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A SEM study on the galvanic protection of zinc-rich paints

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The research is focused directly to the cahodic protection mechanism of zinc-rich paints (ZRP). It is based on a systematic scanning electron microscope (SEM) observation of cross-sections of several ZRP coatings exposed for different time intervals to a 3% (by weight) sodium chloride solution. The effect of vehicle (binder) used in the paint formula and the effect of zinc particle content are considered.

As the anodic behaviour of zinc particles depends very closely on coating microstructure, SEM observation of the latter is very useful to investigate the galvanic performance of ZRP. This study confirms that high zinc particle contents and the use of ethyl silicate as a vehicle favour the degree and duration of the cathodic protection.

Depending upon whether the zinc particles act anodically or not their attack mechanism is radically different. Accordingly, two attack mechanisms of the zinc particles are proposed.

1. Introduction

As early as 1944 Evans and Mayne [1] demonstrated the excellent properties of zinc-dust as an anticorrosive pigment and suggested the dual steel protection mechanism of zinc-rich paints (ZRP). Such dual action, now universally accepted, was not demonstrated experimentally until 1963 [2]. After an initial short-lived period of cathodic protection, where the zinc particles act sacrificially protecting the steel substrate (cathode), an inhibition or pore sealing process provides a subsequent longer period of protection.

This paper is focused directly on the cathodic protection mechanism of ZRP. The research is based on a systematic scanning electron microscope (SEM) observation of cross-sections of different ZRP coatings exposed to a 3% NaCl solution. It should be noted that metallographic studies in the literature showing the transit of ZRP from intact to attack state are very rare.

2. Experimental procedure

Four commercial zinc-rich paints (Table I) were air-sprayed on to white metal shot-blasted hot-rolled steel to form a dry film thickness of approximately 50 to 60 μm. Two zinc contents in vehicles of ethyl silicate and polyamide-cured epoxy were studied. All the samples were prepared in duplicate.

The specimens were exposed to a 3% (by weight) NaCl solution, and the rest potential was recorded at different time intervals with a microvoltmeter (Solartron 7060) and a saturated calomel electrode (SCE).

The panels were lifted out of the solution after exposure periods of ten and thirty days, and cross-sections, made perpendicular to the exposed surface, were observed by SEM. A JEOL JXA-840 electron scanning microscope fitted with a source for energy dispersion chemical analysis (EDAX) was used.

A series of specimens was removed from the solution after 30 days to identify the corrosion products by X-ray diffraction.

3. Results

3.1. Potential against time measurements

Fig. 1 shows the variation of rest potential with time in the ZRPs tested.

3.2. Characterization of the intact coatings, prior to exposure to the saline solution

The EDAX study showed that the zinc particles were constituted mainly by zinc (about 98%) and iron (about 2%). Silicon and aluminium were also detected in the spaces between the zinc particles; this was not surprising taking into account the presence of SiO_2 and bentonites in the paint formulae (Table I).

The SEM study revealed frequent cracking in the ZRP coatings with the highest zinc contents (Fig. 2). These faults were even more obvious in the ethyl silicate type formula, due to defective wetting characteristics of the binder [4]. Micrographs in Fig. 2 clearly show how the interconnection between the zinc particles diminishes, together with the number of contacts between them and the steel base, as the percentage of zinc in the coating is reduced. The zinc particles, before exposure, had a certain internal porosity, which seems to affect the form of subsequent attack under certain situations, as will be seen later.

3.3. Characterization of exposed coatings, after being in contact with the saline solution

Micrographs in Figs 3 and 4 show the ZRP coatings after 10 and 30 days of contact with the 3% NaCl solution. The zinc particles tend to be attacked forming corrosion products within the coating. The

