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Anticorrosive Pigments for Chemically and Thermally Resistant Coatings

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Summary: The present state in the field of organic coatings requires such an anticorrosive pigment, which is adapted in its properties to the binder concerned and will contribute to the overall protection properties of the pigmented coating film at max. The paper presents as an example of thermally and chemically stable pigments the compounds based on mixed metal oxides. Other pigments exhibiting prospective results for the coating applications comprise the pigments of lamellar shape, which in addition to their alkalizing properties contribute to increasing the barrier and simultaneously inhibition mechanism by protective action of the coating.

Introduction

The conservation of metals in their pure form is possible only by their protection, which is secured by the chemical or electrochemical reactions of anticorrosive pigment with the metal alone or with the corrosion medium penetrating through the coating. The present-time task is devoted to investigating such anticorrosive pigments, which can be considered harmless from the environment protection point of view and, at the same time, highly efficient in their corrosion-inhibition action.[1,2] The toxic pigments could be replaced in practice with zinc phosphate $Zn_3(PO_4)_2.2H_2O$. At present there exist a series of anticorrosion pigments based on phosphate anions.[3] Also a phosphate-molybdate anion is possible, the applicable cations comprise Zn^{2+}, Al^{3+}, or Ca^{2+} and others.[4] A further possibility consists in using aluminum polytriphosphate as an anticorrosion pigment for water-dilutable and solvent-type coatings.[5] Aluminium polytriphosphate can be modified with Zn^{2+} ions, which results in an increase in the anticorrosive efficiency of the pigment concerned. The anticorrosive efficiency of primers can be secured by introducing the pigment acting on an ion-exchange principle.[6] This concerns the pigments consisting of silicate anions and Ca^{2+} cations.

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Futher compounds distinguished by their anticorrosive effects are represented by barium metaborate, calcium, zinc, or strontium phosphosilicate, calcium borosilicate, and zinc molybdate.[7] Also the zinc and zinc lead(II) salts of organonitrogen compounds, organozinc compounds and calcium cyclotetraphosphate show an anticorrosive activity. A separate and rather problematic group of anticorrosive pigments consists of the so-called „core" pigments , the core of which is created by an inert carrier bearing an active component.[8] Examples of such pigments comprise iron (III) oxide, the surface of which is treated with zinc phosphate. [9] A possible solution is presented also by calcium carbonate, zinc oxide,[10] or calcium molybdate. As a replacement of standard anticorrosive pigments with the pigments of an equal activity but without harmful effects the spinel-type ferrites or the rutiles based on mixed metal oxides show to be prospective candidates.[11,12]

Effect of polymeric binders on the inhibitive efficiency of coatings

An appropriate formulation of the protective coating creates a general protection by increased life expectancy of the operational coating on the substrate. A key component determining the coating quality is the polymer matrix. No protective high-quality system can be obtained if no anticorrosive high-quality pigment is used in a combination with a high-quality binder. Properties of the binder, such as hydrolytic stability, chemical resistance[13], glass-transition temperature, cross linking degree, and polymer purity in certain limits are the parameters affecting principally the functional properties of coating.

Pigments in organic coating

For the behavior of anticorrosive coating from the corrosion protection point of view the properties of pigment component are determining items in addition to chemical and physical effects. It is not possible, however, to consider the pigment separately, but the pigment-binder system is always to be taken as a whole. The dispersing behavior of the system and the thickness of the film obtained are two remaining factors, which have a great significance from the application technique point of view. It is evident here that the quality of resulting film is affected by such factors as particle size distribution of individual pigments[14]. These parameters are then in a narrow connection to permeability for water and gases and through these characteristics also to the corrosion protection and efficiency of the film.[15] Pigmented organic coatings, which do not contain any corrosion-inhibitive matter (an anticorrosive pigment or organic corrosion inhibitor) can exhibit only the so-called barrier effect if attacked by corrosion-initiating species. This effect is, to a large extent, connected with the nature of chemical binder, the size and shape of filler (inert pigment) particles, the additive content and, eventually, with the fractions of individual components being present in the coating formulation.

