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Study of the Resistances of Organic Coatings to Filiform Corrosion

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Summary: The filiform corrosion is a special-type atmospheric corrosion, which broadens below the organic coatings and is characterized by its manifestation in the form of fibres or filaments. An important factor for broadening the filiform corrosion involves also the barrier or chemical resistance of the organic coating. The paper deals with the modes of filiform-corrosion initiation and evaluation thereof under nonpigmented organic coatings based on various binder bases. Also the possibility of retardation of the filiform corrosion by means of zinc powder and the effects of lamellar pigment on the filament shapes are studied.

Introduction

The development and usage of new, steadily improved systems of surface protection is affected by a series of factors, among which the most important ones are the effects on environment and economics of surface treatment procedures.[1] Just the problems connected to the anticorrosive protection of metals lead us to the region connecting the corrosion engineering to the surface protection by organic coatings.[2] In the past a series of papers was devoted to investigating the corrosion processes of metals alone without any respect to this surface protection by organic coating films. On the contrary another series of papers was directed to the organic coating alone from the polymer matrix, pigment, and filler points of view, with respect to combination of individual components of coatings, the physical and chemical properties thereof.[3] It is evident that a future task will concern investigation of the corrosion processes running not at an unprotected metal, but in the system, where the metal will be fitted with organic protective film or with several layers of protective coats. A further shift in knowledge will be, therefore, conditioned by understanding and describing the processes running at the surface under the coating film.[4] At present it is possible to gather some knowledge to several points, concerning the corrosion processes under an organic coat.

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Blistering

The blistering is one of the earliest signs of disturbing the protective coating functions.[5]. The blisterst can be defined as local regions, in which the coating loose its adhesion to metals substrate, where the water accumulation takes place and wherein the corrosion processes start to run.[6] The appearance of blisters on the coating can be explained by one of four basic possible mechanisms:[7]

a) Formation of blisters by a volume expansion originating in the swelling
b) Formation of blisters due to absorption or formation of gases
c) Osmotic formation of blisters
d) Formation of blisters due to the phase separation in the film formation

The corrosion mechanism in the blistering-attacked region consists in the action of locally cumulating water at the coating/substrate interface. The ferric ions are concentrated at the blister vaults, where the oxygen concentration has its highest value. In these locations also the cathodic reaction is running, and, on the oposite, the anodic reaction runs.

Flash corrosion

Under the term "flash corrosion" a really heavy problem is to be understood, which overwhelmingly concerns water-dilutable coatings. Defects of this type occur only in a case, when the coating film undergoing the drying-out process was subjected to a high relative moisture effect.[8,9] The film formation at aqueous latex coatings runs under the evaporation of water through particle coalescence, the deformation thereof and, at the end, through the diffusion of polymeric chains among individual particles.[10]

Rusting following the blasting operation

At the surface pretreatment of metals by blasting, when the blasting operation was peformed using steel grit there can appear scratchs or the particles can get jammed in the substrate metal. The unfavourable result can be hindered by a two-stage blasting operation or by a chemical cleaning of the metal surface.[11]

Anodic subcorroding

The anodic subcorroding represents the corrosion reactions running under the organic coatings, in which the driving force is exhibited by the anodic corrosion reaction.[12,13] The anodic subcorroding takes place when the steel substrate takes the role of anode, through the imposed potential. Without imposing the potential the protection of steel fails to a high degree through the cathodic subcorroding mechanism. The anodic corrosion running below the protective films has not been studied so intensely as the cathodic subcorroding processes.

Cathodic subcorroding

When the steel material fitted with a coating is permanently exposed to an electrolyte (as the case is with ships, pipelines, tanks for salt solutions, and the like) it possible to protect steel by imposing potential - the cathodic protection. An disadvantage of this protection is that in the vicinity of the place of coating damage the adhesion of coating to steel is mostly lost. This loosing of adhesion is usually designated as the cathodic delamination. The cathodic delamination takes place also in the case, where no potential was imposed. It is proven that the cathodic reaction leads to an increase of pH value under organic coating.[14]

Filiform corrosion

The filiform corrosion a specific manifestation of corrosion attack running under a coating film.[4] The filaments formed by the corrosion products have really various shapes, from the nodular ones to very fine sharply limited filaments. The filament width varies from 0.005 to 0.5 mm. The filaments can grow at a velocity of up to 1 mm/day. The conditions of formation of the filiform corrosion at the steel substrate and also at the galvanized steel substrate fitted with a coating material film rest on the steady exposure to the relative humidity of 70-85 % under simultaneous contamination of the substrate metal with soluble salts. At a really high value of humidity or at the exposure to a water medium the filament corrosion passes to the corrosion case of more general nature, and the thread character is lost.

