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Improved Chemical Resistance of Epoxy Resin-Based Coating Compositions

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ABSTRACT

The chemical resistances of epoxy resin-based compositions are significantly affected by the chemical composition, shape, size and concentration of the inorganic fillers and/or pigments used. Using a microscopic method for evaluating the diffusion of aqueous acid solutions, possibilities were found of increasing the chemical resistance of coating and casting epoxy resin-based compositions.

INTRODUCTION

To obtain an improvement in the mechanical and chemical resistance values of coating composition binders, a comparatively low concentration of fillers or pigments is sufficient if an appropriate interface structure is formed. The structures and properties of coating films depend, to a considerable degree, on the interface composition and also on the structure of the polymer matrix. The binder is modified to a certain extent in the course of its interactions with the respective filler.

From the physical property point of view the fillers may be characterized by the shape and size of their particles. With respect to the particle shapes, the fillers may be divided into different types, namely:

- isomeric fillers, in which the particles are characterized by a mean size on the one hand and by a maximum size on the other; and
- nonisometric fillers that may be

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(a) of layered structure (such as mica); these fillers are characterized by an (equivalent) diameter (*d*) to height (*h*) ratio $d/h > 10$, or
(b) of fibrous structure (such as glass fibers); these fillers are characterized by a fiber length (*b*) to diameter (*d*) ratio $b/d \gg 1$.

Information regarding the chemical properties which significantly affect the chemical coating resistance has not yet been fully evaluated.

EXPERIMENTAL

By following the diffusion of a corrosive medium into hardened epoxy resin-based coating systems, the chemical resistances of individual systems can be quantitatively evaluated. The diffusion has been extensively studied, and a series of mathematical models of the process has been described.[1-6] The basic equation describing the diffusion process involves Fick's second law. For diffusion running in the directions of the x, y and z axes the law is represented by

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + D\frac{\partial^2 c}{\partial y^2} + D\frac{\partial^2 c}{\partial z^2} \tag{1}$$

where D is the coefficient of diffusion, c is the concentration of pigment, and t is the time.

If we consider the diffusion as running only in the x axis direction, then eqn (1) can take the form

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}. \tag{2}$$

On introducing the initial conditions, i.e.

$$c = c_0, \quad x \leq 0 \quad \text{and} \quad t = 0$$
$$c = 0, \quad x > 0 \quad \text{and} \quad t = 0$$

the following equation can then be written

$$c = \frac{c_0}{2}\left[1 - \psi\left(\frac{x}{2\sqrt{Dt}}\right)\right] \tag{3}$$

where ψ is the Gauss error integral

$$\psi_{(\xi)} = \frac{2}{\sqrt{\pi}}\int_0^x \exp\left(-\xi^2\right)\,\mathrm{d}\xi. \tag{4}$$

The diffusion coefficient can then be defined by

$$D = \frac{x_0^2}{\pi t} \tag{5}$$

where x_0 is the depth of diffusion.

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.

RESULTS AND DISCUSSION

Organic and inorganic acids can diffuse into polymeric materials. Therefore, the chemical resistance of anticorrosion coatings and linings is limited in many cases by the chemical resistance of the binder base. The investigation concerns the diffusion of organic and inorganic acids (8% aqueous solutions of formic, acetic, sulfuric or hydrochloric acids) into a low molecular weight epoxy resin of the diene type. An increase in the chemical resistance can be achieved by introducing fillers which are able to react with the diffusing acid.

Inert fillers or pigments (such as TiO_2, graphite, carbon black or chromium oxides) present in an epoxy composition increase the diffusion of the aggressive (corrosive) medium, since penetration at the pigment/binder interface occurs along a pigment particle (Fig. 1(a)). One possible way of reducing the rate of diffusion of acids into the epoxy resin involves reaction of a reactive pigment with the diffusive medium (the acid). Pigments based on heavy metal oxides were introduced into the epoxy resin matrix via complete homogenization. Selection of the pigments was governed by their basicities and reactivities to dilute acids. The

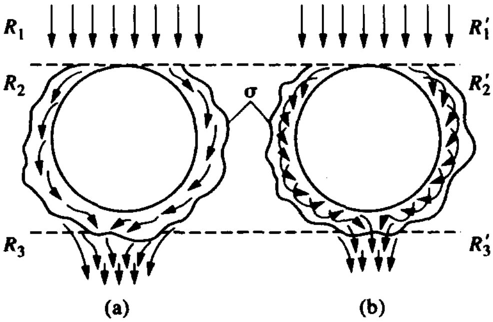

Fig. 1. Diffusion of acids at the pigment/binder interface: (a) inert pigment; (b) reactive pigment.

reactive pigment series involved the use of MgO, ZnO and CaO, with TiO_2 (rutile) being used as inert pigment.

