

The mechanism of the anticorrosive action of calcium-exchanged silica

R Romagnoli,^{1,2} M C Deyá,³ B del Amo²

1 Professor Facultad de Ciencias Exactas, UNLP

2 Investigador CONICET

3 Becario CONICET

CIDEPINT – Centro de Investigación y Desarrollo en Tecnología de Pinturas (CIC-CONICET). Calle 52 e/ 121 y 122. (1900) La Plata. Argentina

Summaries

The mechanism of the anticorrosive action of calcium-exchanged silica

The objectives of this work were to study the efficiency and the mechanism of the anticorrosive action of calcium-exchanged silica in paints. The anticorrosive properties of the pigment were evaluated by following the electrochemical behaviour of a steel electrode in the pigment suspension and analysing the protective layer formed on it. In a second stage, solvent-borne paints were formulated with 30% by volume (v/v) of the total pigment content. The selected PVC/CPVC (pigment volume concentration/critical pigment volume concentration) ratio was 0.8. Two resins were chosen as film-forming materials: an alkyd and an epoxy. The performance of the resulting anticorrosive paints was assessed by accelerated (salt-spray and humidity chambers) and electrochemical tests (corrosion potential, ionic and polarisation resistance).

It was demonstrated that the anticorrosive performance of paints pigmented with calcium/silica is at least equal or better than that obtained with paints containing zinc phosphate. Good correlation was obtained between accelerated and electrochemical tests.

Steel passivation by calcium-exchanged silica is a complex process accomplished by the high pH of the pigment suspension and the deposition of a siliceous film on the steel surface.

Le mécanisme de l'action anticorrosive de la silice qui a été l'objet d'une échange par le calcium

Les objectifs de cette étude étaient d'étudier l'efficacité et le mécanisme de l'action anticorrosive dans les peintures de la silice qui a été l'objet d'une échange ionique par le calcium. Les propriétés anticorrosives ont été évaluées selon le comportement électrochimique d'une électrode en acier dans la suspension du pigment et l'analyse de la couche protectrice qui s'y est formée. Au cours d'une deuxième étape des peintures diluables au solvant ont été formulées avec 30% en volume (v/v) du contenu pigmentaire total. Le rapport CPV/CPVC (concentration pigmentaire volumique/concentration pigmentaire volumique critique) était de 0.8. Deux résines ont été choisies pour la formation de feuillet: une résine alkyde et une résine époxy. La performance des peintures anticorrosives qui en sont venues a été évaluée par le moyen des essais accélérés (enceintes d'essais en brouillard salin et en humidité) et des essais électrochimiques (potentiel de corrosion, résistance ionique, résistance de polarisation).

Il a été démontré que la performance anticorrosive des peintures pigmentées par calcium/silice au moins égalait, ou même éclipsait celle qui était obtenue par les peintures contenant le phosphate de zinc. Il y avait une bonne corrélation entre les essais accélérés et les essais électrochimiques.

La passivation des aciers par la silice/calcaim est un procédé complexe mené à bout grâce au pH pigmentaire élevé et à la déposition des feuillets siliceux sur la surface de l'acier.

Der Mechanismus der antikorrosiven Wirkung von Kalzium-ersetzten Silikaten

Das Ziel dieser Arbeit war es, die Wirksamkeit und den Wirkungsmechanismus der antikorrosiven Wirkung von Kalzium-ersetzten Silikaten in Farben zu erforschen. Die antikorrosive Wirkung des Pigmentes wurden mittels der elektrochemischen Reaktion einer Stahlelektrode in der Pigmentsuspension beurteilt, und durch eine Analyse der schützenden Schicht die sich auf der Elektrode gebildet hat. In einem zweiten Schritt wurden lösungsmittelhaltige Farben hergestellt mit einem Silikatgehalt von 30% bei Volumen, bezogen auf den gesamten Pigmentgehalt. Wir wählten ein PVC/CPVC (Pigmentvolumenkonzentration zu kritischer Pigmentvolumenkonzentration) Verhältnis von 0.8. Wir verwendeten zwei verschiedene Harze als Filmbildner in diesen Farben: ein Alkyd und ein Epoxidharz. Die Leistung der entstandenen korrosionshemmenden Farbe wurde durch beschleunigte Tests (Salzsprüher und Luftfeuchtigkeitsräume) und elektrochemische Tests (Korrosionspotential, ionischer Widerstand, Polarisationswiderstand) ermittelt.

