MATTING OF COATINGS BASED ON WATER-BASED ACRYLIC RESINS

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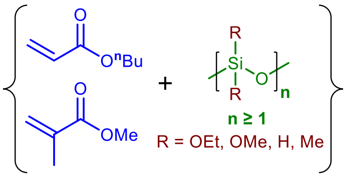
Abstract

This review highlights the main factors that affect a matt appearance of coatings. The physical methods for matting are analyzed, and the application prospects of matting agents are considered. The modern methods of chemical formation of a rough surface for matting of films are presented. It is shown that siloxane derivatives can be effectively used for matting by both physical and chemical methods.



MATTING SURFACE

Key words: matting, acrylic resins, gloss, polymethylsilsesquioxanes.

Introduction

Acrylic resins have been used as film-forming compounds since 1930 [1, 2]. Nowadays, they represent one of the largest classes of products in the paint and coatings industry. These paints are considered the safest and most ecologically friendly products and feature a number of advantages, such as resistance to chemicals and UV light, colorlessness, and transparency [3, 4]. Besides the main properties of the coating, particular attention is drawn to the technological and ecological aspects of their production, and new binding agents are actively being developed in the form of water-dispersion latices, electrostatic application methods, and varnishes that do not require thinners [5].

At the same time, acrylic coatings have a high gloss. Gloss is an optical characteristic of a light-reflecting surface. The degree of gloss shows the ratio between the intensities of specularly reflected light and diffuse light. According to the degree of gloss, coatings can be divided into the following classes: high-gloss, more than 59%; glossy, from 50 to 59%; semi-gloss, from 37% to 49%; semi-matt, from 20 to 36%; matt, from 4 to 19%; deeply matt, no more than 3%. Gloss is measured with a gloss meter at angles of light incidence of 45°, 60°, or 85° [6]. Gloss is determined by different factors. First of all, the solvent, then the drying conditions, the structure of the surface-forming resins; the type, the size, the filler porosity, *etc*.

The goal of this review was to follow the development of concepts about matting of the film surface and to highlight the modern effective methods for matting of water-based acrylic resins.

Matting methods

There are physical [7–13] and chemical [14–24] methods for matting of surfaces. The physical methods include the addition of matting agents and post-processing, such as polishing or etching. The chemical matting involves the synthesis of resins of a certain structure to achieve a matting effect [25].

Dependence of gloss on the parameters of coating formation and other factors

The simplest way to reduce the coating gloss is to change the pigment volume concentration (PVC). PVC is the most important parameter that characterizes the paint formulation, which is defined as the ratio of the volume of pigments and fillers to the total volume of the cured coating, expressed in percentage [26]. Pigments and fillers are dry compounds with a fine, dense, crystalline structure, which are dispersed in the paint. Pigments are divided into inorganic, organic, organometallic, and metallic [27–29]. Titanium dioxide [30] dominates the white pigment market and, from the quality viewpoint, is the most important inorganic pigment. For technical and economic reasons, it is most often used in mixtures with other pigments and fillers [31–38].

High PVC (40–70%) is found in matt paints, lower PVC (<10%) are characteristic of glossy paints and paints with a silky sheen. The higher the PVC value, the lower the content of a film-forming agent in the paint. An increase in the pigment content in the paint can lead to a state when the pigment particles contact with each other. In other words, the critical pigment volume concentration (CPVC) will be reached, and the gloss of the coating film will comprise the lowest value. The CPVC value is determined, on the one hand, by the chemical nature of the film-forming agent and, on the other hand, by the particle sizes of the pigments and fillers. At the CPVC, the solid particles in the coating are so close to each other that they achieve the maximum packing density. The film tension in this case is also maximum; therefore, the coatings with a pigment concentration close to CPVC are prone to cracking [39, 40].

Zhang *et al.* [41] noted that the matting effect can be achieved only when the sizes of the filler particles are commensurate with the film thickness.

