

Mass Transfer of Phosphorus-Containing Corrosion Inhibitors in Epoxy Protective Coatings

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Abstract—Mass transfer of phosphorus-containing corrosion inhibitors in epoxy matrices, which form the layers of anticorrosion primers and coatings, has been investigated. It has been shown that diffusion profiles of phosphonic acid distribution are stepwise, which has been previously observed in a broad range of mineral and organic acids. Penetration rate constants λ of phosphonic acids are comparable with the values that are intrinsic for inorganic acids. The acid-to-water ratio in internal solution in polymer is higher than in outer diffusant solution upon diffusion of phosphonic acids to amine-hardened epoxy matrices. A selective diffusion of phosphate anions has been observed in the solutions of acidic monosubstituted phosphates.

Keywords: corrosion, anticorrosion coating, inhibitor, phosphonic acid, diffusion profile, selective solubility

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Inhibition is one of the most widespread approaches to the improvement of anticorrosion properties of polymer coatings on metals. Salts and adducts of phosphorus-containing acids, such as phosphoric [1], phosphonic [1], and heteropoly acids [2], are the most effective inhibitors in the case of protective coatings.

Introduction of such active inhibitors in the form of microcapsules with a polymer shell [3], which allows separating inhibitor and reactive groups of polymer basis and avoid adverse effect of inhibitor on curing of matrix and adhesion of the coating to the substrate, is a promising approach. In this case, implementation of the protective action of inhibitors starts from the desorption of the inhibitor from microcapsules [4] by the front of penetrating water. A subsequent transfer of inhibitor to the surface of protected metal occurs through the polymer basis, which is usually amine-hardened in the case of cold-curing epoxy coatings.

There are detailed investigations of mass transfer of acids in such matrices [5, 6]; however, there are no data for most of the phosphorus-containing inhibitors.

It should be noted that all polymers with residual functional groups; in particular, crosslinked epoxy resins containing amino groups possess ion-exchange characteristics to a certain extent. This implies that there are fundamental physicochemical reasons for diverse selective sorption of anions and cations. For this reason, the problems of the composition of internal solution of diffusants of the considered class, in

particular, water-to-electrolyte ratio and selective solubility of anions and cations of salt inhibitors in internal solution in polymer, are also of certain interest.

The aim of this work is to study the principles of mass transfer and solubility of phosphorus-containing corrosion inhibitors and their precursors in epoxy amine-hardened matrices and coatings.

OBJECTS AND METHODS OF STUDY

The objects of study are represented both by model epoxy amine-hardened systems and industrial epoxy anticorrosion materials:

—model epoxy composition represented by 100 wt parts of ED-20 epoxy resin—5 wt parts of SKN-26-1A butadiene-acrylonitrile rubber—10 wt parts of DETA diethylene triamine finally cured at 96°C for 6 h;

—ERMP composition represented by 100 wt parts of ED-20 epoxy resin—5 wt parts of SKN-26-1A butadiene-acrylonitrile rubber—13.5 wt parts of *m*-phenylene diamine finally cured at 120°C for 2 h;

—chemically stable ROKOR-793-TRIO epoxy coating (TU 2257-002-11490792-08) finally cured at 96°C for 6 h.

Oxyethylidenediphosphonic acid (OEDPA, CAS no. 2809-21-4), nitrilotrimethylphosphonic acid (NTP, CAS no. 6419-19-8), and adduct of phosphomolybdic acid with dimethylbenzyl amine and phosphate salts of various degrees of substitution were used as corrosion inhibitors and their precursors.

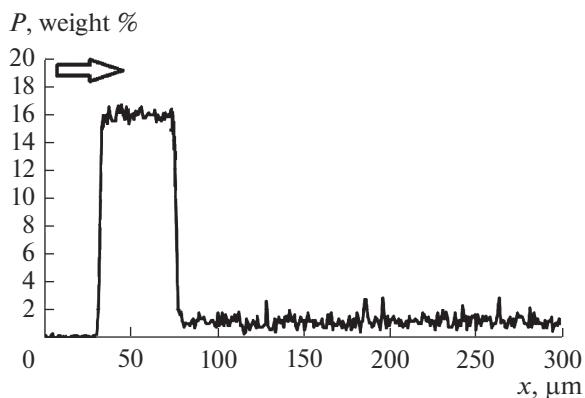


Fig. 1. Concentration profile of phosphorus upon diffusion of 46.8% NTP solution within 6 h at 96°C into model epoxy composition.