Die Tests zeigten daß die korrosionshemmende Wirkung von Farben mit Kalzium/Silizium genauso gut oder besser war als die Leistung von Farben mit Zinkphosphat. Wir fanden auch eine gute Korrelation zwischen den beschleunigten Tests und den elektrochemischen Tests.

Die Passivierung von Stahl durch Kalzium-ersetzte Silikate ist ein komplizierter Vorgang der durch den hohen pH-Wert der Pigmentsuspension und die Absetzung eines Silizium-haltigen Filmes auf der Stahloberfläche erreicht wird.

For correspondence contact

R Romagnoli

Professor Facultad de Ciencias Exactas, UNLP; Investigador CONICET, CIDEPINT – Centro de Investigación y Desarrollo en Tecnología de Pinturas (CIC-CONICET). Calle 52 e/ 121 y 122. (1900) La Plata. Argentina

Tel: +54 221 483 1142

Email: estelectro@cidepint.gov.ar

Fax: +54 221 427 1537

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Introduction

The employment of coatings to protect metals in aggressive environments is of great importance due to damages caused by corrosion. Paints formulated with lead or hexavalent chromium compounds are effective in restraining steel corrosion, but they are particularly hazardous to humans and to the environment. In the search for non-polluting anticorrosive pigments, zinc phosphate was proposed as an alternative inhibitor which, if properly employed, performed adequately in many anticorrosive coatings.¹⁻⁶ A second generation of phosphate pigments was developed by modifying the chemical composition and/or the physical structure of zinc phosphate to improve the corrosion resistance of painted metals.⁶⁻⁸ Finally, to match more demanding applications, a third generation of phosphate pigments based on polyphosphate anions, was introduced on to the market.⁹⁻¹² Zinc phosphate and related compounds may be used with a great variety of binders. For solvent-borne paints, the recommended pigment content was 30% v/v of the total pigment formula and the optimum PVC/CPVC ratio 0.8. A lower PVC value was suggested in the case of water-borne formulations.⁷⁻⁸

Although phosphate pigments dominate the market, many other inhibitors, typically classified as environmentally-compatible products, were developed to match the requirements of anticorrosive protection technology. Ferrites, borates, silicates, semiconductors, ion-exchange pigments, etc, are acquiring increasing importance as alternative products.¹³⁻¹⁸ These inhibitive substances have not been studied as greatly as phosphates; however, in many cases, they exhibit better performance.

Particular attention has been paid to ion-exchange pigments. This term refers to materials produced or derived from reactions of cations (calcium, cerium, etc) and anions (phosphate, chromates, etc) with suitable hydrated inorganic oxides such as silica or alumina.¹⁹

Calcium-exchanged silica is a low specific gravity basic pigment (pH ~ 9) with a relatively high oil absorption compared with other pigments.²⁰ The porosity of this pigment is much lower than that of silica gels and its surface area is ten times that of conventional anticorrosive pigments.¹⁹⁻²¹ This results in efficient exchanging of calcium ions present in solution and the hydroxyl groups found on the surface of the silica gel. This exchange process can be considered as an interfacial acid-base reaction and the

calcium content in the pigment is about 6% by weight.²¹

Calcium-exchanged silica has been evaluated in solvent-based alkyds, chlorinated rubber and two-pack epoxy primers for mild steel. Paint formulations have been developed and optimised for calcium-exchanged silica loadings and pigment/extender combinations, and compared with the corresponding systems based on zinc phosphate and other anticorrosive pigments.¹⁹⁻²¹ Correctly formulated, calcium-exchanged silica primers were found to perform better than all the proprietary pigments tested by different researchers.^{19,20} One of the advantages of this pigment is that lower loadings could be employed, with respect to proprietary pigments.²⁰ The replacement of other pigments by calcium/silica must be done on a volume basis. The alkaline nature of the pigment could result in interactions with acid binders or acid catalysts with consequent effects on viscosity and film curing; these problems can be overcome by appropriate formulation.¹⁹⁻²⁰

It has been reported that calcium-exchanged silicas have the outstanding feature of releasing the inhibitive species in a controlled way, according to the demands of the corrosion process, thus avoiding an unnecessary leaching of the active species. The cations permeating the paint film would release calcium from the pigment and, as a consequence, they would be immobilised on the silica particle. Calcium migrates to the paint-metal interface to form a layer with silica particles. The thickness of the layer, typically 0.25 to 60 μm , depends on the characteristics of the aggressive medium.²⁰

