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Gelatin microgels as a potential corrosion inhibitor carriers for self-healing coatings: preparation and codeposition

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Abstract

Co-deposition of a coating with capsules containing a corrosion inhibitor is one of the methods to protect the material surface against corrosion. This generation of coatings can be regenerated in response to mechanical or chemical damage. The paper presents a method for preparing gelatin microgels that can be eco-friendly corrosion inhibitor reservoir. The influence of temperature, stirring rate, an addition of surfactants (ionic and non-ionic) on microgel quality has been studied. It has been found that the microgels obtained at 80°C from the solution containing non-ionic surfactant at concentration below its critical micelle concentration are the most stable and less polydisperse one. As a proof of concept a Ni-P/gelatin microgels hybrid coating has been obtained by electroless method.

Key words: self-healing; microgel; protective coating; Ni-P coating; corrosion inhibitor

1. Introduction

The selection of a construction material is most often based on a compromise between the desired properties and price. When insufficient surface properties are the only drawback of such a material the top layer is covered by a protective coating. This solution allows to decrease the costs associated with the use of more expensive materials and bringing desired hardness, abrasion resistance or other properties. In the context of corrosion protection both inorganic and organic coatings are applied. They serve to protect various materials – magnesium or aluminum alloys, steel, composites. Preventing and mitigating corrosion issues of structural and functional materials are a vast cost to modern industrialized economies. Until recently the main components of anti-corrosion coatings have been chromium(VI) compounds. However, the current legislation levies by Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) restricts the use of hexavalent chromium, because of their carcinogenicity. The introduction of limitations on the use of compounds containing chromium(VI) has become the impetus for the development of alternative coatings [1]. Nowadays it is important that the protective layer has additional properties being multifunctional. It should smartly defend itself against adverse effects of the external environment and adequately respond to mechanical or chemical damage. Moreover applied technologies need to comply with both health and environmental legislation [2,3]. Self-healing ability is a property of particular relevance for anti-corrosion coatings. Polymer, organosilicon, sol-gel, conversion, metallic or ceramic coatings are used as self-healing layers. Among the self-healing coatings layers containing micro- or nano-capsules are of particular interest [4-8]. They consist mostly of macromolecular compounds, i.e. poly(urea-formaldehyde), epoxy resin, poly(methylmethacrylate), polystyrene [6,7,9]. The capsules may be filled with appropriately selected corrosion inhibitors, for example cerium or magnesium ions, silyl ester, linseed oil, 8-hydroxyquinoline, benzotriazole. Recently emphasis has been put on the search for eco-friendly materials that are the building blocks of corrosion carriers. The results of the studies on the use of silica, titania, CaCO_3 microbeads, halloysite

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3 nanotubes or boehmite nanoparticles have been described. Replacement of the capsules
4 with microgels (micron-sized gel particles) is a new solution. Preparation of microgels
5 containing a corrosion inhibitor is much simpler than capsules synthesis followed by their
6 filling. In this case, the active compound may already be added during formation of the
7 microgel. An example of such systems are polyurea microgel particles containing 2-
8 methylbenzothiazole used in the anti-corrosion applications [10]. According to the best
9 knowledge of authors, there is no data describing the use of gelatin microgel as a carrier for
10 corrosion inhibitor. In other fields of science, especially in the life and health sciences,
11 microgels, including gelatin one, are used much widely. Microgels are carriers of drugs,
12 bioactive substances and nutrients, optical nanobiosensors, agents reducing fat in food
13 products or material for anionic dyes removal [11-21]. Microfabrication technology, reverse
14 micelles via photocrosslinking or water-in-oil emulsion method can be employed to obtain
15 gelatin microgels [22-24].
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30 Research on metal matrix coatings with self-healing properties is relatively new. Such
31 coatings may also be resistant to abrasion or characterized by high hardness in comparison
32 to the most commonly used polymer coatings. The most common metallic coatings are
33 obtained electrochemically as a cathodic coating (e.g. coating by nickel) or an anodic one
34 (e.g. zinc) [25,26]. Cathodic coating must be tight in order to be effective. Otherwise
35 penetration of the substrate via coating pores takes place and corrosion process includes the
36 material on which the coating is deposited. Anodic coating protects the substrate surface
37 from corrosion in the first place. When considering the introduction of microgels filled with
38 corrosion inhibitors to such a type of matrices, the kind of coating we deal with should be
39 taken into account while selecting the active compounds.
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51 Functional diagram of a self- healing coating on the metal matrix is shown in Figure 1. The
52 anodic coating should contain an inhibitor supporting rebuilding of the coating and the
53 cathodic coating should contain an inhibitor supporting repairing of the substrate.
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3 The goal of developing 'green', self-healing coatings is to prepare and incorporate
4 components that regain the functionality in a coating. Herein we describe the first step
5 leading to achieving this goal – preparation of corrosion inhibitor carriers made out of gelatin.
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7 It was selected due to its high availability, suitability to prepare gels in fast and easy way, and
8 the fact that it is a material derived from a renewable source. In presented work conditions of
9 gelatin microgel preparation were optimized. The influence of temperature, stirring rate,
10 addition of surfactants on the microgels properties have been studied. Obtained gel particles
11 were used to create new electroless hybrid coating based on Ni-P matrix. The choice of the
12 matrix was dictated by its properties, as Ni-P coating is employed instead of chromium coating
13 having similar corrosion and wear resistance. In the described application the material has
14 been used for the first time.
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25 26 **2. Materials and methods**

