Provisional chapter

Study on the Anticorrosive Behavior of New Hygiene Structured Pigment Based on Waste Core and Nano Shell in Alkyd Paints

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Additional information is available at the end of the chapter

1. Introduction

Core-shell structured particles are gaining lots of importance recently due to their exciting applications in different fields; these particles are constructed of cores and shells with different chemical compositions which show ultimately distinctive properties of varied materials different from their counterparts, to manipulate the surface functions that can meet diverse application requirements. The purpose of coatings on core-particles is carried out for different reasons like surface modification, increasing functionality, stability, dispersibility, and control release of the core material. The presence of shell can alter some properties of core like surface charge, functionality and reactivity. These new core-shell particles are widely applied in different applications [1-6].

Silica fume is a byproduct of the smelting process in the ferrosilicon industry. The reduction of high-purity quartz to silicon at temperatures up to 2000°C produces SiO_2 vapors, this leads to the oxidation and condensation in low temperature zones to tiny particles consisting of non-crystalline silica.

Silica fume products have very high purity resulting in highly consistent physical properties and particle size distributions. Their complete inertness and neutral pH make these products not capable of altering or initiating reactions when incorporated in catalyzed or multi-component chemical systems. Silica fume is also considered as eco-friendly material as using it converts a waste product into a useful marketable product which leads to a reducing cost [7].

The extremely fine and non-porous nature of pyrogenic silica or fumed silica as it is also known, make it an ideal thickening and bulking agent with outstanding thixotropic qualities. Thixotropic refers to a substances characteristic of reducing viscosity or thickness with extended agitation or shaking. This makes fumed silica ideal filler for paints, thus causing them to thin out during application and regain their viscosity when left to stand preventing drips and runs [8-10].

Titanium dioxide (TiO_2) is the most important white pigment used in the coatings industry. It is widely used because it efficiently scatters visible light, thereby imparting whiteness, brightness and opacity due to its high refractive index; it improves the light and dirt resistance of a formulation. Titanium oxide also possesses low oil absorption, high tinting strength, and inert chemical properties [9-11]. Recently titanium dioxide was found attractive as photo-catalyst, although high photo-catalytic activity is required for titanium dioxide when used as photo-catalysts, low photo-catalytic activity is sometimes preferred for titanium dioxide additives to avoid the degradation of matrix. The catalytic activity of titanium dioxide particles can be enhanced or suppressed by precipitating them on a core of other appropriate pigment to control this phenomenon. These cores layers like silica (SiO_2), alumina (Al_2O_3), or a polymer are often expected to suppress the catalytic activity of titanium dioxide particles [12-15].

Titanium dioxide is commercially available in two crystal structures, anatase and rutile. Rutile TiO_2 pigments is preferred because they scatter light more efficiently. They are more stable and durable than anatase pigments [16]

Titanium dioxide pigments are insoluble in coating vehicles; their performance properties, e.g., chemical, photochemical, and physical characteristics, are determined principally by the particle size of the pigment and the chemical composition of its surface [17].

Although silica fume is a fine lightweight fluffy amorphous powder that possesses suitable values of specific gravity, bulking value and oil absorption which makes it easy to find a new market in different industries, this nature causes the appearance of some problems when applied in paint formulations as they form agglomerations and poor wetting with the binder [18-20].

In this work there is a trial to modify these defects in using silica fume as filler in paints by precipitating very thin layers of a nano-titanium dioxide on its surface in order to get over the defaults caused by silica fume in paint formulations and also to promote its surface properties. Following this trend, silica fume waste was covered with three different layers of nano-titanium dioxide. The effect of these new pigments on different mechanical and corrosion properties of paint films containing them was studied; also the effect of shell-layer thickness on the anticorrosive properties was estimated.

Nano-titanium dioxide properties are different from that of titanium dioxide itself, because materials reduced to the nano-scale can suddenly show very different properties compared to what they exhibit on a micro-scale because of two effects [20-21];

Surface effects [20, 21]

1. More percent of atoms on surface compared to inner atoms can be found.
2. More surface free energy is available: this increased surface area and surface atoms results in the increase of surface energy associated with the particles.
3. Increasing the surface area of a substance generally increases the rate of a chemical reaction.

Volume effects

1. Lower wavelength (higher frequency and higher energy).

2. The average energy spacing increases as the number of atoms are reduced; this enhances the catalytic properties of nanoparticles.

Although these two oxides (SiO_2 and nano-TiO_2) have no significant role as anticorrosive materials [21], the new prepared pigments exhibited good inhibition effect in protecting metal surfaces from corrosion. The use of these pigments can bring about a significant savings besides being eco-friendly by converting a waste product into a useful marketable one which leads to the preparation of a reducing cost anticorrosive pigment. Also, the new formed pigments will combine the properties of both materials and overcome their deficiencies. This study proved that, as the nano-titanium dioxide shell increases, better protection was offered by the prepared pigments.

2. Experimental

2.1. Materials

All the employed pigments, extenders, resins, solvents, additives and chemicals were products of different local and international companies.

Silica fume waste was obtained from ferrosilicon factories in Aswan, Egypt. Its chemical composition is represented in Table (1), the waste was collected from the chimneys of the factory and this may be the cause of its gray color as it contains a very high percentage of carbon resulting from the smelting of this alloy preparation.

Concentration of main constituents	Wt., %
SiO_2	97.98
Al_2O_3	0.39
Fe_2O_3 ^{Total}	1.04
MnO	0.08
CuO	0.02
MgO	0.83
CaO	0.32
SrO	0.003
Na_2O	0.53
K_2O	0.75
P_2O_5	0.07
SO_3	0.005
L.O.I	4.93

Table 1. Chemical composition of silica fume

2.2. Preparation of TiO_2/SiO_2 fume core-shell pigments

Titanium tetrachloride was added in three concentrations 5-10ml to 100ml hydrochloric acid. Silica was impregnated in these three solutions and left for sometime to assure complete covering while stirring. Ammonia solution was then added drop-wisely to these impregnated silicas to adjust their pH; till complete precipitation of the pigments. The formed paste is then filtered through a buchner system and washed very well. This paste was then calcined at 650-750°C.

The preparation of the pigments is represented in the following scheme;

$$TiCl_4/SiO_2 \xrightarrow[NH_4OH]{HCl} TiOH_4/SiO_2 + NH_4Cl \xrightarrow[650-750^{\circ}C]{\Delta} TiO_2/SiO_2 \quad (1)$$

Three concentrations of titanium dioxide and consequently of titanium were deposited on silica surface, these three concentrations were determined using XRF technique. Table (2) includes these results which show that concentrations are ascending from TiO_2/SiO_2 (1) to TiO_2/SiO_2 (3).

