ANNOTATION

on the thesis for the degree of Doctor of Philosophy (PhD)
on specialty 6D074000 - "Nanomaterials and nanotechnology"

of

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Colloid-chemical design of micro- and nanocapsules with protective properties

The relevance of the dissertation research

The development of nanomaterials is currently one of the fastest growing areas in nanotechnology. Protective coatings with autonomous healing or restoration of their protective function are of great interest in the study of surface destruction processes, such as corrosion, biological fouling and other factors affecting metal structures.

Microencapsulation is the process of small particles encapsulation in a thin shell of a film-forming material. The encapsulated substance, called the content of microcapsules, the active or basic substance forms the shells. The shells perform the function the particles separation of one or more substances from each other and from the external environment until the moment of use.

Embedding micro- and nanocapsules with protective coatings is often used to provide one or more active feedback functions. Depending on the morphology of the containers and the filled active agents, coatings with specially targeted self-healing functionality or multi-functional coatings can be created.

Currently, there are problems associated with the use of coatings based on organic substances, since they are inherently susceptible to microbiological contamination. Such coatings may require microbiocidal agents as a protective measure to prevent microbial attack. Biocides are added to the product formulation. This may be due to aesthetic necessity, and the use of biocide can significantly reduce the cost of maintenance, repair and replacement of structural elements. In modern coating protection technology, biocides are mixed with a liquid composition and distributed throughout the dry coating at a concentration designed to withstand the expected product life. However, despite the measures taken with the use of biocides in compositions with organic components of the coating, microbiological contamination is still a widespread and everyday phenomenon, which, however, is often underestimated or not taken into account at all.

In this regard, the research and development of new forms of materials with biocides is an urgent problem of modern science of nanodispersed materials.

The novelty lies in the development of a colloid-chemical scientific platform for the design of micro-and nanocapsules in order to obtain new materials used in the composition of protective coatings.

For the first time, the "green" biocide DCOIT was encapsulated using Pickering emulsions.

The basis and initial data for development of themes

The basis for scientific research is the prospects in the use of Pickering emulsions and the need to research and develop a science-based approach to obtaining nanomaterials with protective properties used in internal and external coatings, engineering, aerospace, construction industry, biotechnology, anti-biofouling.

As initial data, a set of research results on basic research of surfactant compositions for the design and prediction of properties of micro - and nanocapsules of active ingredients with practically important functional properties is used.

The aim of the work

The aim of the work is to develop a scientifically based approach to the design of micro- and nanocapsules with protective properties based on Pickering emulsions to create protective coatings with antimicrobial action.

To achieve this goal the following tasks were set:

1. Establishment of optimal conditions for the formation of Pickering emulsions during polymerization of 3-(trimethoxysilyl) propyl methacrylate with DCOIT biocide, depending on the type and concentration of the initiator, duration and temperature of polymerization to obtain micro- and nanocontainers of a given size and morphology;

2. Study of colloid-chemical properties and the kinetics of biocide release for systems with a polyurethane/polyurea shell and a SiO2 nanoparticle shell with a new green biocide DCOIT for use in indoor and outdoor coatings against biofouling.

3. Investigation of the structure and activity of the obtained micro- and nanocapsules by ERS, IR and NMR spectroscopy to confirm the immutability of the structure and, consequently, the properties of the biocide before and after encapsulation.

4. Identification of the effectiveness of the adding of micro- and nanocapsules with protective properties against biofouling in the selected system by checking the antimicrobial effect of coatings using tests against microorganisms.

5. Development of a scientifically based approach to the formation and design of micro- and nanocapsules with protective properties for the creation of protective coatings with antimicrobial action, which allows to encapsulate the DCOIT biocide into micro- and nanocapsules.

Research methods

A tensiometer PAT-1 was used to measure the interfacial tension of adsorption layers, Malvern Zetasizer NanoZ was used to measure electrokinetic zeta potential and hydrodynamic radius using dynamic light scattering method; the ControlLEO 1550 was used to determine the shape, size, morphology of nano- and submicrocops using scanning electron microscopy method; measurements of the contact angle at the three-phase interface were performed on the Goniometer LC-1 installation; thermogravimetric analysis was used to analyze the encapsulation efficiency by the NetzschTG 209 F1 analyzer; infrared spectra of micro- and nanocapsules was obtained on a Nicolet 5700 spectrometer (Thermo Electron, USA), 1H and 13C NMR spectra were obtained on a JNM-ECA Jeol 400 spectrometer.

Main statements to be defended:

1. Colloid-chemical approach to the formation and design of micro- and nanocapsules synthesized on the basis of Pickering emulsions, allowing encapsulation

of the green biocide DCOIT in capsules with polyurethane/polyurea shells and with a shell of SiO_2 nanoparticles and a core of polymethacrylate.

2. The established optimal conditions and parameters for obtaining of Pickering emulsions and micro- and nanocapsules of 10% DCOIT biocide using SiO_2 nanoparticles at a ratio of m(TPM)/ m(SiO2) = 2.23, by spontaneous emulsification within 24 hours.

