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RESEARCH ON THE INFLUENCE OF ULTRASONIC VIBRATIONS ON PAINT COATING PROPERTIES

Summary

The article describes the application of ultrasonic vibrations to the preparation of paint before the coating process. Ultrasonic processing decreases the viscosity of the paint and the size of its particles. Changing the properties of the paint has a positive influence on the parameters of torch spraying. The results of using ultrasound during the preparation of the paint before the coating process are improved properties of the coating in comparison with those of the coating applied by using the paint without the application of ultrasound.

Key words: *paint coating, properties, ultrasound*

1. Introduction

Coating materials used in machinery are complicated multi-component systems which present a kind of pigment suspension in the solution of a film forming polymer.

The technology of a paint coating process includes preparation, application, and drying. According to the technology, a liquid paint should be easily applied to a surface to create a polymer coating which should provide high quality protection after drying [1].

One of the methods of coating material preparation is based on adding a solvent to the paint. This method involves the following issues:

- several layers of paint that should be applied to a surface,
- defects in the paint coating,
- hazardous conditions during the coating process.

As many other polymer solutions, the coating material is a high viscosity liquid because of the following factors [2, 3]:

- structuring during the aggregation of particles is accompanied with the creation of fragile structures,
- particles and macromolecules which have elongated forms change their space orientation,
- deformation of polymer macromolecules or emulsion drops in the flow.

Viscosity increases during the coating process because of dissolved particles which create complicated structures and the solvent evaporation.

The created structures are destroyed because the outer pressure in the polymer solution increases and the solvent is eliminated. This decreases viscosity. The relation between viscosity and pressure for such type of systems can be presented by the Bingham equation (1):

$$p = p_{\mathrm{B}} + \eta \frac{\mathrm{d}V}{\mathrm{d}x} \tag{1}$$

Here, p is the acting pressure (shear stress), p_{B} is the maximum shear stress by Bingham, η is the viscosity, $\mathrm{d}V/\mathrm{d}x$ is the velocity flow gradient.

Introduction of ultrasonic vibrations is one of the methods for destroying these structures [4,5] changing the acoustic pressure (2):

$$P_{\mathrm{a}}=P_{\mathrm{A}} \sin(2\pi f t) \tag{2}$$

Here P_{A} is the maximum value of acoustic pressure; f is the frequency of ultrasonic vibrations.

Cavitation and acoustic flows are initial mechanical effects which occur by the action of acoustic pressure in a fluid. They create secondary effects such as heating, dispersion, coagulation, oxidation, acceleration of chemical reactions, etc. [6-20].

The intensity of ultrasound processing depends on the absorbing capacity of the processed material, which is determined by the coefficient a in accordance with structural and thermal energy losses (3).

$$a = \frac{2\pi^2 f^2}{\rho c^3}\left(\frac{4}{3}\eta + \frac{(\gamma-1)K}{\gamma C_v}\right) \tag{3}$$

Here, η is the viscosity of the material, f is the ultrasound frequency, K is the coefficient of thermal conductivity, γ is the molar thermal conductivity ratio, C_v is the molar thermal conductivity at constant volume.

On the other hand, the viscosity reduction due to ultrasonic vibrations will increase the influence of secondary effects.

Ultrasonic processing of polymers has been described in a number of articles [10, 16, 20-22].

Investigation results in [10, 16] show that high-intensity ultrasonic vibrations accelerate processes in liquids with high viscosity or density of disperse phase. There are typical examples of this application: polymerization and depolymerization of high-molecular compounds, modification of epoxy oligomers, melt mixing, emulsions, dissolving of sludge, dispersion and uniform spraying of solid particles in polymer materials and technical oils.

The article [21] describes the processes of polymerization and depolymerization. Cavitation is the main cause of depolymerization. Pressure produced under pulsation and bubble bursting cause the destruction of macro molecules. Moreover, this process is accelerated in the presence of gases because vapour and gas bubbles are the sources of cavitation.

