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INVESTIGATION OF MOISTURE TRANSFER THROUGH POLYMER FILMS UNDER THE ACTION OF AN ELECTRIC FIELD

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On the basis of the Nernst–Planck equation, the coefficient of the moisture transfer through sealing polymeter films as a function of the potential difference for a homogeneous electric field is obtained. The equation for engineering calculations of moisture transfer through pressurizing film coatings of dissimilar thicknesses in dc and ac industrial-frequency electric fields is proposed.

Improvement of service reliability for the elements of radioelectronic (REE) and electrical (EE) equipment calls for the search for promising new materials that, while in use, could protect them from the action of external factors, the environmental humidity φ affecting most strongly a variation in the set of element properties [1, 2].

The trend in the theory of reliability is to represent the service reliability of equipment as a set of the longevity and durability of individual elements [3]. Therefore, it is not only of theoretical interest but also of practical interest to search for new sealing materials, capable of improving stability for the elements of the equipment under the action of increased environmental humidity [4, 5]. From economic and structural considerations, these materials are organic polymer dielectrics. However, they should be used strictly selectively, with allowance made for the structure and composition, swelling under the action of moisture, and manifestation of a number of anomalous phenomena in the presence of force and temperature fields [6-8]. Furthermore, allowance made for the moisture transfer through the sealing polymer films in the region of electric fields (EFs) produced by operating elements of REE and EE is practically ignored. Depending on the shape of the sealed elements, these fields can be both homogeneous (HEFs) and inhomogeneous (IEFs). Consequently, moisture transfer between the vapor-air environment, whose φ can often approach unity, and a sealed volume with lowered humidity or between two volumes with dissimilar φ occurs in REE and EE through a polymer film under conditions of the superposition of varied EFs. However, this fact is absolutely ignored in calculations of moisture-transfer properties of organic polymer films used in REE and EE [7, 8].

At the same time, structural defects have been shown to be always abundant even in optically smooth polyethylene (PE) and polytetrafluoroethylene (PTFE) surfaces produced under special conditions [9, 10]. Therefore, even when $\varphi \geq 0.8$, on the polymer-material surface, there is a Kelvin moisture condensation [9], in addition to the water of polymolecular adsorption [1]. For polar hydrophilic polymers, this phenomenon occurs for lower φ, while for nonpolar hydrophobic polymers it occurs for high φ.

As $\varphi \to 1$ the hydrophilic surface is covered with a continuous wetting macroscopic water film, while on the hydrophobic dielectric surface, isolated spherical aggregates appear.

If the air contains gases (for example, ammonia) that, being dissolved in water, produce ions or if in (or on) the surface dielecric layer, there are water-soluble ionic impurities (which is inevitably realized under the industrial conditions of dielectric production, or they are introduced in the processes of manufacturing, transportation, and storage of products as well as in using them) on the surface, then an electrolyte forms, and surface conduction increases by 5-10 orders of magnitude [1-5]. Diffusing thereafter over structural defects that are due to the technological conditions of the production and use of polymer material, the individual molecules of water and their associates, including hydrated ions, increase by several orders of magnitude the specific conductance γ of the dielectric material [1-5]. In the final analysis, this must have an effect on the moisture transfer

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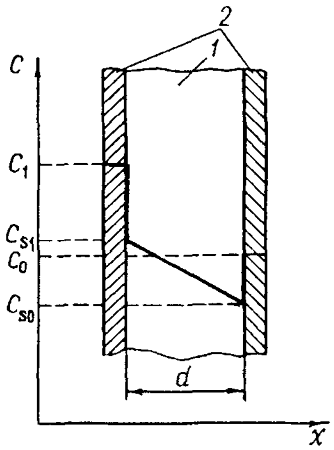

Fig. 1. Change in ionic concentration in a polymer film on two sides of which dissimilar air humidities are maintained (schematically): 1) polymer film; 2) electrolytic solution. The remaining notations are in the text.

through the polymer film since the character of motion for the hydrated ions of both signs is altered due to the action of the force f = qE.

