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### CHANGE OF PROPERTIES AND STRUCTURE OF FILMS DERIVED FROM POWDER PAINTS IN THE PROCESS OF ARTIFICIAL CLIMATIC AGING

The combined effect of artificial climatic factors (ultraviolet irradiation, moisture, temperature) on mechanical properties and surface structure of polymer films derived from powder paints is studied in this article. Methods and equipment for researches are also described. The effect of chemical structure of the film-forming material and hardening agent on the spatial grid structure that defines mechanical properties of the film and their change under climatic factors is reviewed.

**Introduction.** Coatings of powder paints instead of liquid organic paint and varnish materials are increasingly used in modern engineering and construction industry. Motivating factors of application powder paints are: high performance of coatings, wasteless technology (the return of waste in the production cycle), reducing environmental load due to the lack of organic solvents, increasing the productivity of the process of obtaining coatings, etc. A long-term preservation of the integrity of protective coatings that are regularly exposed to adverse weather factors is important for machinery parts and architectural constructions. Nowadays, the most widely used are powder coatings based on the following film formers: epoxy resins, epoxy-polyether oligomer (a combination of epoxy and polyether resins) – hybrid film formers, unsaturated polyether resins [1]. The last decade changes in favor of polyether paints take place at the global market of powder paints, because there is a sharp rise in prices for epoxy resin, and thus, on epoxy and hybrid powder compositions. It is also assumed that the polyether coatings are more weatherproof than epoxy and epoxy-polyether ones, so they are more preferred. Polyether powder coatings contain in their compositions one of the two hardeners, cross-linking oligomer macromolecules with the formation of spatial grid structure.

One of them – triglycidyl (TGIC), which was sufficiently applied for a long period of time, and was recognized in recent years as a harmful agent.

The other, which replaced him – hydroxyalkylamides, is considered to be harmless and known under the trade name "Primidi". Thus, the study of coatings of polyether powder paints cured with TGIC and Primidi in comparison with coatings of hybrid powder compositions is an important task.

**The experimental procedure and the analysis of test results.** The aim of this work – the study of the joint effect of artificial climatic factors (UV radiation, moisture, temperature) on the mechanical properties and structure of the surface of the polymer films of polyether powder paints, cured with Primidi and TGIC, and also hybrid powder coatings.

The objects of study are the films of thickness 0.3-0.4 mm, width of  $(10 \pm 2)$  mm and 100 mm in length, obtained from powder paint samples:

- 1, 2, 3, 4 – polyether, hardener Primidi, the colors red, white, green, black, respectively;
- 5, 6 – polyether, TGIC cure, green, black, respectively;
- 7, 8 – hybrid, the color blue and black, respectively.

The films were obtained on fluoroplastic sheet, with minimal adhesion that enables to separate the films from the substrate edge with a blade. The powder coating was applied through a sieve. To assess the durability, accelerated environmental testings were conducted in accordance with State Standard (GOST) 9.401 (Method 3) simulating service conditions in a moderately cold climate.

Tests were carried out in a climatic test chamber «Feutron» type 3826/16 (Germany) by the following cycle:

- moistening the samples at  $(40 \pm 2)$  °C and a relative humidity of  $(97 \pm 3)\%$  for 2 hours;
- moistening without heating at a relative humidity of  $(97 \pm 3)\%$  C. for 2 hours;
- freezing at minus  $(30 \pm 3)$  °C for 6 h;
- sample irradiation to create a light beam with a surface density of the energy integral radiation  $(730 + 140)$  W/m<sup>2</sup> at the surface density of flow of ultraviolet radiation  $(30 + 5)$  W/m<sup>2</sup> with periodic irrigation with water for 3 minutes every 17 minutes for 5 hours;
- freezing at minus  $(60 \pm 3)$  °C for 3 h;
- aging at 15–30°C and a relative humidity of 80% for 6 hours.

Sampling was carried out in 25, 50, 75, 100 cycles.

