



Creation of Biocidal Coatings using the Stabilization of Silver Nanoparticles in Aqueous Acrylic Dispersions

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Abstract. This article proposes a method for silver nanoparticle (AgNP) stabilization in polymer coatings obtained from aqueous acrylic dispersions. The main objective of the study was to improve the biocidal properties of coatings using AgNPs due to the preservation of their nanoscale state. Two types of AgNP solutions with fundamentally different stabilization mechanisms were synthesized and compared. Two mechanisms were determined: an aqueous electrostatic mechanism with sodium docusate stabilizer (AOT) and a steric, propylene glycol with polyvinylpyrrolidone (PVP) stabilizer. The results showed that both solutions were unstable and prone to precipitation as early as the first day after synthesis. However, the saturation of the propylene glycol AgNP solution with ammonium hydroxide to pH < 9 allowed the strengthening of the electrostatic factor of aggregative stability, providing optimal conditions for mixing with acrylic dispersions stabilized by anionic surfactants. The obtained AgNPs in the acrylic dispersions stabilized over time, and when they became film-forming, stable AgNPs (~20–30 nm) occurred on the surface. As a result, the developed coatings using AgNPs synthesized in propylene glycol in the presence of non-ionic PVP and modified with ammonium hydroxide, demonstrated a high inactivation of bacteria colony-forming units (CFU) (> 60%) within 60 min of contact compared to aqueous AgNP solutions using anionic surfactants as stabilizers, where the decrease in CFU was around 25%.

Keywords: Acrylic dispersion; Aggregative stability; Biocidity; Coatings; Silver nanoparticles

1. Introduction

The prevention of biological corrosion that affects almost all existing types of materials, regardless of their composition, method of production, and use, is currently one of the most important problems. An effective way to protect building structures from bio-damages and prevent the evolution of pathogenic microorganisms in the environment is to form coatings with different compositions on the surface of materials (Tokach and Goncharova, 2016; Bondarenko et al., 2018; Bessmertny et al., 2019; Elnaggar et al., 2019), among which paint and varnish materials can be identified as the most techno-economically beneficial (Tarasova, 2018).

A significant reduction in the number of toxic impurities in the composition of various paints, in combination with uncontrolled sanitary conditions in production, increases the

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risk of microbial contamination (Karamah and Sunarko, 2013; El-Sakhawy et al., 2016). The storage of paintwork materials in liquid form leads to the discoloration of surfaces; changes in rheological characteristics, pH, and coagulation; reduction in molecular weight; destruction of dispersions; and the release of putrid odors and gas. In hardened coatings, it causes visible algae or fungi fouling, the appearance of a green or gray color, and cracking. However, uncontrolled microbial growth can be reduced or prevented using biocides.

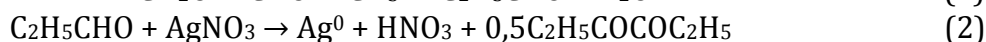
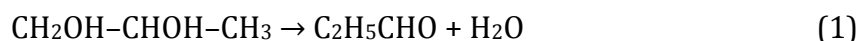
Until recently, the list of substances used for these purposes was quite expansive and included a number of mercury compounds and sulfur- and nitrogen-containing cyclic organic compounds (dithiocarbonate, thiophthalamide derivatives, benzimidazole, and trialkyl tin compounds).

The above-mentioned biocides are highly effective, but their actions reduce biological activity not only in the volume of paint, but also in the environment. In fact, they may be attributed to ecocides. As the United Nations Environment Program was implemented, the list of banned carcinogens continues to grow, which ultimately will drive Russian biocides out of the market.

Colloidal solutions of metallic silver nanoparticles (AgNPs) are promising, as they can meet most of the requirements of the above-mentioned biocides with sufficient control of stabilization (selection and concentration of surfactants, degree of conversion) and environmental conditions (pH, viscosity, electrolytes) (Wang et al., 2018; Adur et al., 2018; Deshmukh et al., 2019).