With allowance made for the proposed mechanism of formations, let us determine the density of the diffusion flux j_i of ions of the ith kind through a polymer film of thickness d that separates the volumes in REE (or EE) with different φ when the concentrations of ions in water films on opposing material surfaces are equal to C_1 and C_0 (Fig. 1). Let the concentration of these ions in the polymer film itself change linearly from the exterior surface toward the interior surface respectively from C_{s1} to C_{s0}. Then

$$\frac{dC}{dx} = \frac{C_{s1} - C_{s0}}{d}. \tag{1}$$

Substituting (1) into the Fick law, we obtain

$$j_i = -D_i \frac{C_{s1} - C_{s0}}{d}. \tag{2}$$

It is easier in practice to determine the ionic concentrations beyond the polymer film in boundary water films (C_1 and C_0) rather than within the polymer film (C_{s1} and C_{s0}). It is assumed that

$$\frac{C_{s1}}{C_{s0}} = \frac{C_1}{C_0}, \tag{3}$$

from which

$$\frac{C_{s1}}{C_1} = \frac{C_{s0}}{C_0} = k_i. \tag{4}$$

From (4), it follows that

$$C_{s1} = k_i C_1\,; \quad C_{s0} = k_i C_0. \tag{5}$$

Substituting (5) into (2), we have

$$j_i = -\frac{D_i k_i}{d}(C_1 - C_0) = \beta_i (C_1 - C_0). \tag{6}$$

It turned out that Eq. (6) is applicable to the diffusion of neutral water molecules from a vapor-air or water medium through a polymer film [11, 12]. When D_i is insignificant (a small free volume ΔV of the polymer) we need to choose a film of very small thickness d so that a sufficient magnitude of j_i could be obtained.

In the general case, the transfer of ions through a polymer film is governed by two factors: their distribution nonuniformity, i.e., the concentration gradient, and the action of an EF. Then, according to the Nernst–Planck equation, we have

$$j_j = -D_i\left(\frac{dC_i}{dx} + \frac{zFC_i}{RT}\frac{d\varphi}{dx}\right). \tag{7}$$

With allowance made for the fact that $E = -d\varphi/dx$, we find

$$j_i = -D_i\left(\frac{dC_i}{dx} + \frac{zFC_i}{RT}E\right). \tag{8}$$

If the flux density j_i is assumed to be constant and the EF in the polymer film is homogeneous, i.e.,

$$\frac{d\varphi}{dx} = \frac{\varphi_s}{d}, \tag{9}$$

we obtain

$$\frac{zFC_i}{RT}\frac{d\varphi}{dx} = \frac{zFC_i}{RT}\frac{\varphi_s}{d} = \frac{\psi}{d}C_i, \tag{10}$$

where

$$\psi = \frac{zF}{RT}\varphi_s, \tag{11}$$

is the dimensionless potential. In view of (11), the Nernst–Planck equation has the form

$$j_i = -D\left(\frac{dC_i}{dx} + \frac{\psi}{d}C_i\right). \tag{12}$$

Having divided the variables and having integrated the equation

$$dx = \frac{dC_i}{j_i/D_i + \psi C_i/d}, \tag{13}$$

we have

$$\psi = \ln\frac{j_i/D_i + \psi C_{s1}/d}{j_i/D_i + \psi C_{s0}/d}. \tag{14}$$

Taking the antilog of (14), we find

$$\exp\psi = \frac{j_i/D_i + \psi C_{s1}/d}{j_i/D_i + \psi C_{s0}/d}. \tag{15}$$

from which

$$\frac{j_i}{D_i}(\exp\psi - 1) = \frac{\psi}{d}(C_{s1} - (\exp\psi)\,C_{s0});$$

$$j_i = \frac{D_i\psi}{d((\exp\psi) - 1)}(C_{s1} - (\exp\psi)\,C_{s0}). \tag{16}$$

We rearrange formula (16), allowing for expressions (4) and (6):

$$j_i = \frac{D_i \psi k_i}{d\,((\exp\psi) - 1)}\,(C_1 - (\exp\psi)\,C_0) = \beta_{ie.f}\,(C_1 - (\exp\psi)\,C_0)\,. \tag{17}$$

Relation (17) holds both for positive ($z > 0, \psi > 0$) and negative ($z < 0, \psi < 0$) ions.

