The Role of Silica Fume Pigments in Corrosion Protection of Steel Surfaces

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1. Introduction

Inorganic Pigments significantly change our surroundings. They are irreplaceable for serving the purpose of imparting color to various compounds. They also add properties such as rust inhibition, rigidity, and abrasion resistance. Pigments are insoluble substances that can be incorporated into a material to selectively absorb or scatter light. Depending on the specific pigment used, different visual effects are produced. Inorganic pigments may be obtained from a variety of naturally occurring or synthetically produced mineral sources. Their applications range from concrete to artist's colors, from industrial paints to toners in photocopiers, from coloring in foodstuffs to raw materials for catalysts. The application properties of pigments depend not only on their chemistry but also on their chemical appearance and to greater extent on the manufacture process (Barnett et al., 2006; Talbert, 2007; Brock, 2000; Baxbaum & Pfaff, 2005).

In comparison with organic pigments, inorganic pigments are generally better to withstand the effects of sunlight and chemical exposure. They provide superior opacity, which means they can render a substance or object opaque by prohibiting light from passing through it. Inorganic colors, however, tend to be less bright, pure, and rich than their organic counterparts. Inorganic pigments also possess less tinting strength; i.e. more pigment is needed to produce the desired effect. This generally makes them more durable. Almost all inorganic pigments are completely insoluble. Consequently they do not bleed or leach out of coatings, inks, or plastics. In addition, inorganic pigments are usually less expensive than similar organic colors (Gysau, 2006; Brock et al., 2000; Baxbaum & Pfaff, 2005; Degryse, 2003).

Nowadays there is evolution in pigment industry, manufacturers are trying to evolve new trends of pigments which are safe, cheap with high efficiency to replace the common and well known pigments, among these new trends of pigments are;

- a. **Substrate pigments**, where at least one additional component (pigment or extender) is deposited onto a substrate (pigment or extender), preferably by a wet method. Weak, medium or strong attractive forces develop between these pigment components during drying or calcining. These forces prevent segregations between components during use (Baxbaum & Pfaff, 2005; Degryse, 2003; Herbst & Hunger 2006).

- b. **Special substrate pigments** include the after-treated pigments and the core pigments. To produce the after-treated pigments the inorganic pigment particles are covered with a thin film of inorganic or organic substances to suppress undesirable properties (e.g. catalytic and photochemical reactivity) or to improve the dispersibility of the pigments and the hydrophilic or hydrophobic character of their surfaces. The particles can be coated by precipitation, by adsorption of suitable substances from solutions (usually aqueous), or by steam hydrolysis (Baxbaum & Pfaff, 2005; Degryse, 2003; Herbst & Hunger 2006; Warson & Finch, 2001; Forsgren, 2006; Vesely & Kalendova, 2008). To produce core pigments. A pigment is deposited on an extender, by precipitation or by wet mixing of the components. In the case of anticorrosive pigments, whose protective effect is located on their surfaces, the use of core pigments can bring about a significant saving of expensive materials. Extender particles are also treated by fixing water-insoluble organic dyes on their surfaces via lake formation (Vesely & Kalendova, 2008; Veleva, 1999).

Titanium dioxide and silica are among the most frequently used fillers in paint and coating formulations. The special properties of the materials should improve the product formulation.

Silica fume is a byproduct of producing silicon metal or ferrosilicon alloys, Silicon metal and alloys are produced in electric furnaces. The smoke that results from furnace operation in tonnage amounts is collected and sold as silica fume, rather than being land-filled. Nowadays, there is increasing environmental concern with regard to excessive volumes of solid waste hazards accumulation. Silica fume which is a fine lightweight fluffy amorphous powder that possesses suitable values of specific gravity, bulking value and oil absorption can find a new market in different industries (Ayana et al, 2005). Silica fume is inert, neutral and of an excellent chemical resistance. It consists primarily of amorphous (non-crystalline) silicon dioxide (SiO_2); its amorphous nature favors safe use from a standpoint of industrial hygiene. It has spherical fine particles less than 0.01μ , the average particle size ranges between $0.1\text{--}0.3\mu$, easy to lump together to form a looser, with high adsorption capacity and gel. Its average granule diameter is $0.15\text{--}0.20\mu\text{m}$, and specific surface area is $15000\text{--}20000\text{ m}^2/\text{kg}$. Major Features of silica powder are its high purity (SiO_2 Content Above 99.5%), hardness 7, high White Reached 96 Degrees, reasonable oil absorption, good dispersion, and stable chemical properties. It improves coatings corrosion resistance, wear resistance, and high temperature resistant properties (Del Amo et al, 2002; Perrera, 2004; Molera et al., 2004; Sorensen et al., 2009).