The porosity of the films was determined by the values of their specific surface area, calculated by the BET (Brunauer, Emmett, Teller). Nitrogen adsorption isotherms were recorded on the device NOVA 2200. Gaseous nitrogen with an operating temperature of 77 K was obtained by evaporation of liquid nitrogen. The measurement error did not exceed 10% of the surface area values.

Mechanical tests were carried out on modern tensile machine T 2020 DC 10 SH (Alpha Technologies UK, USA).

Air temperature – 18°C, the velocity of the upper grip – 10 mm/min, the sample clamping length – 54 mm, number of specimens in the sample – 10.

Tensile strength  $\sigma$  (MPa), elongation  $\varepsilon$  (%), Young's modulus ( $E$ , MPa) as the arithmetic average of ten measurements were calculated by the diagram "tensile stress  $\sigma$  (MPa) – tensile strain  $\varepsilon$  (%)" using a computer program device.

The results of mechanical tests of films before their being exposed to the man-made climate factors are presented in Fig. 1.

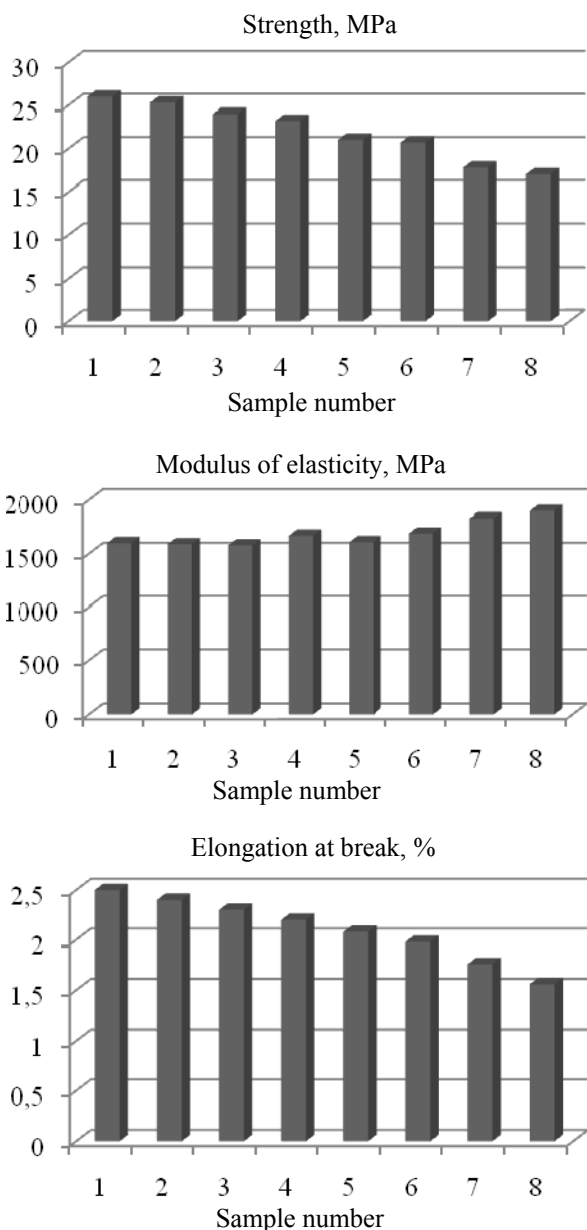


Fig. 1. Strain-strength and elastic properties of films of powder paints

Analysis of the data shows that stronger and more elastic films are formed of polyether paints, especially cured with Primidi. The strength of

samples 1-4 in the average is 24.6 MPa, while the strength of samples 7, 8 – only 17.4 MPa. Elongation at break – 2.35 and 1.66%, respectively. The modulus of elasticity is 1610 MPa and 1865.

Thus, films of polyester of powder paints are stronger than films of hybrid powder compositions by 41%, more elastic – by 42%. The modulus of elasticity of polyether films 16% lower as compared with the hybrid ones, gives the grounds to assert that in the coatings of polyether powder paints smaller internal stresses will develop because of their greater relaxation in the easier deformable film. In turn, small internal stresses in the film provide a greater longevity of the film (the service life of coatings without losing their protective properties).