27 28 29 **2.1 Materials**

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32 Fluorescein sodium salt, sodium dodecylsulfate (SDS), dodecyltrimethylammonium bromide
33 (DTAB) and tetraethyleneglycol dodecyl ether (Brij 30), nickel sulphate, sodium
34 hypophosphite and tri-sodium citrate were received from Sigma–Aldrich. Brilliant Blue FCF
35 analytical standard was received from FLUKA. Gelatin powder pure p.a. and corn oil were
36 received from Avantor Performance Materials Poland S.A.
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42 Critical micelle concentration (CMC) for the above-mentioned surfactants, mol dm⁻³: SDS
43 8.3 × 10⁻³; DTAB 14.1 × 10⁻³; Brij 30 2.3 × 10⁻⁵ [27].
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47 48 **2.2 Methods**

49 50 *2.2.1 Microgels preparation*

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53 Microgels were prepared by water-in-oil emulsion method. 0.5 g gelatin was dissolved in 5 ml
54 of water containing Brilliant Blue FCF in order to facilitate microscopic analysis of the
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3 obtained microgels. The resulting solution was heated to 40 or 80°C and added to 50 ml of
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5 corn oil heated to the same temperature as gelatin solution. The mixture was stirred (stirring
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7 rates from 250 to 1250 rpm) for 10 min and cooled in an ice bath to 4°C. Next 65 ml of
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9 cooled acetone was added and created dispersion was stirred for 1 h at 4°C. The obtained
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11 microgels were filtered off under reduced pressure with fritted funnel (G4, 10-16 µm pore
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13 size) and washed several times with cooled acetone then air-dried at room temperature.
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16 The above procedure was repeated with one of the surfactants: sodium dodecylsulfate,
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18 dodecyltrimethylammonium bromide or tetraethyleneglycol dodecyl either added to the oil
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20 phase (at concentration of 0.25 × CMC, 1 × CMC, 2 × CMC).
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23 Based on the results, the most favorable conditions of microgels preparation were found:
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25 temperature 80°C, stirring rate 1000 rpm, non-ionic surfactant concentration 0.25 × CMC. At
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27 such conditions, fluorescein loaded microgels were obtained then they were co-deposited
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29 with Ni-P coating by electroless method.
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31 32 *2.2.2 Coating preparation*

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34 Coatings were produced on the specimens of d=14 mm made from an alloy steel of AISI 304.
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36 Samples were treated using 1200 grade abrasive paper and ultrasonically cleaned in
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38 acetone. All the specimens were then etched for 10 min in a 0.1 mol dm⁻³ SnCl₂ solution and
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40 washed with distilled water. After that the samples were activated for 10 s in a PdCl₂ solution
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42 (1.4 × 10⁻³ mol dm⁻³), washed with distilled water, and subjected to the bath.
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46 The composition of the bath used for the preparation of Ni-P\gelatin microgels coating was
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48 as follow, g dm⁻³: NiSO₄·6H₂O 22.0; Na₃C₆H₅O₇ 20.0; NaH₂PO₂·H₂O 25.0; dry gelatin
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50 microgels 4.4. Deposition temperature was 40°C, and the pH was adjusted to 9 with 10 wt.%
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52 NaOH.
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54 55 *2.2.3 Microscopic analyses*

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3 Optical microscope images of microgels were taken by an Olympus BX41, model BX41TF
4 equipped with a color digital camera and software XC30 Cell* (The Olympus Soft Imaging
5 Solutions).
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10 Size of microgels was estimated based on microscope images. Microscopic observation of
11 the coating morphology was carried out with a Leica DMRA2 upright epi-fluorescent
12 microscope using a Retiga Exi Fast 1394 camera with a color wheel. For image acquisition
13 Velocity software was used.
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17 18 19 **3. Results and discussion**