Properties of filiform corrosion

The filiform corrosion[5] is a kind of electrochemical atmospheric corrosion, which broadens under an organic coating accross the metallic substrate surface in the form of orientedly growing filaments, which do not intersect each other anywhere. The filiform corrosion was also observed under oxidic layers covering the surface of appropriate metal. The steel, aluminum, and magnesium and the alloy substrates are attacked.[15-17] The corrosion appears at the so-called weak coating places. These places comprise namely unsufficient-thickness places of coating at the edges, local reduction of the coating thickness and mainly the mechanical damages of the coating, exposing the substrate part such as scratches or large pores. This kind of corrosion appears at specific conditions, which can be collected in the following manner:[4,18]

- Sufficiently high relative atmospheric humidity (65-95%) at laboratory temperature
- Sufficient permeability of water vapor through the coating
- Stimulation by impurities such as sulfur dioxide, sulfates, chlorides, acetates
- Presence of coating defects, as especially mechanical damages, pores, air bubbles, salt crystals, or dust particles
- Sufficient adhesion between the substrate and the coating. At insufficient adhesion the standard corrosion runs
- Presence of oxygen in the atmosphere

Other factors, such as temperature, substrate nature and pretreatment thereof, kind of impurity in the atmosphere, value of adhesion and permeability for water vapor, relative humidity value, thickness and kind of coating affect the nature and velocity of corrosion of that kind.

Description of filaments

The corroded surface is characterized by the form of filaments, which grow alongside by each other of a defective coating place, whereat they originated. The filament itself consists of a head and a body. The head is an active corrosion cell and moves at the surface and contains the concentrated electrolyte. A gellike amorfous membrane consisting of hydrated corrosion products separates the head from the body.[4] The trace itself contains the dried out rust. The filament head consists of a front and a backward part. The front side is an anode, whereas the backward part and head vicinity are of cathodic nature. The pH value at the filament front depends on the substrate kind and fluctuates from 1 to 4. The head rear is basic, and some sources report pH value up to 12. The filament widths vary approximately in a range from 0.1 to 1 mm and lengths from 2 to 30 mm and more.

Filament growth

A complete description of the filiform-corrosion mechanism is regrettably not known. Nevertheless, there are no doubts that the filiform corrosion starts with the appearance of an osmotic blister at the coating defect. The blister such formed (a corrosion cell) starts moving in time. It is not quite clear, wherein this movement has its cause. The possible explanation is the action of osmotic pressure in the head or transformation of corrosion products connected with changes in molar volumes. The head movement is, however, conditioned by a loss of the coating adhesion to the substrate in the direction of filament head movement. Literature reports two possible mechanisms of the coating delamination in case of this corrosion kind:[5,19] The so-called anodic and cathodic mechanisms. In both the cases the delamination is caused by hydroxyl ions appearing at the cathodes. The difference is that, which cathode is the main source of hydroxyl ions. The anodic mechanism ascribes the main role to the cathode situated in the rear head of the filament, the cathodic mechanism is ascribed to the cathodes in vicinity of that head. A series of authors propose the cathodic mechanism for the filiform corrosion at steel surface and the anodic one to the aluminum corrosion case.[4,20,21]

Experimental

The present work aimed at the initiation of filiform corrosion at comparing the stability of various organic coating kinds, applied to the substrates of varying composition (steel, aluminum) and pretreatments, to this corrosion kind. Further the effect of pigmentation of the coating, relative humidity, nature of initiation ions, and coating thickness on the filiform corrosion parameters was further sought.

Methods of initiation

In this work four kinds of artifitial initiation of filiform corrosion were tested. The metallic samples were fitted with a coating and following the drying out thereof (3 weeks); closely prior to initiation, fitted with a scratch down (cut) to the metal in a length of about 5 cm. With all the following methods the filiform corrosion was initiated by exposing the system to a medium containing the corrosion stimulators and followed by placing it in certain humid atmosphere.

Method with acetic acid (*Method 1 according CSN 673106*)

The metallic samples covered with an organic coating and fitted with cuts reaching down to the metal were submerged in an aqueous solution containing: sodium chloride ($NaCl$) 50 g/l, concentrated acetic acid 10 ml/l, and hydrogen peroxide 30% 5 ml/l for 1 hour (the aluminum ones for 6 h). After being removed from this solution they were placed in an atmosphere of relative humidity adjusted to 81% for 28 days at 23 °C.

