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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

INCREASING THE CORROSION RESISTANCE OF THE SHIP HOUSING WITH THE USE OF NANOFILLERS IN PAINT COATINGS

Speciality: 3319.03 - "Technology of shipbuilding and ship repair"

Field of science: Technical science

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GENERAL CHARACTERISTICS OF WORK

The relevance of the topic and the degree of elaboration of the problem. Corrosion of metal products, structures and equipment causes significant technical, economic and environmental damage to water transport. Therefore, the requirements for corrosion resistance of ship steel structures are increased, which makes the task of improving protection methods relevant.

Corrosion damage causes irreparable damage to the hull, pipelines and other structures, since corrosion reduces the strength and density of the structures and the hull as a whole. The elimination of the consequences of corrosion destruction requires enormous direct and indirect material and labor resources.

At the same time, most of the parts of the hull elements and ship mechanisms are simultaneously exposed to corrosion destruction and mechanical stresses. Due to corrosion-mechanical damage, a considerable number of floating technical structures are dying.

According to experts, direct corrosion losses account for about 30% of annual steel production, and 10% of the metal is irretrievably lost, dispersed in the form of oxidation products. However, direct metal losses are not determinative, since they do not take into account the indirect costs associated with the failure of metal structures and assemblies. Real damage from an economic point of view in case of a loss of a structure consists of such factors as the cost of lost equipment, the cost of its restoration and repair, losses from idle operation and others.

If the integrity of oil tanks and tanks of sea vessels is violated by gas hydrates or other raw materials for energy resources, environmental pollution occurs. Contamination of the water surface with oil products causes great damage to the environment. Getting to the surface of the water, oil quickly spreads, its heavy fractions settle to the bottom, not only the coastal zone is polluted, but also the bottom of the reservoirs.

In order to improve the anti-corrosion properties of the hull of the vessel, various methods of protection are used. Among them, paint coatings have undeniable advantages. In order to improve the technological properties and reduce the consumption of paintwork pigments, special fillers are introduced: chalk, microasbestos, aerosil, talc, micromica, etc. With the introduction of fillers, the strength and adhesion characteristics of paints are significantly improved, it is possible to more closely fill the slightest irregularities of the painted surfaces.

Paint materials, which include, along with the basic components, any nanostructures and form coatings with a thickness of nanosized dimensions, are called nanolactic materials.

The production and use of nanofillers for ship paints opens new horizons in the use of their unusual properties. Use of nanofillers allows to obtain ultra-thin paint coatings with thickness of 0,01-3500 μm. Representatives of such paint materials are epilams based on organofluorine compounds. Nanofill paints have very high adhesion strength, hydrophobicity, abrasive, chemical and thermal resistance.

To date, there are many methods for protecting the hull from corrosion. However, they do not fully ensure its complete prevention and do not adequately protect against corrosion damage. In the field of metal science, the first issue of corrosion protection was considered by the Russian Academician G.V. Karpenko. His works touched upon the dangers of corrosion fatigue and hydrogen embrittlement, which adversely affect the operation of ship metal structures and lead to huge economic losses.

The dissertation research is based on the scientific works of scientists in the field of protection against various corrosion damage of marine vessels, such as Medvedev M.S., Redreev S.E., Andreev E.M., Boyko I.A., Babkina Z.F., Bilev E.A. The issues of metal strength in a corrosive environment were studied by Dyuryagina A.N., Ponomareva E.B., Tyukanko V.Yu., Shirin S.A., Buinova O.A. Methods of corrosion testing using paint coatings were proposed by Drinberg A.S., the effect of a surface-active medium on corrosion processes is presented in the works of Bolatbaev K.N., Ostrovny K.A., Dyuryagina A.N.

Despite a large number of studies in the field of increasing the corrosion resistance of a ship's hull, today there are few studies on the use of nanofillers in ship paint coatings, due to relatively recent discoveries in the field of nanotechnology and the possibility of using nanoparticles in various industries, in particular, in the preparation of enamels.

The object and subject of the study. The object of the study is to increase the corrosion resistance of hull structures of ships by using nanofillers in paint materials, and the subject of research is the composition, properties and various methods for improving the characteristics of ship paints.

