

УДК 678.4.023

N. R. Prokopchuk, Corresponding Member of Belarus NAS,
D. Sc. (Chemistry), professor, head of department (BSTU);
T. H. Kukhta, department manager (RUE "Institute BelNIIS")

EVALUATION OF INTERNAL STRESS INFLUENCE ON DURABILITY OF POWDER PAINT COATINGS

Method for determination of internal stresses influence on durability of powder paint coatings is developed. The method is based on the difference of thermal-oxidative degradation activation energy of cross E_D -linked film-forming material within loose and metal-bedded film. It is shown that powder paint coatings internal stresses are insignificant as metal-bedded cross-linked film-forming material does not take big deformations of coatings in the process of their formation as well as during the usage. Reduction of thermal-oxidative degradation activation energy of the parameter E_D with such internal stresses is only 3–7 kJ/mol and it does not reduce the coatings durability much in comparison with the influence of the factor of the climatic chamber of UV radiation and high temperatures.

Introduction. The most important indicator of protective coatings functional qualities is their durability. For the certification of paint products the durability of coatings is evaluated in accordance with GOST 9.404–91 by prolonged exposure to artificial climatic factors (UV radiation, alternating temperatures, moisture), excluding the effect of internal stresses σ_{in} in protective coatings on their durability. However, it is known [1] that the internal stresses can reach 8–10 MPa (in coatings of solventborne nitratecellulose paint materials). Obviously, such a large σ_{in} reaching 25% of the tensile strength significantly lowers the potential barrier of breaking chemical bonds in macromolecules of the film former and, consequently, the durability of strenuous coatings. In its origin the internal stresses are of two kinds: the shrinkage arising from the shrinkage of the film material in the formation or operation of the cover; thermal appearing when the temperature changes as a result of conflict between the values of thermal linear expansion coefficients of the material of the protected surface and the polymer film coating.

Earlier we have already [2–5] proposed and implemented in the system of certification tests a rapid method for determining the durability of rubber and thermoplastics based on the relationship between the durability of the polymer material τ and the value of the activation energy of thermal oxidative degradation E_D . Repeatedly, it was shown that the parameter E_D determines the quality of the polymer material and its durability and it decreases under the influence of functional factors. The influence of the internal stress was not considered, i.e. products of polymers have no adhesive contact.

The purpose of this work is to quantify the decrease of the life of the powder paint coatings with internal stresses, reducing the potential barrier of the break of chemical bonds in macromolecules of a film former.

Main part. The objects of the study were unsupported film with a thickness of 0.3–0.4 mm, a width of (10 ± 2) mm and length of 100 mm and a coating on the metal foil with a thickness of 0.1 mm obtained from the powder paints of samples:

1, 2 – polyester film binder, cured by primid the red and the green colours, respectively;

3 – polyester film binder, cured by triglycidyl isocyanurate (TGIC) of green colour.

Mechanical testing on modern tensile testing machine T 2020 DC 10 SH (Alpha Technologies UK) was performed.

Air temperature was 18 °C, the speed of movement of the upper gripping – 10 mm/min, a clamping length of the samples – 54 mm, the number of samples in the sample – 10.

According to the diagram «Voltage tensile σ (MPa) – tensile strain ε (%)» a computer program calculated the unit tensile strength (σ , MPa), elongation (ε , %), Young's modulus (E , MPa) as the average of ten measurements [6].

The activation energy E_a was determined by calculation Broido [7] according to the dynamic thermo–gravimetric analysis. The curves of weight loss TG and the weight loss rate DTG when the temperature is raised to the linear speed of 5,0°C/min were done on a thermo–analytical system TA-4000 module TG15 Mettler Toledo (Switzerland). The sample lot was 10 mg. The air into the electric heat treatment furnace was supplied at a rate of 200 ml/min. Broido method is a method of double logarithm based on the calculation of values

$$\ln \left[\ln \frac{100}{100 - \Delta m} \right], \quad (1)$$

where Δm – weight loss of the sample as a percentage of the weight of the original sample at each of the temperatures within the range of 5–7 degradation of macromolecules.