The depth of diffusion of the acid solutions into the epoxy resin compositions with respect to time was measured microscopically[4] by an indicator method. The diffusion coefficients were then calculated using eqn (5) and subsequent regression analysis of the results obtained.

The pigment base consisted of a low molecular weight resin of the diene type (showing an epoxide equivalent of 0·5154), plasticized with 20% dibutyl phthalate. To this mixture was added 0, 1, 3, 9 or 12% of the respective oxide as either reactive or nonreactive pigment.

The values of the diffusion coefficients depend on the amount of fillers added. The values obtained for various acids indicate that in the epoxy resin matrix the reactions of oxides with the respective acid solutions occur essentially as in eqn (6):

$$MgO + 2\ HCl + 5\ H_2O \rightarrow MgCl_2 . 6H_2O \tag{6}$$

Reactions of this type take place at the surfaces of reactive pigment particles. The reaction products show a definite solubility, which hinders the diffusion effect of acid penetration in subsequent stages, and the whole diffusion process is therefore retarded. The differences between the diffusion of acids into epoxy compositions containing inert and reactive fillers are shown in Figs 1 and 2.

Figure 1(a) represents the state when the nonreactive pigment particle is covered with a polymer mass; with the completion of wetting of

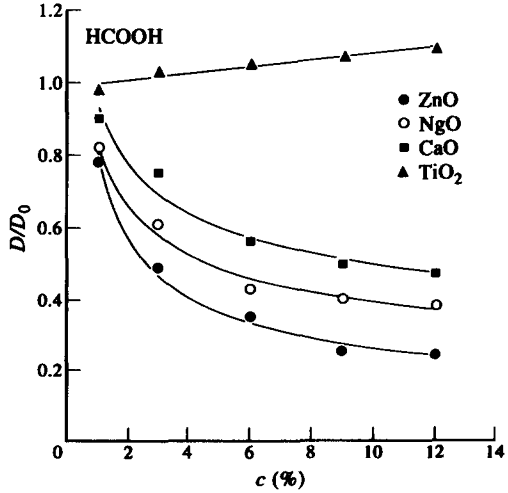

Fig. 2. Relationship between the ratio of diffusion coefficients (D/D_0) and the concentration of pigment (c). D = actual diffusion coefficient, D_0 = coefficient for a filler-free epoxy resin composition.

the pigment particle, there is a wide space at the solid inorganic pigment particle/organic binder interface. In the first stage, physical polymer (epoxy resin) diffusion takes place, the diffusion running at a rate R_1. As soon as the diffusion field impacts on an inert pigment particle the diffusion process runs along the particle at a rate R_2, and the diffusion in the area around the particle occurs more rapidly, depending on the wetting of the particle with the binder (σ) used. The amount of acid diffusing at the pigment/binder interface is governed by the diffusion process and by the wetting qualities in the epoxy resin composition preparation. When we consider the diffusion as running in only one direction (in the direction x), further penetration of the acid into the epoxy resin matrix will show a velocity R_3 which is higher than, or comparable to, the velocity R_1 ($R_1 \leq R_3$).

When using a reactive pigment (Fig. 1(b)), the appropriate stage of the diffusion process will be at a rate R_1', with $R_1 = R_1'$. Where the reactive filler contacts the acid, the above reaction (leading to an appropriate salt) will occur and this binds several water molecules. The pigment–particle surface will thus be coated with the reaction products, which results in a reduction or complete cessation of the diffusion process. The amount of acid which has passed the vicinity of the particle is then at a minimum, and the diffusion-field velocity is thus reduced to a velocity $R_2' \ll R_2$. The small amount of acid which passes to the epoxy resin will move at a rate R_3'.

Table 1 shows experimental values of the diffusion coefficients obtained for the diffusion of acid solutions into the epoxy resin compositions containing various reactive and nonreactive pigments. From the values obtained on measuring the diffusion processes for acids diffusing into the epoxy resin compositions filled with various pigments, it can be concluded that selection of an appropriate pigment for filling the epoxy resin composition may be a way of increasing the lifetime of epoxy resin-based coatings.

Reductions in the diffusion of a liquid medium into epoxy resin-based coating systems are affected by the shapes and sizes of the pigment particles as well as by the chemical compositions of the pigments. Nonisometric pigments acting via a barrier mechanism, in contrast to isometric particles, hinder the diffusion of a liquid medium through the epoxy resin matrix. The diffusion of a liquid medium in the vicinity of pigment particles of various shapes can be envisaged in the following ways:

(a) with spherical particles the corrosive media diffuse along a particle surface to the substrate following the shortest possible path;

(b) chip-shaped particles in a lamellar arrangement exhibit a higher resistance to a liquid medium diffusing through an epoxy resin matrix, the diffusion path being longer; and

TABLE 1
Diffusion Coefficients for Epoxy Resin Compositions of Varying Pigment Concentrations

