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A study on the desorption of phosphonic acids, corrosion inhibitor precursors, from polymer microcapsules

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Abstract

Salts of phosphonic acids are known as efficient corrosion inhibitors in anticorrosive coatings. Incorporation of phosphonates in microscopic capsules into a coating makes it possible to initiate desorption from capsules and diffusion of the inhibitor to the substrate "on demand". The desorption kinetics of phosphonic acids at the initial stage of contact of a capsule with a water flow and until establishment of a stable inhibitor flux has been studied. The diffusion coefficients of the acid extracted from capsules have been estimated. The efficiency of granulation and extraction processes for building microcapsule walls resistant to water and organic solvents has been shown.

Key words: *coating, microcapsule, inhibitor, phosphonic acid, desorption, diffusion, corrosion.*

Salts and adducts of phosphorus-containing acids, including phosphonic ones, are known as efficient corrosion inhibitors [1], including those used in anticorrosive polymer coatings based on chemically resistant epoxide materials [2].

Incorporation of phosphonates into polymer matrices in microscopic capsules ($D \leq 60 \ \mu m$) [3] is a promising technique. Microencapsulation allows one to insulate active components from reactive groups of the epoxy resin and the curing agent at the curing stage, correctly build the coating's polymeric body, and avoid the adverse effect of the inhibitor on the coating adhesion to the substrate to be protected. Ideally, extraction of an inhibitor from microcapsules should begin "upon request", *i.e.*, after establishment of corrosive conditions, for example, at the stage of water diffusion transfer through a coating.

Epoxides are optimum compounds not only for building the matrix of the coating itself but also for the shell of the inhibitor-containing microcapsules since they can be cured both by amines and by acids or acid anhydrides, including phosphonic acids [4].

These classes of curing agents make it possible to obtain cross-linked products that differ in the diffusion characteristics of electrolyte transfer.

Curing by amines produces a matrix characterized by a stepped/abrupt diffusion profile for both mineral and organic acids (HCl, H_2SO_4, H_3PO_4, CH_3COOH, HCOOH). It has been shown that the formation of a stepped profile is due to the presence and number of acid binding sites in the polymer matrix [5, 6]. It is also important to note from the practical point of view that the stepped profile is characterized by the lack of breakthrough of the diffusing acid before the diffusion front.

Curing by acids/anhydrides gives a polymer network containing no binding centers for diffusing acids. In fact, in case of acid-forming anhydrides (phthalic, maleic and succinic), a much lower acid sorption level was found, along with a near-Fickian diffusion profile [5, 6] and Fickian kinetics of diffusant escape. Thus, it can be expected that by varying the type of curing agent, microcapsule shells with various diffusion properties can be obtained from an epoxy resin.

The purpose of this work was to estimate the desorption parameters of corrosion inhibitors from microcapsules when exposed to aqueous media in order to build a model of protective action of inhibited polymer coatings. The main emphasis was on studying the specific features of diffusion transfer of corrosion inhibitor prototypes, namely, phosphonic acids (NTP, nitrilotrimethylphosphonic acid, CAS no. 6419-19-8, and HEDP, hydroxy-ethylidenediphosphonic acid, CAS no. 2809-21-4) eluted from film samples or through microcapsule walls into water.

The subjects of these study included films and microcapsules containing the phosphonic acids mentioned above, both in bound and excessive amounts.

The amount of bound acid M_a, g per 100 g of the resin, was calculated by formula (1)

$$M_a = (M_{pa} \cdot n / M_{er} \cdot N) \cdot 100 \tag{1}$$

where:

M_{pa} is the acid molecular mass,

M_{er} is the molecular mass of the epoxy resin (assumed to be 430 for ED-20 resin),

n is the number of epoxy groups (assumed to be 2 for ED-20 resin),

N is the basicity of phosphonic acids.

Taking into consideration the recommendations [7, 8] on effective basicity of acids ($N_{HEDP} = 4$ and $N_{NTP} = 5$), the following stoichiometric ratios were obtained for curing the ED-20 diane resin ($M_{er} = 430$, $n = 2$): 24 m.p. HEDP and 29 m.p. NTP per 100 m.p. ED-20.

The results of studies on the kinetics and curing completeness show that formulations containing lass than 60% of the stoichiometric amount are cured very slowly and incompletely; synthesis of solid polymers with epoxide curing by HEDP and NTP is possible in the range from 60 to 160% of the stoichiometric amount.