Silica fume is widely used in hydropower projects, refractories, roads, bridges, tunnels, chemical ceramic, rubber and other industries. Because of its fine particles, large surface area, and the high SiO_2 content, silica fume is very reactive material. It can be successfully applied in raising intensity, durability, and it also can improve the material overall performance as filler, used in paint, coating, rubber and other high molecular material (kirubaharan et al., 2009; Guin et al., 2011; Siddique & Khan, 2011, Weil, 2011).

The health problems concerning fumed silica are low; it is not listed as a carcinogen by OSHA, IARC, or NTP. Due to its fineness and thinness, fumed silica can easily become airborne, making it an inhalation risk, capable of causing irritation.

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. This characteristic is also beneficial in the formulation of printing inks which allow for high definition levels during application (Yingchao et al., 2011; Otterstedt & Bradreth, 1998).

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 filler can be used in the following coating and paint industry field (Baxbaum & Pfaff, 2005; Forsgren, 2006; Patton, 1973):

- Industry painting
- Wooding coating
- Anti-corruption coating
- Powder coating
- Architectural Paint
- Water -Proof Paint

Silica fume can benefit (Ayana, 2005; Kirubaharan, 2009):

- For improved abrasion resistance and scratch resistance of the film.
- Gives the highest chemical durability in industrial coatings.
- Offers high loading level leads to reduced formulation cost.

The modern coatings industry utilizes evolving chemistries in its quest to become more efficient in protecting and enhancing the various substrates to which coatings are applied. Further, in order to limit toxic and environmentally damaging emissions, the industry is striving to move away from solvents to water-based employing eco-friendly pigments. This is focused on providing some of the chemical solutions to the many challenges the industry face today in generating modern, safe, low-emission paints and coatings.

Titanium dioxide is a chemically very inert and light resistant material. TiO_2 is mainly known as white pigment (so-called titanium white) and is valued for its brightening effects, and its dirt-repellent properties. TiO_2 particles are used in the coatings industry because of its strong color, high opacity due to their high refractive index, improving the light resistance and dirt resistance of a formulation, low oil absorption, high tinting strength, inert chemical properties and recently attractively as photo-catalyst derived from their photo-catalytic activity. Although high photo-catalytic activity is required for titanium dioxide 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. The insulating layers like silica (SiO_2), alumina (Al_2O_3), or a polymer are often expected to suppress the catalytic activity of titanium dioxide particles (Peter & Robert, 1999; Salamone, 1999; Streitberger & Kreis, 2008; Martens, 1974; Bremmell & Mensah, 2005).

The refractive index is a measure of how light is bent when it passes from one medium to another. The higher the refractive index, the more the light is bent which results in greater

opacity. Rutile TiO_2 has a high refractive index and gives good opacity to coatings. Most mineral fillers have a significantly lower refractive index than TiO_2 and don't contribute to the opacity, but they can be used in conjunction with TiO_2 to achieve opacity at reduced cost. Some minerals, such as amorphous silica (silica fume), have refractive index the same or lower than the resin and will be invisible in the dry film. They can be used to reduce the gloss of a clear coating without creating haze (Bremmell & Mensah, 2005; Shao et al., 2009; Gaumet et al., 1997; Walter, 1991).

This work addresses preparation of new pigments via new method of preparation named "Core-shell", where silica fume which is a cheap and waste material representing the core comprises 90% of the new pigments is covered with a thin layer of titanium dioxide that does not exceed 10% of the pigment comprising the shell. This method of preparation presents a new easy route to obtain high performance pigments with concomitant savings besides being eco-friendly. Presence of titanium dioxide is expected to increase the hiding power of silica fume and consequently increases the new pigments opacity. The combination of these two compounds can lead to the production of new pigments with improved properties different from each of its individual components, overcoming their deficiencies; and consequently changing their efficiency of protection when applied in paints. Titanium dioxide was deposited on silica fume surface in three different concentrations to study the effect of its presence concentration on the anticorrosion efficiency of the new core-shell 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 used has the following chemical composition.