For each polymer, this interval is set experimentally by DTG curve. The beginning of this interval T_n was determined by the intersection of the tangents to the two branches of the DTG, and the end of T – by position of the peak in the DTG curve (Fig. 1).

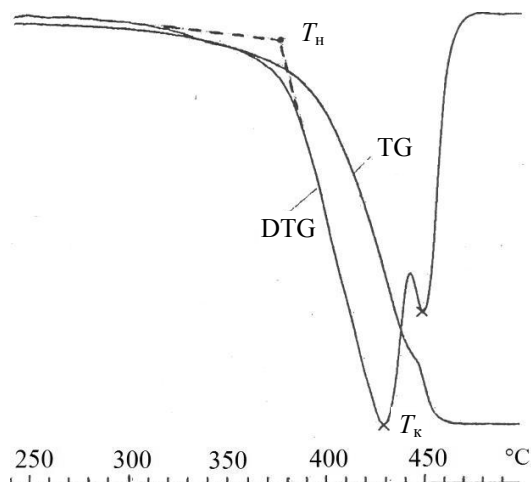


Fig. 1. Curves DTG and TG of polyester powder coatings

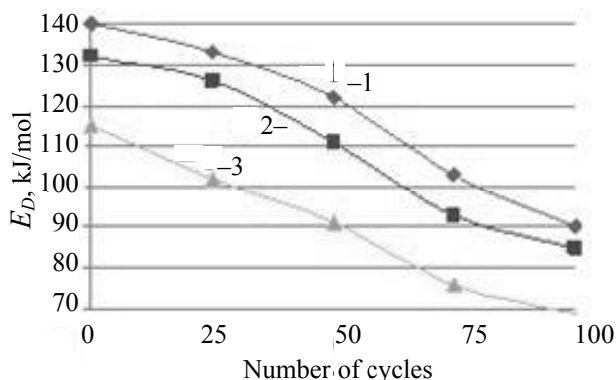
Thus, we first installed the temperature range of 380–430 °C, which determined E_D for polyester powder coatings. Then we plotted linear relationship (Fig. 2) by applying an approximation the method of smaller squares. The slope of the right line to the axis of ordinates was calculated, and then the value of E_D be formula (2)

$$E_D = \text{tg } \varphi \cdot R, \quad (2)$$

where R universal gas constant, $R = 8,31 \cdot 10^3$ kJ/mol.

DSC curves were recorded on a thermal analyzer TA-4000 module DSK30 of the company Mettler Toledo (Switzerland).

Durability of the coatings according to the kinetic theory of strength [8] decreases exponentially with increase of internal stresses in the coatings



$$\tau = \tau_0 \cdot \exp [(U - \gamma \cdot \sigma_{in}) / R \cdot T], \quad (3)$$

where τ_0 – the period of oscillation of carbon atoms bound chemically, constant equal to 10–13; E_D – a potential barrier breaking of chemical bonds; γ – structural-sensitive factor; σ_{in} – internal stress in the polymer coating; T – temperature, K.

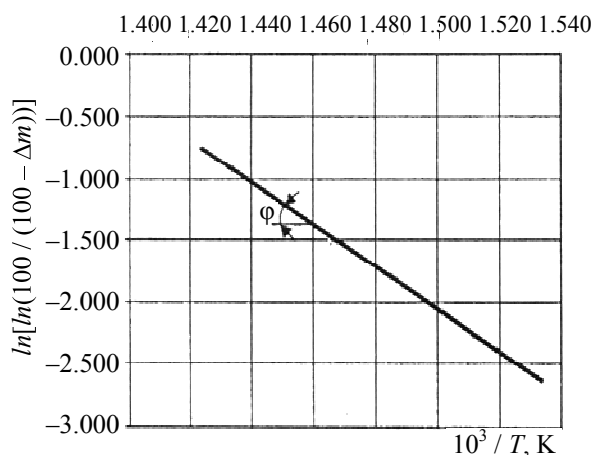


Fig. 2. Example of E_D calculation of polyester powder coatings

Reducing the potential barrier of breaking of chemical bonds in macromolecules film former E_D by the amount of $\gamma \cdot \sigma_{in}$ with destruction adherent film on the foil as compared to the destruction of the free film is due to the weakening of the chemical bonds mechanical tensile stresses (internal stresses and thermal shrinkage). At constant structure of sensitive factor γ in the powder coating the reducing E_D according to the formula (3) is proportional to σ_{in} .

