The impact of external factors on the degradation process of refinish top coatings

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Introduction

Top coatings applied to the motor vehicle body deliver protection and decoration functions. First of all, they protect the vehicle body against the corrosion, yet they determine the appearance and even the price of the vehicle. If we want to buy a second-hand car, we always, in the first instance, pay attention to its appearance, that is, the condition of its top coating, and later to the technical conditions of the vehicle itself. A vehicle with the high mechanical efficiency, but lustreless top coat is less attractive than a car with a well maintained top coating. Thus, the top coatings, apart from their perfect anti-corrosion properties, must be characterised by the resistance to atmospheric conditions and ageing. This refers to both top coatings and refinish coats [1÷3].

Besides the anti-corrosion properties similar to those of the industrial varnish, the refinish coating needs to have nearly identical resistance to the atmospheric conditions in order to make it undistinguishable from the remaining original coating of the vehicle after some time. The top coatings of the motor vehicles are mainly exposed to such factors as: sunlight, particularly UV radiation, acid rain and brine (in winter, the roads are salted) [4÷7].

This paper presents the studies on the behaviour of the refinish coatings exposed to the impact of the experimental external factors depending on the exposure time.

Experimental part

Nowadays, the products based on acrylic resins are most commonly applied in the process of manufacturing the refinish coatings. The majority of coatings applied to brand new cars are made of waterborne products, whereas the refinish coatings are still usually made of solvent-based products. The products based on waterborne acrylic resins have been already present on the refinish product market, but their application in painting workshops involves considerable investments that are necessary to maintain the proper technological requirements while applying such types of coatings. The acrylic coatings, both from waterborne and solvent-based products, are characterised by high resistance to the atmospheric conditions, including the UV radiation.

The research included two systems of acrylic coatings that were aged in different environments. These coatings were made of acrylic resin based products of DuPont and Spies Hecker companies. They are standard refinish products currently used in the painting workshops.

Two systems of top coatings, marked as coatings I and II, were performed. Coating I was made from a clear coat and a layer of the top coat paint. Coatings II presented a three-layer system: the clear coat, the base coat with metallic pigment and the top coat providing protection against the harmful effects of the UV radiation.

The accelerated ageing studies were conducted on these coats under the experimental conditions similar to the vehicle operation conditions.

The refinish coatings were aged under the impact of the following factors:

- UV radiation
- acid rain (aqueous solution of sulphuric acid of pH = 4.3)
- brine (3% aqueous solution of sodium chloride).

The ageing tests under the impact of the UV radiation were carried out in the period of 840 hours in the Ci 3000 W Xenon weather-ometer of Atlas company (according to PN-EN ISO 11341:2005). Xenon arc burner with the power of 4500W emitted the light visible in the spectrum similar to the natural sunlight. The samples for evaluating the ageing time were collected during the exposure period.

As the literature does not provide any exact specification for the chemical content of the acid rain (it is usually assumed to be the mixture of sulphuric and nitric acids of pH 4.3 – 4.5), the ageing tests involved the solution of sulphuric acid of pH=4.3 (measured with MultiLab 540 pH-meter). The coatings were aged for 1200 hours and the samples for tests were successively collected.

Brine was the third factor to which the top coatings were exposed. 3% aqueous solution of sodium chloride which reflected both the content of slush (roads covered with snow are salted or sprayed with brine) and the "atmospheres" of roads located in the coastal areas was used in the experimental tests. A 1200-hour exposure was provided to these coatings. Also in this case, the samples were successively collected for the experimental purposes.

The assessment of the top coating degradation level

In order to evaluate the degradation level of the coating exposed to the atmospheric condition, the following methods were used: dynamic mechanical analysis DMA, optical microscopy and mercury porosimetry.

The visco-elastic properties of polymer materials can be evaluated with the thermomechanical analysis. The sample behaviour under the impact of oscillatory loading was tested using the DMA (Dynamic Mechanical Analysis) method [8, 9]. The tests on the dynamic properties of acrylic coatings were carried out at the following parameters: a type of deformation – shear, frequency 1 Hz, amplitude - 1μm, shear force – 1N, temperature range 20–120 °C, heating rate 3 deg./min.

The following table presents glass transition temperatures T_g and changes of storage modulus G' for both top coatings depending on the type of factor and exposure time.