Comparing polyether powder containing different hardeners, one may notice that Primidi is more preferred than TGIC. The films cured with Primidi are stronger than films cured with TGIC on average by 14%, their elasticity – by 16%. This is due to differences in molecular structure of Primidi and TGIC.

Chemical crosslinking reaction of oligomer molecules of unsaturated polyether with molecules of Primidi proceeds more slowly, requires more time and temperature. However, it forms a more homogeneous, strong and elastic polymer grid.

As a result, the strength and the elongation at break are higher and the modulus of elasticity is lower for the films cured with Primidi. Coating of polyether powder compositions containing Primidi objectively should be more durable than coatings cured with TGIC, due to the development smaller internal stresses in them.

Since films of powder paints are chemically cross-linked mesh structures, mechanical destruction is of fragile nature.

For each sample, there is a ratio:

$$\sigma = K \cdot E \cdot \varepsilon,$$

where  $K = 0,0066-0,0063$  for samples 1-4;  $0,0062-0,0063$  for samples 5, 6 and  $0,0057-0,0055$  for samples 7, 8.

In spatially-linked or cross-linked polymers relationship between molecular weight of the segment between the grid nodes and the molecular weight of the kinetic segment has great influence on their mechanical properties [2].

If  $M_{kc} \ll M_c$  (kinetic chain and flexible grid is quite rare), the change in frequency of the grid has almost no effect on either of high-elasticity deformation, or the glass transition temperature of the polymer. If  $M_c > M_{kc}$ , increasing the frequency of the grid (decrease  $M_c$ ) reduces the deformation of rubbery and increasing the glass transition temperature [2].

At very high frequency of spatial grid highly elastic deformation is impossible and the material at room temperature is in the glassy state. A

change in strength and an increase in the frequency of the grid is expressed as a rule by a curve with a maximum. A small number of cross-links does not complicate straightening of chains during deformation, which leads to an increase in strength. However, the increase in frequency which is more than the optimal prevents orientation processes at a stretching of films, and their strength begins to decline the more than the greater the frequency of the formed spatial grid.

According to the DSC data (Fig. 2), non-adherent films obtained from polyether film former cured with Primidi ( $T_{ct}$  sample N 2 at 62°C) have a lower glass transition temperature. In the curing of the same film former with TGIC, glass transition temperature rises to 6°C (sample N 5 and 6 in Fig. 3).

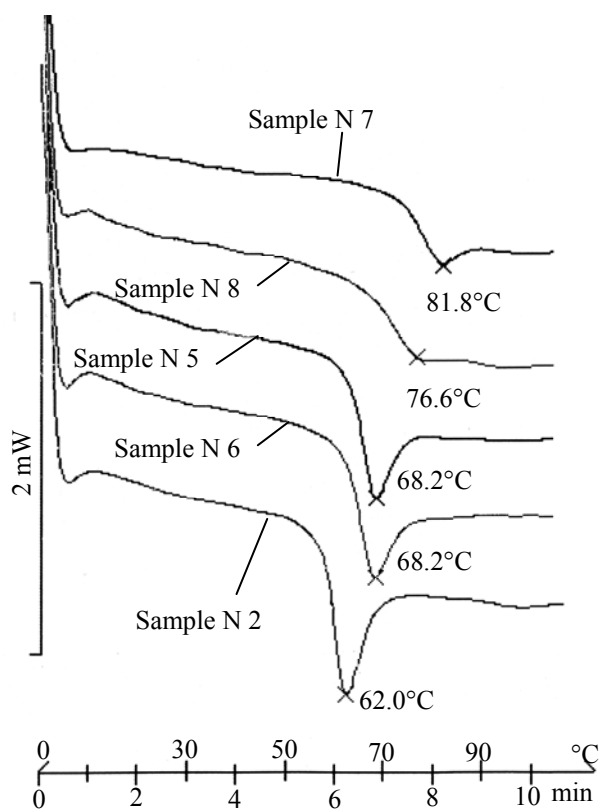


Fig. 2. DSK films from powder paints

Finally film samples N 7 and 8, obtained from hybrid film former (a combination of epoxy and polyether resins) are characterized by the highest glass transition temperature (77–82°C). Thus, there is logical interrelation between the indexes of glass transition temperatures and strength, elasticity modulus, breaking elongation.