Concentration of main constituents	Wt., %
SiO_2	95.54
Al_2O_3	0.34
Fe_2O_3	0.91
MgO	0.70
CaO	0.32
Na_2O	0.39
K_2O	0.80
P_2O_5	0.07
SO_3	0.03
L.O.I	4.93

Table 1. Chemical composition of silica fume

2.1.1 Preparation of $\text{TiO}_2/\text{SiO}_2$ fume core-shell pigments

Titanium tetrachloride was added in three concentrations 1, 2 and 3 ml to 100 ml hydrochloric acid. Silica was immersed in these three solutions and left for sometime to assure complete covering. Ammonia solution was 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 is then calcined at 500-750°C. Three concentrations of titanium dioxide and consequently of titanium were deposited on silica surface, these three concentrations are shown in Table (2).

Pigments	Concentration of TiCl ₄ (wt. %)	Concentration of TiO ₂ (wt. %)	Concentration of Ti (wt. %)
TiO ₂ /SiO ₂ (1)	1	0.42	0.25
TiO ₂ /SiO ₂ (2)	2	0.84	0.50
TiO ₂ /SiO ₂ (3)	3	1.26	0.76

Table 2. Concentrations of titanium dioxide and titanium on silica surface

The scheme of preparation was as follows

2.2 Specification of the physical–chemical properties of the prepared pigments

2.2.1 Specific gravity

Determination of specific gravity was carried out according to (ASTM D5965-96, 2007).

2.2.2 Oil absorption

This was carried out by measuring the amount of flax oil in grams that makes a paste with defined properties out of 100 g of pigments. This determination was carried out using the pestle-bowl method according to (ASTM D281-95, 2007).

2.2.3 Bulking value

Determination of bulking value which expresses the volume of paint for a given weight of a pigment, in which pigments with higher bulking values are considered more economic, is carried out according to (ASTM D 16-62, 2007).

2.2.4 Determining pH of the aqueous extracts of the pigments

The procedure of determining aqueous extract pH was derived from a procedure according to (ASTM D 1583-01, 2007). Suspensions of the pigments were prepared in redistilled water.

2.3 Methods of instrumental analysis

2.3.1 X-ray diffraction

X-ray powder diffraction patterns were obtained at room temperature using a Philip's diffractometer (type PW1390), employing Ni-filtered Cu K α radiation ($\lambda = 1.5404 \text{ \AA}$). The diffraction angle, 2θ , was scanned at a rate of $2^\circ / \text{min}$.

2.3.2 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.

2.3.3 Transmission electron microscopy

Various pigments were examined using (JEOL JX 1230) technique with micro-analyzer electron probe. This technique confirmed the results of the above SEM results besides determining the particle sizes of the prepared pigments.

2.3.4 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 15 paint formulations. These paint formulations contain silica fume, commercial titanium dioxide, silica fume covered with different layer thicknesses of titanium dioxide denoted as $\text{SiO}_2/\text{TiO}_2(1)$, $\text{SiO}_2/\text{TiO}_2(2)$, and $\text{SiO}_2/\text{TiO}_2(3)$ expressing concentration of 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 three groups; each is based on different P/B ratio (group I has P/B 1.74, group II has P/B 2.175 and group III has P/B 3). Paint formulations are given in Tables 5-7, while the physical-mechanical and corrosion properties are represented in Table 8. The corrosion features of the paint films are shown in Figs. (5-7).

2.5 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.

2.5.1 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.

2.5.2 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.

2.5.3 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.

2.5.4 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.

2.5.5 Overall evaluation of the selected physical–mechanical properties of the paints

The measured quantities of physical–mechanical nature including the adhesion of the paint film identified by means of a cross-cut test, impact resistance, and resistance against cupping indicate the elasticity, elongation at break, and strength of the paint film. 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.

2.5.6 The effect of pigment particles on the surface hardness of the paints

Good surface resistance is important for the resistance of the paints against mechanical impacts, scratches, erosion caused by abrasion of dust particles in the outside atmospheric environment. The determination of the surface hardness of the paint film 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%.