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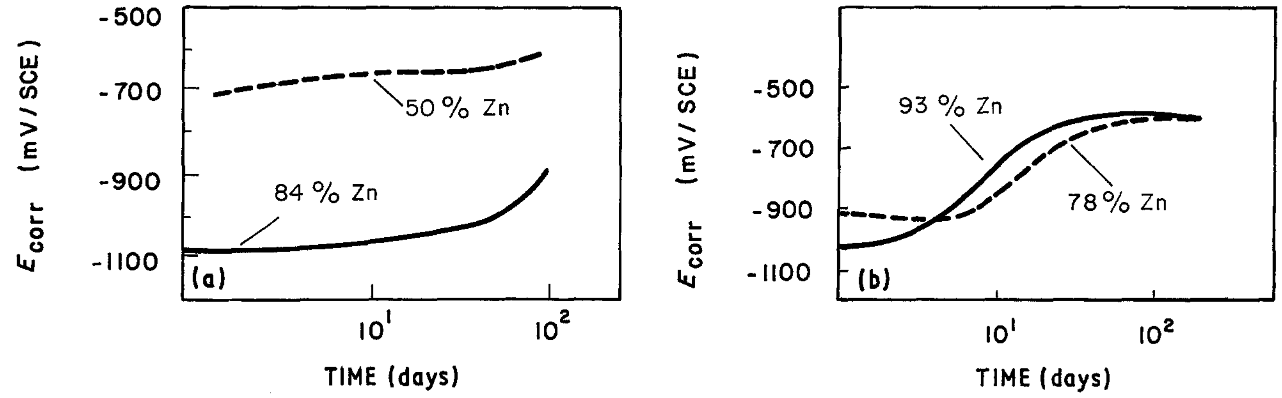


Figure 1 Evolution of rest potential with time for different ZRPs. (a) ethyl silicate, (b) epoxy-polyamide.

diffractograms from X-ray diffraction analysis of these products clearly show the peaks corresponding to zinc oxide, ZnO, and zinc oxychloride, $Zn_5(OH)_8Cl_2$.

4. Discussion

The two basic conditions required for the cathodic protection mechanism in the ZRPs are: (a) a high content in zinc particles, which assures the electrical connection and the electronic conduction between them and with the steel base, and (b) a network of capillaries or ionic conduction paths between the anodic (zinc particles) and cathodic zones (steel). Obviously, the efficiency and duration of the galvanic action will depend upon the possibilities existing for both types of conduction inside the coating. Fig. 5 shows different electronic and ionic conductive paths in the ZRP coatings.

A distinction should be made between chains of zinc particles fully interconnected (Fig. 5a) and chain segments (Fig. 5b), where zinc particles are partially interconnected. As the zinc content increases, there is a "bridging effect" which tends to group the zinc particles together, considerably reducing the electrical resistance of the coating [5]; this effect is favoured in vehicles with defective wetting properties [6]. The zinc particles interconnection may fail if they are covered with polymeric material (vehicle). Consequently, the wetting properties of the vehicle have a decisive influence on both type A and type B electronic conductive paths. It is well known that the non-polar nature of ethyl silicate type binder makes it difficult to wet the zinc particles ("pseudo-wetting" vehicle), whereas epoxy or chlorinated rubber type binders, being of polar nature, wet them relatively easily ("effective-wetting" vehicles) [4].

With regard to ionic conduction, this is affected by macro- and microcracks within the coating (Fig. 5c), internal voids or interstices between zinc particles (Fig. 5d), and vehicle-enriched zones or binder zones