Surface morphology of the film (the film surface in contact with air, and not with the fluoroplastic substrate to eliminate the influence of the substrate was used for the study) were examined using a scanning electron microscope JSM 5610LV (Jed, Japan). is a logical relationship between the values of the glass transition tempera-

tures and the strength, modulus of elasticity, relative elongation at break.

Primidi (sample N 1, 4) is smooth, homogeneous.

Meshwork was formed without significant internal stresses. Surface films of polyether powder paint cured with

The surface of the paint films from the hybrid (sample N 7) is relief, formed under conditions of high internal stresses.

Electron microscopic images (Fig. 3) indicate the different character of the film surface, as well as the size and shape of the pigment particles.

Films of polyether powder compositions containing TIGTS by their character is closer to the films of the polyether oligomer cured with Primidi.

When exposed to weather conditions in the climatic chamber, the stiffness of the spatial grid varies little, so the modulus of elasticity varies within a few percent (up to 10%). However, due to heat, UV radiation, moisture, sections of macromolecules between the grid nodes are broken and the deformability is reduced. At practically linear increase of tension in the film at its stretching and lower relative elongation at break, lower strength is realized. Therefore, with increasing a number of cycles acting on the film, the strength and the elongation decrease. Dependencies of strength and elongation at break on the exposure time have a similar S-shaped character (Fig. 4).

Since the kinetics of radical reactions in solid polymers is highly dependent on the degree of crosslinking of the macromolecules and mechanical stress on their chemical bonds [4] investigated films differ in the rate of aging.

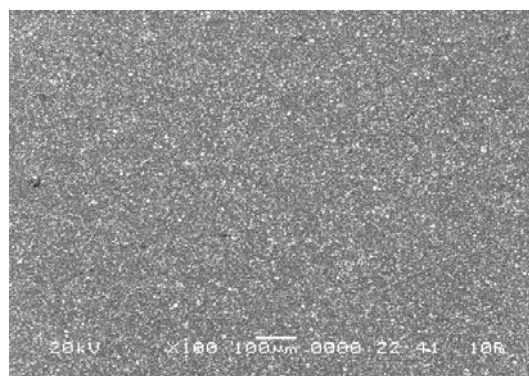
Thus, the films obtained from polyether resins containing Primidi (samples N 1–4) retain 65% of the original strength and 72% elongation at break after exposure to 100 cycles in the climate chamber.

These changes for the films of polyethers cured with TGIC make 60 and 70%, respectively, and for the hybrid films of epoxy polyether resin – 50 and 67%.

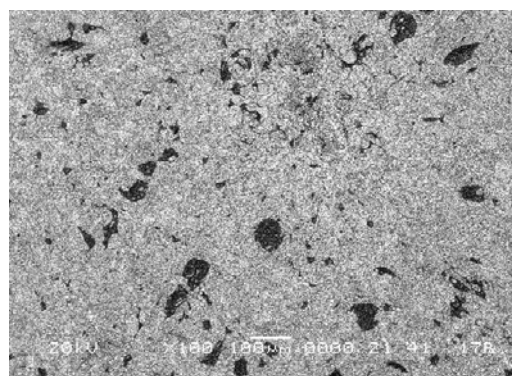
The data obtained by us for the films of powder coatings correspond to the assumption of the kinetic theory of strength [5], according to which the life of a rigid body, including the polymer decreases with increasing mechanical stress  $\sigma$ , acting on the chemical carbon-carbon bonds in the main chain of macromolecules. Degradation rate increases, and longevity of films decreases exponentially:

$$\tau = \tau_0 \exp (U_0 - \gamma \cdot \sigma / R \cdot T),$$

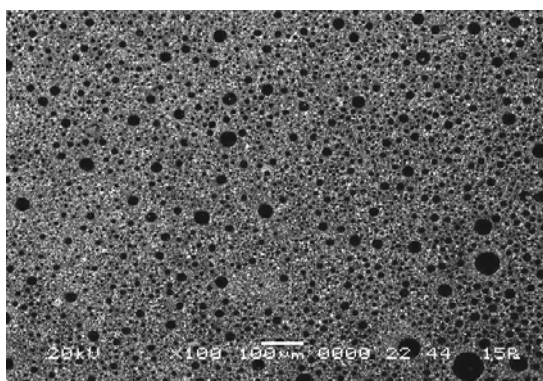
where  $\tau_0$  – the period of oscillation of carbon atoms bound chemically, a constant equal to 10–13 s;  $U_0$  – a potential barrier of break of a chemical bond;  $\gamma$  – structure-sensitive factor;  $\sigma$  – internal stress in the polymer material;  $T$  – temperature, K;  $R$  – the universal gas constant.



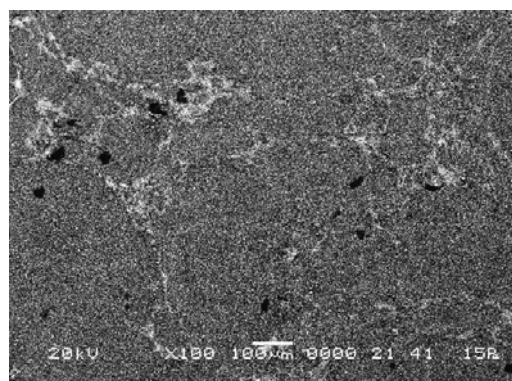
Sample N 1



Sample N 6

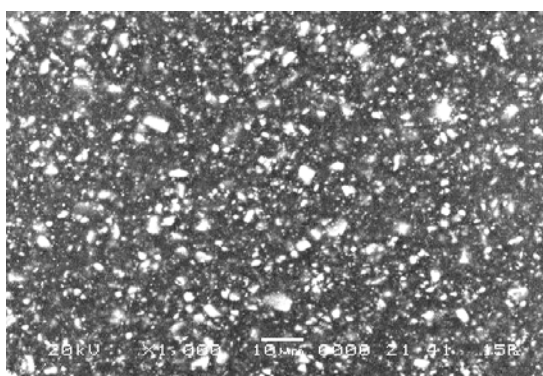


Sample N 4

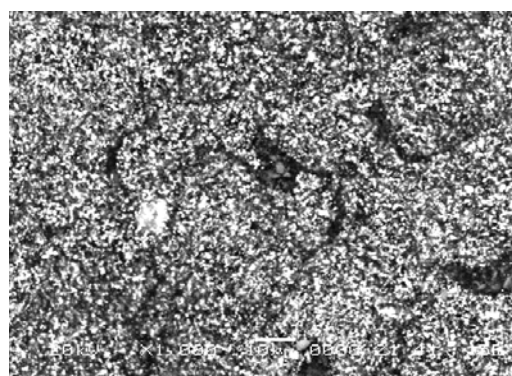


Sample N 7

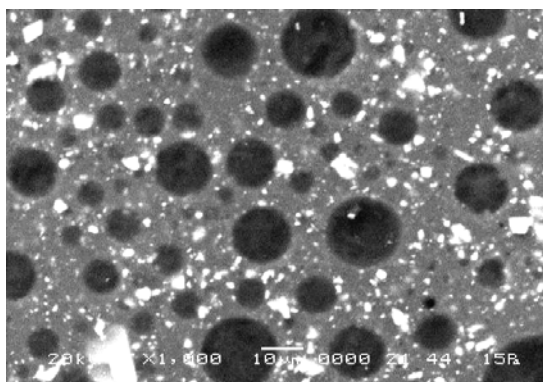
*a*



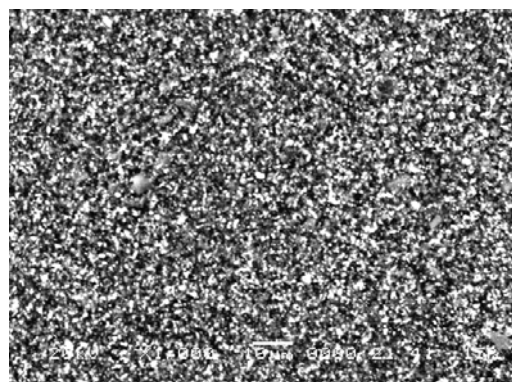
Sample N 1



Sample N 6



Sample N 4



Sample N 7