Three broad viewpoints have built up concerning the possible function of ion-exchange pigments.¹⁹ The ion-exchange theory previously outlined, was the original idea behind the development of this kind of pigment. It was thought that this pigment can undergo an exchange reaction with aggressive ions trapping them or, at least reducing their availability, leaching at the same time calcium ions originally held by the pigment.¹⁹⁻²⁰

The migration theory postulates that both silica and calcium ions are free to move within the film during weathering, and may migrate to the steel/paint film interface in order to build up a protective layer. Occasionally, the pigment may block the pores of the paint film.¹⁹

The pigment/binder interaction theory takes into account the influence that pigments may have on certain important factors, such as cross-linking levels, per-

meability, film porosity, etc, which affect the performance of the coatings.¹⁹ Thus, pigments with an appropriate physical and chemical identity can improve the protective properties of the coating by changing the chemical, physical and structural properties of the film.

The objective of this research was to study the performance of calcium-exchanged silica as an active pigment in anticorrosive paints, paying special attention to the mechanism of the anticorrosive action of the pigment. The inhibitive properties of the calcium-exchanged silica were assessed by electrochemical techniques, employing pigment suspensions. Finally, the anticorrosive performance of the pigment was also evaluated in paints by accelerated and electrochemical tests. From these experiments, some remarks about the mechanism of the anticorrosive action were derived.

Experimental

Pigment characterisation

The composition of the pigment and the pH of an aqueous suspension (water: pigment ratio 20:1) were obtained by current analytical techniques and FTIR spectroscopy.

The ionic exchange properties of calcium-exchanged silica were determined by placing 10g of the pigment in 200mL of 0.2M NaCl and stirring the solution for one day to ensure that the equilibrium was reached. The pigment was then filtered and washed thoroughly with distilled water. Calcium and hydroxyl ions were determined in the filtrate by atomic absorption spectroscopy and acid-base titration, respectively.

The solid residue resulting from the previous extraction was exchanged again with 200mL of 2M KNO₃ solution for one day, with continuous stirring of the suspension. The solid was separated from the resulting solution by filtration. In the filtrate, sodium was determined by atomic absorption spectroscopy and chloride by turbidimetry.

Evaluation of the inhibitive properties of calcium-silica suspensions

The passivation of an SAE 1010 (AISI 1010) steel electrode (area: 15cm²) was studied employing a suspension containing 5g of the pigment in 200mL of distilled water, with different concentrations of sodium chloride: 0.00, 0.01, 0.05, 0.10 and 0.50M. After two days of exposure the plate was removed and observed to detect the onset of corro-

sion. The same experiment was repeated employing different solutions with the above-mentioned concentrations of sodium chloride, without the pigment and at two different pH values: 7.0 and 9.2, respectively. This last experiment was performed to evaluate the effect of the pH on steel passivation in the presence of chloride.

The electrochemical tests were carried out employing an SAE 1010 steel electrode with a surface roughness, measured as mean peak-to-valley height, of $1.40\mu\text{m}$. The corrosion potential was measured with respect to the saturated calomel electrode (SCE), in a pigment suspension in 0.025 NaClO_4 , during 24 hours.

Steel polarisation resistance (with and without IR-drop compensation) was determined in the same pigment suspension and in the same supporting electrolyte. In this case a three electrode cell was employed with a SCE as reference and a platinum grid being the counter-electrode. The sweep amplitude was $\pm 20\text{mV}$ and the scan rate 0.166mVs^{-1} . Anodic and cathodic polarisation curves of the SAE 1010 steel electrode in pigment suspensions of 0.5M NaClO_4 solution were obtained, after 0, 2 and 24 hours of exposure. The cell employed to carry out these measurements was similar to that employed to determine the polarisation resistance. The sweep began in the vicinity of corrosion potential, at a scan rate of 3mVs^{-1} . Both types of measurements were taken employing a Model 273A EG & G PAR Potentiostat/Galvanostat plus Softcorr 352 software.

The composition of the protective layer formed on steel in the pigment suspension (water:pigment ratio 4:1) was determined after two days of exposure. Then, the plate was taken out from the solution and washed with distilled water. The loose material was removed by wiping it with a plastic cloth. The adherent film was removed electrochemically by means of a 2A cathodic current in a 1% v/v sulphuric acid solution.

Paint composition, manufacture and application

The materials used to form the paint films to carry out this research were as follows: medium oil alkyd (50% linseed oils, 30% o-phthalic anhydride, 8% pentaerythritol and glycerol, and 12% pentaerythritol rosinat) and an epoxy-polyamide resin. The solvent employed in the former case was white spirit, while the mixture xylene/methyl isobutyl ketone/butyl Cellosolve (13/45/42%

w/w) was used for the epoxy paint. It was decided to check the anticorrosive properties of the pigment employing solvent-borne paints because their behaviour has been well documented for many years.