Nowadays, many ways to obtain nanoscale substances with high reactivity and varying degrees of stabilization exist (Yuwono et al., 2010; Aripin et al., 2017; Helmiyati, 2019; Kusdianto et al., 2019).

The preparation of colloidal dispersions of AgNPs via reduction in polyatomic alcohol is a dynamically developing direction. In this method, the solvent acts as a reducing agent in contrast to the traditional methods of borohydride and biochemical synthesis. Diols, such as 1, 2-ethanediol (ethylene glycol) or 1, 2-propanediol (propylene glycol) are usually used as solvents. Polyols are soft reducing agents that can reduce silver ions to a null-valence state. The molecular mass used to stabilize AgNPs is 40,000, and the molar ratio (R) of its units with the metal lies in the range of 20–40. If $R < 1$, then the resulting dispersion is unstable. As a result of this reaction, the alcohol is oxidized to the corresponding carbonyl compound, which subsequently reduces the silver to the null-valence state:



Song et al. (2014) proved that the use of polyvinylpyrrolidone (PVP) stabilizers with low molecular weight ($M_w < 29000$) leads to aggregative particle instability, resulting in the aggregation of the particles to micron agglomerates. The researchers also found that AgNPs stabilized by PVP with $M_w = 8000$ tend to form associates, which indicates that they are not sterically stabilized. However, Chou et al. (2004) discovered that with the introduction of carbonate ions into the system, the aggregation of the nanoparticles can be stopped. Therefore, the reduced steric barrier of PVP with low molecular weight can be compensated by increasing the electrostatic barrier. In controlling both effects, it is possible to achieve nanoparticle stabilization in the composition of the polymer dispersion for the subsequent formation of biocidal coatings.

2. Methods

The objects of this research were the following raw materials: industrial aqueous dispersion of polymer, obtained via the emulsion polymerization of methacrylate; butyl

acrylate; and acrylic acid. The following components were used to produce AgNPs: the stabilizers were sodium docusate (AOT, sodium (2-ethylhexyl) sulfosuccinate) produced by Sigma-Aldrich, PVP ($M_w = 10,000$, Sigma-Aldrich), and sodium chloride (Renewal, 0.9% bufus), and the reducing agents were quercetin dihydrate produced by Riedel-de Haën, silver nitrate, isooctane, and CH.DA-brand 1,2-propylene glycol (pure for analysis).

The AgNP colloidal solutions were obtained in two fundamentally different ways: artificial and synthetic.

An artificial method was used to prepare an aqueous AgNP solution by replacing the solvent (of saturated hydrocarbon with water) in previously reduced silver nitrate in the reverse micelle system.

The preparation of the micellar AgNP solution was performed according to the following sequence:

1. The preparation of a surfactant solution of AOT in isooctane of 0.06 mol/l. The addition of a reducing agent, quercetin, at the rate of 200–250 mg per 1 l of AOT solution in isooctane;
2. The preparation of an aqueous solution of 0.25 M silver nitrate in bidistilled water. The resulting mixture with a volume of 10 ml was added to the solution (quercetin/AOT/isooctane) in the amount of 1 l. The liquid turned dark brown for a few minutes, which indicated the beginning of the process of AgNP formation;
3. The addition of distilled water at a 1:1 ratio with stirring resulted in a two-phase system. The prepared mixture was centrifuged at a speed of 3000 min^{-1} to obtain a layer of an aqueous AGNP solution, which was drained from the bottom of the column.

The process of obtaining the finished solution was controlled spectrophotometrically by changing the characteristic peak of silver in the zone of 400–420 nm. The proportion of silver transferred from the ionic to the AgNPs' zero-valent form was rather high (Table 1). A synthetic method was also used to prepare a propylene glycol AgNP solution by reducing the polyhydric alcohols in the presence of a stabilizer, a hydrophilic polymer. A common way to obtain AgNP polyol synthesis solutions is as follows:

1. The preparation of solutions of silver nitrate and PVP in propylene glycol at a concentration of 50 mM. One l of propylene glycol was heated to a temperature of 160°C;
2. The addition of 0.5 l of AgNO_3 and PVP solutions to the heated propylene glycol over 30 min. After full introduction, the system was set 1–2 h at a temperature of 160°C until the reaction was complete.