Research on the application of ultrasonic processing during the preparation of coating material was done in the MADI Laboratory of electro-physical methods of treatment.

Research was done into the following:

- changing of the coating material properties under ultrasonic processing with different parameters,
- influence of the ultrasonic processing of the coating material on the spraying process,
- determination of the paint coating properties achieved by applying the coating material prepared by using ultrasound.

2. Research procedure

Enamel made of alkyd and melamine-formaldehyde resins was used as the test material in the research. The enamel had the following properties:

- the initial viscosity was 910 cPa·s
- the required volume of a solvent was 30%,
- viscosity during the preparation of the paint coating was from 90 to 120 cPa·s.

Properties of the paint and the paint coating were measured during the research.

A rotational viscometer, model Fungilab, was used to measure the viscosity of the paint used as a coating material. The rotational viscometer measured the torque of a spindle rotating in a sample at a specified velocity. The particle size of the paint (the coating material) was measured by a grindometer (GOST 6589-74). It measured the size of particles of the suspension, i.e. the paint (coating material).

The weight of the paint coating was measured with a Const 5 measuring device. The strength of the surface-coating bond was measured with an adhesion tester. It measured the force required to pull off the paint coating from the surface. The surface roughness was measured with a profilometer (model 130), which measured defects of the tested surface. The hardness of the paint coating was measured with a PMT-3 micro hardness tester. It measured the micro hardness of the paint coating by applying a load to its surface. Subroughness of the paint coating was examined with a microscope, CMM-2000. The wear resistance of the paint coating was also measured. The test sample was treated with a grinding wheel, with P320 grain size. The force applied was 20 N. The duration of testing was 60 seconds. Wear resistance can be determined using the following equation:

$$M = \frac{m_1 - m_2}{m_1 - m_0}$$

where

m_0 – mass of the plate before painting,

m_1 – mass of the painted plate,

m_2 – mass of the painted plate after abrasive treatment.

3. Experimental research on the influence of ultrasonic processing on liquid coating material properties

A rod-shaped magnetostrictive transducer was immersed in a tank (50 ml) with the coating material (paint) (Fig.1). The ultrasonic processing of the material was performed under varied conditions, resulting in a number of effects: low amplitude (3 micrometer) – cavitation; intermediate amplitude (10 micrometer) - combined action of cavitation and acoustic flows; high amplitude (20 micrometer) – strong acoustic flows. The frequency of sound waves was 22 KHz. Initial viscosity of the liquid was η_0=910 cPa·s.

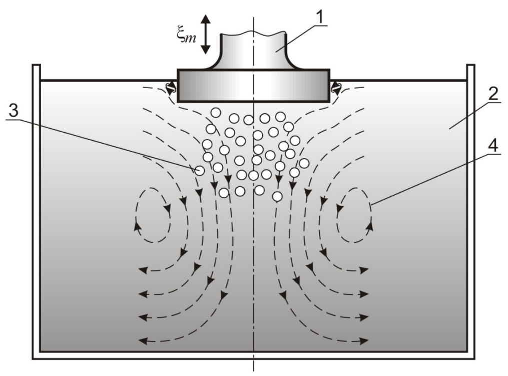

Fig. 1 A schematic of ultrasonic vibrations in liquid.
1- vibration transducer, 2- liquid, 3-cavitation zone, 4- acoustic flows

Viscosity of the obtained samples was measured by a rotational viscometer.

Fig. 2 illustrates how viscosity changes under ultrasonic processing.