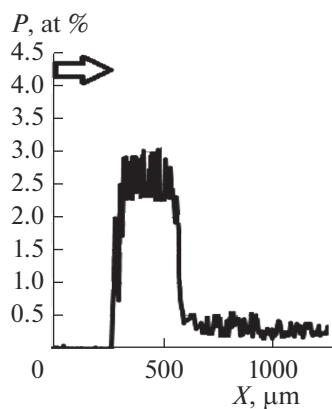


Fig. 2. Concentration profile of phosphorus upon diffusion of 46.8% NTP solution within 168 h at 96°C into ROKOR-793-TRIO coating.

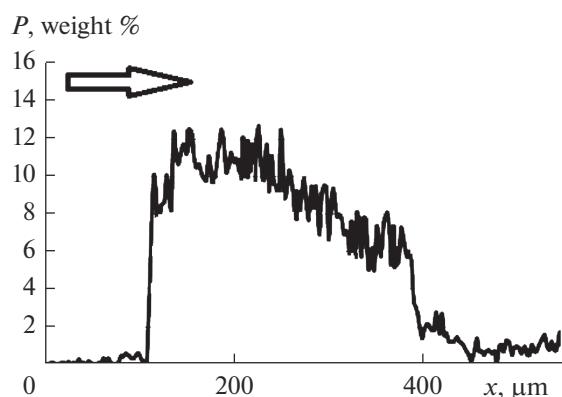


Fig. 3. Concentration profile of phosphorus upon diffusion of 1% OEDPA solution within 168 h at 96°C into ROKOR-793-TRIO coating.

The migration ability and solubility of the inhibitors in epoxy matrix was evaluated according to the concentration profiles of distribution, which were recorded using local X-ray analysis (LXA) [7]. This method provides the concentration distribution of intrinsic elements in inhibitor molecules. This is primarily phosphorus in the substances under study.

The studies were carried out on a JSM-U3 electron microscope equipped with energy-dispersion X-ray spectrometer and a GETAC adapter for digital scanning. GETAC computer program performs ZAF correction for the standardless calculation of the content of elements; LiSi semiconducting detector with hyperfine polymer window with the resolution of 140 eV.

Investigation of the diffusion profiles was carried out both at intermediate stages and at full saturation of the specimen with medium. In the latter case, mean concentration on the area of $10 \times 10 \mu\text{m}$ was also determined.

A transition to the concentration of diffusant was carried out according to the distribution of elements. The electrolyte-to-water ratio in internal solution in polymer can be evaluated according to the values of weight gain at swelling. Gravimetric studies were carried out on Pioneer PA214 analytical scales.

RESULTS AND DISCUSSION

Concentration profiles at diffusion transfer are the initial experimental information, on the basis of which main diffusion and sorption constants can be calculated.

In order to exclude the effect of vitreous state of crosslinked epoxy matrix on the evaluation of the penetration speed of the medium into polymer, the temperature of 96°C was chosen, at which the polymer exists in elastic state and internal stresses are reduced and not critical upon its swelling in medium.

Intrinsic diffusion profiles of phosphorus-containing acids are given in Figs. 1–4. Arrow indicates the direction of diffusion. The penetration speeds λ , $\mu\text{m}/\text{h}^{0.5}$, are given in Table 1.

In the case of the adduct of phosphomolybdic acid (PMA) with two marker elements in anion (Mo, P), the profiles are also stepwise; i.e., diffusion of the whole anion in the polymer matrix is observed.

In this adduct of acid possessing large molecular weight and low solubility (a saturated solution was prepared from 1 g of adduct of PMA in 800 mL of water with adduct precipitate on the bottom), the penetration speed is significantly less than in the case of phosphonic acids and corresponds to $\lambda = 0.5 \mu\text{m}/\text{h}^{0.5}$.