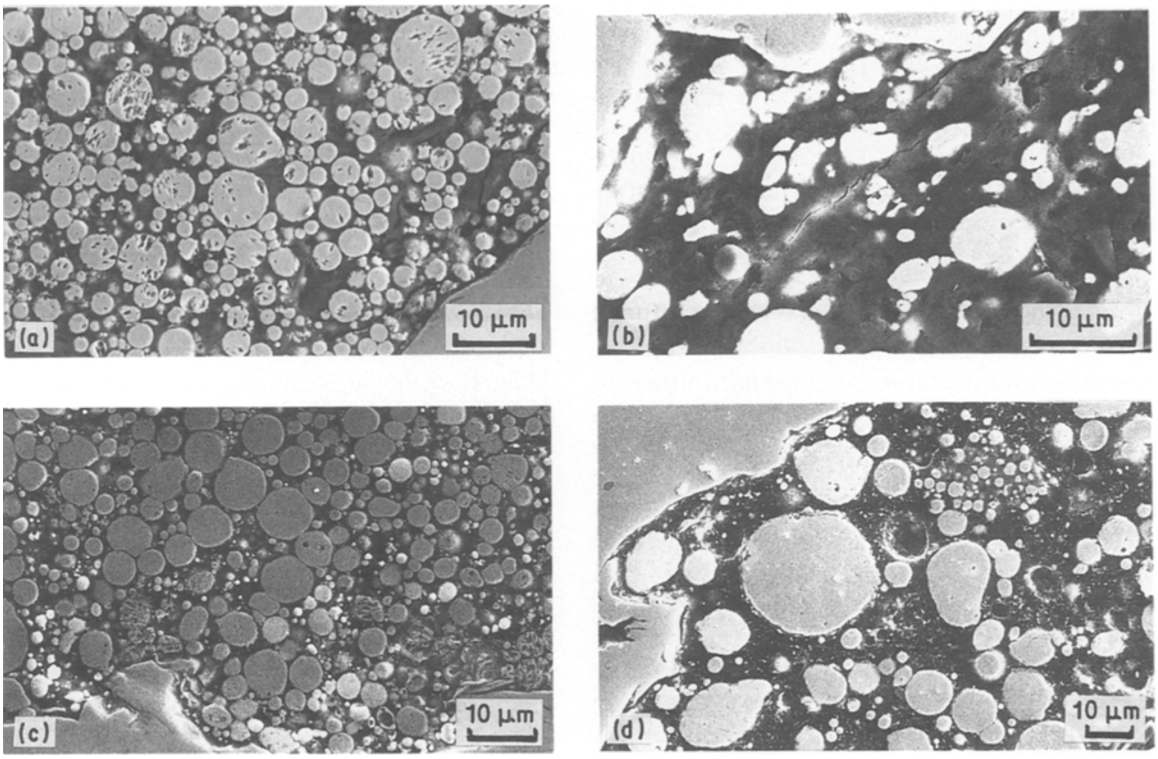


Figure 2 Cross-section SEM micrographs of intact ZRP coatings before exposure to the sodium chloride solution. (a) and (b), 84% Zn and 50% Zn ethyl silicate base, respectively; (c) and (d), 93% Zn and 78% Zn epoxy polyamide base, respectively.