Diffusion of corrosive medium through an organic coating

As it has been already described, each organic coating exhibits a definite permeability to corrosive substances as water, oxygen, Cl^-, SO_4^{2-}, and the like.[16] These substances penetrate to the substrate metal, at the surface of which the corrosion processes are initiated.[17] The corrosive medium components can penetrate through the film on several ways. From the morphology of surface film point of view the small-diameter and large-diameter pores can exist. The small pores having 1-5 nm in diameter or those of an even smaller size arise or decay at the movement of segments of macromolecular binder chains at temperatures above the glass polymer transition. This means that a single-phase system is concerned.[18] The temperature dependence of film penetrability reflects the temperature dependence of macromolecules mobility. If the corrosive substance penetrates these very low-diameter pores through the film, then the so-called activated diffusion is meant. The polymers, which have a high mobility of binder chains, such as elastomeres, are more susceptible to the activated diffusion than the polymer structures of high density. The system containing large diameter pores is designated as a two-phase one, and the shape of these pores does not depend on temperature. The permeability depends, on the contrary, on the properties of diffusing compound. The transport of diffusing substances depends on: the flexibility of macromolecular substances, the density of macromolecular network, the morphology of the structure formed, the glass-transition temperature (T_g) of polymer (binder), the penetrating-substance concentration, the molecular weight of penetrating substances. [13]

All these prerequisites do not consider the chemical reactions running at the diffusion through the film between the diffusing substance and a polymer forming the film structure and at all do not consider the reactions between the diffusing substances and the pigments and fillers contained in the film.[18]

From the corrosion of metal point of view, as it has been already stated, the acid medium is of primary significance, penetrating the protective film not only by physical diffusion, but thanks to the possibility of reaction with pigments, fillers and also binders by chemical diffusion or, maybe, by the physico-chemical art.[19]

Starting with these reasons the work was directed to following the penetration of acid solutions (hydrochloric acid, sulphuric acid, formic acid, acetic acid, and propionic acid) into a chemically resistant binder system - epoxy resin based coatings. Selection of these acids is given by the practical occurrence of hydrochloric and sulfuric acids in "heavy" corrosive atmospheres. This concerns the coatings exposed to atmospheres in chemical and power engineering related plants, but also to contaminated municipal and industrial atmospheres. Organic acids, formic, acetic, and propionic acids, belong among components encountered in foodstuff and also aggricultural plants. Expressive improvement of mechanical and chemical resistances of binders require comparatively low concentrations of fillers or pigments, as far as it is possible to create an appropriate structure of interface. The structure and properties of coatings depend, to a great extent, on the surface properties of pigment particles, on the composition of interface and also on the structure of polymer matrix. Interaction with pigment particles results always in a less or more expressive modification of binder.[20]

Mixed metal oxides as reactive pigments affecting the diffusion of corrosive substances

The spinels involve a large group of double metal oxides characterized by a general formula AB_2X_4 and a crystal structure similar to that of the natural spinel mineral, which is a magnesium aluminate ($MgAl_2O_4$). These mixed metal oxides are solid solutions or compounds consisting of two or more metal oxides.[21] The spinel lattices are rather stable, and the oxides showing this structure are characterized by high thermal and chemical stabilities and a high refractive index.

Thermostable spinel pigments

The outstanding effect of thermal stability of the spinel pigments can be utilized, when also other components of the protective coating exhibit a high resistance to the elevated temperature effects. Of the known polymers which have film-forming properties, the silicone resins are usable as binders for the coating compositions able to resist elevated temperatures. [22]

Experimental

The diffusion methods of investigating the anticorrosive pigments start with the existence of barrier efects and binding the aggresive compounds penetrating the organic coating. The diffusion of corrosively active compounds into the epoxy coating samples prepared was studied by a microscopy method starting with the second Fick law,[23] and independent calculation of the diffusion coefficient (D) was performed by means of the Einstein relation for D. As far as reactive pigments, i.e. the substances capable of chemical reactions with diffusing medium, are used, then the decceleration of diffusion of this medium through the film takes place. Microscopic investigation of the diffusion of aggresive acid medium into pigmented films consisted in measuring the depth of penetration of the medium. When a suitable form of test pieces was used the condition of diffusion in a single direction was satisfied, and the diffusions along the y and z axes could be disregarded.[24] The depth of diffusion can be measured microscopically as a function of time, the time being considered as the time of exposure of the samples to the corrosive medium being investigated.

Anticorrosive action of spinel pigments in coatings

Let us start with the assumption that the primary cause of corrosion at the metal substrate under the protective coating consists in the penetration of surrounding medium through the heterogeneous film created by a polymer matrix with pigment particles which are usually of inorganic nature. From this point of view we can appreciate the importance of the study of transport processes comprising water and corrosive acidic media into the coatings pigmented with spinel pigments. All the binders pigmented to a variable pigment volume concentration (PVC) with spinel like pigments showed a similar behavior for the penetration of acidic (1.0M hydrochloric acid (HCl), 0.5M sulphuric acid (H_2SO_4), and 1.0M acetic acid (CH_3COOH) medium through the coating. The curves obtained indicate that the diffusion of water through the coating layer dependend not only on the kind (defined by chemical composition) of the pigment, but also the pigment volume concentration in the system (Figure 1.). Titanium dioxide, which was used as a representative of inert pigments towards acid media, showed a rising coefficient of diffusion, which entails a higher degree of penetration of coating by the medium and, possibly, a reduction of the resistance of the system to corrosion as a whole. Figure1 depicts the influence of the pigment volume concentration (PVC) on the diffusion coefficient (D) for various spinel-type pigments. The curve/development dependence shows how the cations present in the spinel-crystal lattice affect the transport of acidic medium (0.1M HCl) into the epoxy resin-based coating film. The critical pigment volume concentration (CPVC) values of all the pigments tested lie in a range of 45-55 vol.% and it can be concluded that at such a pigment concentration a sharp growth can be observed for the diffusion of liquid medium. The PVC = 40 vol.% value is an optimum condition for the minimum diffusion of liquids into the coating films.

