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1965

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

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STUDY OF THE DURABILITY OF POLYMER COATINGS AS A FUNCTION OF THE CONDITIONS OF FORMATION AND AGING

(Presented by Academician V. A. Kargin, September 30, 1964)

In work ([1]) it was shown that there is a linear relationship between the adhesion durability of polymer coatings and the internal stresses arising during their formation and aging, as well as during the destruction of free films ([2]). This regularity was used as a criterion for evaluating the durability of the adhesive strength of polymer coatings on various substrates ([3]). It turned out that the relation $\tau = Ae^{-\alpha\sigma}$ is valid not only for the destruction

Fig. 1. Dependence of coating durability on the reciprocal temperature of formation. Left—under irradiation with PRK-2; at different stages of aging: **1**—9 points, **2**—8, **3**—7, **4**—6, **5**—5. Right—in an aqueous medium. **1**—8 points, **2**—6, **3**—4, **4**—2, **5**—1

of films under the action of an external load at different temperatures, but also during the aging of polymer coatings under other conditions (irradiation, aggressive medium), as well as under the combined action of these aging factors under atmospheric conditions and when testing materials by accelerated methods (tropical cycle, GIPI-4 cycle).

It has been shown by many researchers ([4]) that the durability of polymer materials, metals, and alloys depends linearly on the temperature of destruction. In the present work it was found that the dependence of durability on the formation temperature of polymer coatings also obeys the relation $\tau = Ae^{u/RT}$ during aging of coatings under various conditions. The coatings were formed from a modified alkyd resin at temperatures from 20 to 180° on glass and metal substrates.

Aging of the specimens was carried out under the separate action of temperature, radiation from a PRK-2 mercury-quartz lamp, moisture, as well as under atmospheric conditions and according to GIPI-4 cycles.

Figure 2

Figure 2: Figure 2

The durability of coatings during the aging process was assessed by impact strength; the degree of destruction was determined according to the ten-point system adopted in the paint-and-varnish industry.

Figure 1a presents data on the dependence of coating durability on the reciprocal formation temperature, obtained during aging under ultraviolet irradiation from a mercury-quartz lamp. It is seen that as the formation temperature increases, the service life of the coatings decreases. The straight lines obtained at different stages of the aging process intersect at one point at $\tau_0 = 10^{3.35}$. The destruction energy calculated from these data varies within the range from 3 to 10 kcal/mole, depending on the aging time.

An analogous arrangement of the straight lines is observed during thermal aging of coatings at 180°. This direction of the straight lines is associated with the fact that, as the formation temperature rises, significant internal stresses arise in the coatings. Aging of coatings under irradiation or at a temperature higher than the formation temperature is accompanied by a further increase in internal stresses.

Fig. 2. Change in internal stresses during thermal aging of coatings formed at the following temperatures:
1—180°, 2—130°, 3—80°.

Figure 2 presents data on the change in internal stresses during thermal aging of alkyd coatings at 180°, formed at different temperatures. It is seen that coatings formed at 180° are destroyed most rapidly. During aging of coatings formed at temperatures below 180°, a nonmonotonic increase in internal stresses occurs. During the first 300 hours of aging the internal stresses increase, and then slowly relax; at the same time, coatings formed at 130° withstand stresses 1.5 times greater than those formed at 180°. Such a sharp increase in internal stresses under these aging conditions is associated with a decrease in nonequilibrium and further structuring of the alkyd coatings ([5]).

A different dependence of durability on formation temperature is observed during aging in an aqueous medium or in a humidity chamber (Fig. 1b). Under these conditions, as the formation temperature increases, the service life of the coatings increases sharply:

Figure 3

Figure 3: Figure 3

Formation temperature, °C	20	60	80	100	130	150	180
Vapor permeability, mg/cm^2 · day	40	29	23	20	14	10	4

As these data show, coatings cured at a lower temperature ($< 130^{\circ}$) contain a larger number of unsaturated double bonds ([5]), which accounts for the higher value of their vapor and water permeability. Alkyd coatings formed at low temperature lose adhesive strength more rapidly under the action of moisture.

It is also of interest to investigate the influence of formation temperature on coating durability under the combined action of various aging factors under atmospheric conditions, and also in accelerated tests according to the tropical cycle. As can be seen from Fig. 3, the arrangement of the straight lines under atmospheric aging conditions is analogous to that observed during ultraviolet irradiation of coatings. In tests according to the tropical cycle, the dependence $\tau = f(1/T)$ is analogous to aging in an aqueous medium.

It follows from the data presented that the aging conditions do not affect the character of the dependence $\tau = f(1/T)$: regardless of these conditions

for all cases τ_0 proved to be equal to $10^{3.35}$, while the energy of fracture at different stages of the aging process was from 3 to 10 kcal/mole. The conditions of fracture have a significant influence on the direction of the straight lines $\tau = f(1/T)$. Thus, when alkyd coatings are used at high temperature under the action of ultraviolet radiation and in an atmosphere, with an increase in the forming temperature the durability decreases; when aging in an aqueous medium, and also when tested according to the accelerated GIPI-4 cycles, the inverse dependence is observed, i.e., with an increase in the forming temperature the service life of the coatings increases.

Fig. 3. Dependence of the durability of coatings on the reciprocal forming temperature. Left–in atmospheric conditions: 1–9 points, 2–8, 3–7, 4–6, 5–5,

Figure 4

Figure 4: Figure 4

6–4, 7–3, 8–2. Right–according to the tropical GIPI-4 cycle: 9–9 points, 10–8, 11–7, 12–6, 13–5, 14–4, 15–3, 16–3.

Fig. 4. Dependence of the fracture energy on internal stresses during aging of coatings in an aqueous medium

The peculiarity of the self-accelerated fracture of polyester coatings in the aging process under the action of internal stresses consists in the fact that for them an increase in the fracture energy is observed with increasing internal stresses (Fig. 4), whereas in the fracture of materials under the action of an external load the inverse dependence was observed (2, 4). Such an increase in the fracture energy during the aging process does not depend on the conditions and is associated in this case with further structuring of the alkyd coatings, accompanied by the formation of new ether bonds and a decrease in unsaturation, which is confirmed by experimental studies by the IR-spectroscopy method (5).

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Received
26 IX 1964

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Note: Figure translations are in progress. See original paper for figures.