



## ELECTROCHEMICAL DELAMINATION OF ACRYLIC URETHANE COATINGS FROM STEEL

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*We study the adhesion of acrylic urethane coatings on steel by electrochemical delamination. The study established influence of the structure of hydroxyl acrylic oligomers and curing regimes on the electrochemical delamination of the formed acrylurethane coatings.*

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### Introduction

The global paint industry is currently on a declining trend in terms of emissions of harmful and toxic organic solvents. Traditional organic solvent-based compounds are being replaced by coatings with limited or no volatile organic compounds (VOCs), including waterborne dispersion materials) [1, 2]. However, the transition to VOC-limited coatings from traditional compositions presents the following challenges: rheology and viscosity control; control of polymer adhesive film thickness and protective and decorative properties.

VOC reduction is relevant for all coatings with different film-forming systems. This is particularly relevant for acrylic urethane materials, which are widely used in a number of different applications. They are used to produce high quality long-lasting coatings with excellent physical, mechanical and protective properties [3, 4]. They are characterized by fast curing, chemical resistance, weather, water, abrasion, frost and heat resistance. Acrylic urethane coatings have excellent adhesion to various substrates including metal, wood, plastic, concrete, etc. In addition, the finished coatings usually have an excellent appearance.

In competitiveness, coatings manufacturers are forced to minimize not only the VOC content but also that of expensive raw materials in their coatings formulations in order to reduce the cost of their recipes. The cost of the final product and the properties of the paintwork is mainly influenced by the type of hydroxyl-containing polyol used as the main film forming agent in the paint system.

The hydroxyl acrylic copolymers by various manufacturers currently available on the market are often characterized by the same indicators (hydroxyl number (HN), acid number



(AN), viscosity, mass fraction of non-volatile substances in the delivery form, glass transition temperature, etc.). These properties are regulated by changing the composition and ratio of the monomeric units in the hydroxyl acrylic oligomer. Thus, two copolymers with similar physical properties can have different compositions. Such products are positioned by raw material suppliers as analogous. Their replacement in the formulation of coatings can lead to a significant change in the properties of the resulting coatings. In most cases, this is unacceptable to the paint manufacturer and the consumer. When replacing raw materials to make them cheaper, complex checking of the physical-mechanical and protective properties of the coatings is necessary.

This paper presents material on the influence of the structure of the hydroxyl-containing acrylic oligomer and the curing regimes on the adhesion to steel of the formed acrylurethane coatings. We studied adhesion by electrochemical delamination.

The method of cathodic delamination is based on the fact that the destruction of the adhesive contact is caused by the release of hydrogen. This study uses a method in which the substrate under the coating alternately changes sign according to the frequency of the applied voltage. The frequency of the AC voltage was 50 Hz. In this case there is no destruction of the inert anode causing environmental change. The sample is connected to one of the AC voltage source contacts. During the experiment, the current in the circuit changes, which is proportional to the area of the coating delaminated from the substrate if the voltage remains unchanged.

### Study

The research was carried out using compositions containing various hydroxyl acrylic oligomers. The acrylic oligomer in Composition 1 (AO-1) contained mainly secondary hydroxyl groups. The acrylic oligomer of composition 2 (AO-2) contained primary hydroxyl groups. The acrylic oligomer of composition 3 (AO-3) contained both primary and secondary hydroxyl groups in 1:1 molar ratio. The aliphatic polyisocyanate biuret hexamethylene diisocyanate was used as a crosslinking agent and was added to the acrylic compositions at a ratio of  $[-NCO]/[-ON] = 1.0$ .

The acrylic compositions were made to a working viscosity by injecting a mixed solvent (xylene/butyl acetate = 1/1) and applied with a 70  $\mu\text{m}$  thick slot applicator to the steel plates. The films were cured for 14 days at the following temperature regimes:

- at room temperature;
- 1 hour at 40 °C, then at room temperature;
- 1 hour at 60 °C, then at room temperature;
- 1 hour at 80 °C, then at room temperature.

The dry film was 30  $\mu\text{m}$  thick.