Concentration of main constituents (wt. %)	Silica fume	TiO_2/SiO_2 (1)	TiO_2/SiO_2 (2)	TiO_2/SiO_2 (3)
SiO_2	97.98	92.48	89.61	87.88
TiO_2	----	7.52	10.19	12.42
Al_2O_3	0.39	0.36	0.35	0.33
Fe_2O_3	1.04	1.43	1.27	1.23
MgO	0.08	0.60	0.60	0.57
CaO	0.02	0.31	0.33	0.32
Na_2O	0.83	0.18	0.17	0.18
K_2O	0.32	0.95	0.98	0.86
P_2O_5	0.003	0.06	0.06	0.06
SO_3	0.53	0.005	0.005	0.007
L.O.I	0.75	0.62	0.53	0.76

Table 2. XRF analysis results of the prepared TiO_2/SiO_2 pigments

2.3. Methods of instrumental analysis

SEM/EDAX analysis

Energy-dispersive X-ray analysis technique, and scanning electron microscopy, (JEOL JX 840), micro-analyzer electron probe, was used in this work to estimate the particle shapes and to determine the elements deposited on silica surface to estimate the formation of the new pigments.

Transmission electron microscopy

Various pigments were examined using (JEOL JX 1230) technique in order to estimate the particle shapes and to determine the particle sizes of the prepared pigments.

X-ray fluorescence

The different concentrations of each element in the prepared pigments were determined using Axios, sequential WD-XRF spectrometer, PANalytical 2005.

2.4. Formulation of paints based on alkyd resin

2.4.1. Preparation of anticorrosive paint formulations

The prepared pigments were tested in 20 paint formulations. These paint formulations contain silica fume, commercial titanium dioxide, and silica fume covered with different layer thicknesses of nano-titanium dioxide denoted as $SiO_2/TiO_2(1)$, $SiO_2/TiO_2(2)$, and $SiO_2/TiO_2(3)$ expressing concentration of nano-titanium dioxide layers in ascending order from the lower to the higher concentration. All paint formulations were based on medium oil-modified soya-bean dehydrated castor oil alkyd resin. The formulations were divided into four groups; each is based on different concentration of the pigments under investigation ranging from 15-30, and all the groups have the same P/B which is 2.175, this ratio was selected from previous work concerning silica fume in alkyd-based paints [6]. Paint formulations are given in Tables (4-7), while the physical-mechanical and corrosion properties are represented in Table (8). The corrosion features of the paint films are shown in Figs. (4-7).

2.4.2. The effects of the prepared pigments on the mechanical properties of paints

Because the aim of this study was to formulate a pigment whose properties would contribute to the improvement of the mechanical and corrosion qualities of the paints, selected physical-chemical and corrosion tests were carried out.

- **Determining the resistance of paints against impact (ASTM D 5638-00, 2007)**

The result of this test reveals at what height (in cm) of the free fall of a weight onto the paint, the paint film has not yet been disturbed.

- **Determination of paint resistance against cupping in Erichsen apparatus (ASTM D 5638-00, 2007)**

The result of this test reveals the cupping of the test panel with a coating in mm at which the first impairment of the paint occurred.

- **Determination of paint Hardness (ASTM D 6577-00, 2007)**

The result of this test indicates the elasticity of paint film by using the simple pendulum test with a needle, when this needle reaches a groove which is made in the paint film, the time it takes in seconds is the measure of the hardness of paint films.

- **Determining the degree of coating adhesion by means of a cross-cut test (ASTM D 3359-97, 2007)**

The test was performed with a special cutting knife whose edges are 2mm apart. The cut of the created grate was evaluated according to a Gt0–Gt4 scale.

2.4.3. Overall evaluation of the selected physical-mechanical properties of the paints

The physical-mechanical tests nature including the adhesion of the paint film identified by means of a cross-cut test, impact resistance, and resistance against cupping indicating the elasticity of the paint film were measured. Also, good surface resistance is important for the resistance of the paints against mechanical impacts, scratches, and erosion caused by abrasion of dust particles in the outside atmospheric environment. The determination of paint film surface hardness on glass was carried out by means of a pendulum apparatus, the test consists of measuring the number of oscillations of the pendulum that bears onto the paint film with two steel balls. The unit of measuring of hardness is a percentile value related to the hardness of a glass standard that equals to 100%.

The detected results of the mechanical tests were assigned with the corresponding numerical values from the scale for the determination of physical-mechanical properties. The high value of the different mechanical properties means that the pigment contained in the paint has a positive influence on its mechanical properties. This can be clearly seen from data represented in Table (8).

2.4.4. The effect of the prepared pigments on the anticorrosion performance and the chemical resistance of the paints

The primary goal of this study was to prepare a pigment that would increase the anticorrosion performance of the paints. The determination of the prepared pigments properties by means of laboratory tests and electrochemical measurements in corrosive environments was a priority assignment.

2.4.5. Corrosion test evaluation methods

The evaluation of coatings after exposure to the corrosion tests followed methods based on the (ASTM D 714-87) for degree of blistering, (ASTM D 6294-98) for degree of rusting, and (ASTM D 2803-93) for photographic inspection.

2.4.6. Electrochemical evaluation method

Electrochemical Impedance Spectroscopy (EIS) is one of the most modern techniques available to characterize the electrical properties of organic coatings and their adhesion to metal surfaces [22-25]. It is an extremely useful technique in generating quantitative data that relates to the quality of the coat on a metal substrate. EIS is a very sensitive detector of a coated metal condition, its response can indicate changes in the coating long before any visible damage occurs, and it is not an absolute measurement.

In the present study, EIS was employed in order to investigate the effect of different concentration of SiO_2/TiO_2 core-shell pigments in anticorrosive paint formulations based on medium oil alkyd resin using the same P/B which is 2.175. The choice of this P/B was based on a previous study which indicated that this P/B was the best for the performance for similar pigments. The test was carried out in 3.5 wt% NaCl at different immersion times [6].