The simbasis of changes of tensile strength σ_{vn} and of parameter E_D of exposure time in the climatic chamber proves the immutability of factor γ from the exposure time under the influence of climatic factors on artificial film of polyester powder paint cured by primidi and TGIC (Fig. 3).

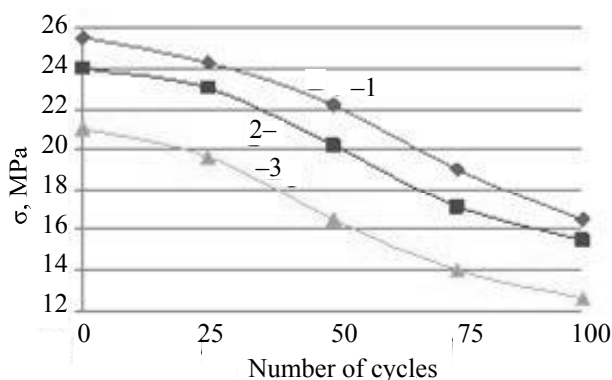


Fig. 3. Changes in tensile strength and the activation energy of thermal-oxidative destruction of unsupported films during exposure in a climatic chamber. Numbers of the curves correspond to the numbers of samples

Since σ and E_D are related by the equation (4), at constant the structure of the films to be conformed at any time of exposure equality

$$\sigma_0 / \sigma_n = E_{D(0)} / E_{D(n)}, \quad (4)$$

where n – number of cycles of exposure on the film in a climate chamber (Table 1).

We have found experimentally (Table 2), that unsupported films (samples 1–3) destroy with parameter values of E_D 140, 132, and 115 kJ/mol respectively, while adherent on the steel foil with a somewhat smaller values: 137, 128 and 108 kJ/mol. Thus, reducing the activation energy of the thermal oxidative degradation of films from polyester powder paint by internal stress is small and corresponds to 3, 4, and 7 kJ/mol for samples 1, 2 and 3 respectively. This is due to minor internal stresses in the powder coating. During the formation of the coating from the powder paints oligomeric macromolecule of foam generator, located

directly on the protected surface, are stapled by the molecules of the hardener into spatial little deformable mesh.

As a result, the coating shrinks slightly, and shrinkage internal stress $\sigma_{in(y)}$ is small:

$$\Delta\sigma_{in(y)} = \Delta\varepsilon \cdot E / (1 - \mu), \quad (5)$$

where $\Delta\varepsilon$ – shrinkage; E – modulus of elasticity of the film; μ – Poisson's ratio. Thermal internal stresses $\sigma_{in(t)}$ resulting from the rapid heating or cooling the coating to a temperature range T , are defined by the equation [1]

$$\sigma_{in(t)} = (\alpha_1 - \alpha_2) \cdot \Delta T \cdot E / (1 - \mu), \quad (6)$$

where α_1, α_2 – thermal linear expansion coefficients of the protective film material and the protected surface, respectively; $\Delta T = T_g - T_e$, T_g, T_e – the glass transition temperature and exploitation temperature respectively.

Table 1

Experimental data confirming the immutability of the film structure from powder paints with their exposure in the climatic chamber

Sample number	Number of cycles									
	0		25		50		75		100	
	σ	E_D	σ	E_D	σ	E_D	σ	E_D	σ	E_D
1	25.5	140	24.3	133	22.2	122	19.0	103	16.5	90
2	24.0	132	23.0	126	20.2	111	17.1	93	15.5	85
3	21.0	115	19.6	102	16.5	91	14.0	76	12.6	69

Table 2

Initial data of TGA and results of calculation of E_D , parameter of free films and unsupported film of polyester powder paint