2.6 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 properties of the prepared pigments by means of laboratory tests and electrochemical measurements in corrosive environments was a priority assignment.

2.6.1 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.

2.6.2 Electrochemical evaluation method

Electrochemical impedance spectroscopy (EIS) 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.

EIS is useful to characterize a painted metal substrate by simultaneously measuring two phenomena: (1) the deterioration of the organic coating caused by exposure to an electrolyte and (2) the increase in corrosion rate of the underlying substrate due to the deterioration of the coating and subsequent attack by the electrolyte.

In EIS, an AC voltage of varying frequency is applied to the sample. It is useful to think of the frequency as a camera shutter that can be very fast (high frequency) for fast reactions and very slow (low frequency) for slow ones. This is the technical feature that allows EIS to gather so much information on an electrochemical reaction in one experiment, and this is why EIS is more useful for coatings than DC electrochemical techniques.

EIS can quantitatively measure both resistances and capacitances in the electrochemical cell. Resistance corresponds to electron transfer reactions such as corrosion, while the capacitance of a metal electrode in contact with an electrolyte is important information for any electrochemical system, for organic coatings, the capacitance measurement is particularly revealing. As the organic coating deteriorates with time during exposure to an electrolyte, EIS can track changes in the capacitance of the coating. The capacitance will change as the coating swells or absorbs water. In addition, changes in the porosity of the coating can be easily measured. EIS can also simultaneously monitor the rate of corrosion of the metallic substrate which generally increases as the protective coating fails, allowing the electrolyte to contact the substrate (Mirabedini et al, 2003; Kendig, et al., 1983; Hernandez et al., 1999; Huang et al., 2008).

In the present work, 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 (1 cm²) as counter electrode. The used electrolyte was 3.5 wt. % 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 15 kHz and 0.3 Hz. 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. Result and discussion

3.1 The physical–chemical properties of the prepared pigments

Silica fume is a fine amorphous kind of silica, while titanium dioxide possess well crystalline particles, since the layers of titanium dioxide were so thin that they do not exceed 10% of the whole pigment concentration as can be seen in Table (3), they do not alter the crystals of silica and hence the XRD charts do not show any difference between the amorphous structure of uncovered silica fume and the silicas covered with the three concentrations of titanium dioxide. This can be clearly seen in Figure (1).

Figures (2 and 3) show the morphology of the prepared pigments using SEM and TEM. From the featured photos it can be seen that, silica fume possess a spherical particle shapes, while titanium dioxide possess platelet structure. The new pigments possess platelet

(1) SiO_2 (2) TiO_2 (3) $\text{SiO}_2.\text{TiO}_2(1)$

Fig. 1. XRD charts of 1. silica fume, 2. Titanium dioxide, 3. Silica coated with titanium dioxide (1), 4. Silica coated with titanium dioxide (2), and 5. Silica coated with titanium dioxide (3)

1. Silica fume

2. Titanium dioxide

3. Silica covered with TiO_2 (1) 4. Silica covered with TiO_2 (2) 5. Silica covered with TiO_2 (3)

Fig. 2. SEM micrographs of 1.Silica, 2.Titanium dioxide, 3, 4 and 5.Silica covered

structures begin to appear with the silica appearing as clouds in the background of the photo due to their purity and fine particles with rods or small plates of titanium depositing on its surface with their amounts increasing from Figure 3d to Figure 3e. These plates provide a reinforcing effect reducing the water and gas permeability, and therefore imparting good anticorrosive properties and special appearance to the paint film when used in paint formulations (Lambourne, 1987).

Figure (4) 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.