The proportion of silver transferred from the ionic form to the zero-valent AgNPs was also quite high (Table 1). The samples of acrylic dispersions containing AgNPs were prepared by simple mixing, adding the solution of AgNPs to the acrylic dispersion in a 1:1 ratio.

A number of methods were used to make further studies and solve the identified problems (Figure 1).

Table 1 Specifications of the AgNP solutions

Indicator name	Aqueous solution	Propylene glycol solution
Color	reddish brown	reddish brown
Position of the main absorbance band (nm)	400–420	380–400
Nanoparticle content (mmol/l)	1–5	4–7

The evaluation of the reaction interaction of the emulsion paint-work materials components was analyzed using infrared spectroscopy. The samples were measured with a Vertex 7010 device produced by Bruker Optics¹ in the mid-infrared range from 370 cm^{-1} to 4000 cm^{-1} . The device was equipped with OPUS software. The samples were in liquid form, and the survey was carried out in the mode of frustrated total internal reflection.

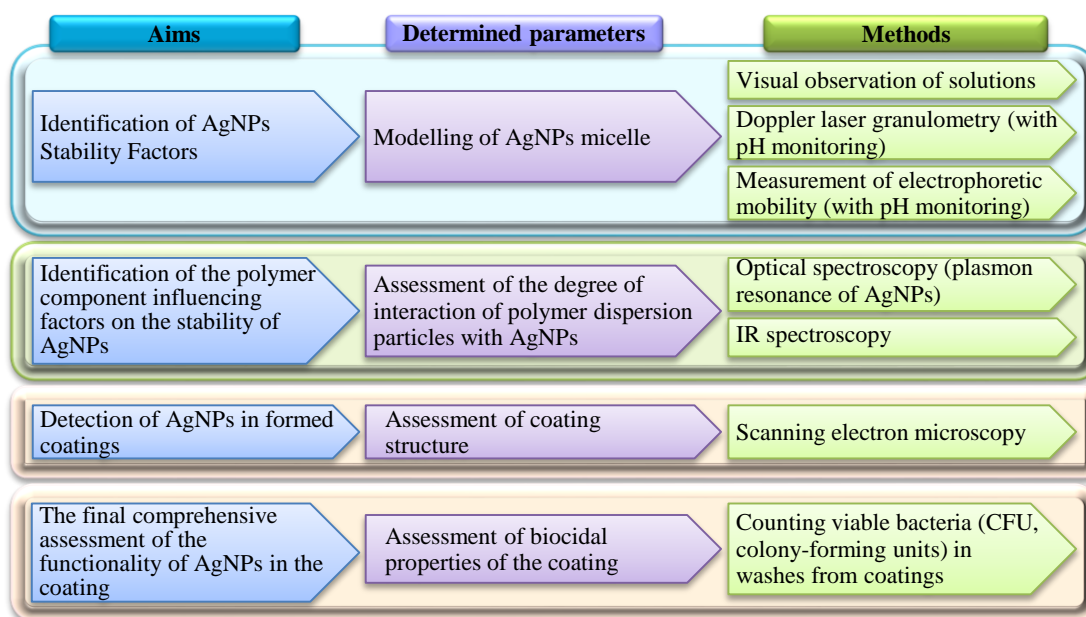


Figure 1 Schematic representation of the methods used in research

An analysis of microstructural features was performed using scanning electron microscopy on a scanning electron microscope Mira 3 FesSem (Tescan, Czech Republic). Recording took place in the mode of high vacuum discharge.

The optical density of the AgNP solutions for the qualitative and quantitative determination of the optical spectrum zones with high absorption intensity was measured via a spectrophotometric method in the ultraviolet and visible spectral regions using a LEKI SS1207 spectrophotometer. The measurements were carried out in quartz cells (1 cm) with respect to the solvent, bidistilled water.