The content of the calcium-exchanged silica in the anticorrosive paint was 30% v/v, with respect to the total pigment concentration. The average size of the pigment particle was $3\mu\text{m}$. Titanium dioxide (12%), barium sulphate (29%) and talc (12%) were incorporated to complete the pigment formula. The PVC/CPVC relationship was 0.8. Pigments were dispersed in the vehicle, employing a ball mill with a 3.3-litre jar for 24 hours, to achieve an acceptable degree of dispersion.²²

SAE 1010 steel panels ($15.0 \times 7.5 \times 0.2\text{cm}$) were sandblasted to approximately Sa 2^{1/2} (SIS 05 59 00), degreased with toluene, and then brushed up to a dry film thickness of $60 \pm 5\mu\text{m}$. Painted panels were kept indoors for seven days before being tested.

The performance of anticorrosive paints in accelerated and electrochemical tests

A set of three panels was placed in the salt-spray chamber (ASTM B 117); rusting (ASTM D 610) and blistering (ASTM D 714) degrees were evaluated periodically. Another set of panels was placed in the humidity chamber at $38 \pm 1^\circ\text{C}$ (ASTM D 2247) and the blistering degree was assessed employing the mentioned specification.

The cells to perform the electrochemical measurements were constructed of 3cm^2 circular zones by placing an acrylic tube, 7.0cm high, on the painted specimen. The cell was filled with the supporting electrolyte, 0.5M sodium perchlorate solution. The ionic resistance between the coated steel substrate and a platinum electrode was measured employing an ATI Orion model 170 conductivity meter at a frequency of 1000Hz . The corrosion potential was monitored against a SCE reference electrode with a high impedance voltmeter.

The polarisation resistance of painted specimens was determined as a function of immersion time, employing the cell described previously, with the SCE as reference and a platinum grid as the counter-electrode. The voltage scan was $\pm 10\text{mV}$ and the scan rate was 0.166mVs^{-1} . Measurements were taken employing a Model 273A EG & G PAR

Potentiostat/Galvanostat plus Softcorr 352 software.

Results and Discussion

Pigment characterisation

The chemical analysis of the pigment revealed that it contained a high amount of an insoluble residue in hydrochloric acid (76.00%), a small amount of active silica coming from silicates (1.04%), and a small amount of calcium (9.32%, expressed as calcium hydroxide). The loss on ignition at 1000°C was relatively high (14.50%). Minor amounts of magnesium (0.07%), sodium (0.08%) and potassium (0.07%) were also detected.

These results clearly show that the pigment is not a true calcium silicate. It seems to be a silica matrix somehow activated with calcium hydroxide. The FTIR spectrum confirmed that calcium-exchanged silica had a matrix of amorphous silica, which could be deduced from the strong absorption band at $\sim 1090\text{cm}^{-1}$ with a shoulder at $\sim 1150\text{cm}^{-1}$. The band at $\sim 790\text{cm}^{-1}$ of lower intensity was also observed.²³ The absorption bands due to the presence of calcium were not detected because the calcium content was only about 5%.

The pigment exchanged different ionic species with the environment. Each 100g of the pigment can exchange 570mg of Na^+ (24.8 milli-equivalents), 250mg of Ca^{2+} (12.5 milli-equivalents), 42.5mg of hydroxyl ion (2.5 milli-equivalents), and 44.4mg Cl^- (1.25 milli-equivalents). These results show that only a small amount of the total calcium (approximately 5%) was exchanged and that sodium is strongly retained by the pigment while the aggressive chloride ion is not exchanged to a great extent. These results contradict those suggested by the ion-exchange theory.¹⁹

Evaluation of the inhibitive properties of calcium-exchanged silica suspensions

The pH of the aqueous extract of the pigment was found to be equal to 9.2. Steel corrosion is restrained in pigment suspensions containing soluble chlorides up to a concentration level of 0.1M . Corrosion developed when chloride concentration was increased to 0.5M . The amount of pigment employed in this test (5g) was able to exchange 0.0625 milli-equivalents (meq) of chloride, while 200mL of 0.1M NaCl contained 20meq of chloride. Thus, the chloride ion provided by the electrolyte solution greatly exceeded the exchange capacity of the pigment. Thus it must be that the

protection afforded by the pigment depends upon the high pH of the suspension rather than upon its ability to exchange aggressive ions. The fact that steel did not corrode in a 0.01M chloride solution at pH 9.2, without the pigment, and it corroded at pH 7 even in the absence of chloride, seemed to confirm that the protection is principally due to the high pH of the pigment suspension.