Method with hydrochloric acid *(Method 2 according DIN 65472)*

The samples were placed in a medium of vapor above 32% hydrochloric acid (HCl) for an hour and afterwards exposed to an atmosphere of relative humidity of 80% and at 40 °C for 28 days.

Method with neutral salt spray fog (*Method 3 according CSN EN ISO 4623*)

The samples were exposed at first to the neutral salt fog (5%) medium for an hour and subsequently to the condensation chamber medium of relative humidity 100% and a temperature of 40 °C for 28 days.

Method of immersion in the solutions of natrium chloride, bromide, sulfate or thiosulfate as effect of the initiation ion kind (*Method 4*)

The samples were submerged in the solutions of natrium chloride ($NaCl$), bromide ($NaBr$), sulfate (Na_2SO_4) or thiosulfate at mass concentrations of 0.1 g salt/l for 30 s. After being removed they were dried with filter paper at places outside cuts, ventilated for 15 min and introduced into the chamber of a similar arrangement as in Method 1.

Description of the tests performed

The steel and aluminum panels were used as substrates. The steel was ground by an abrasive paper and degreased prior to application. With aluminum two pretreatment methods were used: on the one hand pickling in an acid medium and subsequent grinding, on the other pickling in a soda (Na_2CO_3) solution. Various kinds of organic coatings without any content on pigments (only binders alone or binders with a siccative content) were applied onto thus pretreated surfaces. Methods 1, 2, and 3 were used for the initiation. With the samples a scope of filiform corrosion (CSN EN ISO 4623) and coating thickness and with the binders the permeability values for water vapor (μ) and adhesion (Cross-cut test ISO 2409, Pull-of test for adhesion ISO 4624) from the substrates tested were evaluated. The aim consisted in comparing the efficiency of individual initiation methods and determining the effect of binder and substrate types and the substrate pretreatment effect on the manifestation of filiform corrosion. For studying the behavior of filiform corrosion under various organic coatings several tests were performed and the following binder types were tested: polystyrene, chlorinated rubber, two component (2-C)-solvent epoxy resin, 2 -C water-reducible epoxy resin, one component (1-C) polyurethane, epoxyester resin, alkyd resin, silicone resin, aqueous polyurethane emulsion, and aqueous alkyd emulsion.

Effect of relative humidity on the filiform-corrosion manifestation: the samples coated with one component (1-C) polyurethane were exposed to the initiation by the Method 2 and positioned in atmospheres of relative humidity 55, 63, 75, and 81% at 23 °C for 30 days. After ending the test the scope of filiform corrosion, the coating thickness and the maximum and minimum widths of filaments were determined (CSN EN ISO 4623).

Effect of the coating thickness on the filiform-corrosion manifestation: on to the samples the two component (2-C) epoxy resin was deposited in various thicknesses, and the filiform corrosion was initiated by the Method 2.

Effect of the zinc-powder pigmentation on the filiform-corrosion manifestation: paints containing zinc pigment were prepared from 2-C epoxy resin, one component 1-C polyurethane and epoxyester binder with a pigment volume concentration (PVC) value of 50, 55, and 60%. Filiform corrosion was initiated by the Method 1.

Effect of pigment showing a lamellar structure on the filiform-corrosion manifestation: for the pigmentation of 1-C polyurethane and epoxy resin the ferric mica was used and the pigment volume concentration (PVC) values were adjusted to 0, 10, and 20%. The filiform corrosion was initiated by the Method 2.

Effect of the initiation ion kind on the filiform corrosion scope: this test was performed at steel samples fitted with a 1-C polyurethane coating. The initiation was performed by the Method 4; as initiation ions sodium chloride, sodium bromide, sodium sulfate and sodium thiosulfate being used.