Fig. 4. EDAX analysis of silica fume covered with titanium dioxide

Table 3. represents the XRF analyses results of the three prepared pigments besides the uncovered silica fume. From the Table it can be seen that titanium concentration differs in an ascending order from $\text{SiO}_2/\text{TiO}_2$ (1) to $\text{SiO}_2/\text{TiO}_2$ (3), revealing that different concentrations of

Concentration of main constituents (wt. %)	Silica fume	$\text{TiO}_2/\text{SiO}_2$ (1)	$\text{TiO}_2/\text{SiO}_2$ (2)	$\text{TiO}_2/\text{SiO}_2$ (3)
SiO_2	95.54	94.48	93.61	91.78
TiO_2	----	2.85	3.90	5.72
Al_2O_3	0.34	0.36	0.37	0.35
Fe_2O_3	0.91	1.43	1.27	1.23
MgO	0.70	0.60	0.60	0.57
CaO	0.32	0.31	0.33	0.32
Na_2O	0.39	0.18	0.17	0.18
K_2O	0.80	0.95	0.98	0.86
P_2O_5	0.07	0.06	0.06	0.06
SO_3	0.005	0.005	0.005	0.007
L.O.I	4.93	0.62	0.53	0.76

Table 3. XRF analysis results of the prepared TiO_2 /Silica fume pigments Specifications of prepared $\text{SiO}_2/\text{TiO}_2$ pigment properties

titanium dioxide is present on surface of silica and these concentrations do not exceed 10% of the whole pigment concentration.

Specifications of prepared $\text{TiO}_2/\text{SiO}_2$ pigment properties

From Table (4) it is clear that;

- Specific gravity of silica was null, it is a very light fluffy powder, but the prepared $\text{TiO}_2/\text{SiO}_2$ pigments have specific gravity values which are in direct relation with the concentration of titanium dioxide on silica surface.
- Oil absorption of silica is very high and this is expected because of the silica spherical shapes which allow more oil to be deposited in the voids between the particles to form a paste, but $\text{TiO}_2/\text{SiO}_2$ pigments have lower oil absorption than silica. As it is well known that oil absorption expresses how much binder can be consumed by the pigment, and thus how this pigment is economically feasible when used in paint formulations. As the oil absorption is higher, more binder will be needed to completely wet the pigment and form a homogeneous paint film.
- Bulking value (BV) expresses the volume of paint for a given weight of a pigment, therefore pigments with higher bulking values as in silica and $\text{TiO}_2/\text{SiO}_2$ can be considered more economic.
- pH values of the different pigments are neutral.

In general, the new pigments possess better physical properties than either of its components individually. This was obvious from the specific gravity and oil absorption of these core-shell pigments.

Materials	Oil absorption (g/100g)	Sp.Gr.	BV (gal/100b)	pH	Whiteness (%)
SiO_2	819.68	0	0	7	97
TiO_2	22	4.24	2.842	7	95
$\text{TiO}_2/\text{SiO}_2$ (1)	221.84	1.59	7.578	7	97
$\text{TiO}_2/\text{SiO}_2$ (2)	193.64	1.53	7.875	7	98
$\text{TiO}_2/\text{SiO}_2$ (3)	189.88	1.78	6.770	7	98

Table 4. Characteristics of prepared titanium dioxide/kaolin pigments

3.2 The effect of prepared pigments on mechanical properties of paints

Tables (5-7) represent the paint formulations, while Table (8) expresses the results of determining hardness of organic coatings by means of pendulum apparatus; also impact and ductility were determined. Paint films containing silica show the best mechanical properties among the group, while those containing titanium dioxide show the lowest values, this is may be due to the spherical particles of silica which gives the film elasticity due to the voids present between these spheres. This can be in accordance with the properties of silica which are almost in the nano-scale and paint films containing nano-pigments have the following properties;

Constituent (%wt.)	1	2	3	4	5
Fe ₂ O ₃ (Hematite)	10	10	10	10	10
Kaolin	15	15	15	15	15
ZnO	7	7	7	7	7
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	63.5	63.5	63.5	63.5	63.5
Total binder	36.5	36.5	36.5	36.5	36.5
P/B	1.74	1.74	1.74	1.74	1.74
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 of TiO₂/SiO₂ pigments with medium oil alkyd resin (Group I)

Constituent (%wt.)	6	7	8	9	10
Fe ₂ O ₃ (Hematite)	15	15	15	15	15
Kaolin	15	15	15	15	15
ZnO	7	7	7	7	7
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 of TiO₂/SiO₂ pigments with medium oil alkyd resin (Group II)

According to (Guin et al., 2011; Otterstedt & Brandreth, 1998; Salamone, 1999), the main advantages of nano-coating or coatings containing nano-pigments are:

- Better surface appearance.
- Good chemical resistance.
- Decrease in permeability to corrosive environment and hence better corrosion properties.
- Optical clarity.
- Increase in modulus and thermal stability.