20 21 **3.1. Results of preparation of gelatin microgels**

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24 Gelatin microgels were obtained by thermal gelation in water-in-oil emulsion. Microgels
25 preparation procedure follows principles of green chemistry: there is no waste of gelatin, oil
26 phase can be recovered and used again. Both gelatin and corn oil are nontoxic,
27 environmentally friendly, easy to biodegraded products from renewable sources. Diameter of
28 the microgels depends strongly on preparation conditions. Lower temperature and lower
29 stirring rate favor the formation of larger microgels of a diameter up to 200 μm . Microgels
30 sizes up to 100 μm were obtained at stirring rate > 1000 rpm. Figure 2 shows the effect of
31 stirring rate on the size of microgels obtained at 40°C. Increase of the stirring rate is
32 preferable in view of the size of the microgels. Bigger microgels may reduce the stability of
33 plating bath and affect the coating properties.
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46 One of the methods to prevent aggregation of the particles in their preparation process is the
47 use of surfactants. During preparation of gelatin microgels three types of surfactants (anionic,
48 cationic and non-ionic) with equal carbon chain length were used. For our experiments we
49 chose the concentration of surfactants below (when surfactant molecules are in monomeric
50 form) and above their critical micelle concentration (CMC, where its molecules arrange
51 themselves into organized molecular assemblies known as micelles). The addition of a non-
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3 ionic surfactant at concentration of $0.25 \times \text{CMC}$ prevented aggregation of the microgels even
4 at the stirring rate of 1000 rpm, Figure 3. At Brij 30 concentration equal to $1 \times \text{CMC}$ a slight
5 increase in diameter of the microgels was observed. Increasing the surfactant concentration
6 to $2 \times \text{CMC}$ resulted in deformation of the microgels, and in the case of the microgels
7 obtained at higher temperature species with a much thicker wall were also observed, Figure
8 4. In this case blue color, which indicates the presence of an aqueous phase inside the
9 microgels, was not observed. This may be due to the formation of a water-oil-water emulsion.
10 The influence of temperature and Brij 30 concentration on microgels obtaining is presented in
11 Table 1. One can see an increase in diameter of the microgels with increasing the surfactant
12 concentration. Augmentation of temperature to 80°C causes a decrease of microgels size
13 about 30%, more or less, for particular concentration of Brij 30. Addition of ionic surfactants,
14 DTAB and SDS, to oil phase resulted in increase in the degree of aggregation of microgels
15 and their deformation. Both surfactants added at a concentration of $1 \times \text{CMC}$ caused a
16 complete inhibition of the microgel formation. At neutral pH gelatin is amphoteric, its
17 positively charged residues (lysine and arginine) can interact with SDS whilst negatively
18 charged ones (glutamic and aspartic acid) may interact with DTAB. Additionally, hydrophobic
19 parts of gelatin molecules can promote interactions with micelles. The literature confirms that
20 SDS micelles could be bound to gelatin [28,29] and that presence of DTAB may cause the
21 refolding of gelatin-strands to the triple helical structure [30,31]. Both phenomena may make
22 formation of microgels impossible.
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44 3.2. Preparation of Ni-P\microgel coating as a proof of concept

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47 Standard components of bath, together with their functions, used for electroless deposition of
48 Ni-P coatings are listed in Table 2. The composition of plating Ni-P baths may vary
49 depending, e.g. on alloy which is coated, but the baths usually contain: a source of Ni ions, a
50 reducing agent, a complexing agent, stabilizers, buffers and some additives that influence
51 the coating properties. Even though the volatile organic compounds are usually not used as
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3 a solvents and baths are water-based whole process generates a lot of wastes. What more
4 plating baths may be unstable due to the fact that nickel may be released in an uncontrolled
5 manner, e.g. in the volume of the solution. A sudden bath decomposition is the reason for
6 increased deposition costs, as well as increase of the amount of wastewater pollutants. This
7 can be reduced to some extent by addition of stabilizing agents that inhibit the reaction of
8 nickel release. Coating is an energetically costly process since the temperature of plating
9 baths needs to be kept around 50-90°C.
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12 Application of self-healing coatings results in great benefits including diminished degradation,
13 extension of the coating lifetime, and reduction of the maintenance cost. Moreover, plating
14 process of such a coating may even be more environmentally friendly. We propose the Ni-
15 P\gelatin microgels bath, the composition of which is reduced to: a Ni and P source, a
16 reducing agent and dry gelatin microgels. The deposition temperature is lower than 50°C,
17 which will lower use of energy. Further work is planned to extend the bath to include surface-
18 active compounds that provide its stabilization. At this stage, however, it can be concluded
19 that the composition of the bath is minimized in comparison to the commonly used solutions.
20 This modification is of great importance since will reduce amount of wastewater and sludge
21 produced during plating process. Plating wastewater contains nickel which is toxic, has long
22 lifetime and can give rise to bioaccumulation [32,33]. What more presence of heavy metals
23 can reduce the efficiency of biological treatments. As an alternative treatment of created
24 wastewater we propose low-cost and environment-friendly solution describe by [34] – use of
25 spent electroless nickel plating baths for preparation of high quality nanometer nickel powder
26 which can be reused.
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49 Figure 5 illustrates the coating surface of Ni-P\gelatin microgels. The addition of fluorescein
50 inside the microgels allowed to track their presence in the coating. Deposition was carried
51 out in the bath for electroless nickel plating of simplified composition described above. Due to
52 sodium citrate used as a complexing agent it was possible to deposit a coating from an
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3 alkaline solution. According to the mechanism of the nickel (Ni-P) coating deposition by
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5 electroless method, increasing the pH of the bath results in an increase in the speed of the
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7 coating preparation. The coating deposition was carried out at 40°C, so at the temperature
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9 no higher than the temperature at which the gelatin becomes liquid. In the case of electroless
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11 nickel plating the temperature and the pH of the solution are the factors that substantially
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13 affect the rate of coating deposition. The lower the temperature and pH, the slower the
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15 deposition. Therefore, the pH of the solution was adjusted to 9. After about 10 minutes of
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17 deposition microgels began to aggregate and block an access of the bath to the substrate
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19 surface, resulting in stopping the process of the coating preparation. Nonetheless it was
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21 possible to deposit the coating. Further works should be focused on selection of additional
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23 components for nickel plating bath that would improve the stabilization of the solution and
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25 allow the extension of the deposition time and thus the thickness of the coating. Such a
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27 composite coating, with an appropriately selected active compound enclosed in microgels
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29 can actively respond to the negative influence of the external environment. Thus the lifetime
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31 of such coatings when compared to plain Ni -P one can be extended.
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33 34 **4. Conclusions**