EIS experiments were carried out using a conventional three-electrode cell. The working electrode was the coated specimen, using a saturated calomel electrode as reference electrode, and a platinum foil ($1cm^2$) as counter electrode. The used electrolyte was 3.5wt.% NaCl solution. EIS measurements were carried out using AC signals of amplitude 5mV peak to peak at the open circuit potential in the frequency range between 15kHz and 0.3Hz. EIS data was collected using Gamry PCI300/4 Potentiostat/Galvanostat/Zra analyzer, EIS300 Electrochemical Impedance Spectroscopy software, and Echem Analyst 5.21 for results plotting, graphing, data fitting & calculating.

3. Results and discussion

3.1. The physical–chemical properties of the prepared pigments

Figures (1 and 2) show the morphology of the prepared pigments using SEM and TEM. From the featured photos it can be seen that, silica fume possesses a spherical particle shapes, while titanium dioxide possesses platelet structure. The new pigments possess the two shapes altered on each other, i.e. micrographs showed that the spheres of silica are carrying on its surface and around the spheres the tiny plates of nano-titanium dioxide that appear as a roughness on the sphere surfaces.

From these two figures, it can be detected that the prepared pigment particles are formed with two shapes and two particle sizes. Both SEM and TEM showed the size of titanium dioxide in the shell to be in the nano-scale indicating the formation of nano-titanium dioxide on micronized silica fume.

These altered shapes of nano-TiO_2/SiO_2 pigments can provide better corrosion protection properties than its individual constituents if applied in paint formulations as these tiny plates are expected to block the voids between the spheres of silica, thus protecting the substrate by providing a tortuous path of the corroding materials diffusion through the pigment particles till they reach the metal surfaces in a very weak condition, and thus exhibiting better protection properties [26].

Fig. (3) shows the EDAX analysis of prepared pigments. EDAX or energy dispersive X-ray analysis can detect the elements on the surface up to one micron depth. As featured from the chart, titanium was detected; this revealed its presence on silica surfaces, and its concentration can be seen in the Table below.

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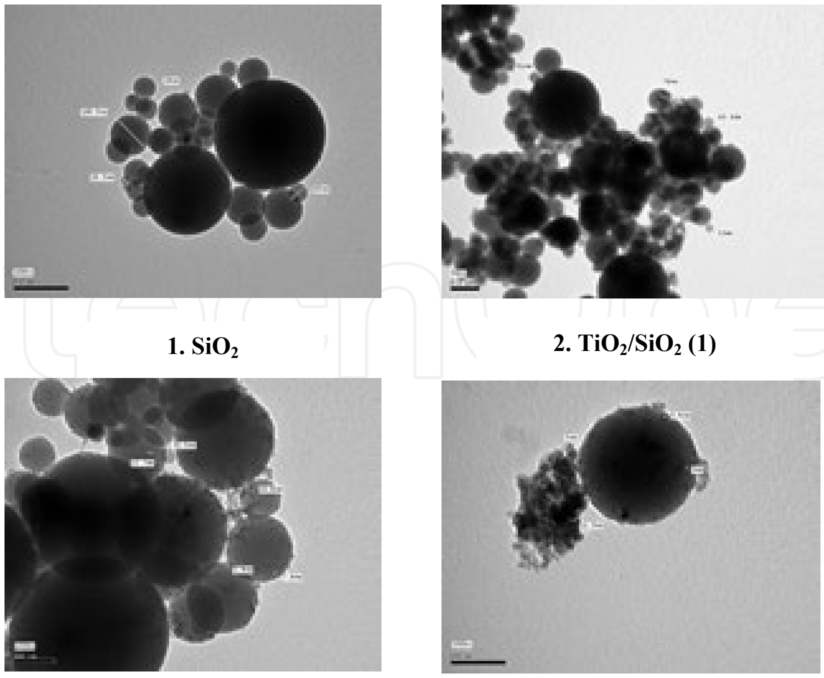
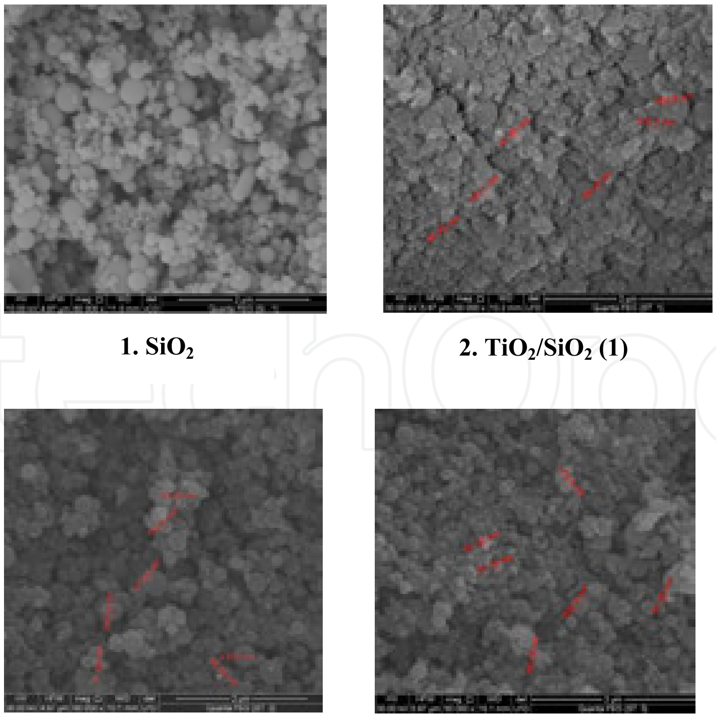


1. SiO_2 2. TiO_2/SiO_2 (1)

3. TiO_2/SiO_2 (2) 4. TiO_2/SiO_2 (3)

Fig. 1. TEM micrographs of silica fume and covered silica with titanium dioxide at magnification of 15x10^{3}X

Figure 1. TEM micrographs of silica fume and covered silica with titanium dioxide at magnification of 15x10^{3}X



1. SiO_2 2. TiO_2/SiO_2 (1)

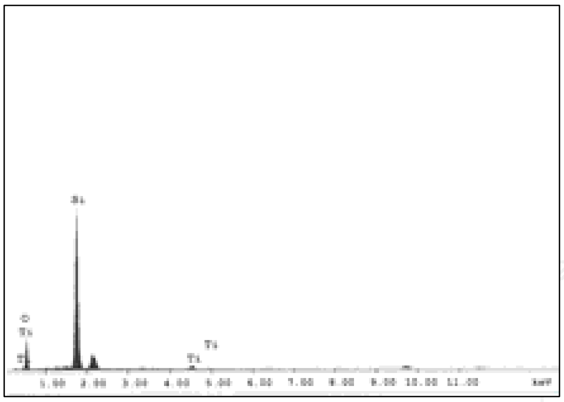
3. TiO_2/SiO_2 (2) 4. TiO_2/SiO_2 (3)

8

Fig. (2): SEM micrographs of silica fume and covered silica with titanium dioxide at magnification of 50x10^{3}X

Figure 2. SEM micrographs of silica fume and covered silica with titanium dioxide at magnification of 50x10^{3}X

Fig. (3) shows the EDAX analysis of prepared pigments. EDAX or energy dispersive X-ray analysis can detect the elements on the surface up to one micron depth. As featured from the chart, titanium was detected; this revealed its presence on silica surfaces, and its concentration can be seen in the Table below.