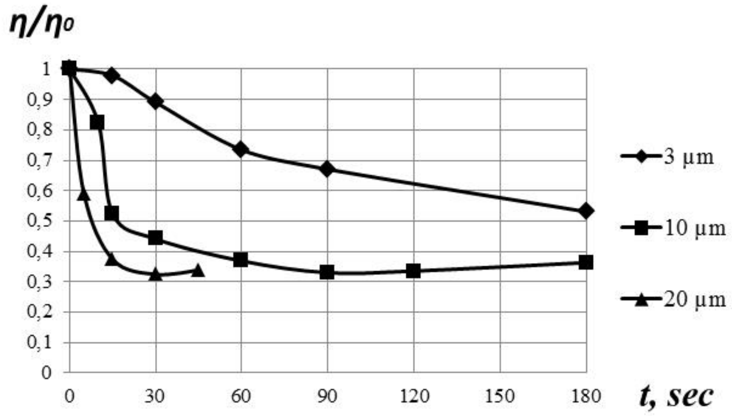

Fig. 2 Viscosity changes under ultrasonic processing

Viscosity decreases during all three conditions of ultrasonic processing (maximum viscosity decreases by about 70 percent) and this decrease becomes sharper with an increase in the amplitude of ultrasonic vibration. The best results were achieved when the amplitude of ultrasonic vibration was 10 micrometer (duration - 90 sec) and 20 micrometer (duration - 30 sec: viscosity decreases by about 70 percent). With a 3 micrometer amplitude, the viscosity decreased only by 50 percent after 180 sec of sonication. This is accounted for by the low lead-in power and the absence of acoustic flows.

Viscosity decreases due to several processes taking place during the ultrasonic processing:

- destruction of macromolecules formed during the process caused by the action of van der Waals forces and capillary forces, the action of shock waves, liquid microjets, microflows, or in the vicinity of cavitation bubbles and friction flows formed by the deceleration of acoustic flows near the surface,
- mixing of the coating material under the influence of acoustic flows. Particles of the coating material become uniform under the influence of sound waves,
- depolymerization, occurring due to the difference between the vibration speed of the solvent and that of the polymer.
- dispersion of pigment particles as a result of cavitation.
- heating that leads to a decrease in viscosity which enhances all the processes listed above.

Dependence diagrams have their breaking points, i.e. points where the positive influence of ultrasonic processing ends and viscosity increases. This phenomenon could be explained by the simultaneous existence of the processes which initiate polymerization during the process of ultrasonic processing:

- increase in the number of free radicals at high temperatures generated by the cavitation bubble collapse,
- deceleration of depolymerization process due to ultrasonic degasification,
- increase in the number of recoverable connections between particles (thixotropic),
- acceleration of the solvent evaporation due to heating,
- possible increase in the lower critical temperature of the solvent leading to the system stratification due to the difference between thermal expanding coefficients of components.

Thus, the process of coating material heating leads to positive and negative effects. Therefore, the coating material temperature during the process of ultrasonic processing has to be determined. Temperature measurement was made for each viscosity measurement of investigated samples (Fig. 3).

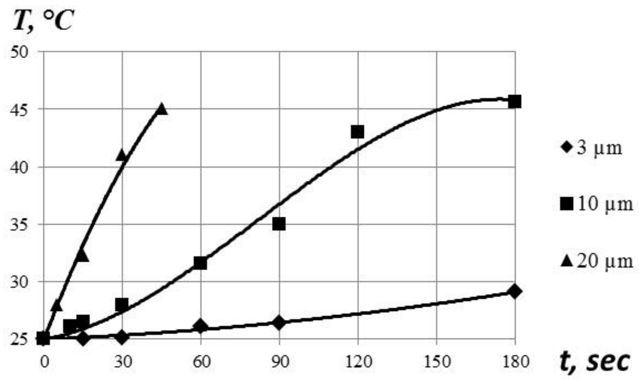

Fig. 3 Heating of the coating material under the influence of ultrasonic vibrations

The influence of heating on the viscosity decrease was determined during the experiment in which the coating material was heated without ultrasonic vibrations. Results of this research were used to create the $\frac{\eta}{\eta_0(T)}$ graph presented in Fig. 4. The critical temperature of about 40°C was identified as the temperature which leads to an intensified polymerization reaction.