As follows from these data and their comparison with the literature data [8–12], the diffusion profiles of phosphonic acids are stepwise, which is intrinsic for the penetration of acids into the epoxy amine-hardened materials [5, 6].

To characterize the diffusion mobility and perform engineering calculations of the time of penetration, the flow rate of diffusion front $\lambda = X/t^{0.5}$, where X is the penetration depth of the front within the period t , is conventionally used. The results of the calculation of the systems and comparison with the literature data for other mineral and organic acids are given in Table 1.

It is clear that the penetration constants of phosphonic acids (NTP and OEDPA) are comparable with those of both phosphoric acid displaying characteristics of volatile acid at the concentration higher than 60% and the temperature higher than 70°C and other inorganic and organic acids in the high concentration range of solutions and high temperatures.

The data on the kinetics of penetration of the diffusion front provide evaluation of the effective diffusion coefficient D to first approximation, according to known [7] equation $D = X^2/(\pi t)$. One example is that the $D = 6.2 \times 10^{-6} \text{ cm}^2/\text{s}$ upon diffusion of the solution of 48.6% NTP at 96°C to the ROKOR-793-TRIO coating.

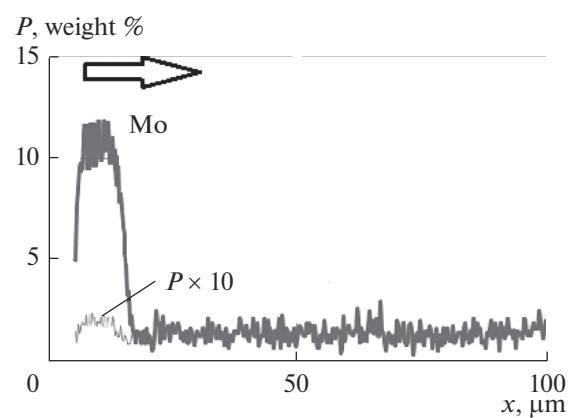


Fig. 4. Profiles of distribution of phosphorus and molybdenum atoms upon diffusion of saturated solution of the adduct of phosphomolybdic acid with dimethylbenzylamine into ED-model at 50°C after 557 days.

For comparison, in the case of hydrophilic polymers, such as poly(vinyl alcohol), the diffusion of phosphoric acid to polymer is characterized by $D = 1.2 \times$

Table 1. Comparison of penetration constants of acids into amine-hardened epoxy compositions

Medium	Polymer	$T, ^\circ\text{C}$	$\lambda, \mu\text{m}/\text{h}^{0.5}$	Reference
46.8% NTP	ED model	96	27	This paper
46.8% NTP	ROKOR-793-TRIO	96	27	
1% OEDPA	ROKOR-793-TRIO	96	22	
20% OEDPA	ED model	96	68	
60% OEDPA	ED model	96	>110	
60% OEDPA	POKOP-5095	96	>34	
Adduct of PMA saturated	ED model	50	0.5	
80% H_3PO_4	ED model	70	32	[5, 6]
70% H_2SO_4	ED model	70	10	
14% HCl	ED model	96	10	
20% HCl	ED model	96	15	
25% HCl	ED model	96	21	
30% HCl	ED model	96	27	
10% H_2SO_4	Bisphenol F	17–30	7.5	[8]
10% H_2SO_4	Novolac	17–30	0.4	
10% H_2SO_4	EP-AM	80	159	[9]
10% H_2SO_4	EP	60	76–75	[10]
10% H_2SO_4	EP	80	105–122	[11]
100% HCOOH	ERMP	70	196	[6]
100% CH_3COOH	ERMP	70	150	
100% CH_3COOH	ERMP	20	75	
0.5 mol/L chloroacetic acid	EP	50	63–74	[12]

Table 2. Calculation of solubility of NTP solutions in the case of chemically stable ROKOR-793-TRIO coating (46.8% NTP solution for 168 h at 96°C)