Element	Wt %	At %	K-Ratio	Z	A	F
O K	43.47	57.83	0.1068	1.0219	0.2401	1.0007
Si K	50.42	37.23	0.4036	0.9861	0.7519	1.0002
Ti K	6.11	3.94	0.0169	0.8790	0.9091	1.0000
Total	100.00	100.00				

Figure 3. EDAX analyses data for TiO_2/SiO_2 core-shell pigments

Fig. 3. EDAX analyses data for TiO_2/SiO_2 core-shell pigments

Constituent (%wt.)	6	7	8	9	10
Fe_2O_3 (Hematite)	18.5	18.5	18.5	18.5	18.5
Kaolin	20	20	20	20	20
$BaSO_4$	10	10	10	10	10
SiO_2	20	---	---	---	---
TiO_2	---	20	---	---	---
TiO_2/SiO_2 (1)	---	---	20	---	---
TiO_2/SiO_2 (2)	---	---	---	20	---
TiO_2/SiO_2 (3)	---	---	---	---	20
Total pigment	68.5	68.5	68.5	68.5	68.5
Total binder	31.5	31.5	31.5	31.5	31.5
P/B	2.175	2.175	2.175	2.175	2.175
Wetting & dispersing agent	1	1	1	1	1
Drier	0.5	0.5	0.5	0.5	0.5
Total	100	100	100	100	100

Table 3. Paint formulations of TiO_2/SiO_2 pigments with medium oil alkyd resin (Group I)

Constituent (%wt.)	1	2	3	4	5
Fe_2O_3 (Hematite)	23.5	23.5	23.5	23.5	23.5
Kaolin	20	20	20	20	20
$BaSO_4$	10	10	10	10	10
SiO_2	15	---	---	---	---
TiO_2	---	15	---	---	---
TiO_2/SiO_2 (1)	---	---	15	---	---
TiO_2/SiO_2 (2)	---	---	---	15	---
TiO_2/SiO_2 (3)	---	---	---	---	15
Total pigment	68.5	68.5	68.5	68.5	68.5
Total binder	31.5	31.5	31.5	31.5	31.5
P/B	2.175	2.175	2.175	2.175	2.175
Wetting & dispersing agent	1	1	1	1	1
Drier	0.5	0.5	0.5	0.5	0.5
Total	100	100	100	100	100

Table 4. Paint formulations containing TiO_2/SiO_2 pigments with medium oil alkyd resin (Group II)

Constituent (%wt.)	11	12	13	14	15
Fe_2O_3 (Hematite)	13.5	13.5	13.5	13.5	13.5
Kaolin	20	20	20	20	20
$BaSO_4$	10	10	10	10	10
SiO_2	25	---	---	---	---
TiO_2	---	25	---	---	---
TiO_2/SiO_2 (1)	---	---	25	---	---
TiO_2/SiO_2 (2)	---	---	---	25	---
TiO_2/SiO_2 (3)	---	---	---	---	25
Total pigment	68.5	68.5	68.5	68.5	68.5
Total binder	31.5	31.5	31.5	31.5	31.5
P/B	2.175	2.175	2.175	2.175	2.175
Wetting & dispersing agent	1	1	1	1	1
Drier	0.5	0.5	0.5	0.5	0.5
Total	100	100	100	100	100

Table 5. Paint formulations containing TiO_2/ SiO_2 Pigments with medium oil alkyd resin (Group III)

Constituent (%wt.)	16	17	18	19	20
Fe_2O_3 (Hematite)	8.5	8.5	8.5	8.5	8.5
Kaolin	20	20	20	20	20
$BaSO_4$	10	10	10	10	10
SiO_2	30	---	---	---	---
TiO_2	---	30	---	---	---
TiO_2/SiO_2 (1)	---	---	30	---	---
TiO_2/SiO_2 (2)	---	---	---	30	---
TiO_2/SiO_2 (3)	---	---	---	---	30
Total pigment	68.5	68.5	68.5	68.5	68.5
Total binder	31.5	31.5	31.5	31.5	31.5
P/B	2.175	2.175	2.175	2.175	2.175
Wetting & dispersing agent	1	1	1	1	1
Drier	0.5	0.5	0.5	0.5	0.5
Total	100	100	100	100	100

Table 6. Paint formulations containing TiO_2/ SiO_2 Pigments with medium oil alkyd resin (Group IV)

3.2. The effect of prepared pigments on mechanical properties of paints

Table (8) shows the results of determining hardness of organic coatings by means of pendulum apparatus, impact resistance and ductility. Paint films containing silica showed the best mechanical properties among the group, while those containing titanium dioxide showed the lowest values, this is due to that fine silica fume is used as additive that enhance the surface smoothness and dispersability of the media into which they are added, these fine silica particles have a lower coefficient of friction than titanium dioxide and other popular fillers. On a molecular level, these particles are perfectly spherical in shape and move more freely to provide a superior tactile feel [27], and thus better mechanical properties were obtained.