The formation of the coating film is a well-studied process [42]. During drying, the solvent or moisture evaporates, increasing the PVC, which leads to the formation of a viscoelastic system and precipitation of matting agent particles. A micro-rough structure is formed on the surface of the coating film [43].

The roughness of the coating film surface is the most important factor that affects the coating gloss. A smooth surface of the paint film will reflect most of the incident light, and the gloss value will be very high. In contrast, a rough surface will reflect and scatter the incident light, so the gloss level will be lower. The degree of roughness can be expressed as an average value. Zhang *et al.* [41] calculated that the surface will have a very low gloss at an average height of the roughness of the film surface $h = 1.1$ μm.

The surface formation can be affected by the selection of the solvent. When the evaporation rates of different solvents in the system are very close, it is easy to form a glossy surface. In contrast, if the evaporation rates of solvents in the system are very different, this will contribute to the formation of a micro-rough structure.

If a chemical reaction of curing/cross-linking occurs in the system, then the matting efficiency of the coating will depend on the rate of this reaction. Therefore, the reaction components in the system, the initiator, the curing agent, and the curing temperature will directly determine the gloss of the coating surface. A slow curing process tends to result in a matt film, whereas a fast curing process helps to obtain a glossy surface.

The molecular structure of the resin itself also affects the surface gloss. Yomg [26] demonstrated that gloss is strongly connected with the molecular refraction (R) of the film-forming compound. The higher the value of R, the higher the gloss value. Amorphous polymers in the form of films or rather large plates can be studied using conventional refractometers [38].

To ensure the transparency of coatings, when selecting a matting agent, it is necessary to pay attention to the difference in the refractive indices of the binding and matting agents. If the difference in the indices is small, the matting agent will not reduce the transparency of the applied film. These mixtures will transmit visible light well. For most of the resin binding agents, the refractive index ranges from 1.4 to 1.6. Synthetic silica has a refractive index of 1.47, which renders it as an important raw material for the production of matting agents. If there is a difference in the refractive indices, incident light will undergo scattering within the paint film, where it is either absorbed or reflected by the substrate, or in the case of pigmented finishes, absorbed or scattered internally by the pigments in the film.

The matting effect and gloss of films can vary greatly depending on the viewing angle (usually gloss is measured and compared at 85°, 60°, or 45°). When using roll coatings in high-rise buildings, an observer may find that the color of the film changes from top to bottom. To reduce this effect, the matting agents are selected that have minimal differences over a wide range of viewing angles. More often, the particle size of the matting agent is selected: a larger particle size results in the lower variability [44, 45].

Physical methods of matting of acrylic resins. Matting agents

At present, the addition of matting agents is the most popular method of matting surfaces of acrylic resins [43]. The principle of matting in this case is based on imparting a certain microheterogeneity to the surface of the coating during its formation, which contributes to the scattering of the light falling on it [7, 44, 46–49]. Fillers with a high specific surface are usually used as such additives [50]. The materials used as matting agents can be divided into two categories: organic and inorganic. The most common organic matting agents are as follows:

– synthetic wax (polyethylene, polypropylene, polytetrafluoroethylene) and their modified derivatives; they feature the MMs of approximately 1800–8000 g/mol and can be added to the system *via* dissolution, preliminary aqueous emulsification or micronization [51];

– microsphere particles, namely, resin spheres prepared by dispersion polymerization (polymethylurea (PMU), polystyrene, melamine–formaldehyde resin).

Inorganic matting agents are mainly synthetic silica [8, 52], natural diatomite, kaolinite, and titanium dioxide [48]. They tend to precipitate, are difficult to disperse again, and enhance the viscosity of the system. They can impair the physical properties of the coating film: weather resistance, UV resistance, and elasticity.

Synthetic silicas have a high ability to reduce gloss, but do not reduce the transparency and purity of films, and also increase their resistance to scratching [39]. They are the most favorable matting agents which provide a good matting effect [36, 37] and have a relatively low cost.