Sample 1			Sample 2			Sample 3		
$T, ^\circ\text{C}$	$m, \%$	$E_D, \text{kJ/mol}$	$T, ^\circ\text{C}$	$m, \%$	$E_D, \text{kJ/mol}$	$T, ^\circ\text{C}$	$m, \%$	$E_D, \text{kJ/mol}$
Unsupported film								
375	92.13	140	381	91.04	132	377	90.84	115
385	89.85		391	88.51		387	87.19	
395	86.44		401	84.69		397	83.00	
405	81.66		411	79.27		407	76.98	
415	75.47		421	71.82		417	70.75	
425	58.17		431	58.09		427	64.75	
Coatings for metal								
373	93.36	137	381	92.63	128	374	91.95	108
383	92.26		391	90.04		384	89.68	
393	89.62		401	86.60		394	86.31	
403	85.37		411	81.64		404	82.23	
413	78.10		421	75.06		414	77.74	
423	64.87		431	66.66		424	69.78	

Because T_g films is 62–76°C, and the average $T_e - 40-70^\circ\text{C}$, ΔT is small. The coefficient of linear thermal expansion of steel and cross-linked films are also close. As a result $\sigma_{in(t)}$ are small and do not cause a significant reduction in the parameter E_D , and hence the durability of the powder paint coatings. For example, the durability of the coating (sample 1), calculated by express method [6] excluding the internal permanent stress in the temperature of 40°C is

$$\tau_{40^\circ\text{C}} = 2.74 \cdot 10^{-3} \cdot \left[10^{-0,1167 \cdot 74 - 0,090} \cdot e^{\frac{74}{2,601}} \right] = \\ = 2.74 \cdot 10^{-3} \cdot \left[10^{-8,726} \cdot 2.27 \cdot 10^{+12,0} \right] = 11.7 \text{ years}$$

whereas with regard to the internal stress

$$\tau_{40^\circ\text{C}} = 2.74 \cdot 10^{-3} \cdot \left[10^{-0,1167 \cdot 77 - 0,090} \cdot e^{\frac{77}{2,601}} \right] = \\ = 2.74 \cdot 10^{-3} \cdot \left[10^{-9,076} \cdot 7.19 \cdot 10^{+12,0} \right] = 16.5 \text{ years.}$$

Evaluation of the impact of various factors on the reduction of operational durability of the coating of polyester powder coatings cured by primid can be estimated as follows. According to [6, 9], the main destroying factors of protective coatings that reduce the potential barrier of the breaking of chemical bonds E_D film former are: ΔE^{clim} – reduction of E_D as a result of exposure in the climatic chamber; ΔE^{UV} – decrease of E_D by internal stresses in the coatings; $E^{mech.ef.}$ – reduction of E_D as a result of static and dynamic loadings on the coatings. The following values were obtained by depleting factors $\Delta E^{clim} = 50 \text{ kJ/mol}$; $\Delta E^{UV} = 10 \text{ kJ/mol}$; $\Delta E^{in.st.} = 3 \text{ kJ/mol}$; $\Delta E^{mech.ef.} = 3 \text{ kJ/mol}$.

If we exclude all destructive factors other than temperature, E_{calc} – the durability of the material will be

$$E_{calc} = E_D = 140 \text{ kJ/mol.}$$

Then at the average operating coating temperature 40 °C their durability will be

$$\tau_{40^\circ\text{C}} = 2.74 \cdot 10^{-3} \cdot \left[10^{-0,1167 \cdot 140 - 0,090} \cdot e^{\frac{140}{2,601}} \right] = \\ = 242 \text{ years.}$$

The durability of coatings with the impact of climatic factors is determined by the value

$$E_{calc} = E_D - \Delta E^{clim} = 140 - 50 = 90 \text{ kJ / mol}$$

and is at 40°C

$$\tau_{40^\circ\text{C}} = 2.74 \cdot 10^{-3} \cdot \left[10^{-0,1167 \cdot 90 - 0,090} \cdot e^{\frac{140}{2,601}} \right] = \\ = 75 \text{ years.}$$

Hence the reduction in durability due to the impact of climatic factors on the coating will be

$$\frac{242 - 75}{242} \cdot 100 = 69\%.$$

Similarly the influence on the coatings of UV radiation is done

$$E_{calc} = E_D - \Delta E^{clim} - \Delta E^{UV} = 140 - 50 - 10 = \\ = 80 \text{ kJ / mol.}$$

Fall of durability due to climatic factors and UV radiation is

$$242 - 219 = 23 \text{ years (90.5%).}$$

Consequently, UV radiation decreases durability of coatings on 90.5 – 69.0 = 21.5%.