In general, TiO_2/SiO_2 pigments showed almost similar mechanical properties as silica but with lower values, and better than paint films containing titanium dioxide. This can be attributed to that the mixed pigments have a wide range of particle sizes, where the smaller nano-titanium dioxide particles may actually fit into the interstices between the larger particles of silica fume, thus taking up volume originally filled by the binder with pigment volume. In this case, the additional pigment does not compromise the mechanical properties of the film, also nano-titanium dioxide pigments did not provide the necessary range in particle size required to achieve a high degree of pigment packing leading to less mechanical properties than paint

Table 7. Physical, mechanical and corrosion results of paint formulations containing TiO_2/ SiO_2 Pigments with medium oil alkyd resin

Parameter	Group I					Group II					Group III					Group IV				
Drying time, hr.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Surface dry	——— 1 - 2 ———																			
Thorough dry	——— 3 – 4 ———																			
Adhesion	Gt0	Gt0	Gt0	**Gt0**	**Gt0**	Gt1	Gt0	Gt1	**Gt1**	**Gt1**	Gt1	Gt0	Gt1	**Gt1**	**Gt1**	Gt1	Gt0	Gt1	**Gt1**	**Gt1**
Hardness, Sec (90µ)	57	67	75	73	72	60	65	67	65	62	78	82	88	86	82	78	82	88	82	80
Ductility, Mm	6.3	3	6.7	6.5	6.4	6.7	2.7	6.4	6.1	5.8	6.4	4.3	6.6	6.2	5.6	6.4	4.3	5.4	5.2	5.1
Impact resistance, g.m.	0.74	0.33	0.74	0.75	0.64	0.75	0.28	0.93	0.88	0.75	0.74	0.26	0.96	0.88	0.74	0.74	0.26	0.74	0.64	0.54
Corrosion resistance																				
Degree of Blistering	6D	8M	4M	6MD	6M	4MD	8F	8F	8MD	8F	4D	6D	8MD	8M	8M	8MD	8M	8M	8F	8F
Degree of rusting	3-P	2-G	3-G	3-G	3-S	5-G	6-G	4-S	3-S	3-G	5-P	4-P	7-G	7-G	8-G	5-S	4-S	9-S	9-G	10
Filiform corrosion	——— Fig.1-FA ———																			

films containing silica fume. Also, the presence of the upper layers of nano-titanium dioxide precipitated on silica surface disturb the texture of silica by altering their platelet particles between the silica spheres leading to less homogenous texture and thus less mechanical properties. Paint films containing titanium dioxide exhibit poor mechanical properties among the entire group.

In general the mechanical properties of paint films in all the groups can be arranged as follow;

Paint films containing SiO_2> TiO_2/SiO_2(1)> TiO_2/SiO_2(2)> TiO_2/SiO_2(3)> TiO_2

3.3. The effect of prepared pigments on anticorrosive properties of paints

Table (8) features the results of determining the anticorrosion performance of paint films through blistering on paint surface and rust under film. The method classifies the osmotic blisters to the groups according to their sizes designated by numbers 2, 4, 6, and 8 (2 denotes the largest size, 8 the smallest one).

To the blister size information on the frequency of occurrence is given. The highest occurrence density of blisters is designated as D (dense), the lower ones as MD (medium dense), M (medium) and F (few). In such away a series from the surface area attacked at least by the osmotic blisters up to the heaviest occurrence can be formed as follows: 8F-6F-4F-2F-8M-6M-4M-2M-8MD-6MD-4MD-2MD-8D-6D-4D-2D.

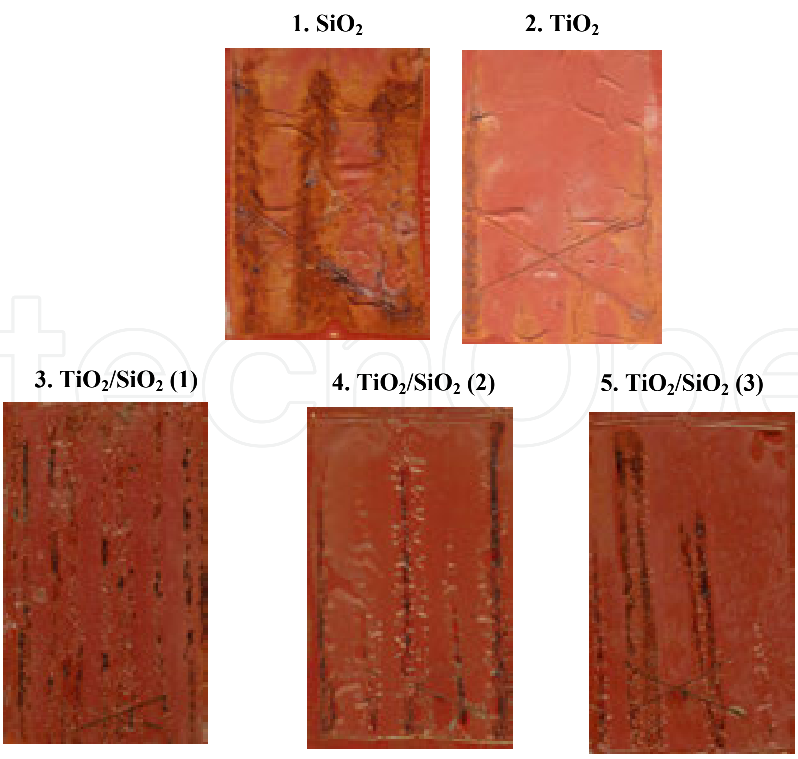


Figure 4. Photos of paint films of Group I after immersion in 3.5% NaCl after 28 days

Fig. 4. Photos of paint films of Group I after immersion in 3.5% NaCl after 28 days

Figure 5. Photos of paint films of Group II after immersion in 3.5% NaCl after 28 days

Fig. 5. Photos of paint films of Group II after immersion in 3.5% NaCl after 28 days

As can be detected from Table (8) and Figures (4-7) that paint films of group IV were better in their performance than the other groups in rust under paint films. In general the performance in corrosion protection of the groups can be arranged as follows;

Group IV > Group III > Group II > Group I

Also it can be detected that, paint films containing SiO_2/TiO_2 (3) were better in its anticorrosive performance than those containing SiO_2/TiO_2 (2) and both were better than SiO_2/TiO_2 (1), this may be due to that in case of anticorrosive pigments whose protective effect is located on their surfaces where nano-titanium dioxide is located, the direct contact with the matrix and hence their interaction with it will be the main reason of their protection properties. It was found that polymer/nano-particle have unique properties resulting from the large fraction of atoms that reside at the surface leading to strong interfacial interactions with the polymer matrix, which can improve the protective characteristics of organic coatings [28-32, 33]. Also, it was considered that the pigments, which induced a very strong polymer-pigment interaction, resulted in coatings with a better dispersion of pigments and stability, and were resistant to corrosion by inducing barrier properties [34, 35].