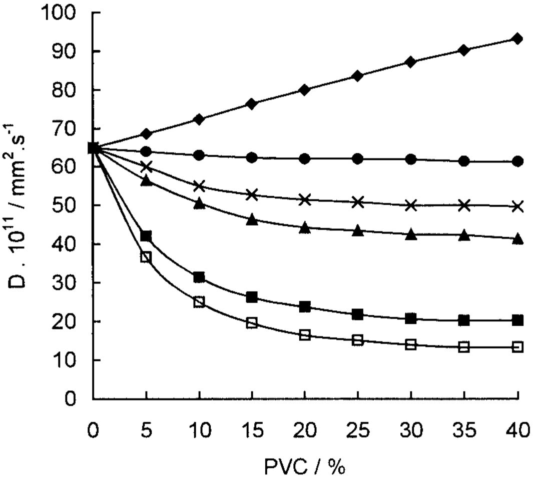

Figure 1. PVC dependence of the coefficient of diffusion (D) for 1.0M HCl into the coatings;

◆ = TiO_2, ● = $ZnAl_2O_5$, × = $TiMgO_5$, ▲ = $ZnFe_2O_4$, ■ = $ZnMgFe_2O_5$, □ = $MgFe_2O_4$.

Quite generally, the transport phenomena take part in all corrosion processes, and the appropriate pigmentation can reduce the diffusion of medium and thus prevent appearance of the primary corrosion cause. The capacity to neutralize the penetrating substances protects also, to a certain extent, the binder, by stopping chemical attacks on the molecular chain thereof. Based on the results obtained a model situation can be assumed, according to which at the surface of spinel pigment particles the salts (of appropriate acids) are formed.[23] This eliminates the chemical diffusion component. Also, an important role is here played by the degree of wetting of the pigment particle by the organic binder. An objective representation of the diffusion of corrosive media at the pigment/binder interface for both inert and reactive (spinel-type) pigment is given in Figure 2.

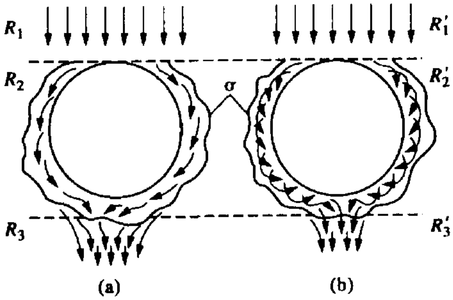

Figure 2. Scheme of diffusion of corrosive media at the pigment/binder interface; (a) inert pigment, (b) reactive pigment.

In the first stage the physical diffusion through the coating takes place, the diffusion running at a rate (R_1). At a moment when the diffusion field contacts an inert pigment tiranium dioxide (TiO_2) particle a change in the rate of diffusion takes place to a rate (R_2), which is determined by the degree of wetting (σ) of the pigment achieved during the dispersion process. The pigment particles act in this case as heterogeneties at a rate of diffusion $R_2 >> R_1$. If we consider the diffusion running only in one direction (along axis x) the rate of diffusion (R_3) will be higher than or equal to the rate R_1. If spinel-type pigments are used then in the phase of diffusion $R_1 = R_1'$. On contacting a reactive spinel and an acidic medium the reaction to the appropriate salt will take place, which also bind several water molecules. The particle surface becomes afterwards a coating consisting of these reaction products, which considerably reduces the diffusion process for the original medium. The rate of diffusion $R_2' << R_2$.