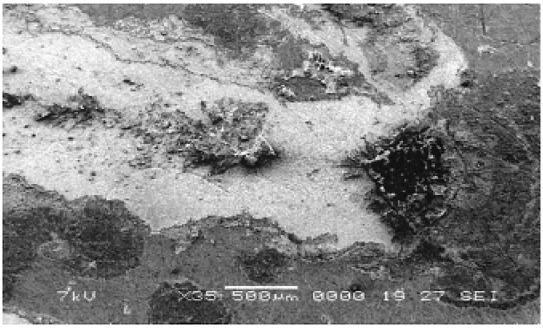
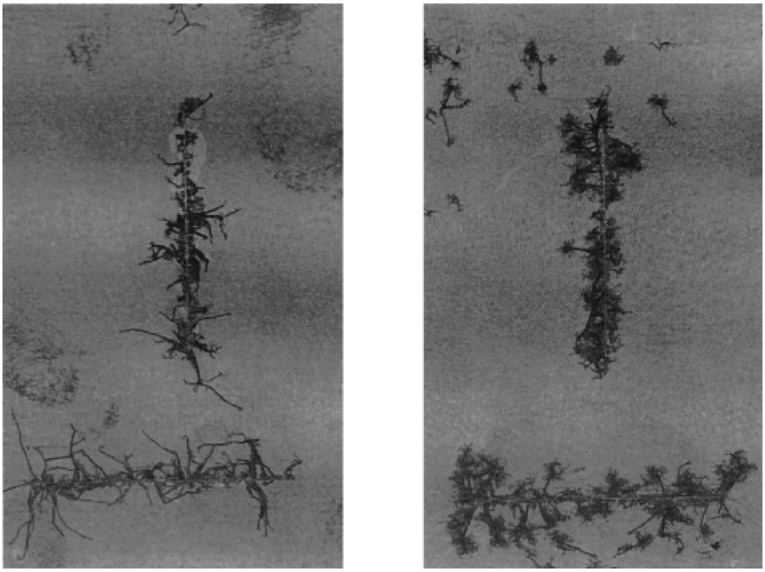


Figure 1. SEM photo of filament under coating based on 1-C polyurethane (35x).

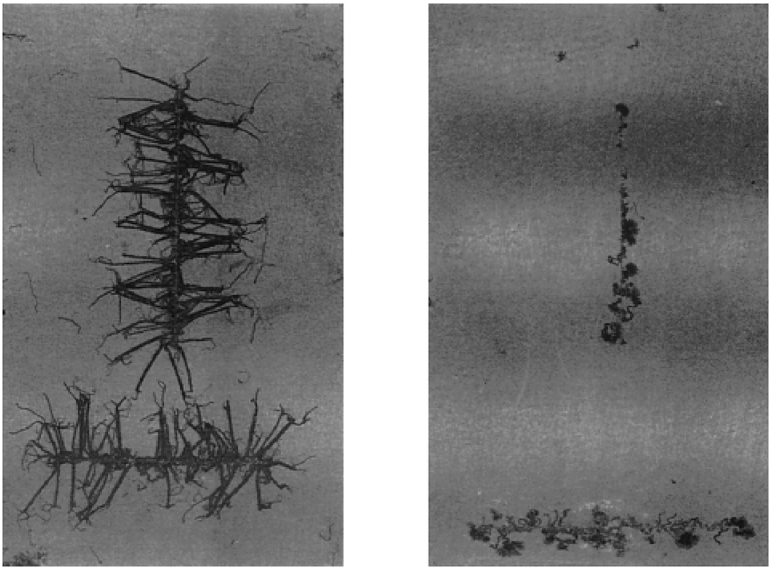


2-C epoxy resin based coat

2-C water-red. epoxy resin based coat

Figure 2.Photographic presentation of testing the filiform corrosion (steel, Method1).

Figure 1 presents scannin electrone microscopic (SEM) photo of filament under coating based on 1-C polyurethane. Figure 2 and Figure 3 give photo of filament under the coatings (based on 2-C epoxy resin, 2-C water-reducible epoxy resin, 1-C PUR , and silicone resin for steel substrates.



1-C PUR resin based coat

Silicone resin based coat

Figure 3. Photographic presentation of testing the filiform corrosion (steel, Method 1.

Conclusion

The binders were ordered by the surface size attacked by filiform corrosion. This order depends on the nature of substrate and the pretreatment thereof and further on the kind of initiation method used. The highest resistance values were observed in all cases of the substrates and the pretreatments thereof using by the silicone, polystyrene and chlorinated-rubber coatings. The relative humidity value showed the effects on the filiform corrosion parameters. With the growing relative-humidity value also the width and length of corroded filaments showed rising. Method 3 (positioning at 100% relative humidity) did not initiate this kind of corrosion, what confirmed the statement that at the relative humidity values higher above 96% this kind of corrosion passes to blistering.

In case of 2-C solvent epoxy resin the increasing coating thickness at steel surface entailed reduction of the filiform corrosion scope. This coating showed the highest barrier capacities of all tested binders. The coatings pigmented with zinc powder at steel and aluminum substrates showed an excellent resistances to filiform corrosion.

All the tested ions were capable of initiating the filiform corrosion. The ion kind affected as the scope of corroded surface so as the density of filaments along the section. The most effective initiator was sodium thiosulfate. Under the coatings of 1C polyurethane pigmented with ferric mica no filiform corrosion was observed. The surface was attacked by surface corrosion. In case of high solid epoxy resin the filiform corrosion was initiated and manifested the dependence of PVC value of ferric mica on the scope of corroded surface and filament density alongside the section.

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