The significant increase in glass transition temperature along with the increased exposure time indicating the additional hardening of the coating was observed for the coating I exposed to the UV radiation. The increase of storage modulus was just slight, which resulted in greater hardness and brittleness of the coating. Coating II (with additional top coat providing the protection against the UV radiation) is characterised by the lower glass transition temperature. Also in this case, the aged sample demonstrated the increased glass transition temperature at the increasing exposure time in the weather-ometer. Coating II was also hardened under the impact of the UV radiation, however, to a smaller degree in comparison with coating I.

Acid rain did not influence the value of glass transition temperature of coating I, whereas there was a 3-fold decrease in the value of the storage modulus at the increasing exposure time. This indicates the degradation of the coating. Coating II behaved differently. A slight increase in the glass transition temperature and the increased storage modulus could be observed in this case. This indicates the increased hardness and stiffness of the coating.

Table 1

Changes of glass transition temperature and values of storage modulus for coatings I and II depending on the exposure time and a type of the factor

Type of factor	Ageing time, h	Glass transition temperature T_g, °C		Storage modulus G' at 20°C, MPa	
		Coating system of type		Coating system of type	
		I	II	I	II
UV	0	76.5	70.5	1500	1300
	400	95.6	76.4	1600	1650
	840	94.1	80.5	1650	1850
Acid rain	0	76.5	70.5	1500	1300
	600	77.8	73.2	500	1500
	1200	78.0	75.7	400	1700
Brine	0	76.5	70.5	1500	1300
	600	76.0	71.3	900	1500
	1200	83.5	76.2	500	1550

Coating I has low resistance to the brine. The decrease in the value of the storage modulus by as much as 75% and the increase in the exposure time show the considerable degradation of the top coating. Higher temperature T_g and the increased exposure time indicate that the coating is becoming harder, and at the same time more brittle. Coatings II are more resistant to brine than coatings I. At the increasing exposure time, they are becoming slightly hardened, which is suggested by the minor increase in the glass transition temperature and the increase in the storage modulus value.

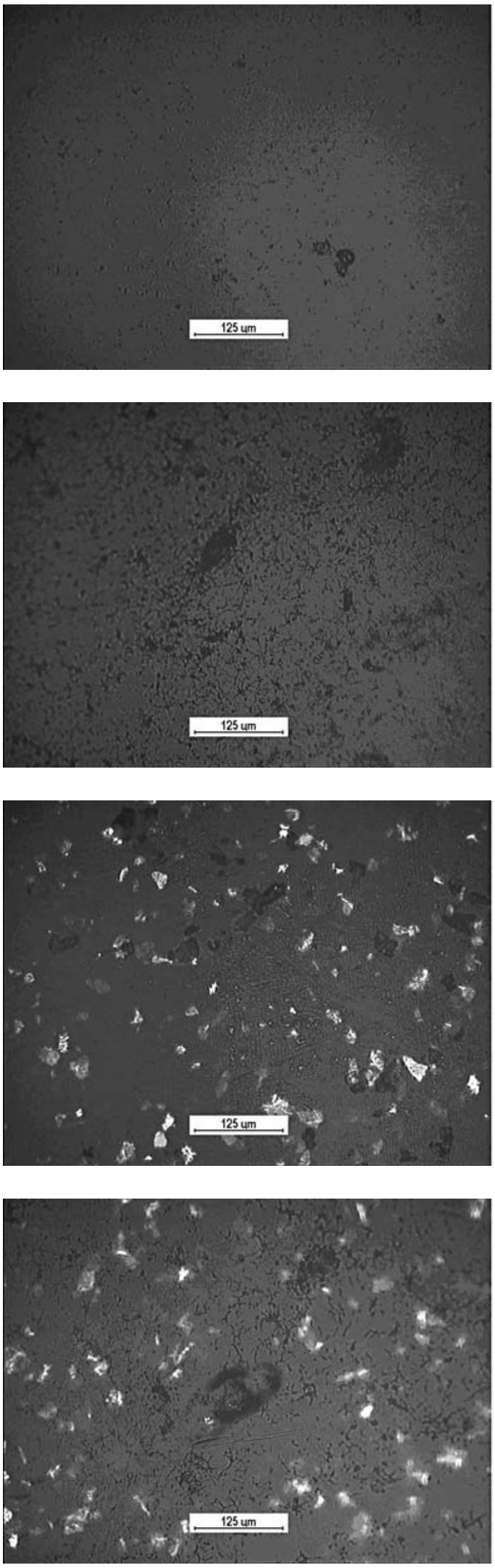
The ageing effects were also evaluated by observing the changes of the tested acrylic top coatings with the optical microscope. The optical microscope of Nikon company was used.