The matting effect of silica is affected by particle size [49, 53]. The standard particle sizes are within 2.8–14.5 μm. The particles with the sizes of 4–6 μm are used in thin coatings for synthetic leather and printing inks, 6–8 μm particles—in coatings for wood and metal, 8–14 μm particles—in finishing coatings where a strong matting effect is required. Silicon dioxides with larger particle sizes are generally more easily dispersed and have a minimal effect on the system viscosity. An important control parameter is the particle size distribution. The narrower the particle size distribution, the more uniform the properties of the resulting material will be.

The presence of pores ensures low bulk density, better dispersion and oil absorption. A fundamental property for effective matting is the pore volume. According to the pore volume, silica used for matting can be divided into the following categories: medium with a pore volume of 1.2 mL/g and large with a pore volume of 1.8–2.0 mL/g [54]. With a pore volume of 2.2, the particles do not have sufficient mechanical strength and decompose during dispersion. The particles with a large pore volume have a lower density and a lower propensity to precipitation, providing high oil absorption, which leads to an increase in the viscosity [55, 56].

However, silicas are hydrophilic and their use as fillers in organic systems is not very effective. Surface treatment with paraffin and PE waxes improves the compatibility of silicon dioxide with organosoluble systems, ensures the stability of mixtures, allows for preventing the sedimentation and improving the redispersion, and can improve the mechanical properties of the coating [50, 53, 57]. With this type of treatment, a continuous shell does not form around silica.

Ou *et al.* [25] modified chemically the silica surface with vinyltriethoxysilane and obtained 3.5 μm particles with a solid content of 15%. The resulting matting additive was included in the composition of a composite for hybrid membranes: acrylic resin/micro-SiO_2/PMU. The effect of the composition of the resulting composites on gloss was studied. The experimental data showed that the addition of only SiO_2 to the acrylic resin reduces the system viscosity and leads to a high-gloss surface. In the system containing all three components, a gradual increase in the viscosity was observed, and the hybrid films demonstrated lower gloss with increasing SiO_2 content. Thus, with the addition of 5 wt % of SiO_2, a matting surface was formed, while at 7%, the maximum viscosity of 36.3 MPa was achieved and the film gloss decreased to 18.9. The authors did not obtain a stable latex using only micro-SiO_2 without PMU, since at the molecular level, the modified silica does not dissolve in acrylic resins, which leads to its aggregation.

Xu and Zhang [45] obtained silica from sodium silicate with the surface modified with trimethylsilyl groups. According to the results of transmission electronic microscopic analysis, resulting SiO_2 has a porous structure, its particles have improved dispersion ability, as well as significantly reduced agglomeration. The modified filler was used for matting acrylamide paints. The work includes the data on their physical properties, namely, viscosity, adhesion, and hardness. The gloss of the films decreases with increasing particle sizes of the modified matting agent. At large particle sizes (10.2 and 17.7), very strong surface roughness is observed according to the results of scanning electron microscopic (SEM) analysis. The surface modifier hexamethyldisilazane improves the compatibility of silica with the acrylamide.

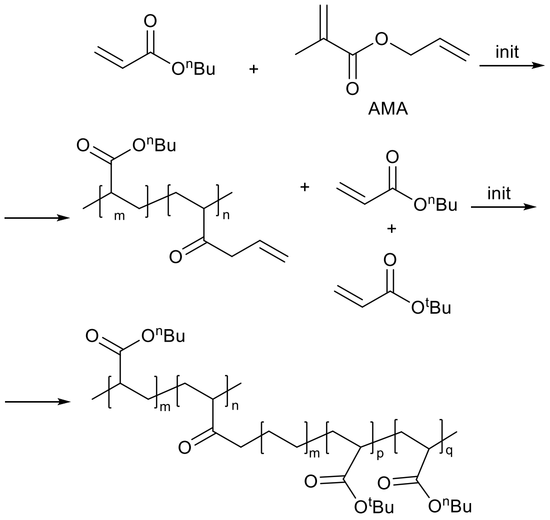
The matting additive should have such properties as a highly developed surface, thermal and chemical stability, absence of odor and color, and, more importantly, commercial availability. In our opinion, polymethylsilsesquioxanes meet all these requirements and will prove to be effective matting agents. Polymethylsilsesquioxanes, hydrogels and MQ copolymers exhibit quite high compatibility with carbon-chain and silicone polymers [58, 59]. The modification of the surface of these compounds with various functional groups makes their use effective for a larger number of systems [60]. In our opinion, they can also be effective matting additives.