The purpose of the study. The purpose of this study is to apply effective methods to improve the quality of paint materials and coatings that protect hull structures of ships from corrosion destruction based on the rational use of nanofill materials.

The main objectives of the study are:

1. Overview of main directions of vessel hull protection against corrosion.

2. Substantiation and selection of methods and means of paint materials quality research.

3. Analysis of composition and properties of fillers of ship paint materials.

4. Conducting experimental studies to identify rational compositions and properties of ship paint materials.

5. Feasibility study of the use of nanofillers in the production of paintwork materials.

Research methods. In this work, theoretical and experimental research methods (analysis, synthesis, method of collecting facts, analogies, comparison, induction, deduction, classification, observation) are used. Calculation methods confirmed the feasibility of using nanofillers in the production of paintwork materials in order to increase the corrosion resistance of the ship's hull.

The work was performed using modern equipment, including:

- electron scanning microscope JEOL JSM 6610lv;
- energy dispersive analysis module Oxford X-Max (S1XMX1002);
- desktop installation JEOL JFC-1600;

- universal cutting vertical mill VLM-2;
- laser granulometer MASTERSIZER 3000.

The main provisions for defense:

- results of physicochemical, morphological and phase analyzes of mineral fillers and nanoparticles of calcite and talcite;
- the identified mechanism, the nature of the interaction of nanofillers with the metal hull of the vessel;
- results of tests of technological and operational properties of various compositions of paintwork materials using calcite and talcite nanoparticles;
- results of corrosion tests of ship hull surfaces painted with PF-115 enamels based on various fillers in aggressive environments; development of requirements for the search for the rational composition and universal quality criterion for ship coatings;
- development of stages of searching for a model formulation with assessment of the impact on the quality of paints and varnishes;
- results of experiments on obtaining highly dispersed powders of nanofillers by dispersion methods;
- established advantages of using nanofillers in marine paintwork: improved protective properties, adjustable viscosity, increased strength, economical use of pigment, high hiding power, low leakage and improved rheological properties;
- test results of the developed compositions of ship coatings for environmental safety and compliance with sanitary and epidemiological standards;
- results of technical and economic calculations of productivity and energy consumption of grinding equipment to assess the efficiency of preparing highly dispersed filler powders;
- results of calculations of the technical and economic efficiency of the developed proposals when using paintwork with nanofillers at the Zykh ship repair and shipbuilding plant.

Practical value of the study. The practical significance of the work is to increase the corrosion resistance of the hull by using nanofill paints, which contributes to the extension of the life of ships. Ship repair costs are reduced and environmental impacts are reduced. The introduction of developed technological measures allows to obtain technical and economic efficiency due to increased corrosion resistance of hull structures of ships.

Scientific novelty of the work. The state of application of paints and varnishes in the "Azerbaijan Caspian Shipping Company" was analyzed. Methods and means of researching paints and varnishes that ensure protection of the corrosion resistance of the hull were substantiated and selected. An analysis was made of the latest modern methods of protecting the hull structure of ships from corrosion.

The features of painting ship hull structures are revealed. Theoretical and technological aspects of the use of nano-fillers in the composition of paints and varnishes for painting the ship's hull have been developed. It has been experimentally established that nanofillers in the composition of paints and varnishes create the possibility of a denser and easier filling of microroughnesses of the painted surface. A new varnish-paint composition has been developed for ship hull structures (AR patent No İ 2024 0121).

It has been determined that the use of chalk nanoparticles in the composition of ship paints and varnishes increases the corrosion resistance of the ship hull by improving the adhesion and strength characteristics of paints and varnishes, leading to an increase in the service life of ships.

Practical and theoretical value of the study. The practical significance of this work is to increase the corrosion resistance of the ship's hull through the use of nanofillers in the composition of paints and varnishes, which helps to extend the service life of ships. Thus, the cost of repairing ships is reduced, and the negative impact on the environment is reduced. The implementation of the methods proposed by the author makes it possible to obtain technical and economic efficiency by increasing the corrosion resistance of ship hull structures.