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37 Gelatin microgels were obtained applying the method of thermal gelling in water-in-oil
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39 emulsion. The process is effective, simple, efficient and has minimal impact on the
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41 environment. Applied materials: gelatin and corn oil are cheap, easily available and easy to
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43 biodegraded. Temperature, stirring rate and the addition of surfactant affect the size and
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45 separation degree of the microgels. The microgels obtained at 80°C with the stirring rate of
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47 1000 rpm and the addition of Brij-30 with a concentration of $0.25 \times \text{CMC}$ were chosen as the
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49 second phase co-deposited with Ni-P coating. The process of coating deposition took about
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51 10 minutes. After this time, microgels began to aggregate in the bath inhibiting the
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53 deposition.
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56 In summary, the work achievements include:
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- determination of the conditions for gelatin microgels preparation;
- selection of bath components and electroless nickel plating process parameters;
- co-deposition of gelatin microgels with Ni-P coating.

A major disadvantage with conventional electroless plating technology is the production of toxic sludge and wastewater. Here we propose composite coating which in comparison with plain Ni-P one is obtained using fewer chemicals. The coating composition is limited to three necessary components. The use of microgels as the second phase may extend the coating lifetime, because the microgels can be loaded with active substances that control the coating wear. In consequence, the overall environmental impact of the metal product (its finishing and use) can be reduced. The changes applied in the process of the coating with nickel substrate preparation by electroless method made progress towards cleaner and more sustainable technology.

Table 1. Effect of temperature and Brij 30 concentration on the size of microspheres.
Stirring rate 1000 rpm.

temperature	concentration of Brij 30	average size of microgels
40°C	0.25 × CMC	97.5 μm
	1 × CMC	79.0 μm
	2 × CMC	49.8 μm
80°C	0.25 × CMC	72.1 μm
	1 × CMC	55.9 μm
	2 × CMC	32.3 μm

Table 2. Standard components of Ni-P plating baths and their functions.

Bath component	Function
sulfate(VI) or nickel chloride	<u>nickel ion source</u> Other nickel salts, e.g. acetate, carbonate or methylsulfate, are rarely used. While choosing a nickel salt it should be taken into account that a chloride anion may have an adverse effect during covering aluminum surfaces or when the Ni-P coating is used to protect against corrosion of iron alloys.
sodium or potassium hypophosphite	<u>reducing agent</u>
mono- and multi-functional carboxylic acids (and their salts), e.g., citric, succinic, lactic acid, organic amines (ethylenediamine, triethanolamine) or amino acids (most of the time - amino acetic acid), ammonia and its salts (chloride and sulfate) as well as boric acid and borates.	<u>complexing agent</u> A complexing agent reduces the free nickel ion concentration and prevents precipitation of a nickel salt, e.g. hydroxy salts or phosphates; slows down the deposition process affecting the uniformity and quality of the obtained coatings.
organic compounds	<u>buffering agent</u> The choice depends on the pH of the working bath.
compounds of the Group VI elements in the Periodic Table, e.g. thiourea, thiocyanates; unsaturated organic acids, e.g. maleic acid; heavy metal cations (Sn^{2+}, Pb^{2+}, Hg^+), anions (AsO_2^-, MoO_4^{2-}, IO_3^-); some surfactants	<u>stabilizer</u> Inhibitor of nickel precipitation reaction.
organic or inorganic additives, e.g. succinic acid	Enhancement of the properties and appearance of the coatings, as well as influence on the process parameters, e.g. by increasing the plating rate.
Most of the baths for electroless Ni-P deposition operates at temperature above 50°C. As the temperature increases the deposition rate increases.	
The pH of the bath is adjusted depending on the type of coating to be obtained. As pH increases, there is a pronounced decrease of phosphorus concentration in the coating.	