The corrosion potential measured over four hours, presented an average value of -380mV which is quite different to the potential of corroding steel in the same electrolytic medium (~ 650 to -700mV). After 24 hours of exposure, the corrosion potential still remained shifted to more positive values (-535mV) with respect to the corrosion potential of bare steel.

There were no significant differences between the polarisation resistance with and without IR-drop compensation. This means that the film by itself did not act as a barrier between the base metal and the suspension. The polarisation resistance with IR-drop compensation, enabled the calculation of the corrosion rate of steel in the presence of the pigment which was lower than that corresponding to steel in the supporting electrolyte. The polarisation resistance was measured after 2, 6 and 24 hours of exposure to the pigment suspension. The value measured after two hours was $21\text{k}\Omega\cdot\text{cm}^{-2}$ which decreased to $8\text{k}\Omega\cdot\text{cm}^{-2}$ after six hours. This last value may stand constant or may vary slightly after one day of exposure. The polarisation resistance of steel in the supporting electrolyte was found to be equal to $0.2\text{k}\Omega\cdot\text{cm}^{-2}$. Relating these values with the amount of dissolved iron, the corrosion rate was found to vary from 1.05×10^{-4} to $2.75 \times 10^{-4} \mu\text{A}\cdot\text{cm}^{-2}$ after six hours of immersion in the pigment suspension. The steel corrosion rate in the supporting electrolyte was $11.0 \times 10^{-3} \mu\text{A}\cdot\text{cm}^{-2}$; this indicated that there was an important reduction in the steel corrosion rate by the presence of the calcium-exchanged silica.

The analysis of the anodic polarisation curve (see Figure 1) showed that the pigment passivated the steel substrate exposed to the calcium-exchanged silica suspension and remained in this state after 24 hours of exposure. The cathodic polarisation curve (see Figure 2) did not show important changes in the oxygen reduction region as time elapsed.

The chemical analysis of the protective layer formed on steel, in the presence and in the absence of 3% sodium chloride, can be seen in Table 1. The protective layer was mainly composed of silica and smaller amounts of calcium. Species in the protective layer, formed on the panels in contact with the 3% NaCl solution, were found to be in lower concentration, probably due to the higher solubility of some compounds in the chloride media. This rule fails with sodium ions which seemed to be strongly retained by the pigment matrix. No chloride was found to be retained by the pigment in both electrolytes. These findings, and the fact that the pigment micelle is attracted by the anode of an electrolytic cell, led the authors to think that the pigment particle was negatively charged so that it attracted sodium ions and repelled negative-charged chloride ions. These results are consistent with those obtained employing coated specimens and seem to confirm the proposals of the migration theory.¹⁹⁻²¹ The presence of silica beneath the coatings was confirmed by Auger Electron Spectroscopy.²⁴

The analysis of the metal surface by SEM revealed that it had several morphologies. There were certain areas covered with a thick layer (see Figure 3a) which seemed to be originated by the deposit of pigment particles (see Figure 3b).

Other regions of the metal surface appeared to be covered with an amorphous iron oxide (see Figure 3c). Some intact areas were also detected when scanning the metal surface; these areas may be passivated because they were free of corrosion in

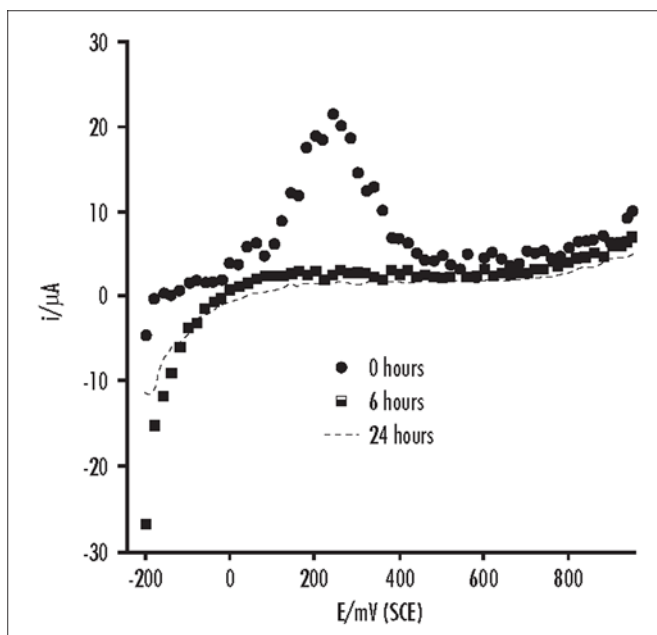


Figure 1: Anodic polarisation curve of the SAE 1010 steel electrode in the calcium/silica suspension in 0.5M sodium perchlorate