Pigment (and concentration)		$D \times 10^{10}$ ($mm^2 s^{-1}$)			
		$HCOOH$	CH_3COOH	H_2SO_4	HCl
MgO	0%	248·05	101·09	2·53	0·95
	1%	207·67	81·84	2·26	0·63
	3%	150·62	67·64	2·24	0·59
	6%	103·77	48·47	2·01	0·41
	9%	90·22	47·03	1·73	0·37
	12%	85·04	46·86	1·58	0·35
CaO	0%	248·05	101·09	2·53	0·95
	1%	220·58	96·32	2·49	0·85
	3%	178·87	85·29	2·24	0·77
	6%	130·21	73·28	2·06	0·72
	9%	112·52	60·74	1·99	0·66
	12%	98·58	53·29	1·90	0·58
ZnO	0%	248·05	101·09	2·53	0·95
	1%	192·53	82·20	1·01	0·32
	3%	113·89	55·69	0·50	0·27
	6%	77·65	45·91	0·39	0·19
	9%	60·15	42·56	0·30	0·15
	12%	59·84	44·91	0·22	0·12
TiO_2	0%	248·05	101·09	2·53	0·95
	1%	240·27	98·53	2·55	0·96
	3%	252·31	96·21	2·59	0·94
	6%	266·37	112·22	2·61	1·20
	9%	271·49	120·27	2·91	1·43
	12%	280·52	133·38	3·12	1·63

(c) lamellar pigment particles, in which the hydrated surface is substituted by a formation of organic chains (the so-called 'silane' surface), are protected against diffusing corrosive solutions of substantially any kind.

Spherical pigment particles were simulated by silicon dioxide precipitated in an amorphous form and introduced into the epoxy resin matrix; the SiO_2 used contained 12% water bound in its structure. The chip-shaped pigment particles were a three-component product composed of mica, quartz and chlorite (magnesium aluminium silicate hydrate).

The two fillers were investigated with respect to their effects on the diffusion of corrosive media into an epoxy resin-based composition. The corrosive media were aqueous formic, acetic, propionic, sulfuric or hydrochloric acids. The fillers were contained in the epoxy resin at concentration levels of 0–12 wt%. Results are shown in Table 2.

TABLE 2
Influence on the Diffusion Coefficient of the Filler Concentration in the Resin Matrix and the Acidic Medium

Medium	*Diffusion coefficient, D × 10^{10} ($mm^2\ s^{-1}$)*								
	0%	*Spherical particles*				*Chip-shaped particles*			
		3%	*6%*	*9%*	*12%*	*3%*	*6%*	*9%*	*12%*
H_2SO_4	183	179	169	144	103	189	115	91	42
HCl	141	135	159	189	175	62	45	34	17
HCOOH	1692	1528	1694	1652	1667	894	651	594	398
CH_3COOH	510	568	552	574	690	495	418	372	302
CH_3CH_2COOH	2816	3352	3271	2890	2931	2274	2007	1850	1528

CONCLUSIONS

From the results obtained, the acids used as corrosive components of application media could be arranged into the following order depending on the depth of their penetration into the epoxy resin-based compositions containing various fillers and pigments:

propionic acid > formic acid > acetic acid > sulfuric acid > hydrochloric acid.

This order applies for both pigment series.

Thus, the depth of diffusion does not depend on either the size of the acid molecules or on their dissociation constants. The order observed can be explained by a different mechanism for reaction of the epoxy resin with inorganic acids compared with organic acids. The inorganic acids tested (HCl and H_2SO_4) are strong acids, i.e. they are almost completely dissociated, and their ions are not able to enter the hydrophobic resin so that attack by these acids takes place only in the surface layer. The organic acids (HCOOH, CH_3COOH, and CH_3CH_2COOH) are relatively weak acids and are therefore much less dissociated; they act as solvents, their action resulting in swelling of the resin, and segments of the macromolecular resin chains are separated. The vacant spaces thus formed can be penetrated by further organic acid molecules which are then fixed in the chain by hydrogen bond formation with the secondary and tertiary amino groups of hydroxy groups of the epoxy resin. This process is not necessarily reversible, and free acids remaining in the resin can cause cleavage of the chains, resulting in degradation of the polymer.

With respect to the fillers used, it was found that the nonisometric particles present in an epoxy resin matrix operate quite effectively via the barrier mechanism. A decrease in the penetration of acids into the epoxy resin-based compositions was observed, however, in case of isometric particles. A strong barrier effect was evident, especially with the samples filled with mica chips.

Thus, the diffusion processes are affected not only by chemical reactions between the binder and the diffusing medium, but also by physical aspects of the diffusion process, in which the pigment/filler particle shape plays an important role. Of further relevance to the diffusion of liquids into a pigmented coating system are reactions between the pigment/filler particles and the diffusing medium (which in the investigation reported here was aqueous acid).

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