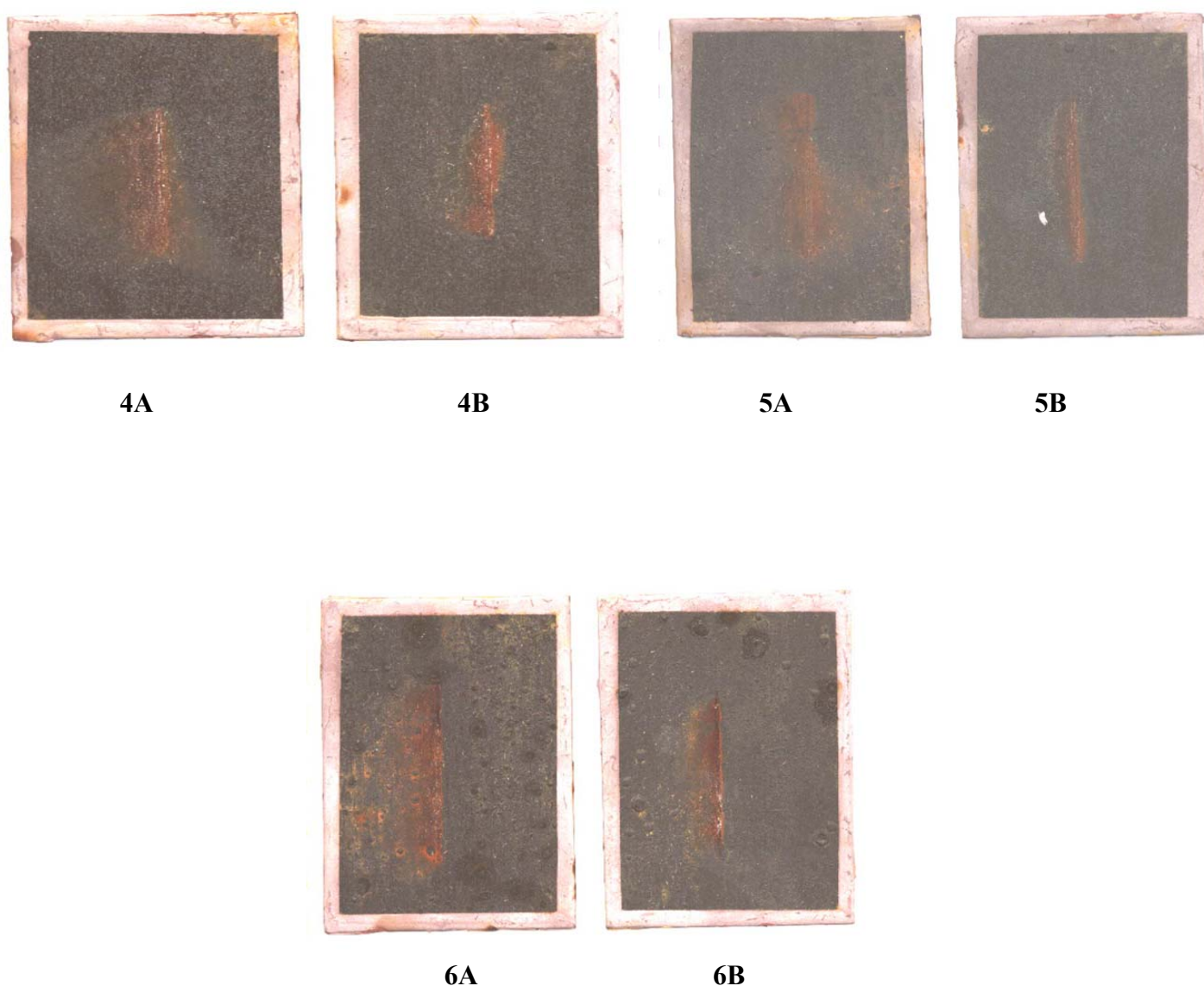


Figure 9: Pictures of coated panels for formulations no. 4, 5& 6 after 28 days immersion in 3.5% salt solution