The addition of matting agents is a simple strategy for producing a rough surface, but this method has limitations. The matting agent must be selected and well dispersed, otherwise the filler will precipitate, flocculate, and impair the properties of the resulting films. If the film-forming compound itself is matting, these limitations disappear [15].

Chemical methods of matting of acrylic resins. Self-matting films

There are many methods for producing matt coatings, which are based on creating micro-wrinkles in them in order to increase diffuse reflection. The current trends in this area call for abandoning the use of a filler and forming the required surface roughness chemically [61].

Yong and Liang [15] reported a new film-forming acrylic polymer resin which has a low-gloss surface and high transparency owing to the control of the film morphology at a submicron level. The resin does not contain matting agents. The microstructure of the film is controlled by changing the content of the cross-linking agent, namely, allyl methacrylate (AMA) from 0 to 0.4 wt %. The resin samples were obtained by copolymerization, adding AMA to the reaction mixture (Scheme 1).

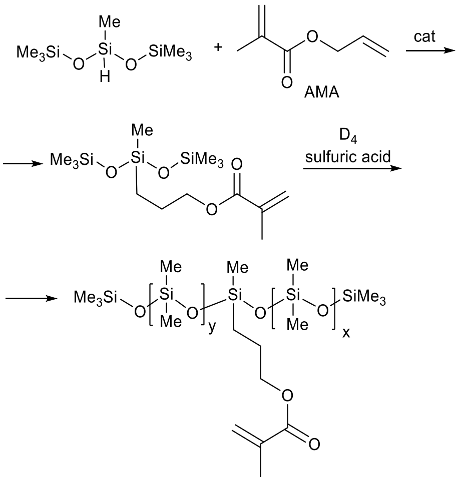


Scheme 1. Synthesis of the low-gloss acrylic resin that does not contain matting agents.

The gloss level of only 4 was achieved at an incidence angle of 60° and the content of the cross-linking additive of 0.2 wt %. The authors concluded that this content of the cross-linking agent is optimal. With an increase in the content of AMA, the film surface, according to the results of SEM analysis, became too rough.

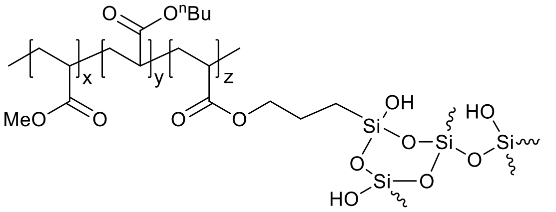
A rough surface was chemically formed by Zhang *et al.* [41]. The comb-shaped copolymers of acrylates and siloxane were obtained. The emulsion polymerization was performed using oligosiloxanes modified with methacrylic groups, rather than AMA (Scheme 2). The presence of methacrylic groups provided these compounds with good affinity for the polymer matrix. The authors managed to obtain the comb-shaped copolymers in all cases with an oligomeric siloxane chain length from 4 to 20 units. We assume that other silicone oligomers compatible with acrylic/methacrylic latexes can also be used for their matting.

Xiao *et al.* [16] used a cross-linking agent based on AMA modified with 1,1,1,3,5,5,5-heptamethyltrisiloxane to obtain a styrene–acrylic copolymer. It was obtained by hydrosilylation in the presence of Speyer's catalyst. The surface gloss was regulated by the amount of the cross-linking agent. The gloss values were reduced from 135.9 to 39.2. The roughness of the films was studied using atomic force microscopy. Based on the results obtained, the authors concluded that the organosiloxane chain migrates to the surface of the emulsion coating film during the film formation.