Let us analyze partial cases of Eq. (17):

(a) $\psi = 0$, which signifies either $z = 0$ (neutral particles, for example, water molecules), or the absence of an EF in the polymer film ($\varphi_{\mathrm{film}} = 0$), or both of them combined:

$$\lim_{\psi\to 0} j_i = \frac{D_i k_i}{d} \lim_{\psi\to 0} \frac{\psi}{(\exp\psi) - 1} \lim_{\psi\to 0} (C_1 - C_0 \exp\psi)\,. \tag{18}$$

With

$$\lim_{\psi\to 0} \frac{\exp\psi}{(\exp\psi) - 1} = \lim_{\psi\to 0} \frac{1}{\exp\psi} = 1\,, \quad \lim_{\psi\to 0} (C_1 - C_0 \exp\psi) = C_1 - C_0 \tag{19}$$

allowed for, we obtain Eq. (6).

(b) The same ionic concentration on opposing surfaces of the film ($C_1 = C_0 = C$). In the presence of an EF,

$$j_i = -\beta_{ie.f}\,C\,. \tag{20}$$

This corresponds to the electrical conductivity in electrolytes. For neutral particles ($z = 0$ and $\psi = 0$), $j_i = 0$.

(c) If the film is impermeable to particles ($\beta = 0$), it is natural that the flux density is zero.

Thus, the hydrated ions that diffuse through the polymer-material film, except for the last case, must produce additional moisture flux. To calculate it, let us assume that the hydration number for ions of this kind (the number of water molecules that form a hydrated ionic shell) is n_{iw}. Then, in the absence of an EF, from (6) we have

$$j_{iw} = \beta_i \frac{m_i}{m_w} n_{iw}\, m_w\, n_1 - n_0 = \beta_i \frac{m_i}{m_w} (n_{iw}\, m_w\, n_1 - n_{iw}\, m_w\, n_0) = \beta_{iw}\,(C_{1w} - C_{0w})\,. \tag{21}$$

In the presence of an HEF, from (17) we obtain

$$j_{iw}^{e.f} = \beta_{iw}^{e.f}\,(C_{1w} - C_{0w} \exp\psi)\,, \tag{22}$$

where

$$\beta_{iw}^{e.f} = \frac{D_i \psi k_i m_i}{d\,((\exp\psi) - 1)\,m_w} \tag{23}$$

is the moisture-transfer coefficient due to the diffusion of hydrated ions of the ith kind in an EF for $D = \mathrm{const}$.

Thus, provided that there is additivity, the overall coefficient of moisture transfer $\beta_{e.f}$ in an HEF with allowance made for all the hydrated ions will be

$$\beta_{e.f} = \beta_w + \Sigma\,\beta_{iw} + \Sigma\,\beta_{iw}^{e.f} = \beta_w + \beta_w' + \beta_w^{e.f} = \beta_0 + \beta_w^{e.f}\,. \tag{24}$$

Then the total density of the moisture flux through the polymer film that is in the HEF will be determined as

$$j_{e.f} = \beta_{e.f}\,(C_1' - C_0')\,, \tag{25}$$

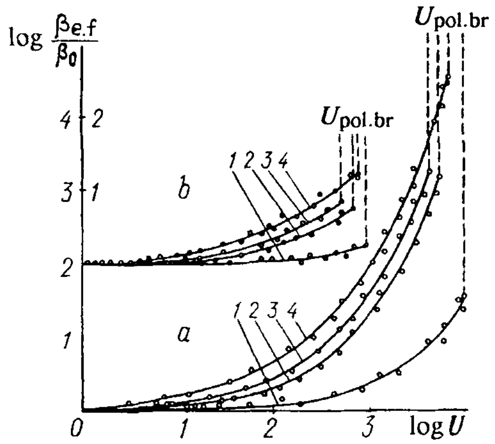

Fig. 2. Logarithm of the moisture-transfer coefficient ratios $\beta_{e.f}/\beta_0$ vs. the logarithm of the voltage U of an external EF for polymer films in a dc HEF (a) and in an ac HEF (b): 1) PTFCE; 2) PE; 3) PVC; 4) PS.