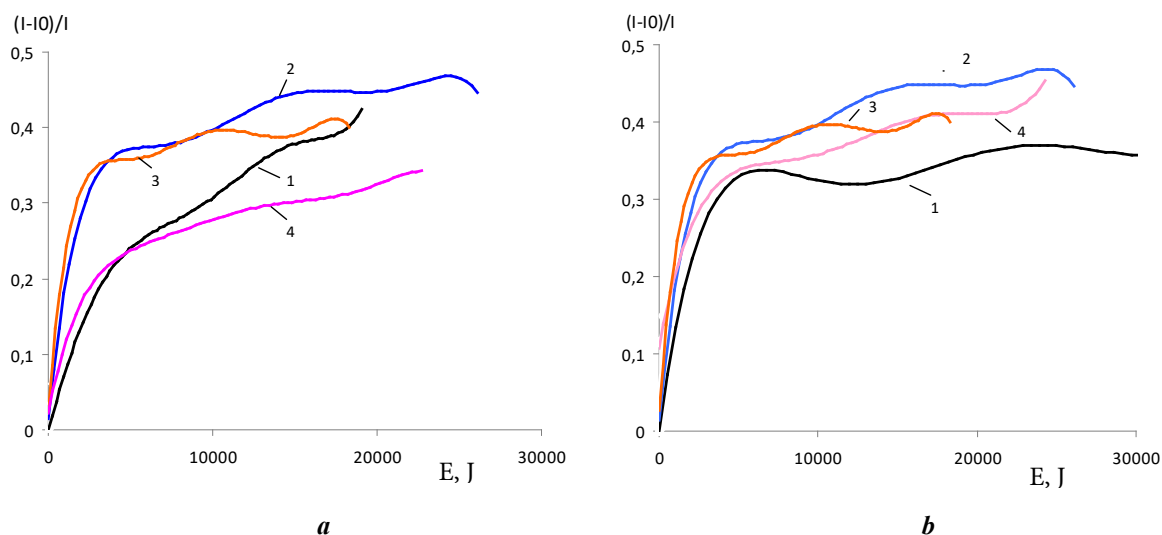
The adhesion of acrylic urethane coatings to steel was assessed by plotting the relative change in current against the delamination energy. For this purpose, an incision was made in the coating to the steel of a certain area using a calibrated cutting tool. The plates were placed in 0.5M aqueous solution of NaOH, through which AC voltage was passed. The electrodes used were a stainless-steel plate and an acrylurethane-coated plate.

Fig. 1 shows the correlation between the relative current and delamination energy of acrylic urethane coatings on steel.



On the one hand, the increase of curing temperature of acrylic urethane coatings should lead to a reduction in the relative current at the same applied delamination energy due to an increase of the density of the chemical lattice, preventing the diffusion of electrolyte and water to the substrate. On the other hand, an increase in curing temperature should result in an increase in current due to the build-up of internal stresses in the forming coatings.

By Fig. 1 the locations of the relative current vs delamination energy dependencies indicate this conflict.



**Fig. 1** Dependence of change in relative current on delamination energy of acrylicurethane coatings on steel formed on the basis of compositions with secondary OH-groups (a); primary OH-groups (b). The curing temperatures: 1 – 20 °C; 2 – 40 °C; 3 – 60 °C; 4 – 80 °C

The slices were made of these curves at delamination energies of 10,000 J and Table 1 was made.

The adhesion of acrylic urethane coatings is relatively high at the first curing mode. The increase of the curing temperature (transition to the second mode) leads to a sharp increase of the relative delamination current. However, a further increase of temperature (transition to curing modes 3 and 4) leads to its reduction.

It is evident that at room temperature curing (mode 1) an underdeveloped three-dimensional polymer film lattice is formed. High temperatures are required for the formation of allophanate, biuret chain fragments because the activation energy for their formation is 3-3.5 times higher than the reaction between hydroxyl groups and isocyanates. The incomplete three-dimensional chemical lattice weakly prevents the formation of intermolecular (dipole-dipole, dispersion) and chemical (chemisorption) bonds between functional groups of the polymer chain and the active centers on the metal surface. The low delamination of acrylic urethane coatings based on AO-1 and AO-2 oligomers in curing mode 1 (Table 1) is due to the high concentration of "polymer-metal" physical and chemical bonds.

The transition to the second and third curing regimes, with a curing time of 1 hour at 40 and 60 °C, leads to an increase of the chemical lattice density. The observed increase in delamination of formed coatings based on acrylic oligomers AO-1 and AO-2 (Table 1) indicates an increase of steric hindrances in the formation of "polymer-metal" physical and chemical bonds.

In contrast, a transition to the fourth curing regime, with films cured at 80 °C for 1 hour, leads to a sharp decrease of AO-1 and AO-2 based coatings delamination degree. In this curing



regime, the three-dimensional acrylicurethane lattice is the most advanced, with high steric hindrances for the formation of metal-polymer adhesion bonds. The poor delamination of these films is obviously caused by the low diffusion of corrosive agents (water, oxygen, electrolytes) to the substrate through the film.

**Table 1.** Relative corrosion current values at a delamination energy of 10,000 J, for coatings with NCO/OH = 1:1

Temperature mode	AO-1	AO-2	AO-3
№ 1	0.31	0.33	0.43
№ 2	0.41	0.42	0.41
№ 3	0.39	0.41	0.42
№ 4	0.27	0.37	0.44

### Conclusions

According to the study, the structure of hydroxyl acrylic oligomers significantly affects the adhesion of acrylic urethane coatings. The coatings based on acrylic oligomer with secondary hydroxyl groups (AO-1) have the highest adhesion among the coatings formed at a stoichiometric NCO/OH ratio.

The best adhesion of the coatings is formed at curing modes 1 and 4. At mode 1 – by a more complete interaction of functional groups of polymers with metal active centers, and at mode 4 – by a denser three-dimensional chemical lattice preventing the diffusion of corrosive agents.

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