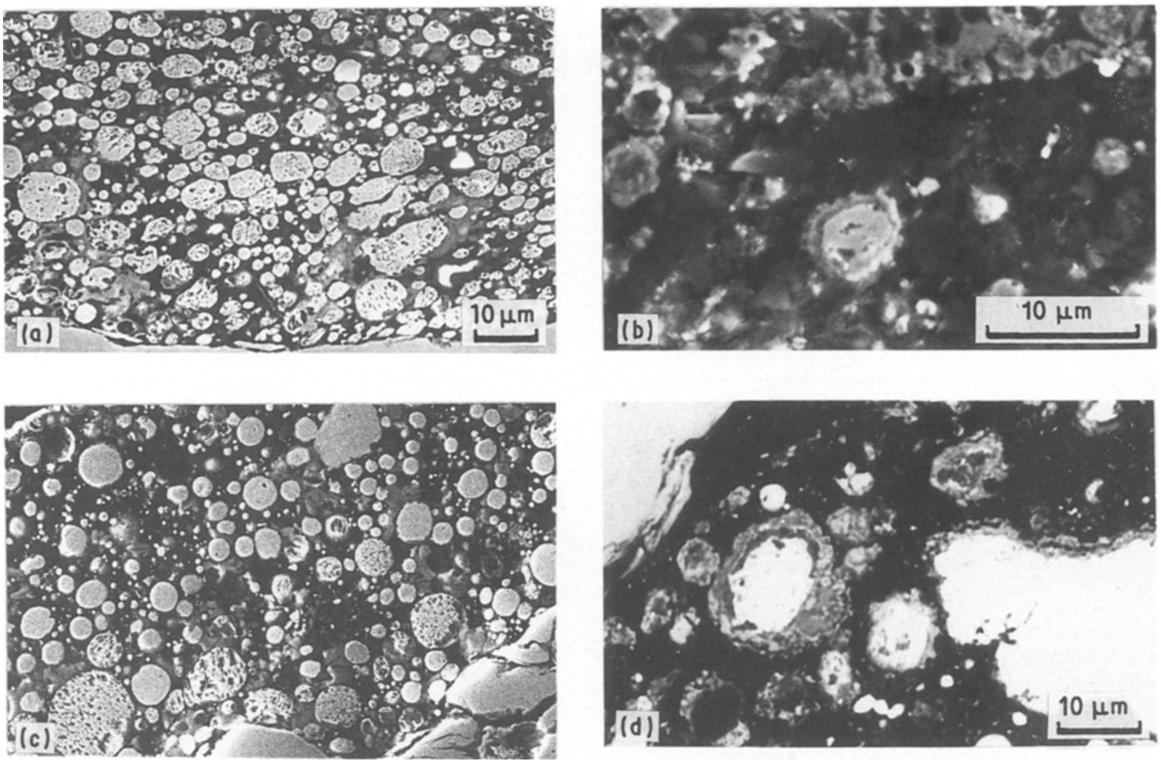


Figure 3 Cross-section SEM micrographs of exposed ZRP coatings after 10 days in contact with the sodium chloride solution. (a) and (b), 84% Zn and 50% Zn ethyl silicate base, respectively; (c) and (d), 93% Zn and 78% Zn epoxy polyamide base, respectively.

(Fig. 5e). When the zinc particles content is high and the vehicle wets them with difficulty, macro- and microcracks are frequently formed in the ZRP coatings, together with voids between zinc particles. The electrolyte filling the cracks contributes to the ionic conduction. The same can be said of that filling the voids between zinc particles, although in this case portions of polymeric material alternating with voids hinder the ionic conduction. The presence of vehicle-enriched zones, together with zinc particles-enriched zones, is a typical situation of coatings with high pigment volume concentration (PVC), where uniform pigment distribution is difficult to achieve. The ionic conduction through these vehicle-enriched zones encounter the same difficulties as normal paint films [7]. In general, as the PVC of ZRP is reduced, the