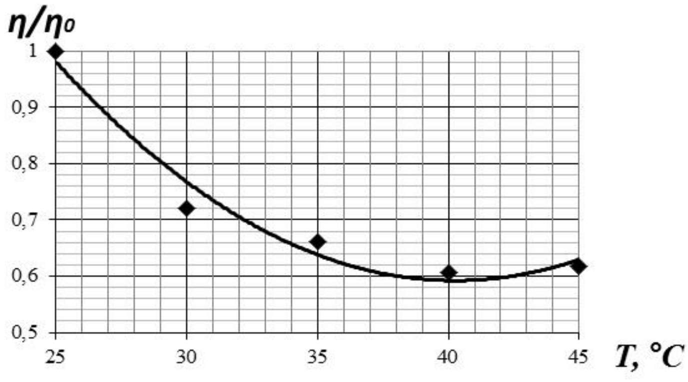

Fig. 4 Changes of coating material viscosity during heating

The assessment of ultrasound effects without heating was done by comparing the data related to the viscosity change caused by heating with the temperature data in each research point, and by the mathematical simulation based on the data available in the diagram shown in Fig. 3. The ultrasound effects without heating are shown in Fig. 5.

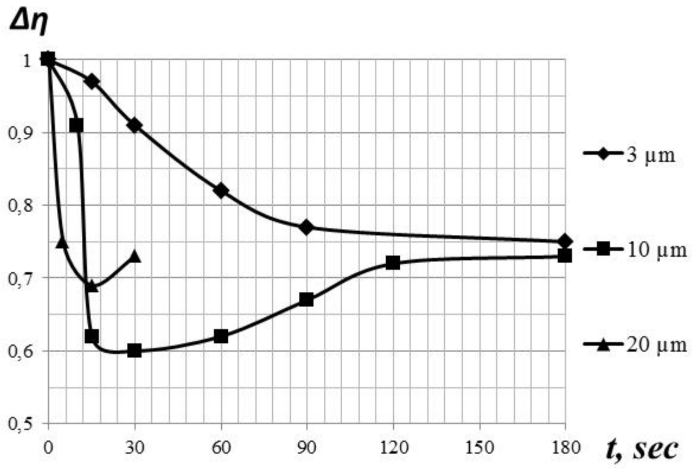

Fig. 5 Effects of ultrasonic processing without heating obtained by mathematical simulations

The strongest effect of ultrasonic processing on the viscosity decrease is noted under the intermediate condition when the duration of ultrasonic processing is 15-60 seconds. Viscosity decrease under the influence of all the other factors except heating is about 55-70 percent. The maximum influence of ultrasonic processing is noted when the duration is 60 seconds and the viscosity decrease is 65 percent. During that time, the temperature of the coating material rises by 7°C.

The particle size was measured after the ultrasonic processing in different conditions determined by the maximum size of particles in the paint composition.

Table 1 Changes in the particle size of the paint

Particle size	*Without processing*	ξ_m=3 µm t=180 sec	ξ_m=10 µm t=60 sec	ξ_m=20 µm t=15 sec
D_{max},, µm	10	9.16	7.5	10

A small decrease in the particle size during the ultrasonic processing with a wave amplitude of ξ_m=3 µm and processing time of 180 sec is explained by cavitation which occurs only in accidental parts of the treated volume. The absence of acoustic flows does not allow other parts to be involved in the space under the influence of cavitation. The main cause of that are acoustic flows with an amplitude of ξ_m=20 µm and processing time of 15 sec, which do not grind pigments. The pigment size decreases because of a simultaneous action of cavitation and acoustic flows with an amplitude of ξ_m=10 µm and processing time of 60 sec, when all parts are in the space under the influence of cavitation.

A correlation between the general type diagram which shows the viscosity change (Fig. 6) and the rheological curve of structured fluids (Fig. 7 [3]) should be noted. There are 3 zones:

- a small viscosity decrease connected with resistance to,
- a large viscosity decrease under the influence of ultrasound,
- a gradual viscosity increase.