Approbation and implementation of research results. In the workshop of the Bibi-Heybat ship repair plant of the Azerbaijan Caspian Shipping Company, several paint samples were created on the basis of the obtained nanofillers. The PF-115 paint sample obtained on the basis of nanochalk was experimentally tested in 2023 at the Zykh ship repair and shipbuilding plant of Azerbaijan Caspian Shipping Company during the repair of the Balakan ferry of project 11611A.

The main results of the dissertation work were reported and discussed at:

- Scientific and methodological seminars of the department "Shipbuilding and ship repair" ASMA, 2016-2023;
- International scientific and technical conference dedicated to the 95th anniversary of the birth of H. A. Aliyev, Baku, 2018;
- International scientific conference "Current problems and ways to solve them in the production of building materials," dedicated to the memory of professor B.S. Sardarov, Baku, AASU, 2018;
- XXIII Republican scientific conference of young scientists and doctoral students, Baku, 2019;
- International conference of young scientists "Youth in Science" on the theme "Principles of selection of marine paint and coating materials and coating systems," Minsk, 2019;
- International scientific and technical conference "Technical operation of water transport: Problems and ways of development." Petropavlovsk - Kamchatsky, 2020.
- XVI International Scientific and Technical Conferences "Problems of Water Transport" Baku, 2017-2022;
- International scientific and technical conference "Modern problems and prospects for the development of the electric power industry", Baku, 2022.

The name of the organization where the dissertation work was completed. The dissertation work was completed at the Azerbaijan State Marine Academy at the Department of Shipbuilding and Ship Repair.

Publications on the topic of the dissertation. The main provisions of the research were published in 22 scientific articles - 9 articles in the collections of international scientific conferences and 13 articles in the journals of the Higher Attestation Commission (including 2 articles abroad and 1 article in the SOCAR Proceedings journal, included in the Scopus international citation system).

The applicant's personal contribution to the research conducted. From the claimant's point of view, the relevance of the research was justified, the main goal and the tasks proposed to achieve this goal were formulated. The implementation of the research was carried out, theoretical and practical issues were solved independently. Processing, systematization and discussion of the results were carried out. The presented dissertation is a completed scientific research work, written by the plaintiff himself, covering the set of scientific and practical propositions and results put forward for defense.

The total volume of the dissertation, indicating the symbols indicating the volume of the structural sections of the dissertation separately for each section. Dissertation structure - title page (379 characters), content (2392 characters), introduction (11,080 characters), 3 chapters (Chapter I - 50,301 characters, Chapter II - 51,552 characters, Chapter III – 61,216 characters, Chapter IV – 38,063), main conclusions (4,921 characters), list of references, applications (24,730 characters). The total volume of the dissertation work is 230 pages, printed on a computer, including 41 figures, 31 tables, 2 charts, 49 applications, a list of used literature, consisting of 161 titles, 203,879 characters excluding images, tables, applications and bibliography.

MAIN CONTENT OF THE WORK

The introduction substantiates the relevance of the topic and the degree of development of the problem, identifies the object and subject of the study, defines the purpose and objectives of the study, indicates the research methods, the main provisions submitted for defense, the scientific novelty of the work, the practical and theoretical value of the study, approbation and implementation of the research results, publications on the topic of research and the structure of the work.

In the first chapter, an analysis of literary and production sources was carried out in the main areas of protection of the hull from corrosion.

An analysis of the literature shows that among the methods for protecting the hull from corrosion, the most reliable and effective method is to protect the surface with paint coatings and materials. A comparative analysis of the functional properties and technical level of ship paint materials established the main reasons for the poor quality of paints.

It was revealed that domestic ship paint materials are significantly inferior to foreign ones both in terms of production quality, level of functional properties, and in terms of stability of physical and chemical indicators and completeness of the nomenclature.

The reason for the poor quality of paint materials, first of all, is the lack of development and research, the lack of local resources, as well as a limited range of alkyd, oil, polyvinyl butyral and phenolic paints.

It has been established that a large number of different paint systems and paint grades are used in ship repair and shipbuilding. A wide range of coatings and materials is associated with the complex operating conditions of hull structures of ships as a whole with the aggressiveness of corrosion and the feature of hull materials.