Preparation of the novel lamellar pigments

Due to the fact that the single layers cannot protect the metal effectively it is necessary to create a system consisting of several layers.[25] The top layer of coating system has to secure primarily the protection of coating system to the degradation by ultravioleght

(UV) radiation and in addition to it has an important anticorrosion function.[26] In this connection we speak on the barrier protection. An efficient barrier can be formed only from the binder, which is characterized by a low permeability for liquids and gases, and this function can be improved by using nonisometric, i.e. platelike or also flakelike pigments. The mechanism of active anticorrosion effects can be with barrier mechanism combined also in a single-layer system, which should comprise both the mechanisms.[27] The lamellar-pigment particle pigmented organic coatings are to be considered the composite materials. The matrix (binder) and also reinforcement (pigment) act with a synergic effect on the final physicomechanical properties. The strength, toughness and resistance to temperature and moisture liquid effects at the corrosion loading undergo raising. An important protection factor concerns also the adhesion properties[28] of the coatings formed. The adhesion of coating to the substrate, so as the adhesion of individual layers one to another are tightly conected with phenomena, such as osmotic blistering, peeling and cracking of the coating films. Improving the mechanical properties by using suitable pigments raises the stability of coating at changes in temperature and at mechanical loading. The connection with anticorrosion function of coating consists in a prerequisite that if no mechanical failure of the protective film takes place the corrosion of substrate does not run. The proper logic of anticorrosion protection starts with creating such a barrier by using the coatings to guarantee a tight insulation of the metal substrate from the environment[29]. The anticorrosion properties of these nonisometric pigments consist in a reduction of the velocity of diffusion of the corrosion medium in the direction to substrate metal (Figure 3.).

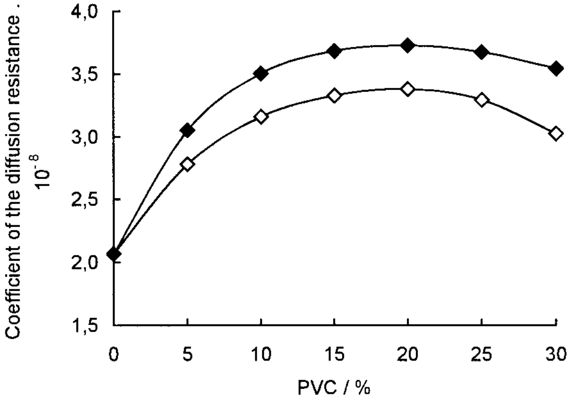

Figure 3. The dependence of coefficient of the resistance to diffusion of 1-C polyurethane coating on the concentration of surface treated iron muscovite;
◇ = iron muscovite, ◆ = lamellar zinc ferrite.

A disadvantage of natural mineral specularite consists primarily in the dark gray to black color and also the sedimentation in the binder resulting from a high specific mass. These disadvantageous negative properties are on the opposite not shown by the muscovite having been subjected to a surface pretreatment (hematite layer).[30]

Another type of such lamellar pigments, verified in a laboratory scale, goes out of the synthesis of primary starting reactants with lamellar particle shapes, which at a cautious calcination passes to a product showing no crystal system changes and thus no changes in their form. As an example zinc ferrite can be named for which as a starting ferric oxide –the specularite (a lamellar ferric oxide) with lamellar particle shapes (Figure 4.).

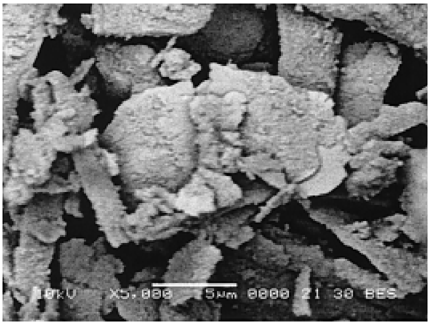

Figure 4. Morphology of lamellar particle of zincferrite (5. 000x).

Conclusion

The type of pigment used exhibits a considerable effect on increasing the chemical stability, resistance to the penetration of acid medium through the coating and thus also the corrosion protection of protected metal substrate. The results obtained, relating to the diffusion of corrosive medium through the coating pigmented with spinel pigments allow to take some general conclusions: the spinel pigments are active compounds capable to take an active part on the diffusion of corrosive medium through the film. This medium is mostly of acidic nature, or the gaseous substances are concerned. The spinel pigments actively protect the polymer film matrix by the reaction with diffusing medium to the degradative reactions causing the change of polymer structure due to effects of this difusing substance. Based on these conclusions it is possible to imagine the spinel pigments as reactive particles, on the surface of which at the diffusion of corrosive substances through the polymer film chemical reactions take place, which lead to the formation of less corrosive substances. The improvement of physicomechanical properties of the coatings is significant primarily in increasing the adhesion to the substrate material. The higher adhesion means a lower tendency to the formation of osmotic blisters and thus to the subcorrosion effects. The anticorrosion properties of these nonisometric pigments consist in a reduction of the velocity of diffusion of the corrosive medium in the direction to substrate metal. The lamellar surface treatment of muscovite by ferric oxide gives the pigments for the anticorrosive coatings acting as corrosion barriers.

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