Scheme 2. Formation of the siloxane oligomers with methacrylic groups.

The self-matting acrylate polymer (Scheme 3) obtained by Xie *et al.* [17] demonstrates good latex stability and does not contain an external powdered matting agent. γ-Methacryloxypropyltrimethoxysilane (γ-MPS) was used as a cross-linking agent at the stage of emulsion copolymerization.



Scheme 3. Schematic structure of the γ-MPS-modified acrylic polymer.

According to the performed investigations, the additive can regulate the surface micro-roughness. The surface roughness increases with an increase in the γ-MPS content, and at 7% content of γ-MPS, the gloss value reaches 6.3. It was shown that the resulting acrylates exhibit microphase separation, which, in combination with the surface roughness, plays a key role in achieving a stronger matting effect. In addition, due to the introduction of γ-MPS, the cross-linking density and hydrophobicity increased, and the thermal stability, tensile strength and water resistance of the films were improved.

Siloxane derivatives have long been proven themselves as the best additives and modifying agents for various systems. In the case of water-based acrylic resins, due to the low surface tension, an organosiloxane chain readily migrates to the surface of the emulsion coating film during the film formation process. Siloxane chains impart the necessary surface roughness and cause microphase separation in the coating film. This leads to increased light scattering on the film.

Conclusions

The chemical strategies for forming the surfaces of acrylic films are widely used in laboratory practice. One of the popular types of reagents includes siloxane derivatives, which are known for their unusually low viscosity coefficients, high permeability, optical transparency, low surface tension, and good dielectric properties. The advantage of the joint use of acrylic polymers and siloxanes is the combination of two effects in the resulting film: the formation of a microrough surface and microphase separation. Together these components contribute to achieving a stronger matting effect.

Nevertheless, a simple method for adding matting agents is still actively utilized, and the search for new, more available organosilicon compounds that can be used as matting additives remains an urgent task.

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References

1. A. D. Yakovlev, Chemistry and Technology of Paint and Varnish Coatings: Textbook for Universities, 3rd ed., KHIMIZDAT, St. Petersburg, **2008** (in Russian).
2. W. Freitag, D. Stove, Paints, Coatings and Solvents, 2nd ed., Wiley, **2008**.
3. I. A. Tolmachev, N. A. Petrenko, Water-Dispersion Paints (with Formulations), Paint-Media, Moscow, **2015** (in Russian).
4. E. E. Kazakova, O. N. Skorokhodova, Water-Dispersion Acrylic Paint and Varnish Materials for Construction Purposes, Paint-Media, Moscow, **2003** (in Russian).
5. T. Brock, M. Groteklaes, P. Mischke, European Coatings Handbook, Th. Schafer, Hanover, **2000**.
6. ISO 2813-2014. Paints and varnishes—Determination of gloss value at 20°, 60° and 85°, **2014**.
7. T. Shitova, N. Yevtyukov, A. Yakovlev, V. Shibalovich, *Paint Varnish Mater.*, **1982**, *3*, 44–46.
8. F. Nsib, N. Ayed, Y. Chevalier, *J. Appl. Sci.*, **2008**, *8*, 1527–1533. DOI: 10.3923/jas.2008.1527.1533
9. Patent US 6103004A, **1995**.
10. Patent JP 2005509072A, **2001**.
11. Patent US 10793727B2, **2018**.
12. Patent WO2019028312A1, **2018**.
13. Patent EP 1323786A1, **2001**.
14. Gh. J. I. Peerzada, M. Prajakta, V. Rajesh, C. Ramalingam, *Silicon*, **2020**, *12*, 1337–1354. DOI: 10.1007/s12633-019-00229-y
15. Q. Yong, C. Liang, *Polymers*, **2019**, *11*, 322. DOI: 10.3390/polym11020322
16. J. Xiao, Z. Qiua, W. Yang, J. Qiu, T. Yang, Y. Xu, Y. Zeng, F. Wang, S. Li, *Prog. Org. Coat.*, **2018**, *116*, 1–6. DOI: 10.1016/j.porgcoat.2017.12.004
17. T. Xie, W. Kao, Z. Zhang, Y. Liu, Z. Li, *Prog. Org. Coat.*, **2021**, *157*, 106300. DOI: 10.1016/j.porgcoat.2021.106300
18. I. Calvez, C. Szczepanski, V. Landry, *Prog. Org. Coat.*, **2021**, *158*, 106369. DOI: 10.1016/j.porgcoat.2021.106369
19. J. Xiao, Z. Qiua, W. Yang, *Prog. Org. Coat.*, **2018**, *116*, 1–6.
20. Y. Meng, P. Lv, Q. Liu, B. Liao, H. Pang, W. Liu, *New J. Chem.*, **2019**, *43*, 19193–19199. DOI: 10.1039/C9NJ04538D
21. Y. Meng, Q. Yong, B. Liao, W. Zeng, H. Pang, *New J. Chem.*, **2020**, *44*, 13971–13978. DOI: 10.1039/d0nj02378g
22. J. Marcu, E. S. Daniels, V. L. Dimonie, C. Hagiopol, J. E. Roberts, M. S. El-Aasser, *Macromolecules*, **2003**, *36*, 328–332. DOI: 10.1021/ma021288a