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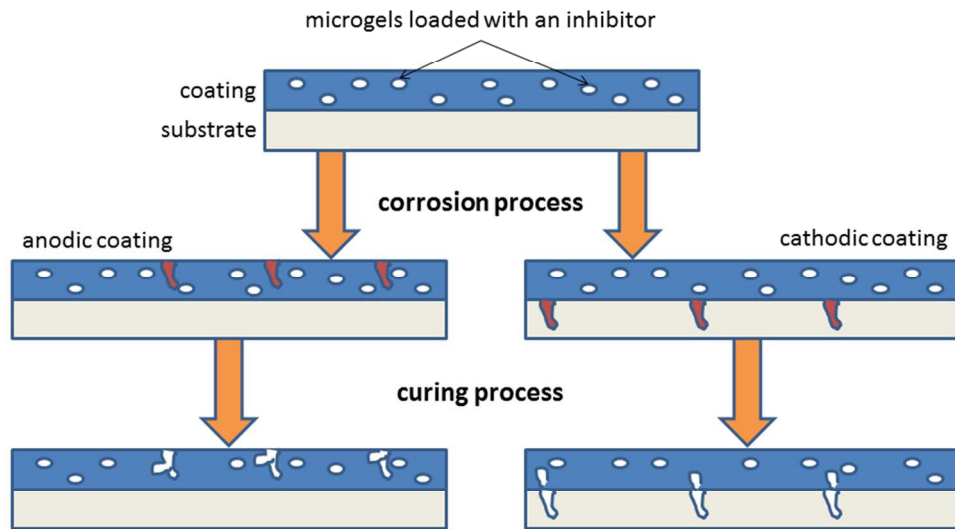
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Figure captions

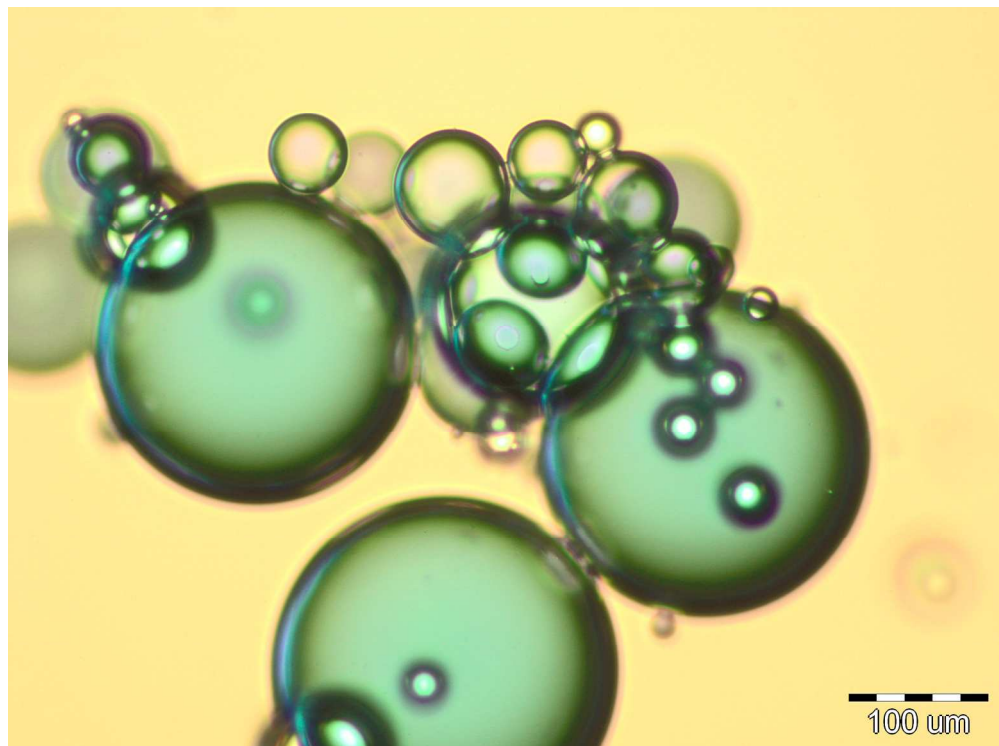
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- Fig.1 Schematic description of corrosion and curing processes for metallic coatings.
- Fig.2 Gelatin microgels obtained at 40°C using various stirring rates, rpm: 250 (a); 750 (b) and microgels' size (c).
- Fig.3 Gelatin microgels obtained at 40°C (a) and 80°C (b) with 0.25 × CMC concentration of Brij 30, stirring rate 1000 rpm.
- Fig.4 Gelatin microgels obtained at 80°C with 2 × CMC concentration of Brij 30, stirring rate 1000 rpm.
- Fig.5 Ni-P\gelatin microgels coating surface analyzed by fluorescence optical microscope.

