Introduction Technological advance in the field of paintwork materials (PWM) that requires enhancement of coating protective properties under severe service conditions, as well as solution of a number of ecological and economical problems, has resulted in the development of brand new PWM - powder ones. Within relatively short period of time these materials proved themselves to be quite promising, with their formulation being one of the highest priorities of the current material science development. At the present time powder paints in terms of coatings manufacture technology, durability, as well as ecology and economics, have practically no alternatives. Absence of solvents in powder paints dramatically reduces environmental pollution, with absence of expenditures connected with organic solvents (30-70% of liquid PWM makeup), treatment of air and sewage waters. On top of that, the technology of powder paint coating fabrication is non-waste (production waste is fully recyclable), less energy-consuming (no power is required for solvent evaporation, the costs of production premises ventilation drop), more automated (maintenance personnel and production floor are reduced), more manufacture efficient (several times). Now the most wide-spread are powder paints on the basis of the following filming agents: epoxy resins, epoxy- polyester oligomers (combination of epoxy and polyether resins), hybrid filming agents; not-saturated polyester resins [1]. In selection of powder paints one of the most important properties is resistance to weather conditions. The influence of ambient environment leads to energy absorption in ultraviolet band of electromagnetic spectrum. This energy has negative effect both on film-forming polymer, and the pigment resulting in loss of glitter and change of color. Due to tendency to chalking epoxy and hybrid paint coatings are usually not recommended for use in the open air. Polyether materials form coatings that provide good resistance to the influence of ultraviolet rays. Composition of polyether powder paints contain curing agents that cross-link oligomer macromolecules and form low-molecular polymer spatial cross-linked structure. Powder paints with extensively used curing agents were selected for the research. One of them is triglycidyl isocyanurate(TGIC) which was used for rather long period of time, but lately regarded as a harmful reagent in some European countries. Another one is hydroxyalkylamide considered as harmless and known under the trade name “primide”. Therefore, study of environmentally resistant polyether powder paint coatings cured with TGIC and primide, as compared to coatings of hybrid powder makeup is a crucial task. Work objective is to quantitavely evaluate destructive factors that influence polymer protective coatings made of powder paints when in service; propose empiric exponential relationship between durability of metal tiles and asbestos cement boards coatings and activation energy of thermal oxidative breakdown of filming agent for polyether powder paints; develop express method for evaluation of these coatings durability with regard to influence of environmental factors. Experimental procedure Subjects of the research were films of 0.3-0.4 mm in thickness, (10 ± 2) mm in width and 100 mm in length, and coatings of 0.1 mm in thickness fabricated of powder paints, samples of: - 1, 2, 3, 4 - polyether paint, curing agent - primide, colors - red, white, green and black, correspondingly; - 5, 6 - polyether paint, curing agent - TGIC, colors - green, black, correspondingly; - 7, 8 - hybrid paint, colors - blue and black, correspondingly. The films were formed on fluoroplastic sheet. Powder paint was deposited through the sieve. The tests were performed in the climatic chamber “Feutron”, type 3826/16 (Germany) according to the following cycle: - moisture treatment of samples at temperature (40 ± 2) oC and relative humidity (97 ± 3)% for 2 hours; - moisture treatment free of heating at relative humidity (97 ± 3)% for 2 hours; - freezing at temperature minus (30 ± 3)oC for 6 hours; - irradiation of samples by creating light flux with surface density of total radiation energy (730 + 140) W/m2 with surface density of UV radiation flux (30 + 5) W/m2 and periodic sprinkling with water for 3 minutes in each 17 minutes for 5 hours; - freezing at temperature minus (60 ±3)oC for 3 hours; - conditioning at temperature 15-30oC and relative air humidity of 80% for 6 hours. Samples were taken each 25; 50; 75; 100 cycles. The films were artificially aged under influence of UV and IR radiation by means of dummy emitter of sunlight SOL 1200S (Germany). Artificial ageing mode: - temperature in the climatic chamber - 50°C; - relative air humidity - 60%; - UV radiation mode - 57.7 W/m2; IR - 730 W/m2; - visible range - 320 W/m2. Total optical radiation flux from dummy emitter HSA 1200S at a distance of 60 cm from radiation source was 1,107.7 W/m2. Magnitude of samples radiation energy from dummy emitter for 600 hours amounted to 2,393 MJ/m2; 1,200 hours - 4,786 MJ/m2; 2,400 hours - 9,572 