To determine the number of bacteria of the *E. coli* family, 1 cm^3 was taken from two successive dilutions of the suspensions and introduced into two sterile petri dishes. The first dish was used for less diluted (10^3 times) suspension and the second for more diluted sown product (10^4 times). The dishes with the product introduced into them were poured with a selective diagnostic agar nutrient medium. The inoculations in the dishes were incubated at $37 \pm 1^\circ\text{C}$ for 24 h. Interscience software was used to count the number of colonies.

3. Results and Discussion

3.1. Structure of AgNP Micelles and Achievement of Their Stability

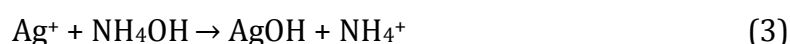
To study the structure of the AgNPs' colloidal micelles and the selection of optimal conditions for their stabilization, electro-kinetic potential was studied, which was quantitatively determined by the strength of the electrical double layer of adsorbed ions on the surface of the suspended AgNPs in the solution (ζ -potential). To achieve this, two samples of the AgNP solutions were synthesized via the polyol synthesis of stabilized PVP (Mw = 8000) in propylene glycol and a reverse-micellar stabilized anionic surfactant (AOT)

in water. The AgNPs obtained from the reverse-micellar method were stabilized predominantly by an electrostatic barrier and a predominantly steric polyol method.

The process of AgNP restoration occurred from an aqueous solution of silver nitrate under the action of reducing agents. In addition, the structure of the AgNPs' core was represented by the silver atoms and silver ions $\{m [\text{Ag}^0] n\text{Ag} + (n-x) \text{NO}_3^-\} x\text{NO}_3^-$ associated with it. This was confirmed by the weakly positive particle charge at $\text{pH} \approx 4$ in both preparation methods.

It is possible to stabilize a nanoparticle due to the amplification of a double electric one, possibly due to the introduction of electrolytes into the system, which can add a crystal lattice on the surface of AgNPs. Therefore, it is possible to exchange counter-ions at the synthesis stage. So, in the case of the introduction of ammonium hydroxide ammonia (NH_4OH) into aqueous or propylene glycol AgNP solutions, the potential-determining AgNO_3 to a sol of AgOH stabilized with NH_4^+ ions takes the following structure: $\{m [\text{Ag}^0] n\text{OH}^- (n-x) \text{NH}_4^+\} x\text{NH}_4^+$.

This contributes to the formation of silver hydroxide on the surface of AgNPs:



For a detailed study of the effect of NH_4OH on the stability of AgNPs, the ζ -potential was studied with increasing pH of the medium from the neutral level, as obtained during synthesis in the presence of ammonium hydroxide (Figure 2).

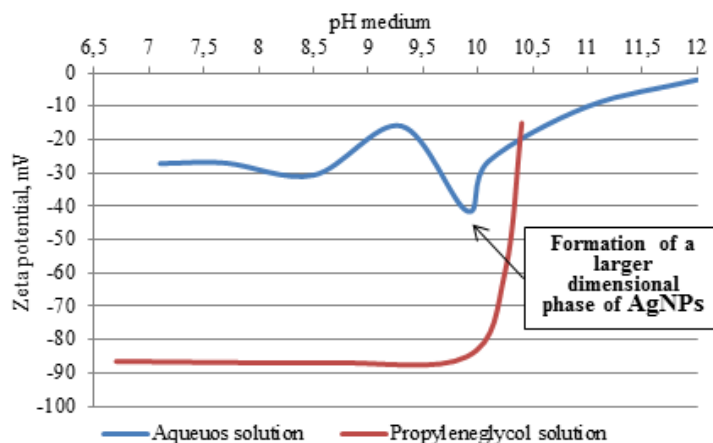
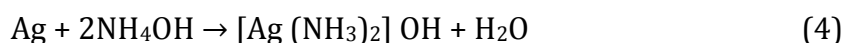


Figure 2 The dependence of the electrokinetic activity of SNP solutions on the pH level of the medium

The further addition of AgNPs and ammonium hydroxide to an aqueous solution of ammonia hydroxide resulted in a decreased ζ -potential to a critical level (less than 20 mV in modulus).

