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Epoxy coating destruction as a result of sulphuric acid aqueous solution action

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ABSTRACT

Destruction of epoxy coatings was examined under the influence of ageing with sulphuric acid aqueous solutions (3, 10 and 20%). The ageing caused oxidation, blistering and porosity increase of examined coatings as well as their surface roughness increase.

1. Introduction

Some of the most dangerous factors that induce failure of polymeric coatings are aggressive media which cause chemical destruction of coatings as a result of leaching, hydrolysis and oxidation. Such wear can be seen in lower protective efficiency resulted from cracking, blistering, increase of pore volumes and pore number as well as from loss of adhesion to the substrate. Action of aggressive media deteriorates also decorative properties (colour fading and gloss loss) [3–10,14].

Polymeric coating destruction induced by aggressive media increases if coatings are subjected to other factors, such as: humidity, heat, mechanical load, and erosive particle (hail, sand, soil lumps, and stones) impact [12,16–19].

Ageing of polymeric materials subjected to aggressive media consists, first of all, in oxidation leading in result to the formation of carbonyl groups C=O [2,6,15]. Spectrophotometric detection of such groups is very easy for many polymers because the absorption band corresponding to the valence vibrations of C=O group is very strong. Very often, formation of carbonyl groups is the first evidence of polymer material ageing and infrared spectra allow not only identification of such groups but also their quantitative estimation [1,5,6].

Oxidised surface layers of polymeric coatings show increased brittleness which results in cohesion loss in the pigment/binder resin system. In the next stage of coating ageing, pigment and filler particles are released from surface layers which leads to the increase of surface roughness [6]. In turn, higher surface roughness results in lower protective efficiency. This is due to the fact that resultant micro-roughness cavities gather contaminants and humidity. This is conducive to the development of biological corrosion which brings about etching pits in the coating structure and overcolouring on its surface [24]. Moreover, surface roughness increase results in loss of coating gloss which determines decorative properties [12].

Coating destruction resulting from aggressive media action affects coating hardness decrease. This is also evidenced by progressive oxidation process of polymeric material with ageing duration [6,9].

Ageing processes that occur in coatings contribute to the development of pores in their structure [13,20,22,23]. In effect, a coating loses the tightness as a result of generation of pathways that conduct aggressive media to the metal substrate [16–18].

Aggressive media action results in cracking and blistering of polymeric coatings. Coatings aged with aqueous solutions of sulphuric acid are especially prone to blistering [6,9].

Therefore, under the influence of aggressive media, polymeric coatings undergo both chemical and mechanical destruction which results in decrease of their operational durability [9,12].

2. Experimental

2.1. Materials and samples preparation

Painting material was obtained by blending epoxy paint with a polyamide curing agent (30% by mass). Epoxy coatings were

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applied, by air-spraying, on an apparent substrate (polyester sheet) as well as on steel substrate, according to the Polish Standard PN-79/C-81514.

Coatings were subjected to a two-stage hardening process; first: for 24 h at 20 °C, next: for 30 min at 120 °C. Then, they were acclimatised for 10 days at the temperature of 20 °C and the relative humidity of 65 ± 5% (according to the Standard PN EN 23270:1993).

Before ageing investigation, epoxy coatings were separated from the apparent substrate and during subsequent examination process were used in the form of free strips of coating layer. The following values were measured prior to ageing: coating thickness (acc. to PN-EN ISO 2808:2000), hardness (acc. to the Buchholtz method, PN-EN ISO 2815:2004) and coating surface roughness (acc. to PN-87/M-042251, PN-ISO 8501-1:1996, PN-ISO 8501-1Ad 1:1998).

The tested coatings (free as well as applied on steel substrate) were three-layered and had the mean thickness of 120 μm.

2.2. Methodology of ageing investigation on epoxy coatings

Epoxy coating samples were prepared according to the standard PN-EN ISO 1513:1999. Ageing of epoxy coatings under the influence of sulphuric acid aqueous solutions (3, 10, 20%) was carried out by immersion, according to the standards PN EN 2812-1:2001, PN EN ISO 2812-2:2000. The ambient temperature was 20 °C. The maximum ageing period was 1320 h.

2.3. Methodology of investigation on epoxy coating destruction

Destruction of aged epoxy coatings was analysed on the basis of microscopic investigation using SEM Hitachi S2460N. Its X-ray microanalyser with energy dispersion system (EDS) enabled also to chemical composition of coating surface layers examine. The EDS spectra were acquired using Voyager system Version 3.0. The elements were analysed employing qualitative and internally calibrated quantitative spectra at maximum excitation depth equal 1 μm.

Coating surface roughness was measured using T2000 Hommel Profilometer.