MJ/m2. Films porosity was determined by their specific area values calculated by BET method (Brunour, Emmet, Teller). Nitrogen adsorption isotherms were read out on instrument NOVA 2200. Gaseous nitrogen with operation temperature of 77 K was obtained by evaporation of liquid nitrogen. Measurements error did not exceed 10% of specific area values. Mechanical tests were conducted on tensile testing machine T 2020 DC 10 SH (Alpha Technologies UK, USA). Ambient air temperature - 18oC, speed of top grip motion - 10 mm/min, clamping length of samples - 54 mm, number of test samples - 10. By diagrams “tensile strain σ (MPa) - tensile deformation ε (%)” using the instrument computer program, the rupture resistance (σ, MPa), relative elongation (ε, %), Young elasticity modulus (E, MPa) were computed as mean arithmetic of ten measurements. The value of activation energy Ea was determined by Broido computational method on the basis of dynamic thermogravimetric data [2]. Morphology of films surface (in research film surface being in contact with air and not with fluoroplastic substrate was used in order to exclude influence of substrate) was studied on scanning electronic microscope JSM 5610LV (Jeol, Japan). Research results and discussion Results of films mechanical tests before influence of artificial climatic factors are given in fig. 1. Sample number образца Durability, MPa Sample number образца Elasticity modulus, MPa Sample number Номер образца Relative elongation at rupture, % Fig. 1 - Deformation-durability and elastic properties of films made of powder paints Data analysis shows that more durable and elastic films are formed from polyether films cured with primide in particular. Durability of 1-4 samples on the average is 24.6 MPa, whereas durability of 7, 8 samples is only 17.4 MPa. Relative elongation at rupture - 2.35% and 1.66%, elasticity modulus 1,610 and 1,865 MPa correspondingly. Therefore, films of polyether powder paints are more durable than films of hybrid powder compositions by 41%, and more elastic by 42%. Less than by 16% elasticity modulus of polyether films as against hybrid ones gives ground to believe that smaller inherent stresses will be developed in coatings of polyether powder paints due to their greater relaxation in film that is easier deformed. In its turn, small inherent stresses in the film provide its longer service life (service life of coatings without loss of their protective properties). Comparing compositions of polyether powder, containing different curing agents, one may note that primide is more preferable than TGIC. The films cured by primide are more durable than films cured by TGIC by 14% on the average, and more elastic by 16%. This is explained by differences in molecular structure of primide and TGIC. Chemical reaction of cross-linking of unsaturated polyether oligomeric molecules with primide molecules proceeds slower and requires higher temperatures and more time consuming. However, it forms more uniform, durable and elastic polymer network. As a result, durability and relative elongation at rupture is higher, and elasticity modulus is lower for primide cured films. Coatings made of polyether powder compositions containing primide have objectively to be more durable than TGIC cured coatings because of smaller inherent stresses that develop in them. Since films made of powder paints represent chemically cross-linked spatial network patterns, their disintegration has fragile nature. For each sample the following ratio is observed: $\sigma = K \bullet E \bullet \varepsilon$, where K= 0.0066-0.0063 for 1-4 samples; 0.0062-0.0063 for 5,6 samples and 0.0057-0.0055 for 7,8 samples. In spatially cross-linked (network) polymers their mechanical properties are greatly influenced by ratio between molecular mass of section between network nodes and molecular mass of kinematic segment [3]. If molecular weight of kinetic segment (MWk.s) molecular weight of an interval between crosslinks (MWc) (kinematic linkage is flexible and network is sufficiently wide), then variation of network density practically affects neither highly elastic deformation nor temperature of polymer glass transition. But if MWc > MWk.s, then increase of network density (reduction of Mc) results in reduction of highly elastic deformation and rise of glass transition temperature [4]. At very high density of three-dimensional network the highly elastic deformation is impossible, and at room temperature material is in glass state. Variation of durability and increase of network density is, as a rule, expressed by a curve with maximum. Small amount of cross linkages does not hamper straightening of chains in deformation, resulting in the enhancement of durability. Still increase of density over optimal values hinders orientation processes during stretching of films, and their durability starts to degrade the more the larger density of formed three-dimensional network is. According to the data obtained by DSC (differential scanning calorimetry) (figure 2), the lowest glass state temperature have non-adhesive films obtained from