- Easy to clean surface.
- Anti-skid, anti-fogging, anti-fouling and anti-graffiti properties.
- Better thermal and electrical conductivity.
- Better retention of gloss and other mechanical properties like scratch resistance.
- Anti-reflective in nature
- Chromate and lead free
- Good adherence on different type of materials.

In general, $\text{TiO}_2/\text{SiO}_2$ pigments show less mechanical properties than silica, but better than paint films containing titanium dioxide and this is due to that as titanium dioxide layers precipitated on silica surface transfers the particle sizes to the micron-scale and also they 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.

Constituent (%wt.)	11	12	13	14	15
Fe_2O_3 (Hematite)	21.5	21.5	21.5	21.5	21.5
Kaolin	15	15	15	15	15
ZnO	7	7	7	7	7
SiO_2	30	---	---	---	---
TiO_2	---	30	---	---	---
$\text{TiO}_2/\text{SiO}_2$ (1)	---	---	30	---	---
$\text{TiO}_2/\text{SiO}_2$ (2)	---	---	---	30	---
$\text{TiO}_2/\text{SiO}_2$ (3)	---	---	---	---	30
Total pigment	75	75	75	75	75
Total binder	25	25	25	25	25
P/B	3	3	3	3	3
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 7. Paint formulations of $\text{TiO}_2/\text{SiO}_2$ pigments with medium oil alkyd resin (Group III)

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.

Group I					
Drying time, <i>hr.</i>	1	2	3	4	5
Surface dry	1 - 2				
Thorough dry	3 - 4				
Adhesion	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness, <i>Sec (90μ)</i>	60	67	74	72	73
Ductility, <i>Mm</i>	6.3	3	5.3	5.1	5.1
Impact resistance, <i>Kg.m.</i>	0.75	0.325	0.6	0.563	0.525
Corrosion resistance					
Degree of Blistering	10	6M	10	10	10
Degree of rusting	8-G	7-S	7-P	6-G	5-G
Filiform corrosion	Fig.1-FA				
Group II					
Drying time, <i>hr.</i>	6	7	8	9	10
Surface dry	1 - 2				
Thorough dry	3 - 4				
Adhesion	Gt1	Gt0	Gt1	Gt1	Gt1
Hardness, <i>Sec (90μ)</i>	72	73	78	80	82
Ductility, <i>Mm</i>	6.7	2.7	5.8	5.5	5.4
Impact resistance, <i>Kg.m.</i>	0.738	0.275	0.55	0.488	0.45
Corrosion resistance					
Degree of Blistering	4MD	8M	8F	10	4MD
Degree of rusting	5-G	10	7-P	10	5G
Filiform corrosion	Fig.1-FA				
Group III					
Drying time, <i>hr.</i>	11	12	13	14	15
Surface dry	1 - 2				
Thorough dry	3 - 4				
Adhesion	Gt1	Gt0	Gt1	Gt1	Gt1
Hardness, <i>Sec (90μ)</i>	78	82	88	92	92
Ductility, <i>Mm</i>	6.4	4.3	5.2	5.2	5.0
Impact resistance, <i>Kg.m.</i>	0.738	0.263	0.525	0.488	0.425
Corrosion resistance					
Degree of Blistering	4MD	4M	6M	6MD	4MD
Degree of rusting	7-S	10	8-P	6-S	4-S
Filiform corrosion	Fig.1-FA				

8-G, 0.1% general rusting; 7-S, 0.3% spot rusting; 7-P, 0.3% pinpoint rusting; 6-G, 1% general rusting; 5-G, 3% general rusting; 8-P, 0.1% pinpoint rusting; 6-S, 1% spot rusting, and 4-S, 10% spot rusting.