In contrast to this, the third zone of the rheological curve corresponds to the viscosity of a Newtonian fluid with fully destroyed structure (the diagram line is parallel to the axis). It means that the ultrasound application does not lead to a full destruction of structures which have been formed in the coating material. The influence of ultrasound is characterized by a limited value of viscosity decrease.

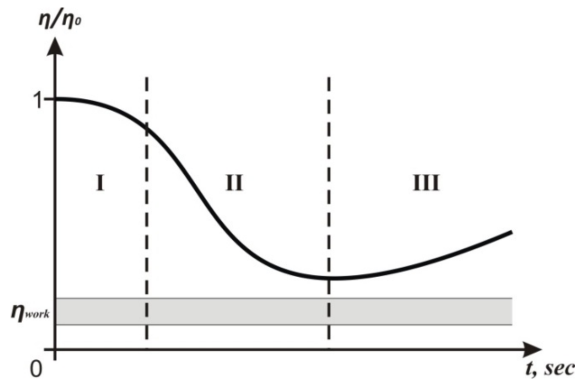

Fig. 6 General view of changes in viscosity

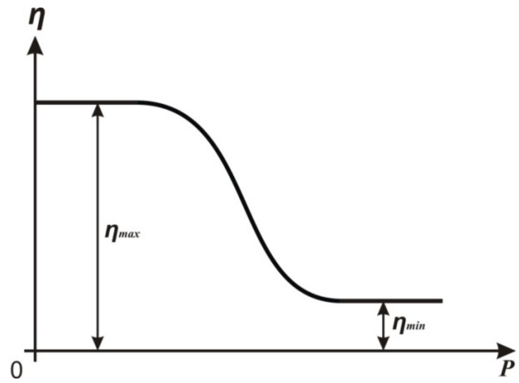

Fig. 7 Rheological curves of structured fluids

Results of mathematically approximated experiments confirm this statement. The obtained approximated interdependence between the viscosity decrease and experimental conditions (experimental data of the first zone were not taken into account) is expressed as follows:

$$\eta/\eta_0=1-(7.17\xi_m^2+62.2\xi_m+251)10^{-5}t+(11.2\xi_m^3-75.8\xi_m^2-563\xi_m)10^{-8}t^2 \qquad (4)$$

The dependence diagram between the viscosity change and the ultrasound processing parameters was obtained using equation (4) is shown in Fig. 8.

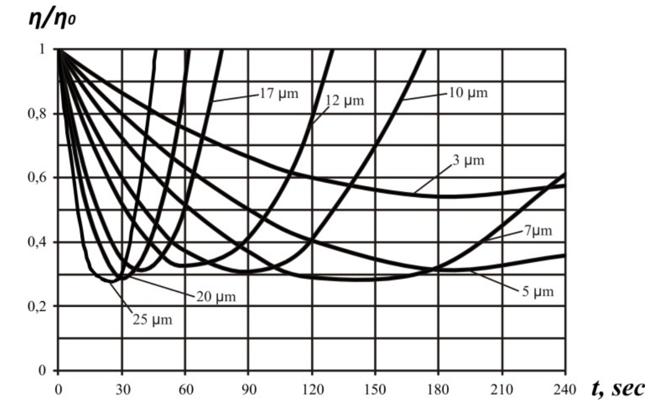

Fig. 8 The dependence diagrams between the viscosity change and the ultrasound processing parameters

The decrease in viscosity is about 70 percent in all processing modes with amplitudes higher than 5 micrometer. The increase in the amplitude has only influenced the rate of viscosity decrease.

4. Influence of the ultrasonic processing of the coating material on the spraying process

Viscosity decreases by about 70 percent under all conditions when the amplitude is higher than 5 micrometer.

Standard equipment (a paint sprayer and an air compressor) was used during the experiment. The diameter of the paint spray nozzle was 1.5 mm, the air pressure was 4 bar. Fig. 9 shows types of spray torches.