primide cured polyether filming agent (glass-transition temperature of sample No 2 is 62°C). During solidification of this filming agent with TGIC curing agent the glass state temperature goes up by 6°C (samples No 5 and 6 in figure 4). Finally, with the highest glass transition temperature (77-82°C) is characterized by samples of films No. 7 and 8 obtained from hybrid filming agent (combination of epoxy and polyester resins). Consequently, logical interrelationship is observed between values of glass transition temperature, durability, elasticity modulus, relative elongation upon rupture of films. Electron micrographs (figure 3) give evidence of different nature of films surface, along with various size and shape of coloring agents particles. Fig. 2 - DSC of powder paint films Surface of films of primide cured polyether powder paint (sample No 1) is smooth and uniform. Network structure is formed free of considerable inherent stresses. Surface of films of hybrid paint (sample No 7), and TGIC cured polyether paint (sample No 6) is texturized, as it was formed under conditions of great inherent stresses. Upon the influence of weather factor on films in climatic chamber rigidness of the three-dimensional network has small variation, so elasticity modulus varies within several percent (10% maximum). However, under impact of heat, UV-radiation and humidity sections of macromolecules between network nodes disintegrate and its elasticity drops. Sample No 1 a) Sample No 7 sample No 1 b) sample No 6 Fig. 3 - Electron micrographs of polymer films with magnification: a - x100; b - x1000 With practically linear rise of film stress upon its extension, and smaller relative elongation of upon rupture lower durability is achieved. Due to this with the increase of the number of cycles affecting films, both durability and relative elongation diminish. Dependences of durability and relative elongation upon rupture on exposure time have similar S-shaped nature (fig. 4). Fig. 4 - Dependence of stress-strain properties of films on time of exposure in the climatic chamber As kinetics of radical reactions in solid polymers has strong dependence on the degree of macromolecules cross-linking and mechanical stress on their chemical bonds [5], the films under study differ in ageing rate. So films obtained from primide cured polyester resin (samples No 1-4) retain 65% of initial durability and 72% of relative elongation upon rupture after impact of 100 cycles in the climatic chamber. Invariance of values of these indices for TGIC cured polyester films is equal to 60 and 70% correspondingly, and for hybrid epoxy-polyester resin films - 50 and 67%. The data we obtained for powder paint films comply with provision of the kinetic theory of strength [6] stating that durability of a solid, including that of polymer, decreases with the increase of mechanical stress σ that affects chemical carbon-to-carbon bonds in the backbone chain. On trials in the climatic chamber polymer films were periodically subjected to 100% moistening. An important role in the reduction of durability and deformation characteristics of stressed composite materials is played by liquid media affecting them on a long-term basis [7]. Cross-linking reaction of polyester binder oligomeric molecules when cured by primide is exercised through chemical interaction of resin molecules terminal carboxyl with hydroxyl groups of curing agent. Polyester resins cured by primide Alongside with that, molecular structure of primide (aliphatic architecture of molecule matrix) provides comparably flexible mobile cross linkage of cured film three-dimensional network and, as a consequence, good mechanical properties and high weathering resistance. With the same TGIC-cured powder polyester paint, terminal carboxyl of the binder interacts with three epoxy groups of the curing agent (figure 5b). Furthermore, ester links are formed and water is exuded which, with large thickness of films, may form defects in the form of punctures. However, this negative effect can be brought to a minimum by using degassing additives in make up of powder paints, along with selection of optimal temperature-time mode of coatings formation. Evaluation of films porosity, made by BET method showed that it practically does not depend on the chemical nature of curing agent used. Values of specific surface area of film samples No. 1-6 varied from 10 to 11 m2/g, i.e., being within the measuring error. For this reason one may say that porosity has identical effect on all film samples during their tests. Whereas differences in mechanical properties and weathering resistance of powder polyester paint films are conditional on different nature of chemical cross-links in the three-dimensional network, i.e., on differences in chemical architecture of curing agent molecules. As a result, individual molecules of polyester resin are cross-linked into the three-dimensional network without emission of volatile low-molecular compound. Enhanced reacting capacity of TGIC epoxy groups provides more easy and quick cross-linking at lower temperatures