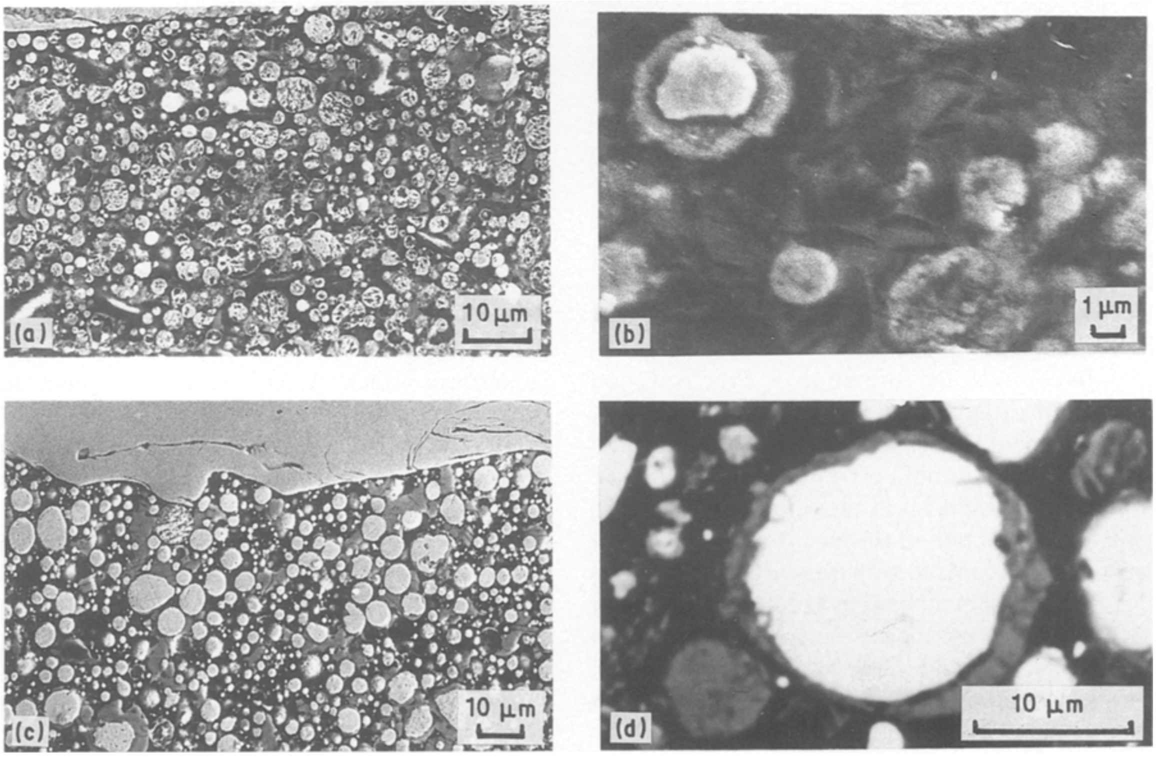


Figure 4 Cross-section SEM micrographs of ZRP coating after 30 days in contact with the sodium chloride solution. (a) and (b), 84% Zn and 50% Zn ethyl silicate base, respectively; (c) and (d), 93% Zn and 78% Zn epoxy polyamide base, respectively.

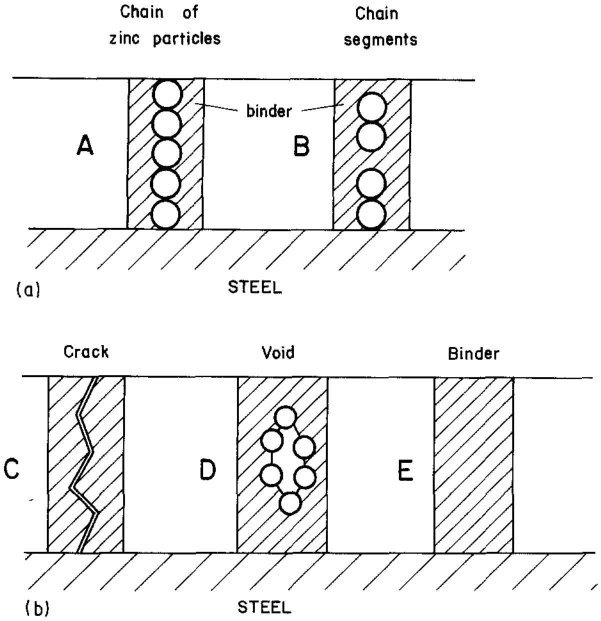


Figure 5 Schematic representation of (a) electronic and (b) ionic conduction paths in ZRP coatings.

possibilities of ionic conduction fall; this occurs to a greater extent in the epoxy vehicle than in the ethyl silicate vehicle.

4.1. The effect of the vehicle

ZRP coatings of ethyl silicate type with a high zinc content (70 to 90%) frequently show type A, C and D paths (Fig. 5). Accordingly, these coatings have a good ionic and electronic conduction, which are the ideal conditions for the cathodic protection mechanism to be operative. The initial rest potential shows very negative values (Fig. 1), −1100 mV/SCE, which are maintained for a relatively long time (30 to 40 days). Due to the presence of a great number of type A paths the whole coating thickness behaves in a similar way; practically all zinc particles provide cathodic protection to bare steel areas. SEM micrographs in Figs 3a and 4a show the development of localized attack on the zinc particles at any deepness of the coating thickness.