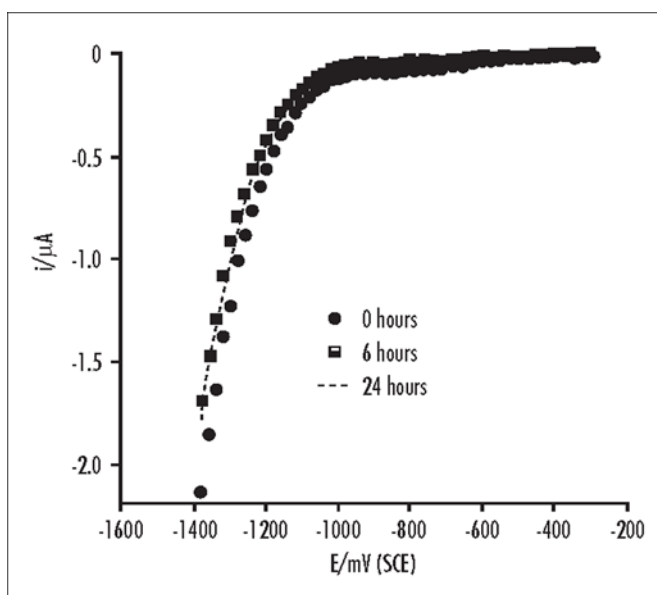


Figure 2: Cathodic polarisation curve of the SAE 1010 steel electrode in the calcium/silica suspension in 0.5M sodium perchlorate

Table 1: Composition of the protective layer formed on SAE 1010 steel in pigment suspensions in different electrolytes

Chemical composition of the film (mg/100cm ²)	Distilled water	3% sodium chloride
Silica (SiO ₂)	153	140
Calcium (Ca ²⁺)	14.7	101
Sodium (Na ⁺)	0.1	18.7
Chloride (Cl ⁻)	below the detection limit	below the detection limit
Ca ²⁺ /SiO ₂ ratio	9.60	7.2
Na ⁺ /SiO ₂ ratio	0.07	13.4

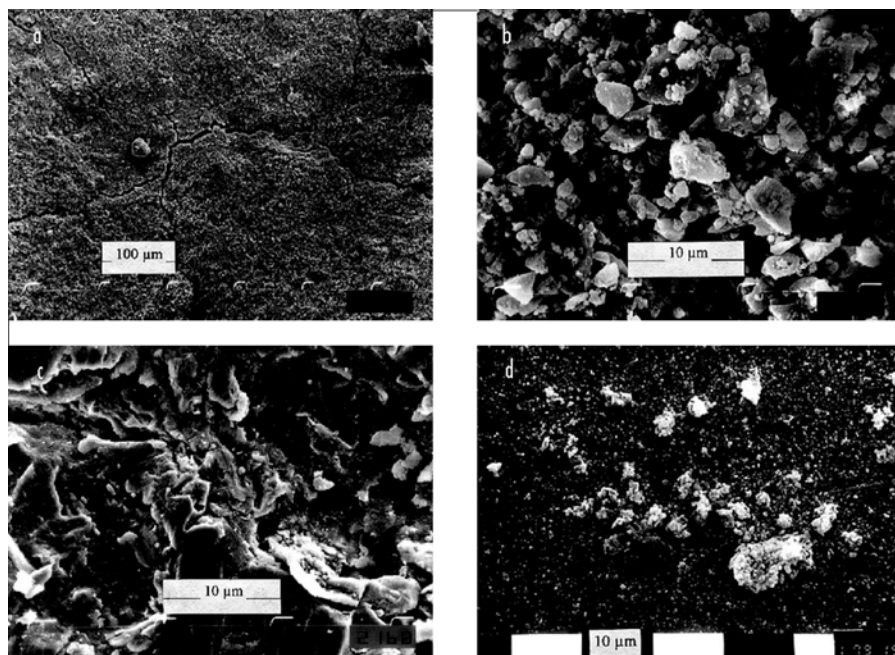


Figure 3: SEM micrograph of the film formed on the steel panel in contact with the calcium/silica suspension in 0.025M sodium perchlorate: a) Thick layer (200X); b) Massive deposit of pigment particles on the steel surface (2000X); c) Amorphous iron oxide (3500X); d) Globular formations formed on corroding areas (2000X)

spite of having been in contact with the aerated pigment suspensions. It is thought that these areas were covered with a thin siliceous transparent film which was found to drastically reduce the diffusion coefficients of iron ions and slow down the rate of the corrosion process.²⁵