*b*

Fig. 3. Electron microscopic pictures of polymer films:  
*a* – 100 times increased; *b* – 1000 times increased

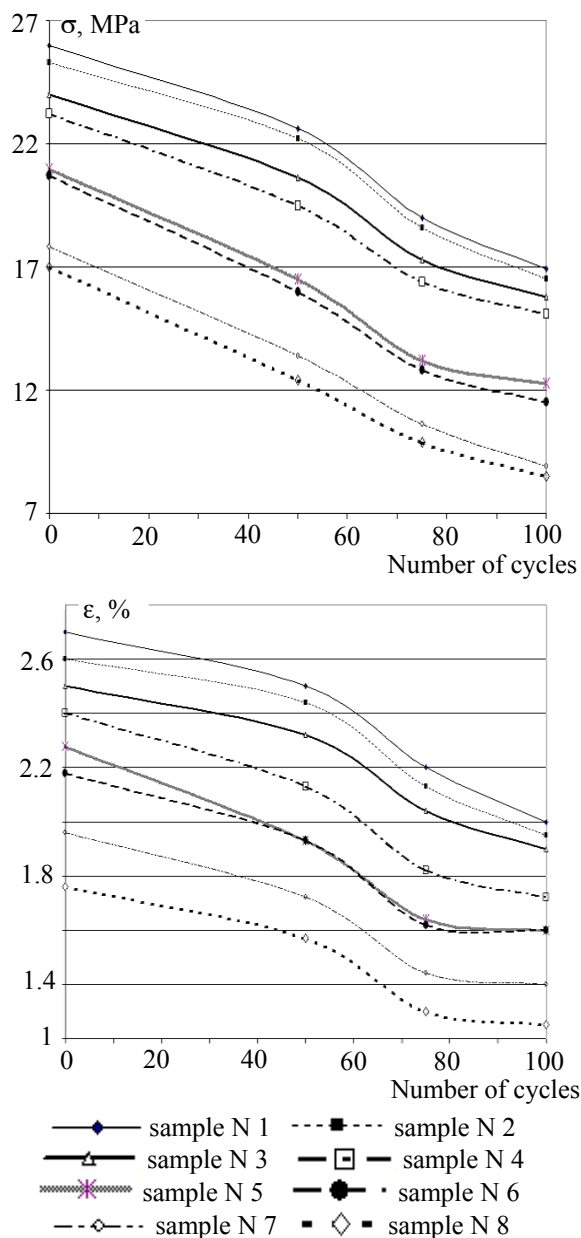


Fig. 4. Dependencies of strength properties of the films on the exposure time in a climatic chamber

When tested in the climate chamber polymer films were periodically subject to 100% hydration. Liquid media acting on composite materials play an important role in reducing the strength and deformation characteristics of the composite materials [6].

Crosslinking reaction of oligomer molecules of polyether binder being cured with Primidi is carried out by the chemical interaction of end carboxyl groups of resin molecules with hydroxyl groups of the hardener (see Fig. 5, *a*).