In highly pigmented ZRP epoxy type coatings, better wetting of zinc particles by the vehicle favours formation of type B electronic conduction paths (in which the connection between zinc particles is only partial) and type E low ionic conduction paths (Fig. 5). In contrast, the formation of Type A, C and D conduction paths is unlikely. This means that only the chain segments in electrical contact with the steel base can provide cathodic protection. Not all of the coating thickness behaves in the same way, as only a relatively small fraction of the zinc particles (the most internal ones in contact with the steel base) act as anodes. This is shown in the SEM micrograph of Fig. 3c. Consequently, the absolute value of potential measurements, initially close to −1000 mV/SCE, declines more rapidly (Fig. 1). As there is a smaller number of particles supporting the cathodic protection process, they are consumed more quickly and become disconnected earlier from each other and from the steel base. Accordingly, the cathodic protection does not last more than 8 to 10 days, in comparison with the 30 to 40 days for a ZRP – ethyl silicate base with similar zinc content (Fig. 1). Once the cathodic protection mechanism is disrupted the form of attack of zinc particles changes drastically (Fig. 4c), as will be discussed later.

TABLE I ZRP coatings composition*

Type of vehicle	Components
Ethyl silicate	Zinc dust†: 84% and 50% (by weight) Ethyl silicate Bentonites (antisettling agent) Silica (extender). Only in the formula with the lowest zinc content Solvents
Epoxy-polyamide	Zinc dust†: 93% and 78% (by weight) Epikote 1001 Versamid Bentonites (antisettling agent) Solvents

*Information supplied by the paint manufacturer.
†Approximate zinc content determined by the gas evolution method [3].

4.2. The effect of zinc content

The possibilities of cathodic protection of ZRP can be enormously restricted on diminishing zinc concentration in the coating. The critical zinc content to ensure cathodic protection depends upon the type of vehicle used in the ZRP formulation. Therefore, whereas the silicate type coating with a zinc content of 70% still maintains its cathodic protection capability quite well after 10 days of testing [8], the epoxy type coating with a zinc content of 78% loses such a capability within the first few days of testing. The decay of cathodic protection can be detected by observing the variation of the rest potential with time (Fig. 1) and the morphology of attack on the zinc particles. When the rest potential become more noble, this attack does not show the formation of internal cavities but uniform dissolution with the formation of corrosion products on the zinc surface (Fig. 3d).

The ethyl silicate based ZRP also loses entirely its capacity to protect the steel substrate cathodically if the zinc content is reduced to 50%. The initial rest potential is now some −700 mV/SCE and the way the zinc particles are attacked is drastically modified. The signs of localized attack disappear and are replaced by a uniform attack of the zinc particle outer surface, as may be seen in the SEM micrographs b and d of Figs 3 and 4. With time this attack advances into the interior of the particle and can even consume it entirely (Fig. 6). It seems strange that the extensive bibliography on ZRP does not reflect this singular relation between zinc particle morphology attack and its cathodic protection capacity.

4.3. Attack mechanisms of zinc particles

Fig. 7 attempts to schematically describe the major differences in zinc particles behaviour depending on whether or not they are in electrical contact with the steel base. In the first case, the zinc particles will only be the site of the anodic reaction of the corrosion

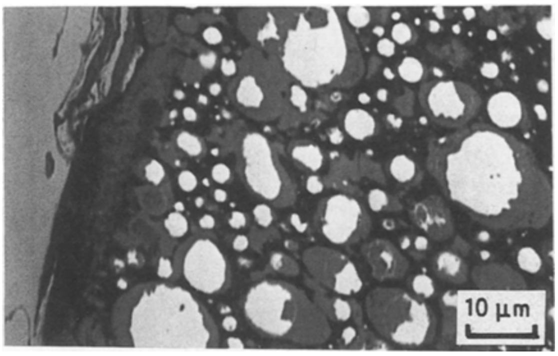


Figure 6 Cross-section SEM micrograph 93% Zn epoxy polyamide base ZRP after 160 days in contact with the sodium chloride solution. The photomicrograph obtained by image-composition shows the strong zinc particle attack.

process, being carried out the cathodic reaction in the bare zones on the steel surface. This involves corrosion products (ZnO, $Zn_5(OH)_8Cl_2$, etc.) forming at a certain distance from the zinc particles, in the capillaries full of electrolyte that facilitate ionic conduction between the anodic and cathodic zones. Conditions favouring the establishment of the capillary network (high zinc contents and "pseudo-wetting" binders) also favour active anodic dissolution of the zinc particles in the cathodic protection process. As the corrosion products are formed at a certain distance from the metal, there is less anodic polarization of the zinc and, therefore, the period during which the cathodic protection performs is more extensive.