Finally, when oxidation started at certain points of the surface, silica precipitated on the oxide particle stopping its growth; globular formations were visualised on the surface (see Figure 3d). The average composition of these formations, obtained by EDAX, was as follows: SiO₂: 18.8%, CaO: 49.2%, and Fe₂O₃: 32.0%. The smaller formations were enriched in iron oxides and depleted in silica and calcium.

According to the foregoing discussion it should be concluded that passivation is a complex process accomplished by the high pH of the pigment suspension and the deposition of silica films on the steel surface. The repassivation of the substrate seemed to be achieved by the formation of globular formations enriched in calcium and silica. These formations plugged the pores of the film. Other contributions, such as the negative charge of the pigment, may result in an improved anticorrosive protection.

The performance of anticorrosive paints in accelerated and electrochemical tests

The steel specimens coated with alkyd paints did not rust after two months of exposure. In the case of epoxy paints, the qualification was nine after nine months of exposure. The blistering degree observed during the exposure to this chamber was 8F for both paints; that is to say only small blisters with a low surface density developed during the exposure time. In the humidity chamber, only the alkyd paints developed blisters of great size (size no 2), and a medium surface density.

The results obtained during the exposure of calcium/silica alkyd paints to the salt-spray test are, at least, equal to or better than those obtained by exposing similar paints containing zinc phosphate.⁴⁻⁵ The only difference noticed with calcium/silica is a small blistering, due probably to some interaction between the

alkaline pigment and the acidity of the binder which caused some delamination of the paint. Blistering may also be increased by the adsorption of sodium ions as a consequence of the negative charge of the pigment. The anticorrosive behaviour of epoxy paints pigmented with calcium/silica is clearly superior to that of equivalent paints containing zinc phosphate.⁵

The corrosion potential of painted steel displaced towards more positive values (see Figure 4), after one day of exposure, with respect to the corrosion potential of steel in the same electrolyte (650 to -700mV/ECS). This behaviour was observed for both types of binders; however, the corrosion potential of steel coated with the alkyd binder evolved quickly to values which are typical of painted steel undergoing corrosion. The higher permeability of the coating resulted in the ingress of water and aggressive agents, and the anticorrosive action of the pigment was highly exceeded.

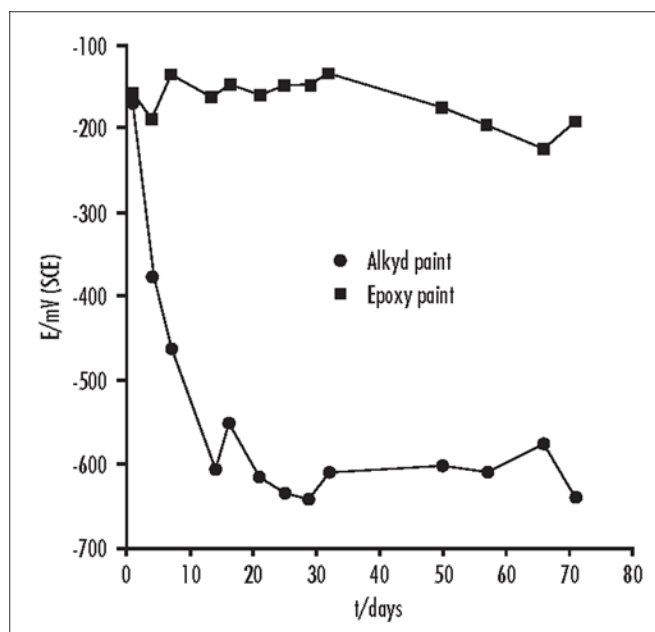


Figure 4: Corrosion potential of painted steel as a function of the exposure time in 0.5M sodium perchlorate solution

In the case of the epoxy paint, it was found that the corrosion potential kept shifted to more positive values over long periods of time. It is thought that the silica particles blocked the pores of the film, thus impeding the diffusion of corrodent species; the pigment could therefore develop its inhibitive action satisfactorily.

The examination of the ionic resistance versus immersion time plots (see Figure 5) showed that alkyd paint did not possess an intrinsic barrier effect while epoxy one showed certain barrier properties because the resistance was above 10⁷Ω.cm⁻².²⁶ The most important fact is that the permeability did not increase significantly during the test period.