This led to the loss of resistance to aggregation and subsequent particle enlargement (Figure 3). This showed an abrupt increase in electro-kinetic potential at $\text{pH} \approx 10$. With the increase in concentration of ammonia in a medium, silver transforms into a more water-soluble form—silver ammonia. This compound in water is a weakly dissociating $\text{Ag}(\text{NH}_3)_2^+$ complex ion and part of the OH^- hydroxide group:



This explained the increase in the AgNPs' solubility, saturation of the medium with electrolytes, and the subsequent decrease in surface charge. In addition, the standard redox potential of the pair Ag^+/Ag was more positive than the pair $\text{Ag}(\text{NH}_3)_2^+/\text{Ag}$ (+0.799 V and -0.373 V, respectively).

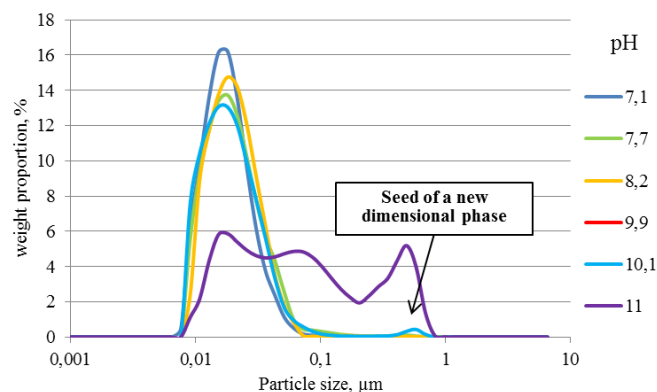


Figure 3 Particle size distribution of an aqueous SNP solution, dependent on the medium's pH

This data can be used to obtain AgNPs in propylene glycol stabilized by PVP ($M_w = 8000$). In the presence of ammonium hydroxide ($\text{pH} = 7\text{--}9$), AgNPs showed a ζ -potential level of 85–86 mV, which indicated their high stability. The particle size at the same time was about 20 nm and did not change during storage for 2 weeks, including in aqueous solutions. Thus, a weak steric barrier on the surface of AgNPs in combination with an increase in the electrostatic factor led to an increase in the nanoparticles' stability.

3.2. Mixture of AgNP Solutions with Polymer Dispersion

Both the aqueous AgNP solution and the modified propylene glycol were mixed with the acrylic dispersion. For each mixture, the absorption spectrum of optical radiation in highly water-diluted solutions was measured (1% of the initial concentration). The ratio of acrylic dispersion to the AgNP solution was 1:1, as it did not cause minimum nor maximum critical values on the spectrum line. Such a low acrylic dispersion content was reasoned by the proximity of the size of polymer particles to the Rayleigh dispersion (< 100 nm), which caused a strong increase in light diffusion with the increase in concentration.

The aqueous AgNP solution (Figure 4), stabilized by electrostatic forces, inevitably reduced its stability over time. This can be explained by the interaction of acrylic acid, which is part of the monomeric composition of polymer, with NH_4^+ counter-ions and surface silver hydroxide. As a result, the growth of nanoparticles continued until there was complete precipitation of a dark precipitate.

More hydrophobic AgNPs stabilized in propylene glycol when introduced to an acrylic dispersion, over time retaining the spectrum with a plasmon resonance in the zone of 420 nm (Figure 5).

This was facilitated by the steric stabilization effect created by PVP. However, at the same time, acrylic copolymers and PVP are not capable of entering joint reactions due to the significant contribution of Van der Waal's forces, characteristic of high-molecular compounds. To confirm the absence of the reaction interaction of combined dispersions of AgNPs and the polymer, the Infra-red-spectra were surveyed.

The analysis of the IR-spectra of the aqueous AgNP solution confirmed the absence of new peaks and showed the decrease in the intensity of the AgNP characteristic spectrum in proportion to its concentration in the acrylic dispersion, which may indicate the absence of a reaction in the combined dispersion.