where C_1' and C_0' are the current moisture concentrations on the opposing surfaces of the film in the HEF. To calculate β_0 and $\beta_{e.f}$, let us resort to the basic relation of mass-transfer theory [11, 12]:

$$\beta_0 = \frac{D}{d}. \tag{26}$$

Accordingly

$$\beta_{e.f} = \frac{D_{e.f}}{d}, \tag{27}$$

where D and $D_{e.f}$ are the overall coefficient of moisture diffusion in a polymer film of thickness d without the field and in an HEF.

As investigation specimens, we chose the typical representatives of flexible-chain polymers that are most frequently used for the purposes of REE and EE insulation and sealing: polytrifluorochloroethylene (PTFCE) – fluoroplastic-3, polyethylene (PE) – 15802-02, polyvinyl chloride (PVC) – C-65, and polystyrene (PS) – UPM-07039. The specimens were prepared as films in a $T-p$ regime [13].

To calculate $\beta_{e.f}$, we adopted the sorption method [1], realized in a thermostated sorption balance [14]. However, instead of a tubular capacitor, use was made of a flat capacitor with Rogowski disk perforated electrodes (for penetration of water molecules), between which a polymer film was placed. The number and sizes of holes were such that they did not disturb EF homogeneity. To avoid edge effects, the film diameter was somewhat larger than the electrode diameter. The quantity $\beta_{e.f}$ was calculated from formula (27), according to [1], as

$$\beta_{e.f} = \frac{d}{\pi^2} \frac{\Delta \ln (N_\infty - N)}{\Delta \tau}. \tag{28}$$

The determination error for $\beta_{e.f}$, with the Henry law being obeyed for different specimens and magnitudes of U, was 10–20%.

Since the magnitudes of β_0, obtained for the films with $d_0 = 2 \cdot 10^{-5}$ m in the absence of EF, differ by several orders of magnitude (PTFCE – $3.6 \cdot 10^{-8}$ m/sec, PE – $9.1 \cdot 10^{-7}$ m/sec, PVC – $1.7 \cdot 10^{-5}$ m/sec, and PS – $4.3 \cdot 10^{-5}$ m/sec, which, on the average, agrees with the data of [11, 12] in order of magnitudes), the results of the experiments are presented as $\beta_{e.f}/\beta_0(U)$ (Fig. 2), where U is the voltage between capacitor plates. In this case, we assumed that $\varphi_{film} \approx U$. As the position of the curves shows, there is a difference between these dependences in dc and ac HEFs ($\nu = 50$ Hz).

In a dc EF (Fig. 2a), even in the region of low voltages ($10^{-2} < U < 10^{-3}\nu$), the $\beta_{e.f}$ of the films increases by several percent. As U increases to $U_{air\ br}$ (the voltage that corresponds to the air breakdown) $\beta_{e.f}$ changes nonlinearly. Weakly polar amorphous PS, characterized by significant porosity, has the highest rate of growth; the values of $\beta_{e.f}$ for a nonpolar PTFCE polymer with an abundant crystalline phase increase the most slowly. The quantities $\beta_{e.f}$ for PVC and PE have intermediate values. The increase in moisture transfer varies from several percents for PTFCE to hundreds of percents for PS. Then, in a moderate interval ($140 < U < 6\cdot 10^3$ V), a very intense $\beta_{e.f}$ increase of 2-3 orders of magnitude is observed for PS, PVC, and PE while, for PTFCE, this index is no larger than one order of magnitude.

In the voltage region $6\cdot 10^3 < U < U_{pol.br}$ for PS, PVC, and PE, $\beta_{e.f}$ increases by an order of magnitude more. When breakdown voltages $U_{pol.br}$ that are characteristic of each polymer are attained, $\beta_{e.f}$ increases stepwise to the values inherent in macroporous materials.