Also, the previous results can be dedicated to that nano-titanium dioxide particles forming the upper layers of the pigment are arranged in alignment on silica surfaces and sometimes in

Figure 6. Photos of paint films of Group III after immersion in 3.5% NaCl after 28 days

Fig. 6. Photos of paint films of Group III after immersion in 3.5% NaCl after 28 days

between its particles. In case of low concentration of nano-titanium dioxide, its small platelet particles order themselves in the interstices positions between the spherical silica particles, these spaces formed between the binder and the pigment particles, even under the best circumstances give the chance for areas arise on the surface of the pigment particle where the binder and the particle may be in extremely close physical proximity but are not chemically bonded. This area between binder and pigment can be a potential route for water molecules to slip through the cured film [2, 36]. As the concentration of nano-titanium dioxide increases, a more close-pack texture locking almost all these positions will be formed leaving no routes for the corroding materials to reach the metal surface and thus better corrosion inhibition can be detected [37, 38].

3.4. Electrochemical Impedance studies

Electrochemical impedance spectroscopy (EIS) was used for the evaluation of the electrochemical properties of painted mild steel with formulations containing different concentrations of TiO_2/SiO_2 core-shell pigments. The painted specimens were tested in 3.5 wt% NaCl at different immersion times.

Equivalent circuit modeling is a standard tool for the interpretation of impedance data. Equivalent circuit consists of R_s which is the electrolyte/solution resistance, followed by a

Figure 7. Photos of paint films of Group IV after immersion in 3.5% NaCl after 28 days

coating capacitance C_c which is in parallel with R_{po} which is the pore resistance; and Warburg impedance Z_w (diffusional element) is also included to represent the electrochemical processes taking place at the paint-metal interface. This element Z_w is often represented as C_{dl} (the double layer capacitance) which is in parallel with R_{ct} (charge transfer resistance) in corroding coated metals.

The values of pore resistance (R_{po}) obtained from impedance data, at different immersion times 1, 7, 14, 21 and 28 days, are listed in Table (8) and shown in Fig. 8.

Group	Paint no.	Pigments in paint formulations	R_{po} (Kohm.cm^2)				
			1 day	**7 day**	**14 day**	**21day**	**28 day**
I	3	[TiO_2/SiO_2(1)]	0.291	0.182	0.164	0.122	0.113
	4	[TiO_2/SiO_2(2)]	0.865	0.409	0.243	0.220	0.191
	5	[TiO_2/SiO_2(3)]	0.758	0.566	0.350	0.290	0.274
II	8	[TiO_2/SiO_2(1)]	0.307	0.191	0.175	0.140	0.109
	9	[TiO_2/SiO_2(2)]	2.680	0.887	0.884	0.412	0.409
	10	[TiO_2/SiO_2(3)]	9.520	3.010	2.770	0.906	0.618

Group	Paint no.	Pigments in paint formulations	R_{po} *(Kohm.cm²)*				
			1 day	**7 day**	**14 day**	**21day**	**28 day**
III	13	[TiO_2/SiO_2(1)]	0.867	0.522	0.490	0.306	0.272
	14	[TiO_2/SiO_2(2)]	2.700	1.000	0.770	0.456	0.408
	15	[TiO_2/SiO_2(3)]	1.686	3.550	1.568	1.080	0.764
IV	18	[TiO_2/SiO_2(1)]	1.211	1.140	0.566	0.406	0.367
	19	[TiO_2/SiO_2(2)]	3.680	1.255	1.170	0.612	0.491
	20	[TiO_2/SiO_2(3)]	126.0	37.80	10.93	4.840	1.800

Table 8. EIS results for different paint formulations in 3.5 wt% NaCl at different immersion times

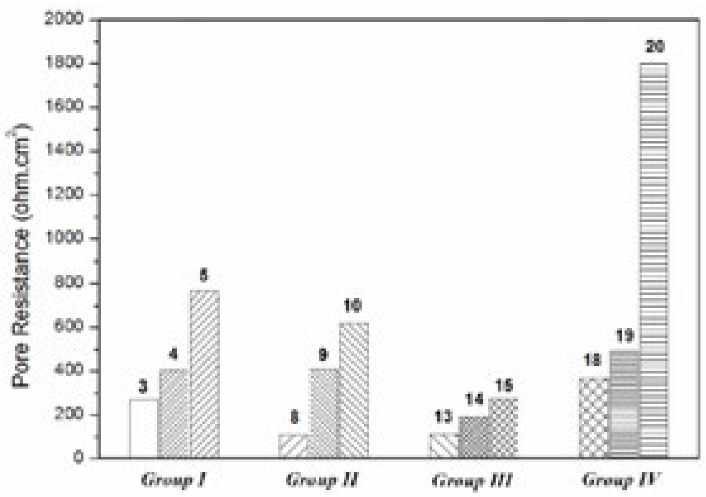


Figure 8. Pore resistance of TiO_2/SiO_2 paint formulations in 3.5 wt% NaCl after immersion for 28 days

Results represented in this table indicated the following;

a. The pore resistance (R_{po}) is clearly higher in case of group IV paint films which contains 30% of TiO_2/SiO_2 pigments, than that of other groups at all immersion times. It is obvious that the rate of corrosion follows the order;

Group IV > Group III > Group II > Group I

b. Concerning the upper layer thickness it was found that the pore resistance (R_{po}) increases in the following order;

Paint films containing TiO_2/SiO_2(3) > TiO_2/SiO_2(2) > TiO_2/SiO_2(1)

c. As shown in Fig. 9, the paint film containing TiO_2/SiO_2 (3) in group IV (paint no. 20) offered the best corrosion resistance even after 28 days immersion in 3.5wt% NaCl solution (1.8K ohm), indicating that paint formulations loaded with 30% of TiO_2/SiO_2(3) pigment is the best among the four groups and they can provide effective protection to carbon steel.

d. The pore resistance (R_{po}) is inversely proportional to immersion times. As paint no. 20 was the best among the groups it was taken as an example to show in Fig. 9 the typical Nyquist plots after different immersion time in 3.5 wt% NaCl.