Technique of desorption studies

Weighed portions of films or microcapsules were placed in a glass extraction cell filled with distilled water. After stirring and settling for 2.5 hours, the resulting solution was decanted into an electrode cell, while a new portion of distilled water was added to the filtered-off microcapsule powder. The amount of desorbed phosphonic acid (PA) was determined from the change in the solution pH. The measuring tools included an I-60 MI ionomer for pH measurements and a Pioneer PA214 analytical balance with 0.0001 g accuracy (OHAUS Corp., USA).

The fraction of the acid eluted from the total amount contained in a weighed portion of granules, $M_{port.}$, was calculated by formula (2)

$$P(\%) = (\Sigma[H^+] \cdot M_m \cdot V)/(M_{port} \cdot M_{pa}/M_{er} \cdot N) \cdot 100 \qquad (2)$$

where:

$\Sigma[H+]$ is the concentration accumulated at the current measurement time,

M_m is the molecular mass of the acid,

M_{pa} is the mass of the acid added to the epoxy resin (*n*, g),

M_{er} is the mass of the epoxy resin (100 h),

N is the acid basicity (4 for HEDP, 5 for NTP).

Electron probe X-ray microanalysis [9] was performed on a JSM-U3 scanning microscope (Jeol, Japan) equipped with an energy dispersive X-ray spectrometer (EDS) and a digital scanning unit (GETAC, Germany). GETAC software makes it possible to use ZAF correction for standardless calculation of the content of elements in a sample being studied.

Polarization microscopy was performed on a POLAR 3 microscope (Altami company, Russia) with PL 5X/0.12 and PL L 10X/0.25 lenses. The image was recorded with a FL3-U3-88S2C-C camcorder (Point Grey Research Inc., Canada). The images were processed with Altami Studio software (Altami company, Russia).

Results and Discussion

Study on the structure of epoxy resin/phosphonic acid composites

Microscopic studies of films have shown that in systems with an excess of acids, crystals of phosphonic acids are formed and distributed in the bulk of the epoxy resin. The composition and detailed structure of hardened compounds with phosphonic acids in the polymer films obtained were studied by electron probe X-ray microanalysis.

Figure 1 shows the surfaces of butt-end chips of a polymer film containing 35 m.p. NTP per 100 m.p. ED-20, or 120% of the stoichiometric amount.
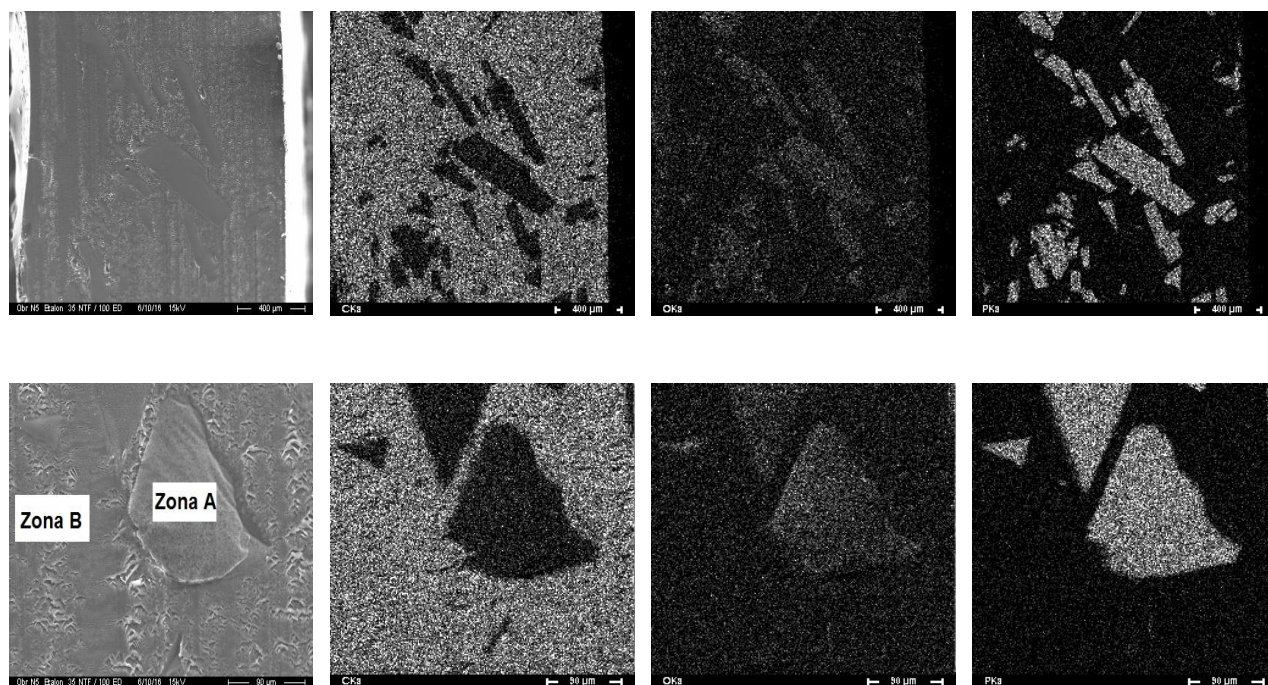
Figure 1. Electron microscopic images of a chip on a surface of 35NTP/100ED film on 400 and 90 μm scales, including that for X-ray radiation of *K*α lines of carbon C, oxygen O, and phosphorus P. The accelerating voltage was 15 keV. The diameter of the studied area was *ca*. 3 μm.

