Model of the kinetics of aging of paint and varnish coatings of cement concrete

V I Loganina1*
1Penza State University of Architecture and Construction, 440028, Penza, St. G. Titova, 28. Russia
E-mail: loganin@mail.ru

Abstract. Information on the kinetics of aging of coatings is presented. The process of moistening was considered as one of the particular cases of aging. During incubation period there is a slight increase, and possibly a decrease in defectiveness. The duration of the incubation period is 0.2-0.5 of the entire durability. The active stage of damage accumulation begins after the incubation period. In the active stage of accumulation of damages, significant changes occur in the structure and properties of the coating (change in color, shine, cracking, etc.). Determined that the beginning of the active stage of accumulation of lesions coincides in time with the first significant changes in the surface area of the coating. It was found that there is a correlation between the experimental data on the kinetics of damage accumulation, the degree of chalking, and surface area. It lies in the fact that the active stage of damage accumulation coincides with the beginning of chalking of coatings. An analytical dependence is proposed that makes it possible to estimate the area of the defective surface of the coating during aging. The dependence of the level of damage accumulation on the duration of tests can be described by a logistic curve (or Pearl curve).

1. Introduction
Coatings for exterior decoration of buildings should perform not only protective functions, but also maintain high decorative properties during operation [1]. The main types of decorative properties of pigmented coatings are shine, color, mud retention and chalking. Such types of destruction of coatings as weathering, cracking, peeling, bubbling, the appearance of corrosion foci on the coating in most cases characterize the deeper stages of destruction of coatings. These types of destruction are used to characterize the protective properties of coatings [2, 3].

Change in shine is the first sign of the beginning of the destruction of the coating. It is caused by the destruction of the surface lacquer layer, leading to an increase in the size and height of the particles and aggregates of pigments protruding on the surface of the coating. As the surface layer of the film former disintegrates, the aggregates and pigment particles are gradually exposed on the surface of the coating, indicating the initial stage of melting of the coatings [4, 5]. According to [6-9], the time to the initial stage of chalking coincides with the time necessary to reduce the gloss by 50% of the initial.

In terms of the kinetic concept of destruction, the aging process of coatings consists of a number of stages and is multilevel. The destruction is preceded by the stage of accumulation of damages of various scales - from the rupture of individual chemical bonds, the appearance of submicro and microscopic cracks to the formation of a main crack [10-12].

Obviously, different rates of damage accumulation in coatings during aging are associated with changes in the coating structure. Under the influence of climatic factors, the destruction of the surface
layers of the coating occurs, leading to an increase in the roughness and, consequently, the surface area of the coating. In addition, the increase in surface area is also associated with the presence of formed macro and micro cracks.

Let us consider the accumulation of damage caused by the influence of climatic factors. In the study, we will restrict ourselves to a certain fixed level, namely: the accumulation of damage, observed visually.

2. Materials and methods
Polyvinyl acetate PVAC, polymer-lime and lime paints were used as paint compositions.

The degree of destruction of the coating surface was estimated from the change in the value of the adsorption of dyes from solutions. The appearance of cracks and other defects on the coating surface was assessed by the change in the color intensity of the solutions after contacting them with the surface of the coating under study. A solution of methylene blue dye in acetone was used.

3. Research results
As an example, the process of moistening was considered as one of the particular cases of aging. Fig. 1 shows the experimental data of the dependence of the level of damage accumulation on the duration of the tests.

An analysis of the data (Fig. 1) indicates that at the first moment of moistening, an increase in the shine of the coatings is observed, due to the plasticizing effect of moisture, which leads to the leveling of the microrelief of the coating surface. This is evidenced by the data on the change in the adsorption area of the dye (curve 3). After 800 hours of moistening, an active stage of damage accumulation is observed (curve 2). Simbatno there is an increase in the surface area of the coating. After 800 h of moistening, the initial stage of chalking is observed. So, after 800 hours of moistening, the degree of chalking of the coating was estimated by 1 point, after 1000 hours - 2 points, after 1200 hours - 3 points.

Fig 1. Change in the surface area of PVAC coating in the process of moistening 1 - the shine change; 2 - change in the level of damage accumulation; 3 - changing the surface area of the coating.

Analysis of the experimental data indicates that the beginning of the active stage of accumulation of lesions coincides in time with the first significant changes in the surface area of the coating (Fig 2, 3). The active stage of damage accumulation begins after the incubation period. The duration of the incubation period is 0.2 - 0.5 of the entire durability. The results of experimental studies indicate that the general nature of the distribution of damage is uneven, which is obviously due to the compositional heterogeneity and heterogeneity of the coating structure, as well as its uneven stress.
state. It was found that the initial defects (color change) are formed spontaneously. Local cracking appears near various inclusions and risks [13-17].