Table 8. Physico-mechanical and corrosion characteristics of dry paint films

As can be detected from Tables (5-8) and Figures (5-7), that paint films of group II were better in their performance than the other groups in the rust under paint films revealing that the P/B 2.175 is better than the other P/B ratios. Also paint films containing SiO₂/TiO₂ (1) and SiO₂/TiO₂ (2) were better in their performance than SiO₂/TiO₂ (3), this may be due to

Fig. 5. Photos of paint films of group I after immersion in 3.5% NaCl after 28 days

Fig. 6. Photos of paint films of group II after immersion in 3.5% NaCl after 28 days

Fig. 7. Photos of paint films of group III after immersion in 3.5% NaCl after 28 days

the photocatalytic effect of titanium dioxide on the surface of silica which is in accordance with its concentration, i.e. as titanium dioxide concentration increases, the photocatalytic effect also increases. This behavior can be also explained according to that as concentration of titanium increases, it alters the silica particles causing random effect between the particles and hence less film compactness leading to easiness of the passage of corroding materials to the metal substrate.

3.4 Electrochemical studies on paint films

EIS was employed to investigate the corrosion protection performance $\text{TiO}_2/\text{SiO}_2$ core-shell pigments in anticorrosive paint formulations based on different P/B ratios on the protection of mild steel substrate in 3.5 wt% NaCl at different immersion times. The results of the analysis and calculations of the impedance data, at different immersion times 1, 7, 14, 21 and 28 days, were listed in Table 9.

Inspections of this data indicate the following;

- The coating resistance (R_c) is clearly higher in case of group II (P/B 2.175) paint formulations than that of other groups at all immersion times. It is obvious that the rate of corrosion decrease in the order: group II > group I > group III.
- The coating resistance (R_c) of paint films containing $\text{TiO}_2/\text{SiO}_2$ (1) and $\text{TiO}_2/\text{SiO}_2$ (2) were better in their performance than $\text{SiO}_2/\text{TiO}_2$ (3).
- As shown in Figure 5, the paint film containing $\text{TiO}_2/\text{SiO}_2$ (1) in group II (paint no. 8) offered a very good resistance even after 28 days immersion in 3.5 wt% NaCl solution (9.809 K ohm), indicating that paint formulations containing $\text{TiO}_2/\text{SiO}_2$ (1) in P/B 2.175

is the best among the three groups and they can provide effective protection to carbon steel.

- d. The coating resistance (R_c) is inversely proportional to immersion times. As paint no. 8 was the best among the groups it was taken as an example to show in Figure 5 the typical Nyquist plots after different immersion time in 3.5 wt% NaCl.

Group	No.	Sample	R_c (Kohm.cm ²)				
			1 day	7 day	14 day	21day	28 day
I	1	SiO ₂	2.197	1.114	0.692	0.541	0.474
	3	TiO ₂ /SiO ₂ (1)	3.271	2.845	2.696	2.388	1.174
	4	TiO ₂ /SiO ₂ (2)	3.923	0.604	0.430	0.374	0.265
	5	TiO ₂ /SiO ₂ (3)	1.038	0.764	0.681	623.7	0.503
II	6	SiO ₂	0.933	0.660	0.658	0.372	0.271
	8	TiO ₂ /SiO ₂ (1)	147.34	25.36	13.09	11.63	9.809
	9	TiO ₂ /SiO ₂ (2)	62.67	9.896	5.693	4.012	3.033
	10	TiO ₂ /SiO ₂ (3)	2.015	1.192	0.790	0.564	0.486
III	11	SiO ₂	0.145	0.135	0.109	0.082	0.042
	13	TiO ₂ /SiO ₂ (1)	1.158	0.700	0.598	0.401	0.355
	14	TiO ₂ /SiO ₂ (2)	1.021	0.513	0.489	0.388	0.329
	15	TiO ₂ /SiO ₂ (3)	0.331	0.105	0.079	0.060	0.056

Table 9. EIS results for different paint formulations in 3.5 wt% NaCl at different immersion times

From the Figure it can be detected that the decrease in coating 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 (Xianming et al., 2009). 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.
- 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 (Del Amo et al., 1999).

Generally, electrochemical studies were in high accordance with accelerated laboratory test results.

3.4.1 Some suggested mechanisms of protection concerning the new prepared pigments

- Silica is used in coatings and paints to increase the scratch resistance. The silica fine particles do not interfere with the visible light, only by a high quality of dispersion,

cloudiness can be avoided and transparency can be achieved. The high tendency of silica particles to agglomerate with each other makes it difficult to assure that every single silica particle can react with the surrounding medium. The reaction of the individual particles with the medium is important for many applications in order to achieve the desired results (Kirubaharan et al., 2009).