Influence of the ultrasonic processing on the spraying process was estimated by comparing topography parameters of sprayed samples prepared by both methods. Standard technology includes 30 percent solvent adding according to the manufacturer's manual, shown in Fig. 9a. Our experiment was done using only 10 percent solvent with the following ultrasonic processing parameters: amplitude ξ_m=10 µm during 60 seconds. In this condition, the influence of ultrasound application was greatest. Viscosity of samples was $0.1\eta_0$. The diameter of the nozzle was 1.5 mm with 4 bar air pressure. Fig. 9b illustrates the obtained spray torches.

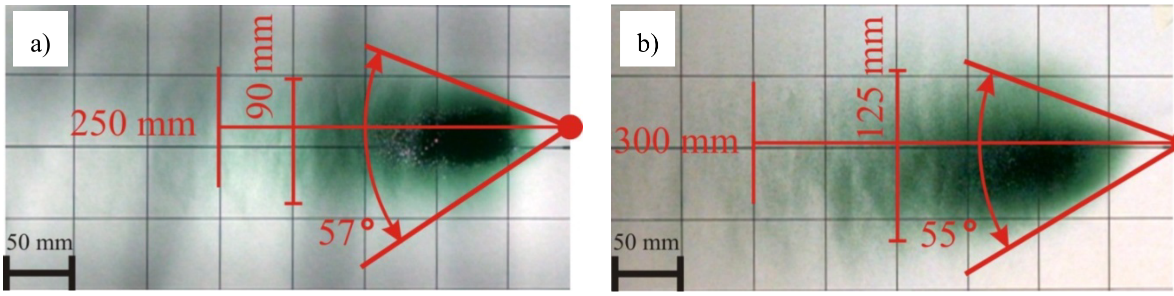

Fig. 9 Spray torches from the coating material prepared by using:
a) – typical technology; b) – developed technology

The angle of spray torch after the ultrasound treatment changed only slightly because the viscosity of samples was the same. The width of the torch rose from 90 mm to 125 mm in the case of spraying the coating material treated by ultrasound. This is connected with a simultaneous increase in the paint density and the velocity of aerosol drops and a decrease in the number of drops which participate in the fogging process. Also, these processes explain the increase in the torch height from 250 to 300 mm.

5. Influence of the ultrasonic processing of the coating material on the coating properties

Metal plates were painted to estimate the influence of ultrasound treatment of the coating material on the properties of the coating. The determined thickness of the paint coating prepared with the ultrasound treatment opened up a possibility to apply the paint coating in one layer in contrast to the standard technology which requires two layers. Thickness of the two-layer coating was 34 micrometer, and that of the one-layer 27 micrometer.

Table 2 Properties of paint coatings

Parameter	*For typical technology*	*For developed technology*
Ra, μm	0.037	0.024
Rz. μm	0.404	0.273
Microhardness, kg/mm^2	2.29	3.1
Adhesion, MPa	4	5
Mass loss, g	0.43	0.27
Properties on the submicro scale:		
Ra, nm	8.7	3-4
F_{ff}, N	1.52 x 10^{-12}	1.36 x 10^{-12}
F_{sv}, N	0.31 x 10^{-15}	0.23 x 10^{-15}

A decrease in the values of amplitude parameters of surface roughness (*Ra* is the average deviation of the profile, *Rz* is the sum of 10 highest profile points) of up to 1.5 times is explained by non-uniform pigment distribution in the upper layer of the paint coating prepared using a typical spraying technology of pressure pulverization of the coating material prepared with ultrasound. Some droplets which have small sizes settle on the surface of the coating at a low speed, which does not allow them to overcome the force of surface tension.

Increased microhardness of a dry film defines the durability of the paint coating which was caused by the ultrasound degassing effect and reduction in the amount of the applied solvent. As a result, the coating has less micropores and the probability of their occurrence during drying decreases.