Reduction of durability of the coating by internal stress is taken into account by the following values of the calculated activation energy of degradation of the film former

$$E_{calc} = E_D - \Delta E^{clim} - \Delta E^{UV} - \Delta E^{in.st} = \\ = 140 - 50 - 10 - 3 = 77 \text{ kJ/mol.}$$

Durability due to climatic factors, UV radiation and internal pressure is

$$\tau_{40^\circ\text{C}} = 2.74 \cdot 10^{-3} \cdot \left[10^{-0,1167 \cdot 70 - 0,090} \cdot e^{\frac{70}{2,601}} \right] = \\ = 16.4 \text{ years.}$$

Reducing the durability of the coating due to these three factors is equal to

$$242 - 225.6 = 16.4 \text{ years (93.2%)}$$

but due to internal stresses only

$$93.2 - 90.5 = 2.7\%.$$

Thus, at a constant average temperature (40°C) of coatings from powder paint polyester cured by primid, climatic factors reduce their durability on 69%, UV – 21.5%, and the internal voltage – only for 2.7% .

So the main factor in destroying the protective coating of powder paint is heat aging of film formers.

Thus, the durability of coatings subjected to simultaneous continuous environmental exposure, UV radiation, and stress at 40°C was 16.4 years, and at 20°C

$$\tau_{40^\circ\text{C}} = 2,74 \cdot 10^{-3} \cdot \left[10^{-0,1167 \cdot 77 - 0,090} \cdot e^{\frac{77}{2,435}} \right] = \\ = 123 \text{ years.}$$

Conclusion. The evaluation of influence on the durability of polyester powder paint coatings of the internal stresses in comparison with other destructive factors in their operation was done. It is shown that three-dimensional network structure of these coatings prevents the development of a considera-

ble shrinkage and thermal stresses, and as a result, decrease of the durability of coatings. It was found that the main role in the destruction of protective coatings belongs to temperature of coatings, and artificial climatic factors, simulating operating conditions of coatings in moderately cold climate and to artificial light photoaging simulating the radiation from the sun.

References

1. Крутько Э. Т., Прокопчук Н. Р. Химия и технология лакокрасочных материалов и покрытий: учеб. пособие для студентов вузов. Минск: БГТУ, 2004. 314 с.

2. Способ определения долговечности эластомеров: пат. 1791753 СССР, МКИ G01N318, G01N1700. № 4843144/08; заявл. 26.09.90; опубл. 30.01.93 // Бюл. № 4. 8 с.

3. Изделия полимерные для строительства. Метод определения долговечности по энергии активации термоокислительной деструкции полимерных материалов: СТБ 1333.0-2002. Введ. 01.01.03. Минск: Минстройархитектуры, 2002. 11 с.

4. Прокопчук Н. Р. Полимерные материалы с повышенной устойчивостью к энергетическим и химическим воздействиям. Первый съезд ученых Республики Беларусь: сб. материалов, Минск, 1–2 нояб. 2007 г. Минск, 2007. С. 349–359.

5. Прокопчук Н. Р. Оценка долговечности полимерных изделий // Стандартизация. 2008. № 1. С. 41–45.

6. Кухта Т. Н., Прокопчук Н. Р. Климатическая стойкость покрытий из порошковых полиэфирных красок // Материалы. Технологии. Инструменты. 2013. Т. 18, № 4. С. 76–84.

7. Broido A., Simple A. Sensitive Graphical Method of Treating Thermogravimetric Analysis Data // J. Polimer. Sci. Part A-2. 1969. Vol. 7. No. 10. P. 1761–1773.

8. Регель В. Р., Слуцкер А. И., Томашевский Э. Е. Кинетическая природа прочности твердых тел. М.: Наука, 1974. 560 с.

9. Кухта Т. Н., Прокопчук Н. Р. Экспресс-метод оценки долговечности покрытий из порошковых красок // Известия НАНБ. Серия физико-технических наук. 2014. № 1. С. 20–24.

Received 21/02/2014