No.	Parameter	Value
1	Thickness of specimen L , μm	1632
2	Mean penetration depth X , μm	344
3	Relative penetration depth $2X/L$	0.425
4	Relative weight gain $\Delta M/M_0$, wt %	8.7
5	Total solubility of electrolyte $C_{\text{el}} = \Delta M/M_0/(2X/L)$, wt %	20.5
6	Content of NTP acid in diffusion zone C_{NTP} , wt %	14.6
7	Concentration of NTP in internal solution $C_{\text{int}} = C_{\text{NTP}}/C_{\text{el}} \times 100\%$, %	71.2
8	Concentration of NTP in outer solution C_{out} , %	46.8
9	Strengthening of internal NTP solution as compared to outer solution $C_{\text{int}}/C_{\text{out}}$, fold	1.5

$10^{-6} \text{ cm}^2/\text{s}$ ($D = 16.1 \times 10^{-6} \text{ cm}^2/\text{s}$ in aqueous solution) [13].

The diffusion coefficient of phosphoric acid in solution rather than in polymer is $D = 1.3 \times 10^{-6} \text{ cm}^2/\text{s}$ at 25°C and the concentration of 16.0 mol/L, $D = 0.9 \times 10^{-6} \text{ cm}^2/\text{s}$ at 0.36 mol/L, and $D = 10.4 \times 10^{-6} \text{ cm}^2/\text{s}$ at 0.04 mol/L [14].

At the same time, the self-diffusion coefficient of water at 25°C is much higher and corresponds to $D = 2.7 \times 10^{-5} \text{ cm}^2/\text{s}$ [15].

Comparison of the diffusion coefficients of phosphonic and phosphoric acids and water shows that diffusion transfer may occur with a predominant penetration of water, as in the case with other acids.

As follows from the theory of mass transfer, the flow of inhibitor leaving through the polymer layer to the boundary with substrate depends not only on the penetration speed (D), but also on the solubility of inhibitor in polymer basis and the composition (water-to-electrolyte ratio) of the internal solution of the inhibitor in the polymer matrix.

The problem of determination of solubility is one of the variants of the problem of distribution of electrolyte in two contact immiscible phases, such as water

and polymer from physicochemical viewpoint. Investigation of the system in sorption equilibrium state is the conventional method. However, this approach may take a long time under real conditions and real low-permeable protective materials.

Another method for the evaluation of the solubility and composition of the internal penetrating solution could be represented by the previously determined principle [5, 6] in the systems with a stepwise diffusion profile on the presence of a linear relationship of a total weight gain (water + acid) and the relative penetration depth of the front of acid:

$$\Delta M/M_0 = C_w + (C_{\text{el}} - C_w)(2X/L),$$

where $\Delta M/M_0$ is the relative weight gain, which corresponds to the penetration depth of front X ; C_w is the equilibrium solubility of water in polymer; C_{el} is the required total solubility of aqueous solution of electrolyte in polymer; X is the mean penetration depth of the front of electrolyte; and L is the thickness of specimen.

Initial data on the sorption and penetration of NTP and the results of calculation of solubility are given in Table 2.

The composition of the internal OEDPA solution also differs significantly from the composition of the internal solution. It is clear from the data (Fig. 5) that the OEDPA-to-H₂O ratio in the internal solution is higher than that in the outer solution; i.e., strengthening of the internal solution as compared to the outer solution is observed.

Thus, the acid-to-water ratio changes both in the case of OEDPA and NTP during penetration of the solution into the epoxy matrix.

It is known [1] that the salts of phosphorus-containing acids, such as phosphonic and phosphoric acids, possess the largest inhibiting effect.

In the case of salt systems, selective permeability of the anion and cation in the inhibitor molecule are also possible, along with the change of the electrolyte-to-water ratio in the diffusion zone. Features of the diffu-

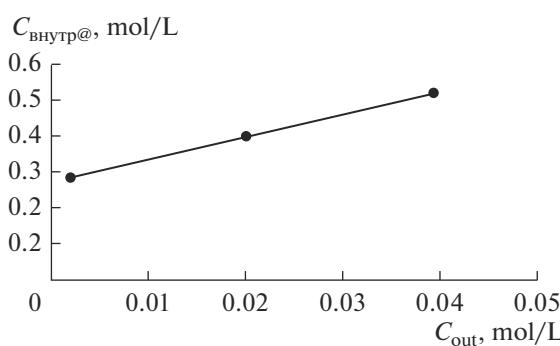


Fig. 5. Concentration of OEDPA solutions in epoxide vs. the concentration of outer solution.