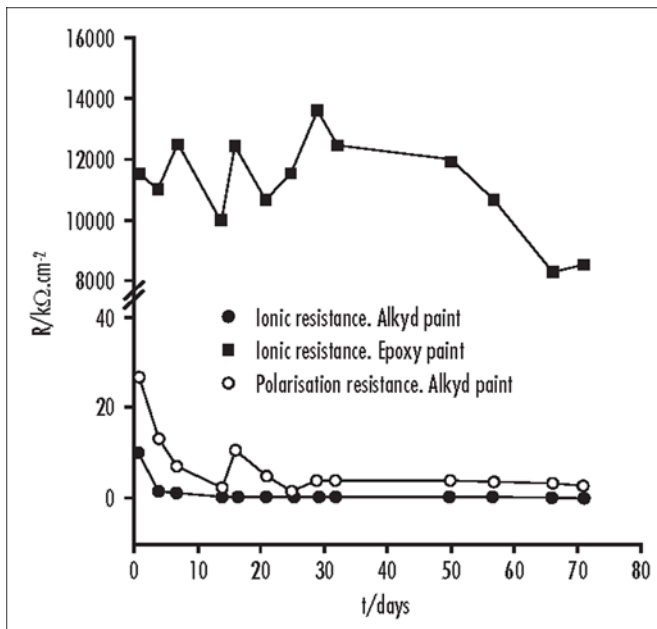


Figure 5: Ionic resistance of painted steel as a function of the exposure time in 0.5M sodium perchlorate solution

The polarisation resistance of the epoxy paints could not be measured due to the high ionic resistance. In this case a linear response, indicating ohmic control may be obtained, or very low corrosion rates (which were difficult to measure with the employed technique) would be measured. In the case of alkyd paints, the barrier effect was lost after the first day of immersion. However, the current passing through the defects of the coating was very low but increased as time elapsed. The electrochemical reactions were highly polarised due to the inhibitive action of the pigment.²⁵ The anodic reaction appeared to be more polarised than the cathodic one. After three weeks of immersion the inhibitive action of the pigment was very much lower, the active areas becoming depolarised, and both reactions proceeded at higher rates (see Figure 6).

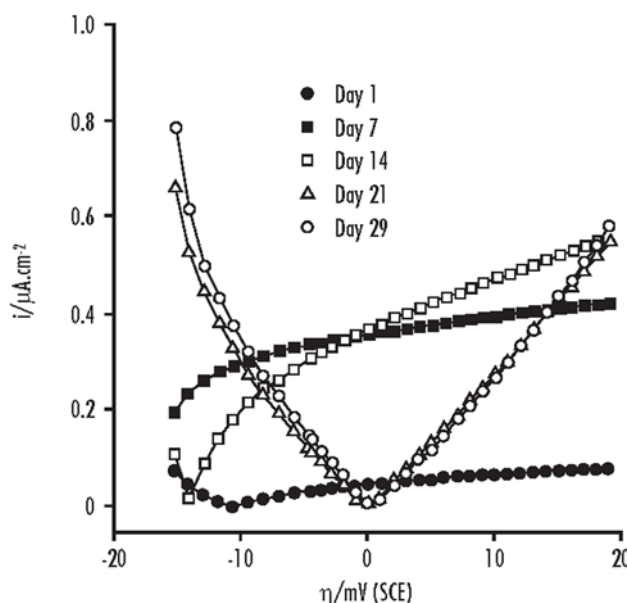


Figure 6: Current-overpotential profiles in the vicinity of the corrosion potential, at different exposure times, of steel coated with alkyd paints

Conclusions

- The protection afforded by calcium/silica ion-exchange pigment relies upon the high pH of the pigment suspension and the composition of the protective layer rather than on its ability to exchange aggressive ions.
- The presence of silica in the protective layer was considered beneficial to restrain steel corrosion.
- The pigment particle was negatively charged so that it attracted sodium ions and repelled negatively-charged chloride ions which accelerated the corrosion processes.
- The results obtained during the exposure of calcium/silica alkyd paints to the salt-spray test were at least equal to or better than those obtained by exposing similar paints containing zinc phosphate. The results obtained with epoxy paints were clearly better when calcium/silica was employed instead of zinc phosphate.
- The excellent performance of epoxy paints was highly dependent on the fact that their permeability did not increase significantly during the test period.
- The inhibitive action of the pigment when the barrier effect of the coating was lost, was easily discerned through the changes in the polarisation curves of alkyd paints.

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