The cleaved surface (Figure 1) contains inclusions 3–600 μm in size and with various shapes, which are deficient in carbon C (dark C*K*α areas), whereas oxygen O (low-contrast O*K*α areas) and phosphorus (luminous P*K*α areas) are in excess.
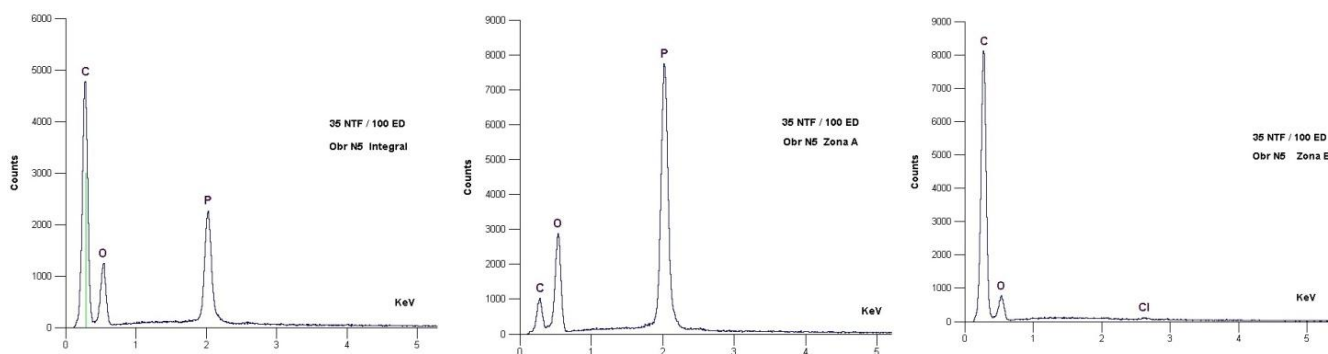

Figure 2. Element spectra recorded integrally on the entire surface of the sample chip and selectively in the zones (Figure 1): Zone A ("acid") and Zone B ("resin").

The combination of the element ratio C/O = 77.1/22.5 in zone B (Figure 2), the chlorine content of 0.35 mass%, and the complete absence of phosphorus allow us to state that the microprobe detected a domain of pure epoxy resin in zone B.

The phosphorus content in zone A (Figure 2) is *ca*. 36.0 mass%, which indicates a point where nearly pure NTP acid is present.

Thus, the polymer film studied contains inclusions of NTP crystals distributed in a matrix of epoxy resin cured by the acid. The matrix also contains micro zones of nearly pure epoxy resin, which allows easy isolation of granules from the film. The cores of the isolated microgranules contain micro volumes of pure NTP in a shell of epoxy resin cured by the same acid.

Two techniques to isolate microencapsulated phosphonic acids were used in the study, namely, extraction and granulation. The resulting microencapsulated precursors of corrosion inhibitors are powders whose dispersivity is determined by that of the starting acid powder and by the isolation method. Subsequent experiments were performed using powders with a mean particle size of *ca*. 60 μm.

The results of polarized-light microscopic studies on the dissolution of the contents of microcapsules placed in water are presented below.
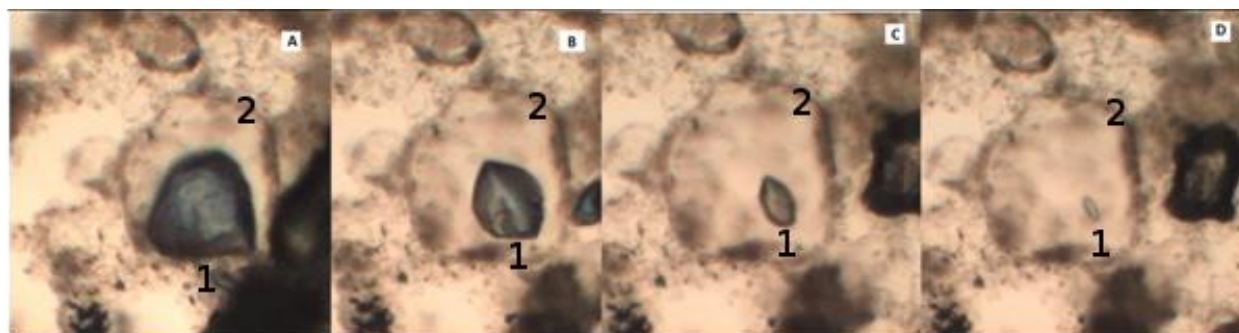