and within shorter time of coatings cure. Meanwhile cyclic TGIC structure specifies higher rigidity of network cross links, with inherent stress slow relaxation. Due to this complex of mechanical properties of films and their weathering resistance worsen. Polyester resins cured by TGIC Analysis of figure 4 shows that after impact of 100 cycles in the climatic chamber the films still retain on the average 65% of initial durability and 72% of relative elongation upon rupture. However, with regard to impact of other operational factors on protective films, like inherent stresses, external mechanical forces, it is reputed that 100 exposure cycles result in complete loss of films service life, as it is common knowledge that durability corresponds to time within which durability and/or elasticity drops twofold. We have established that non-adhesive films of primide-cured powder polyester paint of different colors disintegrate with energy practically identical to activation energy of thermal-oxidative degradation Ed equal to 140±2 kJ/mol. The key prevailing destructive factors that lower potential barrier of filming agent bond opening Ed are: ΔEclim - lowering of Ed due to exposure in the climatic chamber; ΔEUV - lowering of Ed under influence of sunlight-simulating radiation; ΔEin.str - lowering of Ed by inherent stresses that occur due to differences in coefficients of thermal expansion of coating and protected surface; ΔEmech. in. - lowering of Ed due to static and dynamic loads on coatings. The following values of destruction factors were obtained: ΔEclim =50 kJ/mol, ΔEUV = 10 kJ/mol; ΔEin.str.= 7 kJ/mol; ΔEmech. in = 3 kJ/mol. Due to this calculated value of thermal-oxidative degradation activation energy of coatings that determines their durability equals to: Ecalc.= 140-50-10-7-3=70 kJ/mol. Earlier we [8-10] have proposed and implemented in the system of certification tests the express method for determination of rubber and thermoplastic articles durability, which is based on the interrelation between durability of polymer material τ and value of activation energy of its thermal-oxidative degradation Ed. It has been repeatedly demonstrated that Ed determines quality of polymer material and is reduced under influence of service factors. In this work for the first time ever the method is proposed for evaluation of durability of powder paint coatings having tridimensional cross-linked structure. Durability of coatings τTs at set value of service temperature Ts is calculated by empirical formula we have established: , where K = 2.74·10-3 years, α = -0.1167 mol/kJ, β = 0.090 Values of coefficients are established by mathematical treatment of experimental datasets obtained at prolonged (six months) ageing of powder polyester paint films from different manufacturers differing considerably in values of Ed. Calculated durability of polymer coating in years (ttotal) at variable values of article service temperature is determined by the formula: where mi - number of hours of impact at particular values of service temperature; Σmi - total number of hours of impact at variable values of service temperature; τTs - durability of a polymer article in years at particular value of article service temperature. For climatic conditions of Eastern Europe duration in hours was determined for service within one year and at temperatures that develop within materials upon impact on them of direct sun beams (table 1). Table 1 Index name Value Number of hours of temperature impact, h 2,25 1,4 440 200 100 Temperature, oC 20 30 40 50 60 Example of durability calculation for on-metal coatings from polyester powder paint produced by MAV PUPE is given below. Calculated durability of coating in years at temperatures 20,30,40,50 и 60°C is: Calculated durability of coating in years when in service in climatic conditions of Eastern Europe is: Conclusions Express method was developed for evaluation of durability of protective coatings made of powder paints of polyester class. The method is based on empirical exponential dependence of coatings durability on activation energy of thermal-oxidative degradation of powder paint filming agent. Evaluation of the impact of destructive factors acting on macromolecules of protective coatings when in service, and lowering potential barrier of empirical bonds opening of polymer macromolecules was made and, as a consequence, the coating deformation-durability properties and service life. For the first time data was obtained on real service time of powder paint coatings, notably made of local powder paint. Determination of coating durability by express method `is performed in one working day, whereas the method established by standard takes four months. This makes it possible to promptly evaluate quality level of powder polyester paints from different manufacturing companies available on the market of paintwork materials of the Republic of Belarus. Besides, producers of powder paints of polyester class are permitted to noticeably shorten time for the development of new formulations of durable protective coatings.