3. The established features of the prolonged kinetics of DCOIT biocide release from micro- and nanocapsules with protective properties

4. The revealed positive effect of the introduction of the antimicrobial action of the biocide into micro- and nanocapsules with protective properties with a shell of SiO2 nanoparticles and a core of polymethacrylate in protective coatings against mold fungi and bacteria, as well as against biofouling.

Objects of the research

Micro-and nanocapsules based on the biocide 4,5-dichloro-2-n-octyl-4-isothiazoline-3-one (DCOIT), alkoxysilane 3-(trimethoxysilyl)propyl methacrylate, silicon dioxide SiO2 Ludox AS-40, initiator Irgacure 2959 (2-hydroxy-4 ' - (2-hydroxyethoxy) - 2-methylpropiophenone, initiator Irgacure 651 (2,2-dimethoxy-2-phenylacetophenone. Also, micro- and nanocapsules obtained from polyurethane/polyurea and a core from DCOIT. All reagents used in this study are manufactured by Sigma Aldrich Co.

Subject of research

Study of the main regularities and physical and chemical characteristics of the formation and synthesis of micro-and nanocapsules with a polyurethane/polyurea shell and a DCOIT core and synthesis of micro - and nanocapsules with a shell of silicon dioxide nanoparticles and a core of substituted polymethacrylate with DCOIT included in it.

Scientific novelty of the research

1. Encapsulation of the green biocide 4,5-dichloro-2-n-octyl-4-isothiazoline-3-one (DCOIT) with a multicomponent system of 3-(trimethoxysilyl) propyl methacrylate (TPM) /water/SiO2 and also with polyurethane/polyurea shells was carried out for the first time in order to obtain micro- and nanocapsules with protective properties;

2. For the first time, a colloid-chemical approach to the formation and synthesis of micro- and nanocapsules with protective properties based on Pickering emulsions with silicon dioxide nanoparticles for the creation of protective coatings with antimicrobial action confirmed by the totality of the results of modern physico-chemical research methods ERS, IR, NMR spectroscopy.

3. The established possibility of regulating and controlling the encapsulation process with a shell of silicon dioxide nanoparticles and a core of polymethacrylate with DCOIT included in it, obtained on the basis of Pickering emulsions;

4. Positive effect of antimicrobial action of biocides in micro- and nanocapsules with protective properties against biofouling and prolongation of action due to encapsulation was revealed.

The novelty is the development of colloidal-chemical scientific platform for the design of micro- and nanocapsules to obtain new materials used in the composition of protective coatings.

For the first time, encapsulation of the "green" biocide DCOIT was carried out using Pickering emulsions.

Theoretical significance of the obtained results

- Established colloidal-chemical approach to the synthesis of micro- and nanocapsules with antimicrobial action based on Pickering emulsions, stabilized by SiO_2 nanoparticles and expansion of modern ideas on encapsulation of biocides;

- The revealed relationship between the dispersion of emulsions and biocide capsules, as well as the established effectiveness of the encapsulated biocide DCOIT associated with prolonged release kinetics.

Practical significance of the obtained results

- consists in the development of nanomaterials and the creation of micro- and nanocapsules of "green" biocide used to obtain protective coatings against the destruction of surfaces due to biological fouling.

- the results of the study can be used to expand the range of prototypes of capsules with antimicrobial properties with protective bactericidal, antifungal properties.

Substantiation of the importance of the obtained research results

The results of the study are recommended for creating effective, environmentally friendly and at the same time cost-effective micro- and nanocontainers for encapsulating of the "green" biocide DCOIT into the system. The positive effect of the introduction of micro- and nanocontainers on the antimicrobial properties of polymer coatings with the potential for introduction in biotechnology, the production of additives for paints, varnishes, protective coatings of various types has been revealed.

Accordance of the work with the directions of scientific development or state programs

The work was carried out in accordance with the research plan of the K. I. Satpaev Kazakh National Technical University under the budget program: 120 "Grant financing of scientific research" under project "New functional and multifunctional self-healing materials based on nano- and microencapsulated hydrophobic active agents "(2015-2017), as well as under the project No.2018/AP05131984 "Development of a colloid-chemical platform for multi-emulsion encapsulation technology with natural polymers and surfactants" (2018-2020).

Description of the PhD student contribution to the preparation of each publication

The author was studied the involved to the preparation of the dissertation results.

The PhD student's personal contribution to the preparation of each publication consisted in the preparation and study of literary data on the topic of the dissertation, in conducting experimental work, as well as in participating in the interpretation of the results obtained.

The results of scientific work were reported and discussed at the International Scientific Conferences: «III International Conference Industrial Technologies and Engineering - ICITE 2016, 2020», «IX Annual Conference of the Nanotechnological Society-2018», «16th Conference of the International Association of Colloid and

Interface Scientists-2018», «10th international conference Interfaces Against Pollution-2018».

The main results on the topic of the thesis are presented in 15 publications, including 2 articles in a foreign journals with high impact factor (IF 3.99 and 0.367) included in the Scopus database, 3 articles in a foreign journal cited in the Web of Science database, 5 articles in the journals included in the list recommended by the Committee on Control and Supervision in the Field of Education and Science of the MES RK, 4 abstracts at international conferences of the Far and Near Abroad and 1 patent (No. 33998, bulletin number No. 45, 08.11.2019).