23. P. Tiemblo, N. García, in: Handbook of Nanoparticles, Springer, **2015**, pp. 1–35. DOI: 10.1007/978-3-319-13188-7_47-1
24. Patent CN 1024922085A, **2011**.
25. J. Ou, M. Zhang, H. Liu, L. Zhang, H. Pang, *J. Appl. Polym. Sci.*, **2015**, *132*, 1–8. DOI: 10.1002/app.41707
26. Q. Yong, *Polym. Adv. Technol.*, **2022**, *33*, 5–19. DOI: 10.1002/pat.5508
27. Coloring of Plastics: Fundamentals, Colorants, Preparations. Hanser, **2003**.
28. T. V. Kalinskaya, A. S. Drinberg, Colored Pigments, LKM-Press, Moscow, **2013** (in Russian).
29. I. A. Tolmachev, N. A. Petrenko, Pigments and Their Application in Paints. A Short Guide for a Process Engineer, Paint-Media, Moscow, **2012** (in Russian).
30. C. C. Man, W. K. Pei, K. P. Vinoth, L. Siew, *Prog. Org. Coat.*, **2022**, *163*, 106660. DOI: 10.1016/j.porgcoat.2021.106660
31. Optical Properties of Paint Coatings, 2nd ed., Profession, St. Petersburg, **2010** (in Russian).
32. L. G. Gerasimova, O. N. Skorokhodova, Fillers for the Paint and Varnish Industry, LKM Press, Moscow, **2010** (in Russian).
33. T. V. Kalinskaya, A. S. Drinberg, E. F. Itsko, Nanotechnology. Application in the Paint Industry, LKM Press, Moscow, **2011** (in Russian).
34. B. Muller, U. Pot, Paints and Coatings. Principles of Compounding, Paint-Media, Moscow, **2007** (in Russian).
35. R. Lambourne, T. A. Strivens, Paint and Surface Coatings: Theory and Practice, William Andrew Publ., **1999**.
36. Patent US 9028605B2, **2011**.
37. Patent EP 1446447B1, **2001**.
38. I. Y. Averko-Antonovich, Methods of Studying the Structure and Properties of Polymers, Kazan, **2002**.
39. D. Gorbunov, *Paint Varnish Mater. Their Appl.*, **2006**, *2–3*, 18–19.
40. Additives in Waterborne Coatings, G. Davison, B. Lane (Eds.), RSC, Cambridge, **2003**. DOI: 10.1039/9781847550057
41. B. Zhang, B. Liu, X. Deng, S. Cao, X. Hou, H. Chen, *Appl. Surface Sci.*, **2007**, *254*, 452–458. DOI: 10.1016/j.apsusc.2007.06.030
42. The Chemistry and Physics of Coatings, 2nd ed., A. R. Marrion (Ed.), RSC, Cambridge, **2004**. DOI: 10.1039/9781847558206
43. W. Heilen, Additives for Water-Borne Coatings, Vincent Network, **2021**.