In an ac EF (Fig. 2b), up to $U_{pol.br}$, the $\beta_{e.f}/\beta_0$ ratio differs insignificantly from 1 for all the specimens. This is due to the electrolytic material transfer being absent in the ac EF. The hydrate ions execute only oscillatory motions in fluctuation hollows of the polymers. A pronounced $\beta_{e.f}$ increase for PS and PVC in a prebreakdown region of U values derives from the weak unipolar electrical conduction in these polymers. The moisture transfer for PTFCE increases to the smallest degree as in the case of a dc EF.

The rapid increase in $\beta_{e.f}$ for high U ($U_{air\ br} < U < U_{pol.br}$), especially in the dc EF, is due to the generation of numerous ions at the expense of barrier and partial discharges as well as polymer destruction [15, 16].

For $U_{pol.br}$, in the polymer films numerous transverse pores and holes with sizes of tens to hundreds of micrometers form, clearly visible under the microscope in polarized light. Therefore, the moisture transfer increases stepwise and becomes the same as in coarsely divided systems.

By the experiments with polymer films of dissimilar thicknesses $d > d_0$ it was established that, for engineering calculations of the moisture transfer through sealing film coatings in a dc HEF, we can resort to the formula

$$\beta_{e.f} = 3.322\,\frac{D}{d}\,(\exp 5\cdot 10^{-4}\, n_w \psi)\left(1 - \frac{U_{polar}}{U}\right)\log\left(\frac{d}{d_0} + 1\right), \tag{29}$$

where D is the diffusion coefficient for water molecules, which is independent of d and is calculated in the absence of EF; U_{polar} is the potential difference of high-voltage polarization determined experimentally according to Quittner and Beran [17]. The factor $1 - U_{polar}/U$ changes with U in an intricate manner but, on the average, its magnitude can be taken to be 0.5.

In the case of an ac EF, relation (29) has the form

$$\beta_{e.f} = 3.322\,\frac{D}{d}\,(\exp 5\cdot 10^{-4}\, n_w \psi)^{1/2}\log\left(\frac{d}{d_0} + 1\right), \tag{30}$$

which yields that, in relation (30) as compared to (29), the factor $1 - U_{polar}/U$ is absent since, in this case, there is practically no high-voltage polarization of the specimen; the exponent in (30) decreases, too.

The magnitudes of D for the majority of polymer materials can be taken from reference or scientific literature, for example, [1, 3-5, 18]. From our experiments,it follows that n_w has the following values: for PTFCE – 0.1; PE – 0.2; PVC – 0.3; PS – 0.8.

The results obtained show that under the action of an EF, there is an increase in $\beta_{e.f}$ as compared to β_0 of several percent to several orders of magnitude, which is not allowed for in moisture-transfer equations, depending on the type of polymer material. This should be taken into account when we choose the encapsulating shell for the elements of REE and EE with the aim of extending their operating time and improving efficiency.

NOTATION

φ, relative humidity of the ambient medium; E, electric-field strength; j_i, diffusion-flux density; d, film thickness; C, ionic concentration; k_i, coefficient of ionic distribution between the polymer film and the ambient medium; β_i, mass- (or ionic) transfer coefficient; D_i, diffusion coefficient; z, ionic charge number; $d\varphi$, potential difference on the film thickness dx; R, universal gas constant; T, temperature; F, Faraday number; φ_{film}, potential difference on the film; n_{iw}, hydration number of the ions of this kind; m_i, ionic mass; m_{w}, mass of a water molecule; $\beta_{iw} = \beta_i m_i / m_{\mathrm{w}}$, moisture-transfer coefficient due to diffusion of hydrated ions of the ith kind; $C_{1w} - C_{0w}$, additional difference of moisture concentrations on opposing polymer-film surfaces caused by ionic hydration; N_∞, film weight, established as a result of saturation, as $\tau \to \infty$; N, film weight at instant τ; n_{w}, hydration number, averaged over all kinds of ions. Subscripts: i, kind of ion, flux, and component; 1, 0, water films on opposing material surfaces; s1, s0, opposing surfaces of the material itself; e.f, in electric field; w, water; iw, hydrated ion; air br, air breakdown; pol.br, polymer breadown; polar, polarization.

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