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High-solids, one-coat paints based on aliphatic epoxy resin-siloxanes for steel protection

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ABSTRACT

This research involved the design of high-solids, one-coat paints for the protection of metal structures with low maintenance requirements. The main paint components were: (i) an aliphatic epoxy resin cured with an aminosilane and chemically modified with alkoxysilanes as film-forming material, and (ii) rutile titanium dioxide as opaque pigment, a polysilicate strontium and zinc as corrosion inhibitor and, a synthetic calcium silicate and barites as extenders.

Some paints displayed excellent performance in salt spray apparatus (degree of rusting) and in 100% relative humidity cabinet (degree of blistering). Results indicate that as the aliphatic epoxy resin/alkoxide ratio increased, the degree of rusting improved while the degree of blistering worsened, in total agreement with film permeability. In addition, binders based on dimethyldiethoxysilane, methyltriethoxysilane and tetraethoxysilane, in that order, displayed an improved corrosion performance and a decreased blistering resistance. The reactivity of alkoxides and the chemical interaction with the metal substrate supports the obtained results.

Initial gloss and gloss and color retention improved as the alkoxide level increased; no significative differences were registered when the alkoxide type variable was considered.

In summary, the use of alkoxides as modifiers of an aliphatic epoxy resin allowed the formulation of hybrid paints with high anticorrosive and weathering resistance performance. The more suitable hybrid organic–inoganic paint must be selected according to the requirements of each structure in service.

1. Introduction

Silicon derivatives may form inorganic polymers with unique characteristics; that is why, they are being included in the formulation of protective coatings [1]. The alkoxysilanes, silicon derivatives and precursors of the polysiloxanes, are the most commonly used in this area because they have high strength chemical bonds of ≡Si—O-type; this energy exceeds that of the —C—C— in the organic polymers (e.g. epoxy and polyurethane resins) [2] and enhances the film properties.

In general, alkoxysilanes used in paints are modified by the incorporation of hydrocarbon chains linked by covalent bonds to silicon (preferably aliphatic to prevent yellowing that generate the aromatic structures exposed to sunlight). The remaining covalent bonds link the silicon with oxygen atoms and through them with hydrogen or alkyl groups; the chain length of these groups must be less than five or six carbon atoms to facilitate the kinetic of the reactions included in the sol–gel process (polymerization of siloxanes by hydrolysis and condensation reactions). The presence of the hydrocarbon chain makes it more hydrophobic; the hydrophobicity increases with chain length.

It is appropriate to consider some aspects of alkoxides for carrying out their polymerization by sol–gel process: (i) they are soluble in alcohols and in both aromatic and aliphatic hydrocarbons, (ii) their reactivity increases with the number of groups —OH and $—OC_nH_{2n+2}$ in the structure since these allow obtaining macromolecular networks, (iii) the pH plays an important role because values below to the isoelectric point of the silica produce polymeric gels while clearly alkaline values generate colloidal gels of lower density and specific area, and (iv) during aging process, volumetric shrinkage of network occurs spontaneous and irreversibly, with the expulsion of water and alcohol from the pores [3–5].

In paints based only on polysiloxanes, the cracking caused by the high surface tension during aging must be avoided (pressure difference increases as distance between the particles decreases).

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The simplest solution is to allow the evaporation of the reaction products at a very low speed; this method, while effective, is not practical in many cases due to long drying times required (weeks or even months to form a dry system without cracking). The quoted period can be substantially lowered by incorporating chemical additives that modify the surface tension of the interstitial fluid, allowing the quick removal of the volatile components without cracking. It is appropriate to mention that when the polysiloxanes are used in combination with organic resins, cracks are not usually observed during film formation.

The aim of this research was the design of efficient high-solids, one-coat paints recommended for the protection of metal structures exposed to weathering, with low maintenance requirements; they were based mainly on an aliphatic epoxy resin stoichiometrically cured with an aminosilane and chemically modified in several degrees with alkoxysilanes.

2. Materials and methods

The experiments included the following steps: (i) the choice of the aliphatic epoxy resin, (ii) the selection of an aminosilane as curing agent and alkoxysilanes as co-binder, (iii) the design of the pigmentation, (iv) the formulation and manufacture of hybrid paints, and finally (v) the laboratory tests to establish the performance of painted panels.

2.1. Choice of the aliphatic epoxy resin

Epoxy paints are widely known and have achieved high commercial acceptance as protective and decorative paints for application on various substrates (steel, concrete, etc.). Nevertheless, they generally do not have good resistance to UV from sunlight when exposed for long periods [6]. Therefore, it became necessary to develop paints based on epoxy resin with better color and gloss retention. This was achieved by modifying the glycidic epoxy resins (prepared from bisphenol A and epichlorohydrin) with acrylic resins and also with melamine resins co-etherified with epoxy groups and epoxidized polyester resins. It is worth mentioning that the cited developments, although lead to better weathering resistance, simultaneously generate films with less resistance to corrosion than glycidic epoxy resins [7–10].