In contrast, a zinc particle electrically isolated from the steel base cannot be the exclusive site of the anodic reaction (Fig. 7). The two reactions of the corrosion process (cathodic and anodic) will be located on the same surface of the isolated particle wetted by the electrolyte. Corrosion products will form in the immediate neighbourhood of the metal, which will increase electrode polarization and lessen zinc corrosion rate. According to this metallographic study, these different mechanisms affect the zinc particles attack morphology.

The cause of localized attack on zinc particles when they are acting anodically, providing cathodic protection to the steel, remains to be explained. Some zinc particles clearly show a series of porosities, grooves or cavities in the original ZRP coatings, before testing (Fig. 8), which must be related to the pigment manufacturing process. Consequently, it seems reasonable to think that these discontinuities, pre-existing in the zinc particles, have acted as nuclei to initiate and promote the localized attack. Another interpretation could be related to the uneven wetting of the zinc particle by the vehicle. Perhaps both factors act at the same time. In any case, exclusive research into this point would be required to clarify the phenomenon.

5. Conclusions

The conclusions are as follows.

1. The way that the zinc particles in ZRP coatings are attacked is radically different, depending upon whether they are acting anodically or not. In the former case, there is a localized attack at certain points of the zinc surface, whereas in the second case the attack is much more uniform.
2. As the anodic behaviour of zinc particles depends