In this case, complex ether bonds are formed and water releases, which at large thicknesses of films can produce defects in the form of punctures. However, this negative effect can be minimized by using degassing additives in a powder coating

composition, as well as by choosing the optimal time-temperature conditions of coatings formation.

The evaluation of films porosity by the BET method performed by us showed that it is almost independent of the chemical nature of the used hardener. The values of the specific surface of film samples N 1–6 ranged from 10 to 11 m<sup>2</sup>/g, i. e., within the measurement error. Therefore, we can assume that the porosity has the same effect on all the samples of the films when tested. The differences in the mechanical properties and weather resistance of films of polyester powder paints are due to the different nature of a chemical cross-link in the spatial grid, i.e., the differences in the chemical structure of molecules of a hardener.

At the same time the molecular structure of Primidi (aliphatic structure of the molecule basis) provides relatively flexible, movable cross-links of the spatial grid of the cured film and, consequently, good mechanical properties and high weather resistance. In the curing of the same powder polyether paint with TGIC, carboxyl groups interact with three curing epoxy groups (see Fig. 5, *b*).

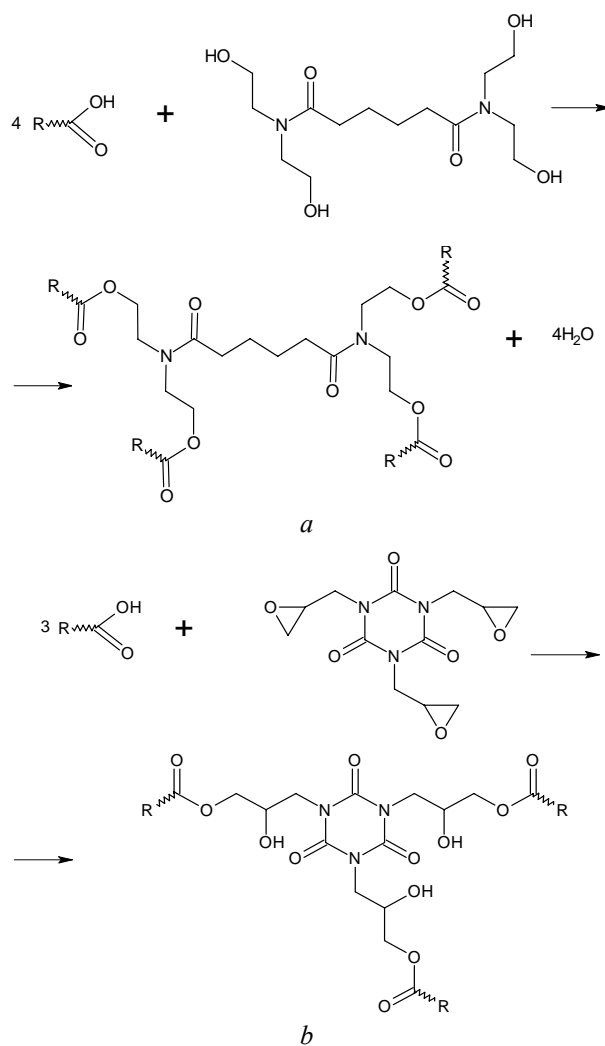


Fig. 5. Polyether resin curing scheme Primidi (*a*) and TGIC (*b*)

As a result, the individual molecules of polyether are sewn in the spatial grid without releasing a volatile low molecular weight compound. The increased reactivity of epoxy groups TGIC provides a quick and easy cross-linking at lower temperatures and the cure time of coatings.

However, the cyclic structure of TGIC causes high stiffness of cross-links in the grid, the internal stress in which relaxes slowly. As a result, a complex of mechanical properties of the films and their weathering becomes worse.

**Conclusion.** The investigations showed that the most promising compositions of powder paints are compositions on the basis of polyether film former containing Primidi as a hardener. These paints, compared with others, form films which are stronger and more elastic, slowly collapsing under the influence of climatic factors. The structure of the film surface is smooth, homogeneous, indicating the absence of significant internal stresses in it.

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