To improve performance against sunlight but without losing corrosion resistance, hybrid systems comprised of aliphatic epoxy resins and polysiloxanes are being studied as finishing paints [11–13]; aliphatic epoxy resins are generally liquid and therefore allow the paint formulation with low level of volatile components [14–16]. Accordingly, for this research, diglycidyl ether of 1,4-butanediol was selected (weight per epoxide WPE, 171).

2.2. Selection of silanes

The aminosilane for curing the aliphatic epoxy resin must be difunctional (two amine hydrogens) with the object of forming a lineal epoxy polymer with superior weatherability. The amino group gives alkalinity in aqueous solution and acts as catalyst of the hydrolysis and condensation reactions; in this way, a few large polymeric units (high molecular weight) are formed.

Taking into account the above mentioned, the aminopropyl methyldiethoxysilane was selected (chemical formula, $C_8H_{21}NO_2Si$; molecular weight, 191.3; equivalent weight, 95.7; appearance, clear liquid; density, 0.916 g cm^{-3}). The equivalent weight of aminosilane and the WPE of the aliphatic epoxy resin were used for the stoichiometric calculation of the amount of curing agent.

Polysiloxanes used as co-binder must have low molecular weight to produce high-solids paints. For this research, the following alkoxysilanes were selected: dimethyldiethoxysilane (formula, $C_6H_{16}O_2Si$; molecular weight, 148.3; aspect, clear liquid; density, 0.851 g cm^{-3}); methyltriethoxysilane (formula, $C_7H_{18}O_3Si$; molecular weight, 178.3; aspect, clear liquid; density, 0.895 g cm^{-3}) and, finally tetraethoxysilane (formula, $C_4H_{20}O_4Si$; molecular weight, 208.3; aspect, clear liquid; density, 0.934 g cm^{-3}). The binders included 30/70, 40/60, 50/50, 60/40 and 70/30 aliphatic epoxy resin/alkoxide (v/v) ratios.

2.3. Design of the pigmentation

The pigmentation included: (i) rutile titanium dioxide with R1 surface treatment according Standard DIN 55912 (density, 4.2 g cm^{-3}; oil absorption OA, 16) as opaque pigment, (ii) a commercial strontium zinc phosphosilicate of easy dispersion (density, 3.3 g cm^{-3}; OA, 34) as corrosion inhibitor and, (iii) a synthetic calcium silicate (density, 2.3 g cm^{-3}; OA, 280) and barites (density, 4.5 g cm^{-3}; OA, 9) in 3.0/3.0/1.0/1.5 (w/w) ratio as extenders.

2.4. Formulation and manufacture of hybrid paints

In this experiment, it was considered sufficient the water supply from the atmosphere and from components of the formulation having water absorbed. For this reason, no water was incorporated in the formulations to not affect the stability of hybrid paints in container.

2.4.1. Volatile organic compounds (VOC)

Aliphatic epoxy-siloxane systems do not require theoretically solvent in the formulation since both film-forming materials are liquids (i.e. 100% solids); nevertheless, it is not possible from a practical standpoint for pigmented systems due to their high viscosity (difficult application, poor film leveling, etc.). Consequently, the hybrid paints were formulated with 90% solids in volume including butyl acetate as solvent.

2.4.2. Pigment volume concentration (PVC)

Preliminary paints were formulated in a wide range of pigment volume concentrations for estimating the critical pigment volume concentration (CPVC). The preparation of the paints and panels was performed as indicated below (surface tension was adjusted in all cases to 40 dynes cm^{-1}).

The CPVC values obtained in previous tests of degree of rusting (salt spray apparatus) and degree of blistering (100% relative humidity cabinet) varied in a narrow range between 32 and 35% for all samples and for dry film thickness between 220 and 230 μm; the low CPVC values are attributable to high OA of synthetic calcium silicate. According to the above, the PVC selected was 32.0%.

It is worth mentioning that the CPVC values, estimated theoretically for all samples through equation $CPVC = (100/\rho)/[(OA/0.935) + (100/\rho)]$ o $CPVC = 1/(1 + OA\,\rho/93.5)$, are placed in the range determined in the quoted previous laboratory tests (ρ is the pigment density).

2.4.3. Manufacture

The pigments were dispersed in the vehicle based on the aliphatic epoxy resin solubilized in butyl acetate. The process was conducted in a high-speed disperser for approximately 25–30 min (7–8 Hegman gauge) and then, the corresponding siloxane was added.

Aliphatic epoxy resin-siloxane paints were prepared in two moisture free containers; one of them with the dispersed pigments and the second with the aminosilane. Prior to the paint application,