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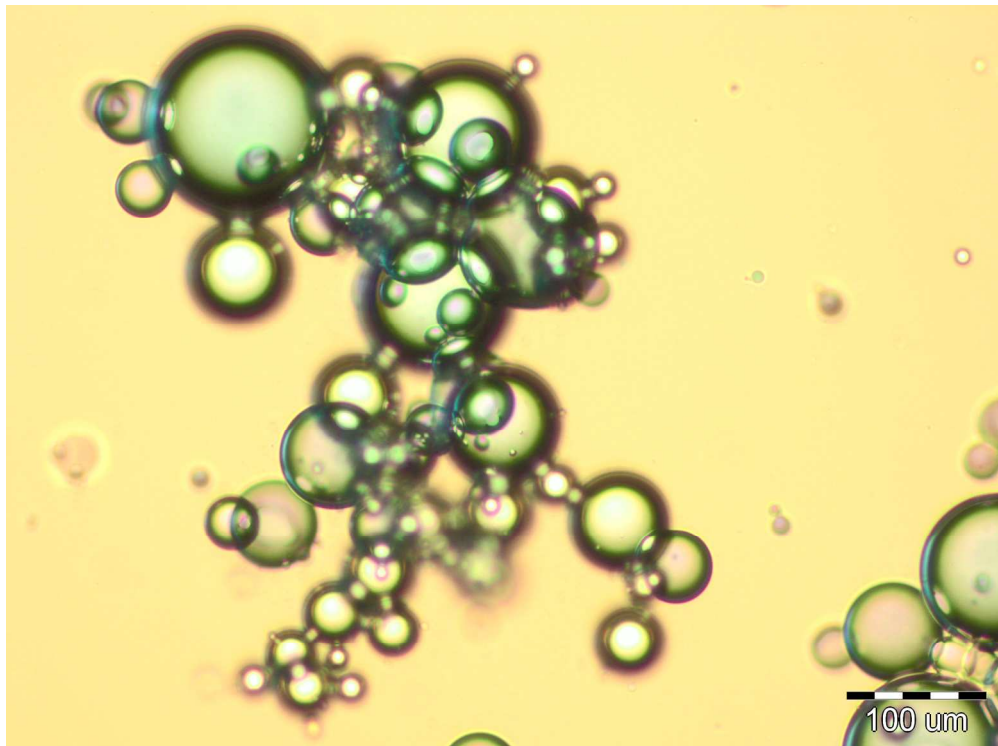
Review



176x130mm (300 x 300 DPI)