Thus, there is a correlation between the experimental data on the kinetics of damage accumulation, the degree of chalking, and surface area - the active stage of damage accumulation coincides with the onset of chalking of coatings. This conclusion is also confirmed by the data in the study of the kinetics of the aging of coatings at UV irradiation (Figure 4). Analysis of the experimental data shows that that the initial stage of chalking of coatings appears after 100 h of UV irradiation. The degree of chalking of coatings after 100 h of irradiation is estimated as 2 points, while an increase in the adsorption area of the dye is observed. The active stage of damage accumulation also begins after 100 h of UV irradiation.

**Figure 2.** Change in the level of accumulation of damage to coatings during aging: 1 - PVAC; 2 - polymer–lime coating; 3 - lime coating.

**Figure 3.** Change in surface area of coatings when moistened: 1 - PVAC; 2 – polymer-lime coating; 3 – lime coating.
There is a change in the surface area of the coatings, caused by a decrease in the quality of their appearance. The intensity of destruction under the influence of climatic factors is not the same at different stages of operation. It was found, that during some incubation period (the duration of which depending on the type of coating can be different), there is a slight increase, and possibly a decrease in defectiveness. Then, in the active stage of accumulation of damages, significant changes occur in the structure and properties of the coating (change in color, shine, cracking, etc.) leading ultimately to failure of the coating.

Analysis of the experimental data (Fig 2) shows that the dependence of the level of damage accumulation on the duration of tests can be described by a logistic curve (or Pearl curve), which has the form

\[
W = \frac{a_1}{1 + \exp(a_2 - a_3 t)}
\]

where \(a_1\) is the saturation level; \(a_2\) and \(a_3\) are empirical coefficients; \(t\) - test time.

The logistic curve reflects two phases of development. The first phase (slow growth) is the incubation period, the second phase (intensive growth) is the active stage. The duration of the incubation period can be determined by the formula

\[
t_{inc} = \frac{(a_2 - 0.28)}{a_3}
\]

duration of the active stage - according to the formula

\[
t_{act} = \frac{2.504}{a_3}
\]

As noted earlier, in the process of aging, an increase in the surface area of the coatings is observed, which is also caused by microcracking. Let us consider the kinetics of destruction of the coating from the point of view of changes in the defectiveness of their structure. Realizing that this assessment is very difficult, (there are various types of defects, their configuration can change in the process of exposure to the external environment, etc.) an attempt was made to estimate in a first approximation the kinetics of changes in the area of the defective surface. Let \(F_x\) be the relative area of the coating occupied by defects, then \((1 - F_x)\) is the relative area of the coating not subject to defects. In the process of exposure to the external environment, an increase in \(F_x\) occurs, i.e.

\[
F_{x}^{\text{fn}} < F_x < F_{x}^{f}
\]

where \(F_{x}^{\text{fn}}\), \(F_{x}^{f}\) are the initial and final relative the coating area with defects.
Let us consider the destruction of coatings as a two-stage process. The rate of change of the defect-free area of the coatings in the incubation period is:

$$\frac{d(1 - F)}{dt_{\text{inc}}} = A_1(1 - F)$$

(5)

where $A_1$ is a coefficient characterizing the rate of change of the defect-free area of coatings during the incubation period.

After a mathematical transformation, we get

$$F_{x}^{\text{inc}} = 1 - (1 - F_{x}^{\text{inc}})\exp(A_1t_{\text{inc}})$$

(6)

At the end of the incubation period, the relative area of the defective surface is

$$F_{x}^{\text{inc,f}} = 1 - (1 - F_{x}^{\text{inc}})\exp\left[\frac{A_1(a_2 - 0.28)}{a_3}\right]$$

Similarly, in the active stage of aging of paint coatings, the rate of change in the defect-free area is expressed

$$\frac{d(1 - F)}{dt_{\text{act}}} = A_2(1 - F)$$

(7)

where $A_2$ is a coefficient characterizing the rate of change of the defect-free area of coatings in the active stage.