- Hydrophobic silica fume is used to enhance water and corrosion resistance this is due to improved pigment stabilization in the coating system combined with the stronger barrier effect inherent to hydrophobic silica fume. This barrier effect in particular is what prevents moisture from penetrating the coating film and reaching the substrate (Guin et al., 2011).

Fig. 9. Nyquist plots for $\text{TiO}_2/\text{SiO}_2(1)$ of group II (paint no. 8) in 3.5 wt% NaCl at different immersion times 1, 7, 14, 21 and 28 days

- Fine Silica fume is used as additive that enhance the surface smoothness and dispersability of the media into which they are added. Their 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 which serve as a matting agent for paints besides being corrosion resistant (Kirubaharan et al., 2009).
- Durability is an important property of titanium dioxide, and since it is present in only very low concentrations in the prepared pigments, its opacity is controlled, but in spite of this it help in increasing the hiding power and durability of the new prepared pigments (Salamone 1999; Patton 1973; Ahmed & Selim, 2010).
- Titanium dioxide can also contribute to some extent to the preservation of the physical integrity of the medium in which it is dispersed by providing protection against cracking, checking, loss of adhesion and loss of tensile strength (Ahmed & Selim 2010; Ahmed & Selim, 2011).
- Titanium dioxide particles forming the shell were arranged in alignment between the silica particles comprising the core. In case of low concentration of titanium dioxide, its

small platelet particles order themselves in between the voids of the spherical silica particles in a close-pack texture locking the voids between silica particles and thus more compact paint film will be formed, prohibiting the formation of blisters or rust under film. As the concentration of titanium dioxide increases, a less compact film will be formed and a disturbance between silica particles occurs, 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 (Forsgren, 2006, Ahmed & Selim, 2011).

- Titanium dioxide is an inert oxide which imparts barrier properties to organic coatings by impeding the transport of aggressive species to the surface of the substrate. Such pigments orientate themselves parallel to the substrate surface and protect the substrate by providing a tortuous path of diffusion to the substrate. In addition, they may have a reinforcing effect on the mechanical properties of the coating. Its platy particles may be one reason of its protection properties; also it gives excellent hiding power to the films. Titanium dioxide is of high cost and its presence in high concentration may lead to the degradation of paint films due to its photochemical reactivity (Sorensen, 2009, Forsgren, 2006; Ahmed & Selim, 2010; Ahmed & Selim, 2011).
- As concentration of titanium dioxide is low, there is no chance for its photochemical reactivity to show itself (Bremmell & Mensah, 2005).

4. Conclusions

1. New pigments based on core-shell method were prepared in this work; these pigments are based on silica fume that is an industrial byproduct which was covered with different concentrations of titanium dioxide.
2. The pigments overcome the low hiding power of silica fume, and the new pigments possess better hiding power that was directly related to the titanium dioxide concentration on the silica surface.
3. The corrosion protection performance was inversely related to the concentration of titanium dioxide, this was because its platy particles alters the spherical silica particles leading to disturbing the texture that leads to less homogenous film and thus less protection.
4. The best corrosion performance among the pigments was $\text{TiO}_2/\text{SiO}_2$ (1) and the best among the groups was group II with P.B 2.175.
5. Electrochemical studies were in high agreement with the accelerated laboratory test.

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The purpose of this book is to present and discuss the recent methods in corrosion evaluation and protection. The book contains six chapters. The aim of Chapter 1 is to demonstrate that Electrochemical Impedance Spectroscopy can be a very useful tool to provide a complete evaluation of the corrosion protection properties of electro-coatings. Chapter 2 presents results of studies of materials degradation from experimental electrochemical tests and theoretical calculations. Chapter 3 deals with the presentation of the corrosion and corrosion prevention of the aluminum alloys by organic coatings and inhibitors. Chapter 4 addresses the new method of pigment preparation that can improve protection efficiency. The effectiveness of plasma deposited films on the improvement of carbon steel corrosion resistance is discussed in Chapter 5. Chapter 6 deals with the conjugation of carbon nanotubes with organic-inorganic hybrid to prepare hybrid coatings that combine high anti-corrosion efficiency with elevated mechanical resistance.

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