Figure 3. Screenshots in polarized light of the process (from left to right) of dissolution in water of the contents of a NTP-containing microcapsule obtained by the extraction method. 1 – NTP crystals; 2 – microcapsule shell.

As one can see, the microcapsule shell retains its initial dimensions and continuity even if the microcapsule contents (NTP) is completely dissolved in water. It has also been shown in the course of testing that the NTP-containing microcapsules obtained by the extraction technology are stable in the presence of typical organic solvents used in paint formulations.

Figure 4 shows the comparative kinetics of desorption of phosphonic acids into water from films and microgranules obtained from formulations with various acid amounts.
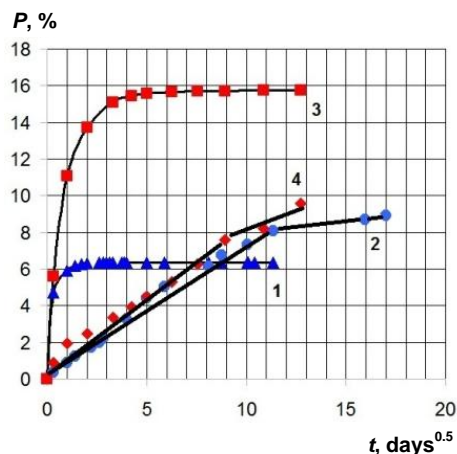
Figure 4. Kinetic plots of desorption of phosphonic acids into water from a powder and films of cured ED-20 epoxy resin in $P \sim t^{0.5}$ coordinates. 1, HEDP powder; 2, HEDP film; 3, NTP powder; 4, NTP film.

Films

As one can see from the data presented in Figure 4, the desorption kinetics of phosphonic acids from film samples (2, 4) is linear in Fickian coordinates (mass gain – square root of time), $P(\%) - t^{0.5}$ (day$^{0.5}$).

The difference in the slopes of straight lines 2 and 4, which amount to 0.5820 (R^2 = 0.9908) and 0.7666 (R^2 = 0.9833), respectively, indicates that the nature of the acid and its content affect the rate of acid migration in the polymer matrix and its long-term removal from the protective coating film.

In the very initial region (at $t^{0.5} \sim 0.1$) there is an abrupt change in the pH and acid concentration in the solution. The P value for curves 2 and 4 amounts to 0.2% and 0.6%, respectively.

Thus, two important regularities of phosphonic acid leaching from films can be stated:
1. Acid desorption is observed if its content in the matrix is below the stoichiometric value, which means that the acid is not completely bound in the reaction with the epoxy resin; in this case, about 6 mol. parts of the acid out of 19 mol. parts initially added to the formulation is desorbed.
2. The leaching rates, which are estimated by the slopes for HEDP and NTP in the linear region, are similar.

Granules

Unlike the film samples, desorption from small granules (curves 1, 3) with a mean size of 60 μm is characterized by a one-and-half orders higher abrupt increase in concentration, *i.e.*, to 6–16%.

To determine the concentration dependence of the desorption properties in the resin/acid systems (Figure 5), we studied microgranule samples with the acid (NTP/HEDP) content varied in both directions from the stoichiometric amounts.
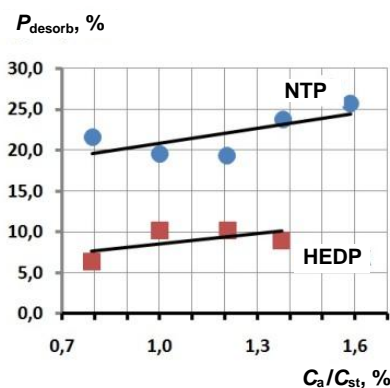
Figure 5. Dependence of desorption amount *P*, % of a phosphonic acid on its content C_a/C_{st} in an epoxy polymer at 96°C.