Solving equation (7), we obtain

$$F_{x}^{\text{act}} = 1 - (1 - F_{x}^{\text{inc,f}})\exp(A_2t_{\text{act}})$$

At $t > t_{\text{inc}}$, taking into account formulas (6), (8), the change in the relative area of the defective surface during aging obeys the dependence

$$F_{x} = (F_{x}^{\text{inc,f}} + F_{x}^{\text{act}}) = 2 - \left\{\left(1 - F_{x}^{\text{inc,f}}\right)\exp\left[\frac{A_1(a_2 - 0.28)}{a_3}\right]\right\} \ast (1 - \exp(A_2t_{\text{act}}))$$

Equation (9) characterizes the kinetics of the change in the relative area of the defective surface of the coatings during aging and allows, in the first approximation, to speak about the mechanism of destruction of coatings.

4. Summary

It was found that the process of destruction of coatings under the influence of climatic factors can consist of an incubation period and an active stage of damage accumulation. The duration of the incubation period, depending on the intensity of the impact of external factors, the type of coatings can be 0.2 - 0.5 of the entire durability of the coatings. The beginning of the active stage of accumulation of lesions coincides in time with the first significant changes in the surface area of the coating. A model is proposed that characterizes the kinetics of changes in the relative area of the defective surface of the coatings during aging and allows, in the first approximation, to speak about the mechanism of destruction of coatings.

5. References

[1] Verkholtantsev V V 1985 Methods for predicting the durability of coatings Paints and varnishes and their application 4(49)

[2] Karyakina M I 1988 Testing of paint and varnish materials and coatings (Moscow: Chemistry) 272

[3] Suhareva L A 1984 Durability of polymer coatings (Moscow: Chemistry) p 240

[4] Elambasseril J, Ibrahim R N, Das R 2011 Evaluation of fracture characteristics of ceramic coatings on stainless steel substrates using circumferentially notched tensile specimens Composites part b-engineering 42(6) 1596-1602

[5] Hong Wei, Guo Fangwei, Chen Jianwei 2018 Bioactive glass-chitosan composite coatings on PEEK: Effects of surface wettability and roughness on the interfacial fracture resistance and in vitro cell response Applied surface science 440 514–518
[6] Loganina V, Fediuk R, Usanova K, Timokhin R 2020 Regularities of Change in the Properties of Paint Coatings on Cement Concretes at Moistening Lecture Notes in Civil Engineering 70 1–14
[7] Loganina V 2019 Durability of Paint and Varnish Coatings Depending on the Quality of their Appearance IOP Conference Series: Materials Science and Engineering 471(2) 022044
[8] Loganina V I 2010 Regularities of quality change of the appearance of paintwork coatings of cement concretes in the aging process Materials Today: Proceedings 19 2210–2212
[9] Loganina V 2017 Forecasting of trouble-free operation of the protective and decorative coatings for building products and structures ARPN Journal of Engineering and Applied Sciences 12(17) 5180–5184
[10] Pak Sung-Nam, Yao Zhongping, Ju Kyong-Sik 2018 Effect of organic additives on structure and corrosion resistance of MAO coating VACUUM 151 8–12
[11] Klyuev S V, Khezhev T A, Pukharenko Y V, Klyuev A V 2018 Fiber concrete for industrial and civil construction Materials Science Forum 945 120-124
[12] Begich Y E, Klyuev S V, Jos V A, Cherkashin A V 2020 Fine-grained concrete with various types of fibers Magazine of Civil Engineering 97(5) 9702
[13] Klyuev S V, Klyuev A V, Khezhev T A, Pukharenko Y V 2018 High-strength fine-grained fiber concrete with combined reinforcement by fiber Journal of Engineering and Applied Sciences 13 6407-6412
[14] Klyuev S V, Khezhev T A, Pukharenko Y V, Klyuev A V 2018 Fibers and their properties for concrete reinforcement Materials Science Forum 945 125 – 130
[15] Amran M, Fediuk R, Vatin N, Mohammad Ali Mosaberpanah, Aamar Danish, Mohamed El-Zeadani, SV Klyuev, Nikolai Vatin 2020 Fibre-reinforced foamed concretes: A review Materials 13(19) 4323
[16] Makhmud Kharun, Sergey Klyuev, Dmitriy Koroteev, Paschal C Chiadighikaobi, Roman Fediuk, Andrej Olisov, Nikolai Vatin and Nataliya Alfimova 2020 Heat treatment of basalt fiber reinforced expanded clay concrete with increased strength for cast-in-situ construction Fibers 8 0067
[17] Afonso R G de Azevedo, Sergey Klyuev, Markssuel T Marvila, Nikolai Vatin, Nataliya Alfimova, Thuany E S de Lima, Roman Fediuk and Andrej Olisov 2020 Investigation of the potential use of curauá fiber for reinforcing mortars Fibers 8 0069