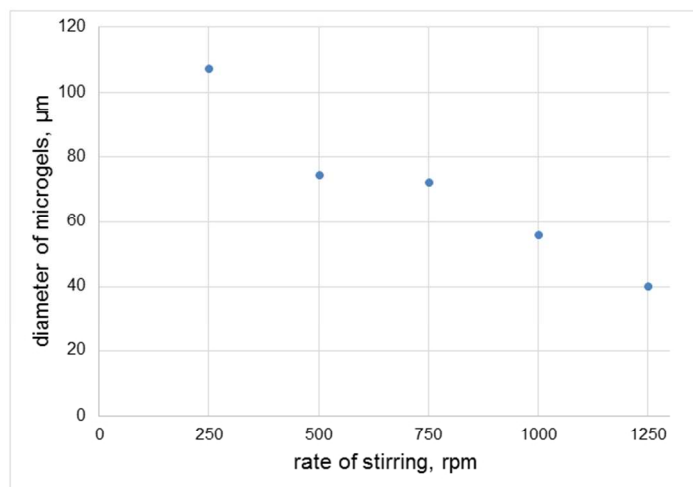
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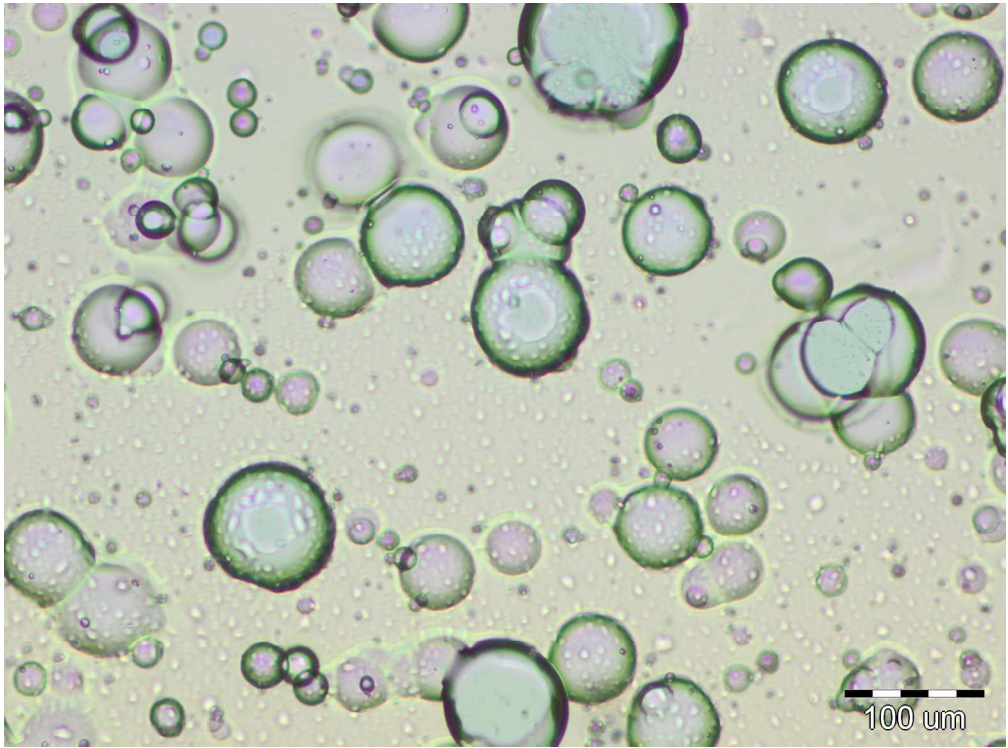
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Review