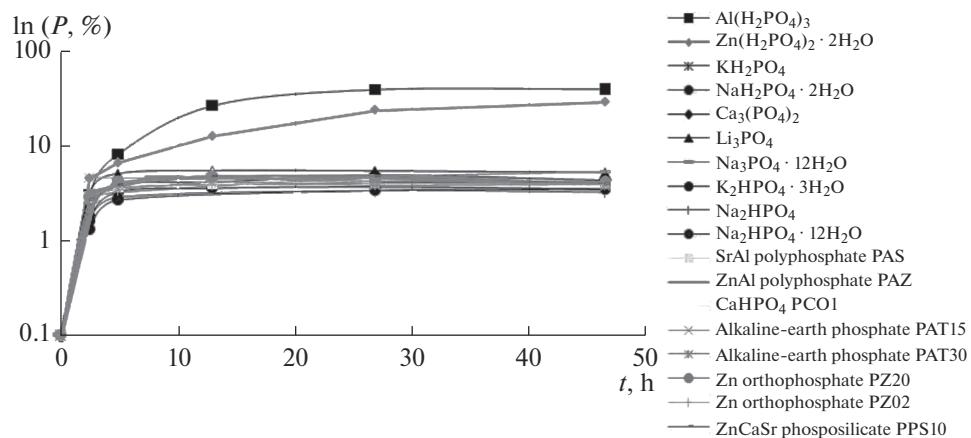


Fig. 6. Variation of weight gain $\ln(P, \%)$ in logarithmic coordinates vs. time ($\sqrt{t}, \text{h}^{0.5}$) of epoxy model in phosphate solutions at 96°C .

sion of salt systems into epoxy polymer matrices were not previously studied.

The ratio between diffusing ions including those in equilibrium is interesting both from the viewpoint of theoretical study of the diffusion of electrolyte solutions into polymers and from the practical viewpoint of the evaluation of the composition of inhibitor permeating to the metal substrate.

In Fig. 6, the kinetics of the weight gain of model epoxy systems in various phosphates are given.

As follows from the data, swelling became stationary after 2160 h at high temperature (96°C) (Figs. 6–8, Table 3).

Analysis of the data (Table 3) shows that partially substituted amphoteric metal (Zn and Al) phosphates, which are of largest interest as effective corrosion inhibitors, possess significantly higher sorption (28–38%) than alkali and alkaline-earth metal phosphates (3–5%) of all degrees of substitution.

Based on LXA data of partially substituted phosphates, such as $\text{Zn}(\text{H}_2\text{PO}_4)_2$, $\text{Al}(\text{H}_2\text{PO}_4)_3$, KH_2PO_4 , and NaH_2PO_4 , the cation-to-anion ratio in internal solution (after full saturation of the specimen) was evaluated and compared to the external solution (from which diffusion occurred).

The profiles of distribution of P, Al, and Zn (Figs. 7, 8) of amphoteric metal phosphates demonstrate full penetration of medium into the polymer at 96°C after 2160 h.

During long-term diffusion experiments of acidic monosubstituted amphoteric metal phosphates possessing high diffusion activity and high sorption, no concentration gradient along the thickness of marker elements in anion and cation is observed. This indicates stationary distribution of the diffusant components along with stabilization of the weight gain and

allows one to calculate the steady-state cation-to-anion ratio in internal solution in a polymer (Table 4).

Analysis of the results states that the ratio between marker elements of anion (P) and cation (Al, Zn, Na,

Table 3. Weight gains of the epoxy model specimens in phosphate solutions under stationary conditions (2160 h, 96°C)