44. S. Maskery, *Pigm. Resin Technol.*, **1973**, *2*, 11–19.
45. Q. Xu, Z. Zhang, *Nano Brief Rep. Rev.*, **2018**, *13*, 1850137. DOI: 10.1142/S1793292018501370
46. T. Fletcher, *Prog. Org. Coat.*, **2002**, *44*, 25–36. DOI: 10.1016/S0300-9440(01)00206-5
47. Z. Wicks, F. N. Jones, S. P. Pappas, Organic Coatings, Science and Technology, Wiley, New York, **1999**.
48. N. A. Kovrizhkina, V. A. Kuznetsova, A. A. Silaeva, S. A. Marchenko, *Aviation Mater. Technol.*, **2019**, *57*, 41–48. DOI: 10.18577/2071-9140-2019-0-4-41-48 (in Russian).
49. J. Braun, *Coat. Technol.*, **1991**, *63*, 43–51.
50. L. Simpson, *Prog. Org. Coat.*, **1978**, *6*, 1–30.
51. M. Gunde, M. Kunaver, M. Cekada, *Dyes Pigm.*, **2007**, *74*, 202–207. DOI: 10.1016/j.dyepig.2006.01.049
52. M. J. Sailor, Porous Silicon in Practice: Preparation, Characterization and Applications, Wiley, **2012**.
53. V. Kuznetsova, E. Timoshina, G. Shapovalov, V. Zheleznyak, *Trudy VIAM*, **2023**, *128 (10)*, 132–144. DOI: 10.18577/2307-6046-2023-0-10-132-144
54. J. Rouquerol, D. Avnir, C. W. Fairbridge, D. H. Everett, J. M. Haynes, N. Pernicone, J. D. F. Ramsay, K. S. Sing, K. K. Unger, *Pure Appl. Chem.*, **1994**, *66*, 1739–1758. DOI: 10.1351/pac199466081739
55. J. M. Rosenholm, C. Sahlgren, M. Lindén, *Curr. Drug Targets*, **2011**, *12*, 1166–1186. DOI: 10.2174/138945011795906624
56. A. Al Othman Zeid, *Materials*, **2012**, *5*, 2874–2902. DOI: 10.3390/ma5122874
57. J. Braun, D. J. Fields, *Coat. Technol.*, **1994**, *66*, 93–98.
58. M. V. Mironova, G. A. Shandryuk, I. B. Meshkov, *Russ. Chem. Bull.*, **2021**, *70*, 2200–2207. DOI: 10.1007/s11172-021-3333-x
59. M. V. Mironova, G. A. Shandryuk, A. A. Shebeko, I. B. Meshkov, V. G. Kulichikhin, A. M. Muzafarov, *Polym. Sci., Ser. B*, **2020**, *63*, 199–208. DOI: 10.1134/S1560090421030118
60. I. B. Meshkov, A. A. Kalinina, V. V. Kazakova, A. I. Demchenko, *INEOS OPEN*, **2020**, *3*, 118–132. DOI: 10.32931/io2022r
61. F. Nsib, N. Ayed, Y. Chevalier, *J. Appl. Sci.*, **2008**, *8*, 1527–1533.
62. T. Xie, W. Kao, L. Sun, J. Wang, G. Dai, Z. Li, *Prog. Org. Coat.*, **2020**, *142*, 105569. DOI: 10.1016/j.porgcoat.2020.105569