Analysis of the concentration dependences of the desorption of phosphonic acids around the stoichiometric ratio shows that desorption increases as the acid content in the polymer increases. The desorption amount ranges within 5–10% for HEDP/ED formulations and 20–25% for NTP/ED formulations. Thus, desorption of NTP is much higher than that of HEDP in a broad concentration range of the acid/resin ratio (from −20% to +60% with respect to stoichiometry).
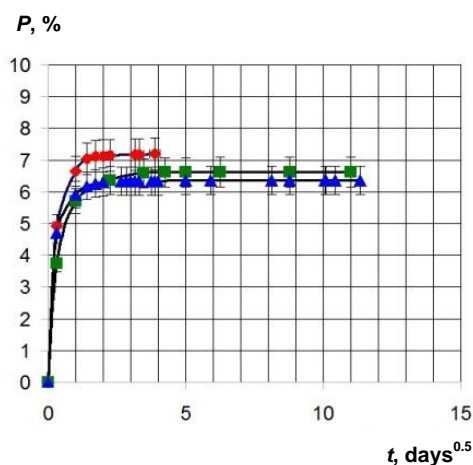

Figure 6. Reproducibility of the kinetics (*t*, day$^{0.5}$) of the HEDP fraction (*P*, %) desorbed from a powder (relative error 7%).

The curves in Figure 6 demonstrate a satisfactory reproducibility of results, for HEDP in particular, among different series of desorption experiments performed at different times with microgranules newly obtained from newly prepared resin/acid polymer formulations.

The stability of desorption results allows us to state that the granulation method for the preparation of encapsulated inhibitors is suitable for industrial production and application.

Estimation of the diffusion coefficient during desorption

The diffusion coefficients of HEDP and NTP from films and microgranules can be calculated from the initial stage of the desorption kinetic curve at $\gamma = M_t/M_\infty < 0.6$ [9].

In this region of the desorption curve in $\gamma \sim \sqrt{t}$ coordinates, the desorption equation (3) has a known form for film samples [9]:

$$\gamma = 4\sqrt{\pi} \cdot \sqrt{(DT/L^2)}, \tag{3}$$

and the diffusion coefficient is calculated by formula (4), where $G = d\gamma/d(\sqrt{t})$.

$$D = \pi/16 \cdot G^2 \cdot L^2 \tag{4}$$

For cylindrical granules (at $h \gg R$, where h is the cylinder height and R is its radius), the formula for the diffusion coefficient does not change (4a),

$$D = \pi/16 \cdot G^2 \cdot L^2, \tag{4a}$$

while for a spherical granule, formula (2) takes the form (5).

$$D = \pi/36 \cdot G \cdot R^2 \tag{5}$$

The calculated diffusion coefficients are shown in Table 1.

Table 1. Diffusion coefficients of NTP and HEDP during desorption of the acids into water at +22°C from polymer samples shaped as microgranules ($d_{av.} = 60$ μm) and films, as calculated from the initial desorption stage ($\gamma < 0.6$).

| no. | Sample | Diffusion coefficient D, $10^8 \cdot cm^2$/s | | |
| | | Film | Microcapsule shape | |
			cylinder	sphere
1	Film with HEDP	2.00	–	–
2	Microcapsules with HEDP	–	1.65	0.73
3	Film with NTP	10.50	–	–
4	Microcapsules with NTP	–	2.57	1.14

The effective diffusion coefficients for HEDP granules, both in cylindrical and spherical approximation, are somewhat lower $(0.73–1.65) \cdot 10^{-8}$ cm^2/s) than the D value for the film. The effective diffusion coefficient for NTP granules, $(1.14–2.57) \cdot 10^{-8}$ cm^2/s, is also lower than that for the corresponding film $(10.5 \cdot 10^{-8}$ cm^2/s). The diffusion mobility values can be used in initial engineering evaluations of the extraction of acids from microcapsules in the course of coating development.

Conclusions

1. The principal possibility of microencapsulation of phosphonic acids using the technology for epoxide oligomer curing on crystal surfaces has been demonstrated.
2. The shells of the resulting microcapsules ensure efficient extraction of an acid with water from the microgranules into the polymer coating matrix. The extractable acid fraction is up to 10% for HEDP/ED formulations and up to 25% for NTP/ED formulations.
3. The microcapsules are resistant to the action of water at 96°C and to the action of typical organic solvents at ordinary temperatures.
4. The diffusion characteristics of the transfer of phosphonic acids have been determined. The permeability of HEDP-containing capsules ($D = (0.73–1.65) \cdot 10^{-8}$ cm^2/s) is somewhat lower than that of NTP-containing capsules (D = $(1.14–2.57) \cdot 10^{-8}$ cm^2/s).
5. The reproducibility of results for different series of desorption experiments allows us to state that the methods for the preparation of encapsulated inhibitors are suitable for industrial production and application.

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