No.	Salt	Weight gain	Form of distribution by phosphorus
1	$\text{Al}(\text{H}_2\text{PO}_4)_3$	38.2	Full penetration
2	$\text{Zn}(\text{H}_2\text{PO}_4)_2$	28.0	Full penetration
3	Na_3PO_4	5.2	
4	Li_3PO_4	5.0	
5	$\text{Zn}_3(\text{PO}_4)_2\text{PZ20}$	4.2	
6	$\text{Ca}_3(\text{PO}_4)_2$	4.2	
7	KH_2PO_4	4.0	
8	NaH_2PO_4	4.0	
9	$\text{CaHPO}_4 \text{PC01}$	3.9	
10	$\text{ZnCaSr @фосфосиликат PPS10}$	3.9	
11	$\text{Zn}_3(\text{PO}_4)_2\text{PZ02}$	3.8	
12	Alkaline-earth phosphate PAT30	3.8	
13	Alkaline-earth phosphate PAT15	3.7	
14	K_2HPO_4	3.4	
15	Na_2HPO_4	3.3	

Table 4. Variation of concentration of metal cation relative to phosphate anion upon diffusion of salts from saturated solution to epoxy polymer coatings after 2160 h at 96°C (up to P_∞)

Diffusant	Out, mol/L	Coating	Weight gain P_∞ , %	Me-to-P ratio in internal solution in polymer as compared to outer solution (salt)
Zn(H_2PO_4) ₂	1.00	P-5095	13.7	0.130
Al(H_2PO_4) ₃	1.23	P-5095	16.3	0.052
Al(H_2PO_4) ₃	1.23	P-793	11.4	0.035
Al(H_2PO_4) ₃	1.23	ED model	38.2	0.012
KH ₂ PO ₄	0.64	ED model	4.0	0.014
NaH ₂ PO ₄	0.46	ED model	4.0	0.080

and K) of diffusants in internal and outer solutions during diffusion of salt inhibitors differs significantly

and the internal diffusant solution in a polymer is significantly depleted by Al, Zn, Na, and K cations (by

1–2 orders) as compared to the outer solution, from which diffusion occurred.

It can be suggested that “token diffusion,” which retains electroneutrality of internal and outer solutions, is a possible mechanism of such separation of ions.

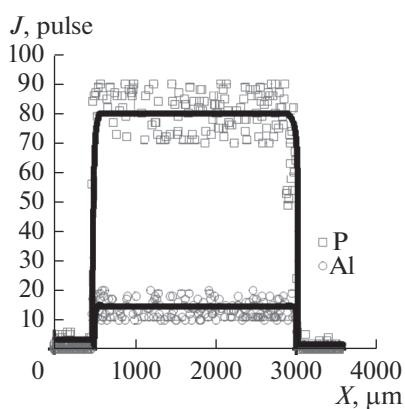


Fig. 7. Profiles of distribution of P and Al. Phosphate $Al(H_2PO_4)_3$ diffuses into the ROKOR-793-TRIO polymer at 96°C within 2160 h.

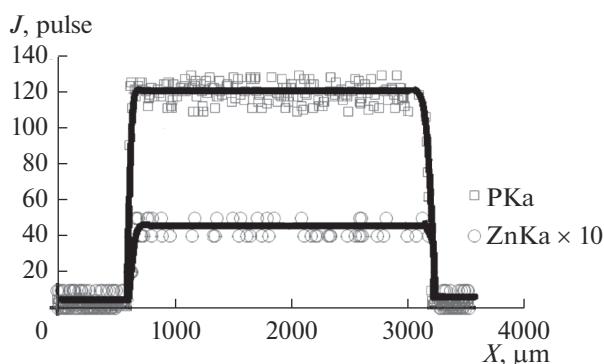


Fig. 8. Profiles of distribution of P and Zn. Phosphate $Zn(H_2PO_4)_2$ diffuses into the model epoxy polymer at 96°C within 2160 h.

CONCLUSIONS

1. Break/stepwise profiles have been detected during the investigation of the diffusion of phosphonic precursors of corrosion inhibitors into amine-hardened epoxides, which have been previously observed in a broad range of mineral and organic acids. The penetration rate constants λ of phosphonic acids are comparable to the values in inorganic acids.

2. During diffusion of phosphonic acids into amine-hardened epoxy matrices, internal solutions strengthen and the acid-to-water ratio in internal solution (in polymer) is higher than in the outer diffusant solution.

3. A selective solubility of cations and anions of the solutions of acidic monosubstituted phosphates has been detected; a predominant diffusion of phosphate anions has been observed.

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SPELL: 1. diffusant