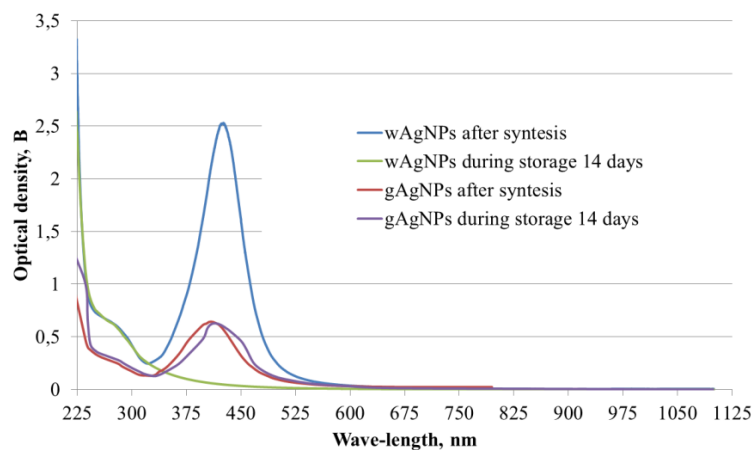


Figure 4 Optical density of acrylic dispersion with aqueous (wAgNPs) and glycolic (gAgNPs) SNP solutions after synthesis (without storage) and during storage (14 days)

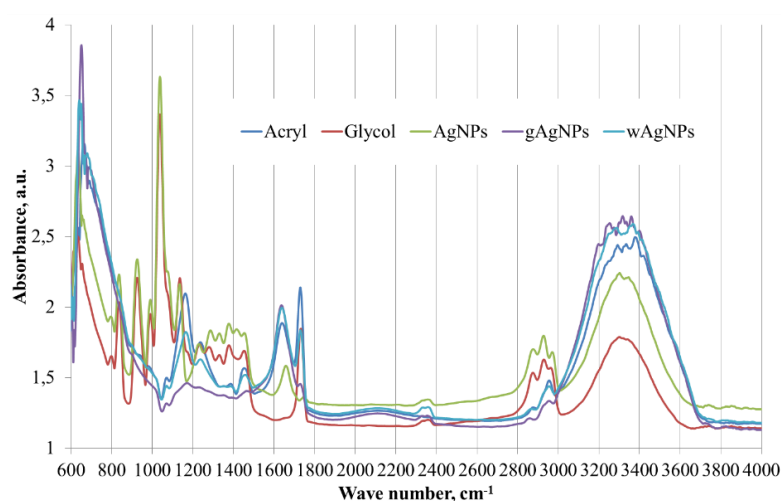


Figure 5 IR absorption spectra of acrylic, aqueous, and glycolic SNP solutions

This conclusion can be also applied to the glycol AgNP solution combined with an acrylic dispersion.

3.3. Mechanism of Structure Formation of Aqueous Polymer Dispersions with AgNP Solutions

To determine the structure of the hardened coatings on the basis of acrylic dispersion and AgNPs, studies using scanning electron microscopy were conducted (Figure 6).

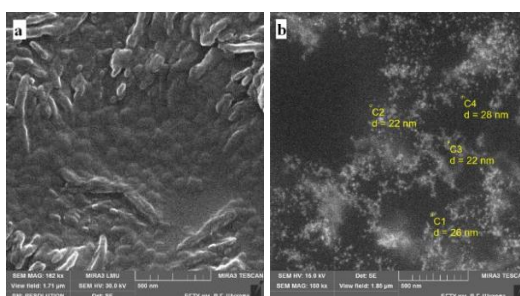


Figure 6 Scanning electron microscope photomicrographs of acrylic coatings formed using: (a) aqueous; and (b) propylene glycol SNP solutions

The coating obtained using an aqueous AgNP solution showed a strong roughness (Figure 6a). This is explained by the lack of coalescent in the final stage of drying. Separate nanoparticles in this coating could not be isolated even at high accelerating voltage (30 kV). The coatings obtained using AgNPs in propylene glycol showed a more uniform surface structure (Figure 6b). This can be explained by the fact that propylene glycol acts as a coalescing agent. PVP-stabilized AgNPs form some steric volume around them, which stabilizes them and prevents agglomeration. Providing the volume associated with the steric barrier, the average AgNP density decreased and became lower than the density of acrylic, as a result of which it was possible to achieve their flow upward onto horizontal surfaces.