Changes in chemical structure of epoxy coating surface layers were analysed using PerkinElmer microspectrophotometer I-Series$^{\text{TM}}$. The registered FTIR spectra were mean values of 35 measurements. The spectra were analysed using the program IMAGE (PerkinElmer). Investigation consisted in "step by step" registration of infrared absorption spectra (FTIR) from chosen areas of the coating sample (squares of 50 μm side). The result of investigation was distribution of so called total absorbance related to the sample surface.

Porosimetric investigation on epoxy coating structure was carried out with the method of mercury porosimetry using the Autopore II (Micromeritics) apparatus.

Coating hardness was measured according to the Buchholtz method (PN-EN-ISO 2815:2004).

Estimation of dynamic tensile strength (rheological properties) of epoxy coatings was carried out using PL-DMTA (dynamic mechanical thermal analyser) apparatus manufactured by Polymer Laboratories. The tested probes (coating strips) were subjected to initial static tensile at the tension of 2.5/3 MPa and subsequently—to sinusoidal tensile cycles with the frequency of 1 Hz. Deformation amplitude was 16 μm. Coating specimens were tested in the range of temperature from 0 °C to 200 °C, at a heating rate 3 °C/min. Characteristics of dynamic storage modulus E', dynamic loss factor (tg δ) and coating elongation versus the temperature of epoxy coating sample were obtained. Dynamic storage modulus E' expresses potential energy accumulated by perfectly elastic materials during the deformation cycle. Dynamic loss factor—tg δ corresponds with the relation of loss modulus E'' to dynamic storage modulus E'. Loss modulus E'' expresses energy dissipated in the form of heat by perfectly viscous materials during their deformation.

3. Results and discussion

X-ray investigation showed that epoxy coating surface layers underwent oxidation by aggressive media. The highest oxidation degree showed surface layers of the coating aged with 20% sulphuric acid aqueous solution. Oxygen content in these layers was 31% (in the case of 1320 h ageing duration) and was three times higher than that in unaged coatings. Oxygen content in epoxy coating surface layers increased with ageing duration and aggressive medium concentration (Fig. 1).

It was stated that a significant effect of ageing on coating hardness (measured acc. to PN-EN ISO 2815:2004) decrease which evidences a progressive oxidation of epoxy material [6,15].

The higher the aggressive medium concentration, the lower coating hardness as a result of brittleness increases with coating oxidation level increase. In the case of ageing with 20% sulphuric acid aqueous solution, Buchholtz hardness decreased by 26% (from the value of 81—for the unaged coating, up to 60—for 1080 h aged coating).

Changes that took place in the structure of epoxy coatings subjected to sulphuric acid aqueous solution are reflected in the FTIR spectra, which can be seen in Fig. 2.

Infrared spectroscopic investigation proved formation of carbonyl groups characterised by the appearance of an absorption band at 1766–1721 cm^{-1}. The absorption intensity of this band increased with ageing duration and with aggressive medium con-

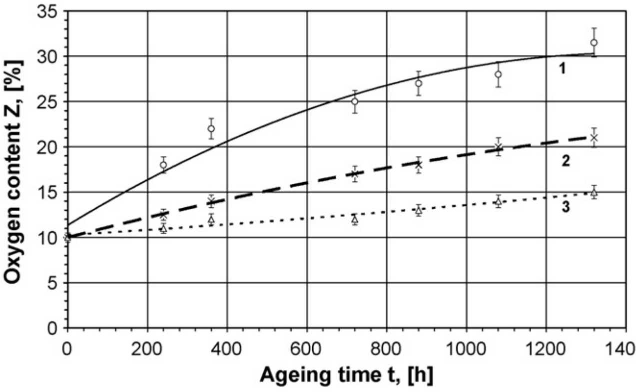

Fig. 1. Oxygen content in epoxy coating surface layers subjected to the action of sulphuric acid aqueous solutions: 3% (curve 3), 10% (curve 2), and 20% (curve 1).

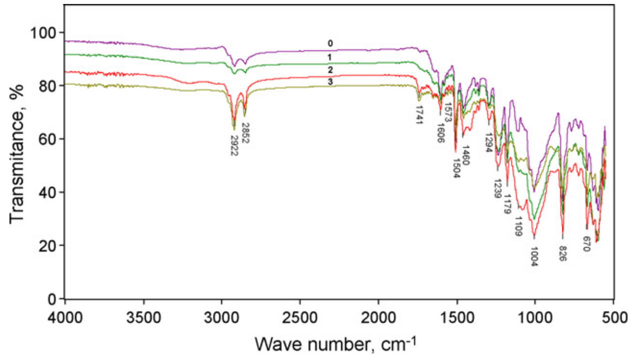

Fig. 2. FTIR spectra of epoxy coatings subjected to sulphuric acid aqueous solutions for 1080 h: 3%—curve 1, 10%—curve 2, and 20%—curve 3 (unaged coating—curve 0).