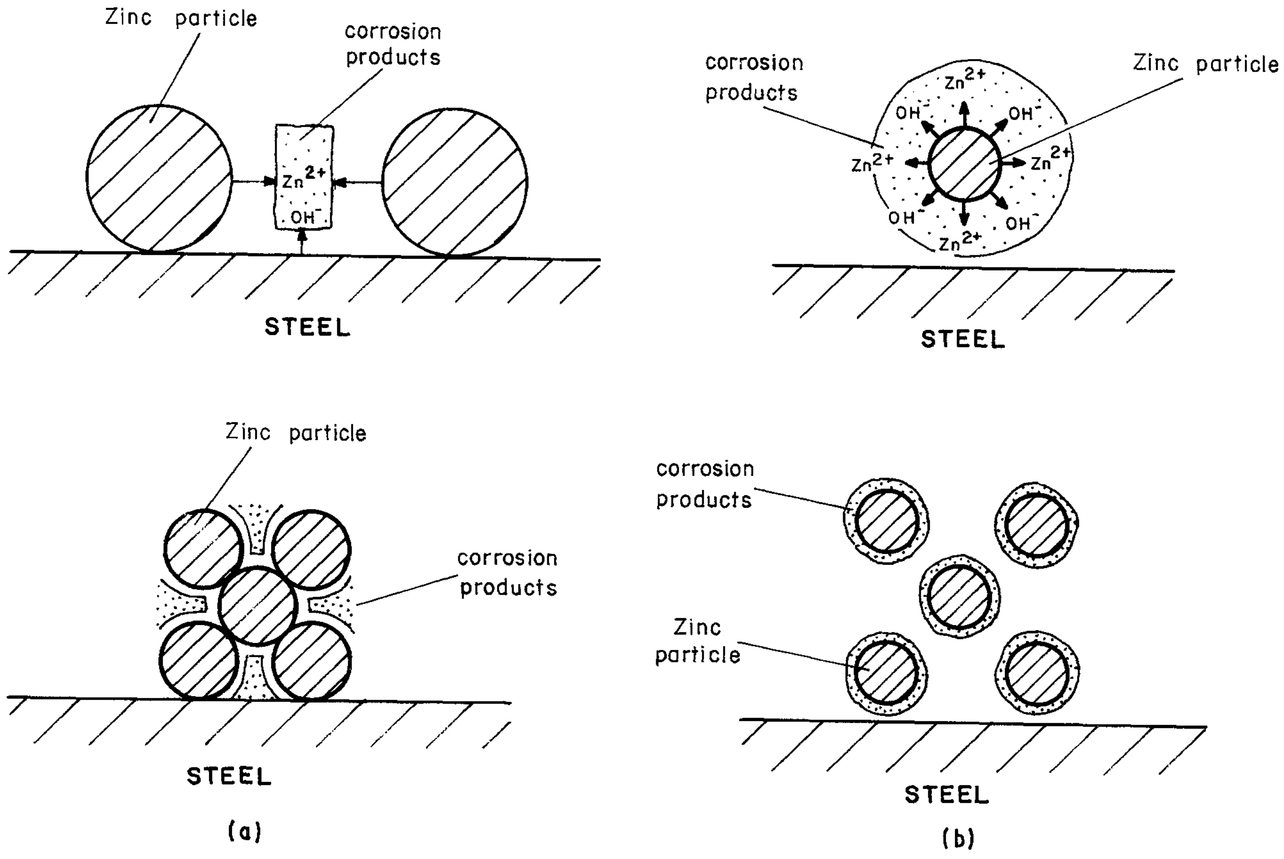
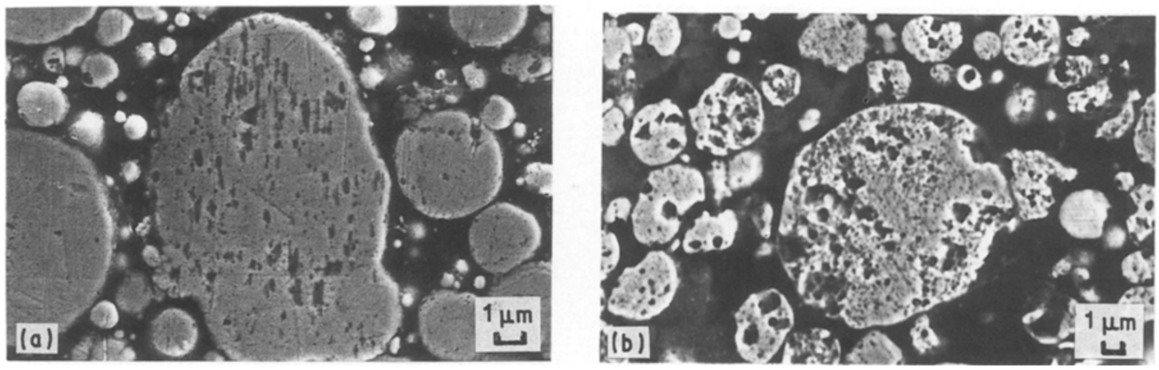


Figure 7 Idealized representations of zinc particles attack in ZRP coatings. (a) zinc particles in electrical contact with steel, (b) zinc particles isolated from steel.



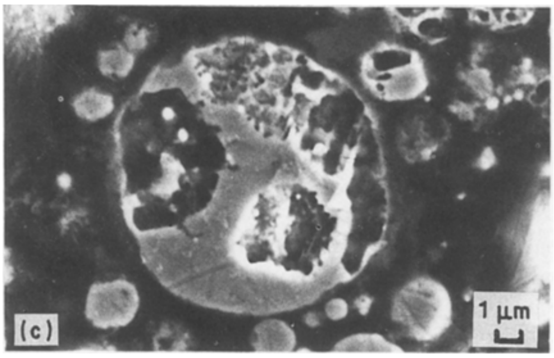


Figure 8 Localized attack, in the form of caverns or cavities, of the zinc particles in a 84% Zn ethyl silicate ZRP. (a) before testing; (b) after 10 days of contact with the sodium chloride solution and (c) after 30 days of contact with the sodium chloride solution.

very closely on coating microstructure, SEM observation of the latter is an extraordinarily useful tool to investigate the galvanic performance of ZRP.

3. This study confirms that high zinc particle contents and the use of ethyl silicate as vehicle favour the degree and duration of the cathodic protection.

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