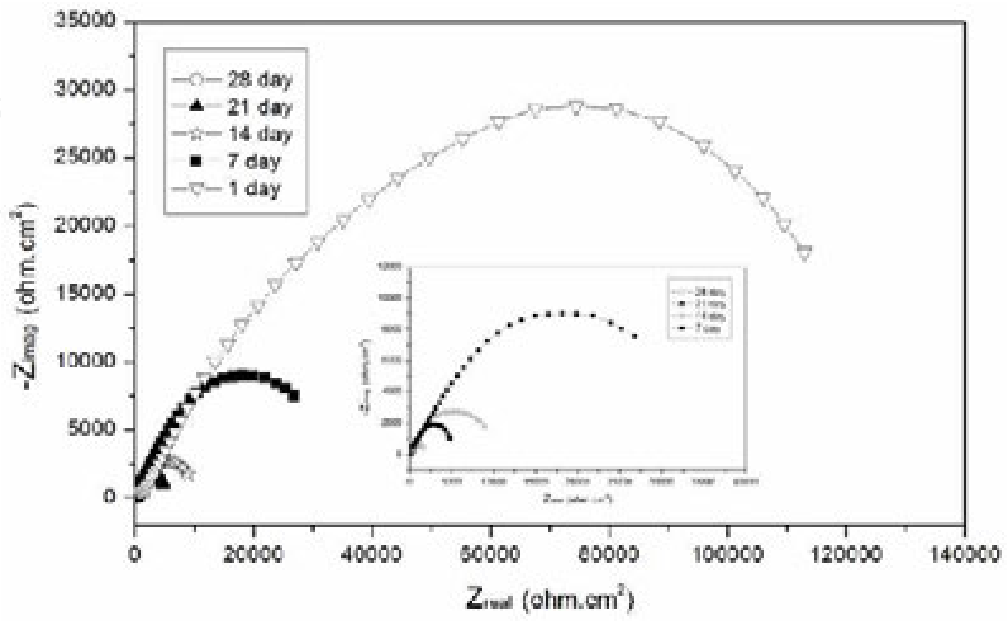


Figure 9. Nyquist plots of paint formulations containing TiO_2/SiO_2 (Sample 20) in 3.5 wt% NaCl at different immersion times 1, 7, 14, 21 and 28 days,

The decrease in pore resistance may be due to the penetration of water and movement of ionic species among the coating layer, increasing the coating conductivity. This can be explained according to the following steps;

- Initially, the electrolyte penetrates through the coating layer, and sets up conducting paths at different depths within the coating [39]. With increase immersion time, the electrochemical reactions at the interface between the coating and the metal surface make progress where the electrolyte phase meets the metal/oxide interface and a corrosion cell is then activated [40].
- This step is followed by that the barrier properties of the coating are decreased, suggesting a decrease in the coating resistance, i.e. decrease the radius of the semi-circle [41-43].

Generally, electrochemical studies were in high accordance with accelerated laboratory test results which revealed that group IV was the best and paint films containing TiO_2/SiO_2(3) showed the best corrosion inhibition behaviour among all paint films of the groups.

4. Conclusions

Hybrid pigments were prepared based on silica fume waste in the bulk covered with different layers of nano-titanium dioxide to overcome the deficiency of forming silica fume agglomerations due to its fine particles and promote its surface properties. The pigments were tested as anticorrosive pigments in paints based on medium oil alkyd resin. The study showed that as the thickness of the nano-titanium dioxide layers increases better corrosion protection performance was exhibited by paint films, and the study also revealed that the pigment loading in paint formulations is directly proportional to corrosion inhibition.

Electrochemical studies showed that pore resistance was in inverse relationship with the concentration of the prepared pigments, showing that as pigment concentration increases less pore size was detected and hence better corrosion protection was performed and these results are in high agreement with the accelerated laboratory test.

Acknowledgements

This work was supported by Science and Technology Development Fund (STDF) under project number 1242.

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References

[1] Ahmed, N.M., Selim, M.M. Anticorrosive performance of titanium dioxide-talc hybrid pigments in alkyd paint formulations for protection of steel structures. Anti-Corrosion Methods and Materials 2010; 57 (3) 133-141.

[2] Ahmed, N.M., Selim, M.M. Innovative titanium dioxide-kaolin mixed pigments performance in anticorrosive paints. Pigment & Resin Technology 2011; 40 (1) 4-16.

[3] Ahmed, N.M., Mohamed, H.A. Performance of phosphate-alumina pigments in waterborne paints for protection of cold-rolled steel. J. Coating Technology and Research 2011; 8 (2) 201-210.

[4] Caruso, R.A., Susha, A., Caruso, F. Structural Control of TiO_2 Networks Using Polymer Gel Templates. Chem. Mater. 2001; 13 (1) 400-409.

[5] Daniel, M.C., Astrue, D. Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology. Chem. Rev. 2004; 104 (2) 293-346.

[6] Ahmed, N.M., Abd El-Fattah, H.T.M. The Role of Silica Fume Pigments in Corrosion Protection of Steel Surfaces. In: Reza Shoja Razavi (Ed.), Recent Researches in Corrosion Evaluation and Protection, InTech; 2012. p. 67-90.

[7] Abu-Ayana, Y.M., Youssef, E.A.M., El-Sawy, S.M. Silica fume-formed during the manufacture of ferrosilicon alloys-as an extender pigment in anticorrosive paints". Anti-Corrosion Methods and Materials 2005; 52 (3) 345-352.

[8] Youssef, E.A.M., Ahmed, N.M., Abd El-Ghaffar, M.A. Characterization and evaluation of silica fume as an extender pigment for surface coating applications. Pigment & Resin Technology 1998; 27 (2) 88-98.

[9] Siddique, R. Utilization of silica fume in concrete: Review of hardened properties. Resources, Conservation and Recycling 2011; 55 (11) 923-932.

[10] Boddy, A.M., Hooton, R.D., Thomas, M.D.A. The effect of the silica content of silica fume on its ability to control alkali-silica reaction. Cement and Concrete Research 2003; 33 (8) 1263-1268.

[11] Panjehpour, M., Ali, A.A.A., Demirboga, R. A Review for characterization of silica fume and its effects on concrete properties. International Journal of Sustainable Construction Engineering & Technology 2011, 2 (2) 1-7.

[12] Ahmed, N.M., Abdel-Fatah, H.T.M., Youssef, E.A. Corrosion studies on tailored Zn Co aluminate/kaolin core–shell pigments in alkyd based paints. Progress In Organic Coatings 2012, 73 (1) 76-87.

[13] Pagliaro, M., Ciriminna, R., Palmisano, G. Silica-Based Hybrid Coatings. Journal of Materials Chemistry 2009; 19 (1) 3116-3126.

[14] Giner, V.T., Ivorra, S., Baeza, F.J., Zornoza, E., Ferrer, B. Silica fume admixture effect on the dynamic properties of concrete. Construction and Building Materials 2011; 25 (8) 3272-3277.