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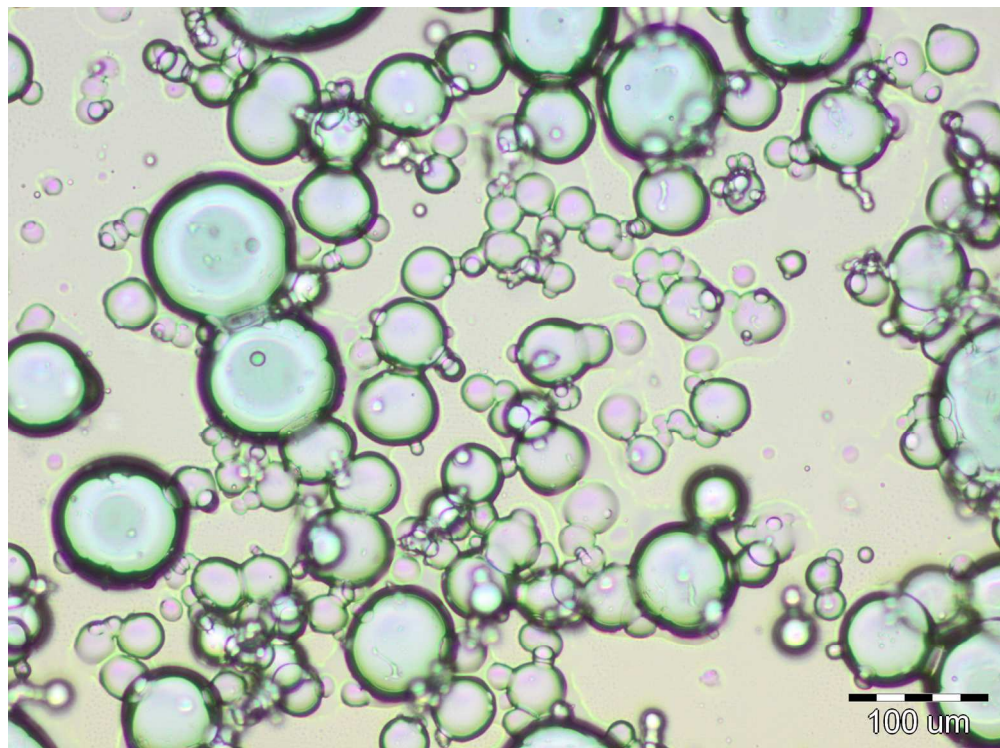
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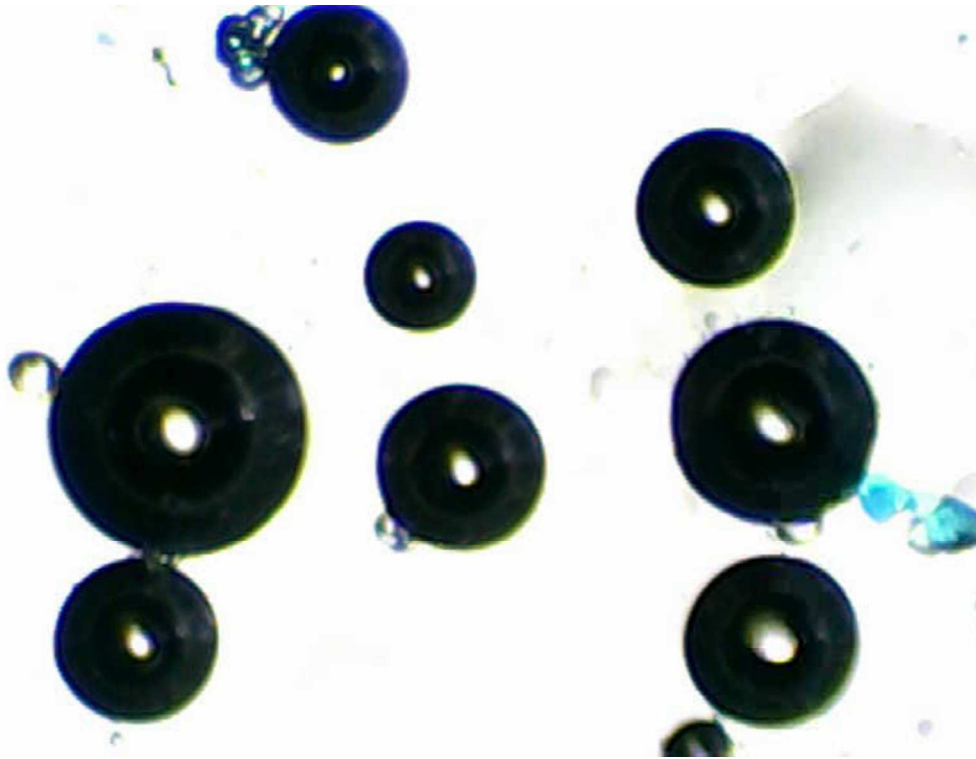
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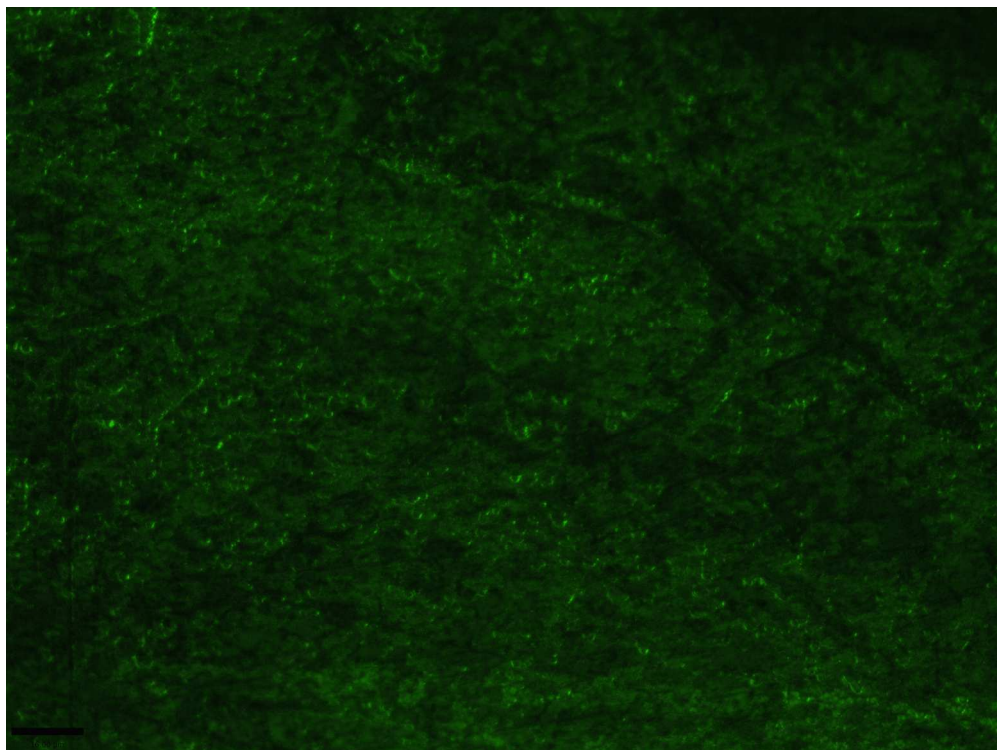
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54x40mm (300 x 300 DPI)

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117x88mm (300 x 300 DPI)

Review