Adhesion increase is connected with the application of one-layer technology in which, great amounts of the coating material flow into microdepressions of the surface due to the gravity force, decreasing the gripping square end. Adhesion increase is also connected with the vaporization of the reduced solvent, which results in micropores at the boundary line and to depolymerization effect which improves the spraying process.

Improved wear resistance is connected with decreasing the amplitude parameter value of roughness at the micro and the submicro scale and with increasing the paint coating durability. Properties of the paint coating at the submicro scale were investigated by the atomic force microscopy. Topographies of paint coatings were obtained at the 3.5x3.5 micrometer size, shown in Fig. 10. Increased roughness on the paint coating surface after ultrasonic processing is explained by erosive disruption of pigments under collapsing and fluctuating cavitation bubbles, which leads to saturation of the upper layer by pigments. Parameter scan was done to control the following:

- constant height *Ra* to determine roughness parameters at the submicro scale,
- lateral friction contact to estimate the friction force F_{ff} change,
- vertical viscosity contact to determine viscosity of the surface F_{sv} [23].

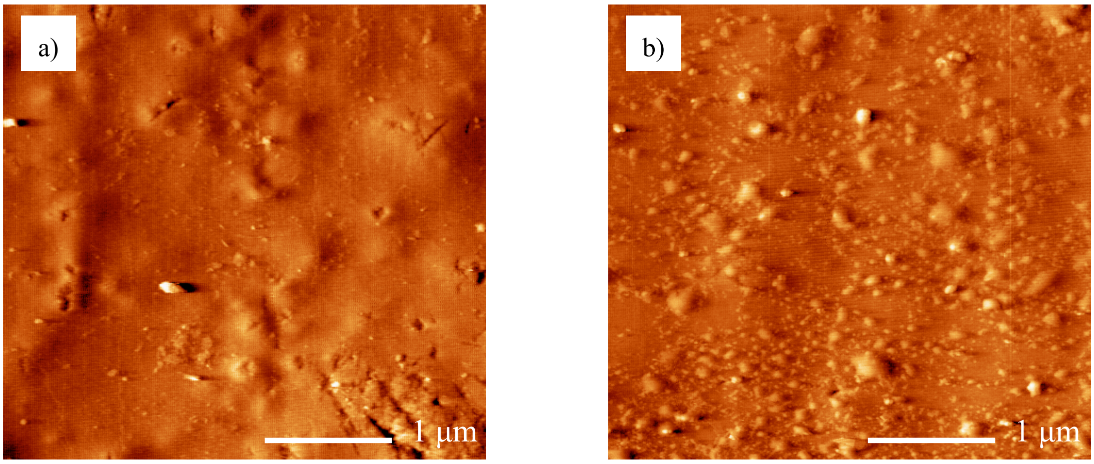

Fig. 10 Topography of the paint coating surface created using pressure atomization on the coating material prepared by: a) – typical technology; b) – developed technology

Amplitude parameters of the paint coating generated from the coating material prepared with the application of ultrasound decrease by more than two times. This shows the aligning of the surface layer. Such a decrease has a positive influence on brightness and wear resistance of the coating.

6. Conclusions

Ultrasonic processing of coating materials includes different processes which lead to a decrease in viscosity and initiation of polymerization reaction.

Grinding of pigments particles, which are component parts of coating materials, occurs only in the processing mode with low (3 micrometer) and medium (10 micrometer) amplitudes, and it is initiated by the collapsing of cavitation bubbles.

The ultrasound treatment of the coating material reduces the required solvent capacity and subsequently results in the changes of torch spraying parameters.

The application of ultrasonic processing during the preparation of coating material decreases the number of paint layers, reduces defects of paint coatings, and eliminates hazardous work during the coating process.

The coating produced by using a coating material processed by ultrasound is characterized by improved properties and improved condition of the surface layer at the micro- and the sub-micro scale.

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