[15] Vila-Gonzalez, C.A., Cruz-Silva, R., Menchaca, C., Sepulveda-Guzman, S., Uruchurtu, J. Use of Silica Tubes as Nanocontainers for Corrosion Inhibitor Storage. Journal of Nanotechnology 2011; 11 (1) 1-9.

[16] Tarrío-Saavedra, J., López-Beceiro, J., Naya, S., Gracia, C., Artiaga, R. Controversial effects of fumed silica on the curing and thermomechanical properties of epoxy composites. eXPRESS Polymer Letters 2010; 4 (6) 382-395.

[17] Xianming, S., Tuan, A.N., Zhiyong, S., Yajun, L., Avci, R. Effect of nanoparticles on the anticorrosion and mechanical properties of epoxy coating. Surface & Coatings Technology 2009; 204 (2) 237-245.

[18] Peter, H., Robert, V. High grade kaolin fillers–production review: Industrial Minerals. Applied Clay Science 1999, 54 (1) 25-37.

[19] Salamone, J.C. Concise polymeric materials encyclopedia, CRC press 1999. p. 477.

[20] Shao, Y., Li, Y., Du, Y., Wang, F. Enhancement of the Protectiveness of Epoxy Coatings with Surface-Modified Nano-Titanium Particles. Corrosion 2006; 62 (6) 483-490.

[21] Lewis, O.D., Critchlow, G.W., Wilcox, G.D., De Zeeuw, A., Sander, J. A study of the corrosion resistance of a waterborne acrylic coating modified with nano-sized titanium dioxide. Progress in Organic Coatings 2012; 73 (1) 88-94.

[22] Scully, J.R., Hensley, S.T. Lifetime Prediction of Organic Coatings on Steel and a Magnesium Alloy using Electrochemical Impedance. Corrosion 1994; 50 (9) 705-716.

[23] Wei, D.F., Chatterjee, I., Jones, D.A. Evaluation of Corrosive Degradation in Coated Steel Using Alternating Current Impedance Spectroscopy. Corrosion 1995; 51 (2) 97-104.

[24] Tsai, C.H., and Mansfield, F. Determination of Coating Deterioration with EIS: Part II. Development of a Method for Field Testing of Protective Coatings. Corrosion Sciences 1993; 49 (9) 726-737.

[25] Mansfield, F., Kendig, M.W., and Tsai, S. Evaluation of corrosion behavior of coated metals with AC impedance measurements. Corrosion 1982; 38 (3) 478-484.

[26] Walter, G. Laboratory Simulation of Atmospheric Corrosion by SO_2-II. Electrochemical Mass Loss Comparisons. Corrosion Sciences 1991; 32 (15) 1041-1048.

[27] Lambourne, R. Paint and surface coatings, Ellis Horwood Ltd. Pub. 1987, p. 131.

[28] Guin, A.K., Nayak, S.K., Rout, T.K., Bandyopadhyay, N., Sengupta, D.K. Corrosion behavior of nanohybrid titania–silica composite coating on phosphated steel sheet. J. Coat. Technol. Res. 2012; 9 (1) 97-106.

[29] Chen, C., Khobaib, M., Curliss, D. Epoxy Layered-Silicate Nanocomposites. Prog. In Org. Coat. 2003; 47 (3) 376-383.

[30] Voevodin, N.N., Balbyshev, V.N., Khobaib, M., Donley, M.S. Nanostructured coatings approach for corrosion protection. Prog. In Org. Coat. 2003; 47 (4) 416-423.

[31] Kirubaharan, A.M.K., Selvaraj, M., Maruthan, K., Jeyakumar, D. Synthesis and characterisation of nanosized titanium dioxide and silicon dioxide for corrosion resistance applications. J. Coat. Technol. Res. 2012; 9 (2) 163-170.

[32] Mathiazhagan, A., Joseph, R. Nanotechnology-A New Prospective in Organic Coating – Review. International Journal of Chemical Engineering and Applications 2011; 2 (4) 225-237.

[33] Vesely, D., Kalendova, A. Anticorrosion efficiency of $Zn_xMg_yAl_2O_4$ core-shell spinels in organic coatings, *Progress in Organic Coatings* 2008; 62 (1) 5-20.

[34] Hegedus, C.R., Kamel, I.L. Polymer-Filler Interaction. Effects on Coating Properties. J. Coat. Technol. 1993; 65 (822) 37-43.

[35] Rong, M.Z., Zhang, M.Q., Zheng, Y.X., Zeng, H.M., Walter, R., Friedrich, K. Improvement of tensile properties of nano-SiO_2 /PP composites in relation to percolation mechanism. Polymer 2001; 42 (1) 167-183.

[36] Quanxiang, Y., Yun, L., Jizu, Y. Preparation of titanium dioxide compound pigments based on kaolin substrates. J. Coat. Technol. Res. 2010; 7 (2) 229-237.

[37] Sorensen, P.A., Kiil, S., Dam-Johansen, K., Weinell, C.E. Anticorrosive coatings: a review. J. Coat. Technol. Res. 2009; 6 (1) 135-176.

[38] Barranco, V., Feliu Jr., S., Feliu, S. EIS study of the corrosion behavior of zinc-based coatings on steel in quiescent 3% NaCl solution. Part 2: coatings covered with an inhibitor-containing lacquer. Corrosion Science 2004; 46 (9) 2221-2240.

[39] Del Amo, B., Romagnoli, R., and Vetere, V.F. Steel Corrosion Protection by Means of Alkyd Paints Pigmented with Calcium Acid Phosphate. Ind. Eng. Chem. Res. 1999; 38 (3) 2310-2314.

[40] Shao, Y., Jia, C., Meng, G., Zhang, T., Wang, F. The role of a zinc phosphate pigment in the corrosion of scratched epoxy-coated steel. Corrosion Science 2009; 51 (1) 371-379.

[41] Panjehpour, M., Ali, A.A., Demirboga, R. A Review for characterization of silica fume and its effects on concrete properties. International Journal of Sustainable Construction Engineering & Technology 2011; 2 (2) 1-7.

[42] Torii, K., Kawamura, M. Pore structure and chloride ion permeability of mortars containing silica fume. Cement and Concrete Composites 1994, 16 (4) 279-286.

[43] Kaiser, J.P., Zuin, S., Wick, p. Is nanotechnology revolutionizing the paint and lacquer industry? A critical opinion. Science of the Total Environment 2013; 442 (1)282-289.