The exemplary photos enlarged to 200 times are presented in Photo 1.

By analysing the obtained microscopic pictures, the conclusion can be drawn that the majority of changes at the tested top coatings are observed for coating I. Coatings II with an additional acrylic top coat are by far more resistant to the aggressive external factors such as acid rain or brine. Similar effects could be observed for the UV radiation.

The distribution of pore sizes and volumes, and consequently the effect of factors resulting in the ageing of the top coatings were evaluated on the basis of the porosimeter measurements. The measurements were carried out with Auto Pore IV 9500 mercury porosimeter of Micromeritics company. The volume of mercury intruded into the pores of already degassed material was determined for fixed consecutive increasing levels of pressure. The distribution of the macro-pore volumes was determined on the basis of the Washburn's equation [10].

The exemplary distributions of the pore volumes in the selected sample depending on the exposure time of a specific factor (impact of the acid rain – Photo 2) and the comparison of behaviours of coatings I and II exposed to one factor at the same time (exposure to the UV radiation, Photo 3) are presented below.



1
2
3
4

Photo. 1 Changes of the acrylic top coating. 1 – non-aged coating I; 2 – coating I after 1200 hrs of ageing with the solution of sulphuric acid ; 3 – non-aged coating II ; 4 – coating II after 1200 hrs of ageing with the solution of sulphuric acid

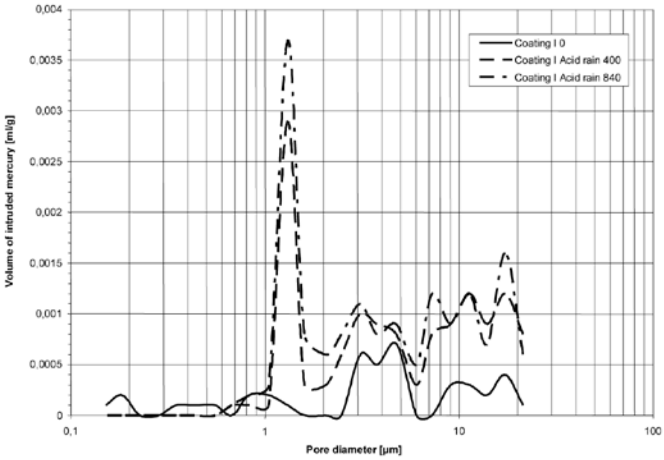


Photo. 2 Distribution of pore volumes in coating I aged with the acid rain depending on the exposure time

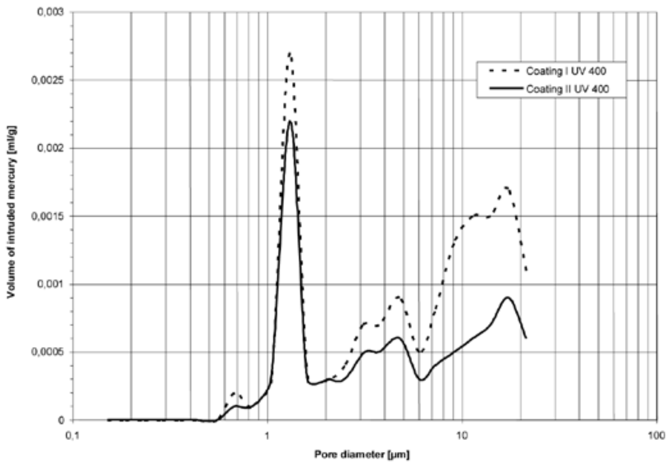


Photo. 3 Comparison of coatings I and II aged with UV radiation for 400 hrs

For coatings I, the clear growing tendency for the sample degradation at the increased exposure time to the specific factor can be observed. This is caused by the increased quantity of pores previously present in the material and the formation of new ones having different average diameters. Coating II is characterised by greater resistance to the external factors than coating I. The quantity of new pores is smaller and the quantity of already existing ones is increasing slower. The positive impact of the UV radiation on coating II resulting in the additional hardening of the paining coat was also observed.

Summary

This paper presents the assessment of the impact of types of factors resulting in ageing of the refinish acrylic top coatings and the time of their exposure. It can be stated that the three-layer acrylic coatings (type II) are much more resistant to the external factors than the two-layer coatings (type I).

Besides the resistance to the external factors, to which the motor vehicles are exposed, the three-layer coatings provide additional aesthetic quality. They are usually metal-effect coatings.

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