3.4. Evaluation of the Microbicidal Action of Paint Coatings with AgNPs

The bactericidal effect of nanoparticle solutions is reasoned by the formation of silver cations, which in turn combine with the sulfhydryl groups of the active sites of thiol-containing enzymes, irreversibly inhibiting biochemical reactions and reducing the adenosine triphosphate activity of myosin, thereby disrupting cell metabolism (Loponov, 2005). The methods for determining the number of bacteria of the Enterobacteriaceae family were based on the inoculation of a certain amount of product and its dilutions on agar-selective diagnostic media, incubating the seeds, and counting typical colonies.

The wipes analysis (Figure 7) showed that samples of hardened acrylic copolymers without AgNPs showed a characteristic strong seed content. The mixture of acrylic dispersion with the aqueous AgNP solution showed a 25% decreased colony-forming units (CFU). Such a low result can be explained both by a decrease in silver activity due to ammonia and an agglomeration of AgNPs and their sedimentation in the coating.

For the propylene glycol AgNPs, a more significant reduction in CFU (> 60%) was observed, which is uncharacteristic for the action of PVP or propylene glycol. Higher biocidity is based on a small particle size, compared to an aqueous AgNP solution, and their significant release to the surface.

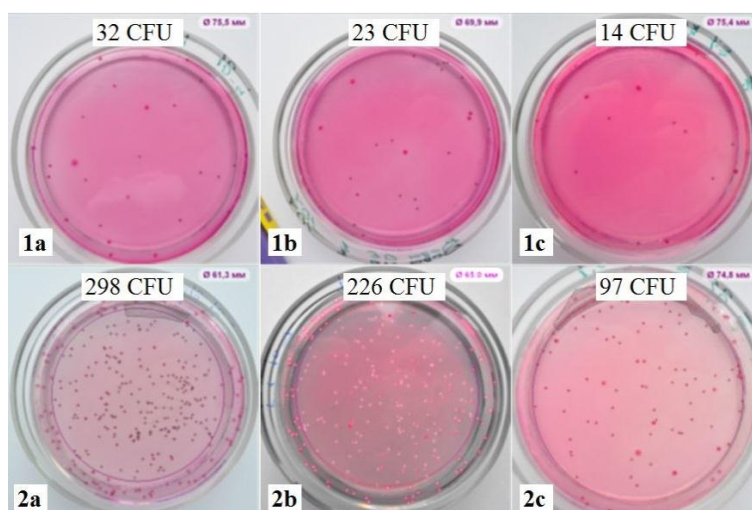


Figure 7 The results of washout diluted (1) 10^4 times and (2) 10^3 times from coatings without AgNPs: (a) with an aqueous; (b) propylene glycol; and (c) AgNP solution

4. Conclusions

To achieve the biocidal effect of acrylic-based coatings, it is most efficient to use AgNPs synthesized as a result of polyol synthesis using PVP of relatively low molecular weight ($M_w < 10,000$). Low molecular weight PVP weakly inhibits the surface of AgNPs, and as a result,

their activity is preserved. The addition of ammonium hydroxide to a pH of < 9 enhances the electrostatic aggregate stability factor, providing optimal conditions for mixing with acrylic dispersions stabilized by anionic surfactants. This allows AgNPs to maintain their dimensions (~20–30 nm) until the polymer dispersion is dry and is also found on the surface of formed coatings. As the final result, the aforesaid coatings demonstrate high bacteria CFU inactivation (> 60%) within 60 min of contact compared to aqueous AgNP solutions using anionic surfactants as stabilizers, where the decrease in CFU is around 25%.

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