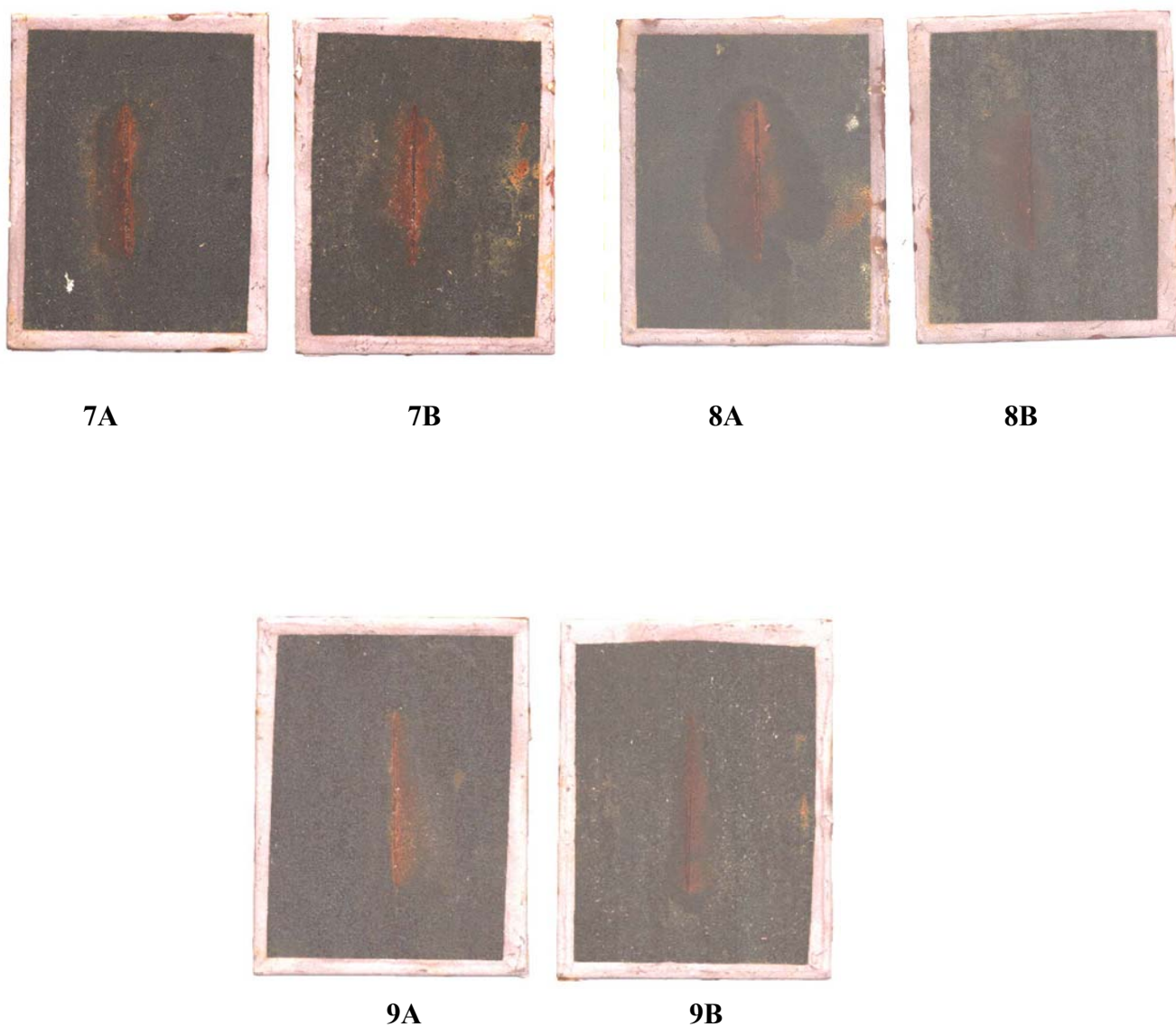


Figure 10: Pictures of coated panels for formulations no. 7, 8 & 9 after 28 days immersion in 3.5% salt solution