It was revealed that at present, the painting of hull structures on the vessels of the Azerbaijan Shipping Company is mainly carried out by paint materials of foreign manufacturers, such as Jotun (Norway) and International (England).

It has been established that the choice of ship paint materials and paint coating systems is currently made by shipbuilding and ship repair enterprises without fully taking into account the main functional and consumer properties of the materials used, as well as without taking into account operating conditions.

It has been found that when choosing paints, it is not enough to take into account only the type of environment, it should also focus on a number of technological, operational and economic factors. It was revealed that the main factors in the development of paints are: the required durability of the coating, the material of the painted structure, repairability, processability of the material application, compatibility with other methods of protection, the necessary degree of surface preparation, requirements for decoration, fire safety and explosion safety, economic feasibility, as well as sanitary and hygienic requirements [72][1].

It was determined that in the paint industry the possibilities of nanotechnologies are not sufficiently studied and applied, the production of environmentally friendly fillers and durable paints on polyester, polyurethane and acrylate bases has not been developed and mastered.

Insufficient scientific and technical developments aimed at improving the quality of paint materials on ship repair have been established. It is indicated that by developing and mastering the production of ship paint materials, using nanofillers, it is possible to achieve an extension of the life of the ship's hull.

The Rules of the Register, which are applied to paints used in shipbuilding, are systematized. The main physicochemical and technological characteristics of paints for painting the hull of the vessel have been determined. Special attention is paid to the technological process of applying paint materials to the hull of the vessel [114][2].

It was established that for hulls of ships operated in Caspian Sea, the use of paint materials using nanofillers from local raw materials is promising. The importance of comprehensive research aimed at protecting ship hulls from corrosion by developing paints using nanofillers is justified.

It has been established that the traditionally established organizational structure of painting production in ship repair and shipbuilding is not effective enough and hinders its further technological, technical and economic development.

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[1] Люблинский Е.Я. Коррозионностойкие газотермические покрытия / В.М.Вяльцев, В.Г.Зильберберг // Физико-химическая механика материалов, – Москва: – 1998. №2, – с. 95-96.

[2] Тюканько В.Ю., Островной К.А., Дюрягина А.Н. Микроструктурирование ЛКП в присутствии кислот растительных масел // Сб. тр. пятой СПб. Межд. конф. молодых учёных «Актуальные проблемы науки о полимерах». – Санкт-Петербург: – 2009, – с.23-28.

The feasibility of creating specialized divisions at domestic enterprises that carry out a full range of painting work on the orders of shipowners is indicated.

The second chapter presents methods and tools for studying the main properties of paint materials, taking into account the aggressiveness of sea water and the grade of shipbuilding steel. The main criteria for the selection of paint materials are defined in accordance with the Rules of the Register of Russian Shipping.

Methods of obtaining nanofillers for ship paints are classified. It is indicated that dispersal methods are based on the production of nanoparticles by mechanical grinding, and condensation methods are based on the growth of nanoparticles from individual atoms.

Dispersing methods are recognized as the best and effective methods for producing nanofill for ship paints when macrobodies are ground to nanosize.

Analysis of nanofill production methods revealed that with precise control of concentration and composition of surfactant stabilizer, dispersing methods make it possible to obtain nanofillers with size in the range of 10-50 nm, which is acceptable for introduction into ship paints.

It is indicated that the selection of paint materials should be carried out on the basis of an assessment of the complex of technological and operational properties of paint materials aimed at ensuring reliable protection of the hull of the vessel.

The creation of a modern quality control laboratory and the improvement of the technology for the preparation of paint materials is justified. It is indicated that the use of nanofillers in paint materials has good prospects and creates prerequisites for the development of effective paint coatings for ship hull structures.

It has been established that various fillers can be used to impart desired properties to paintwork materials, which provide increased strength, thermal conductivity, resistance to various external factors and improve the appearance of the surface.

By analyzing the main physical and chemical characteristics of natural fillers, it was found that highly dispersed talc - magnesium silicate meets the requirements in terms of its technological properties and can be used as a filler in the composition of paint and varnish materials. It has been established that the addition of talc to the composition of paints and varnishes increases strength, improves resistance to temperature extremes, resistance to mechanical damage and defects.

An analysis of the main physical and chemical characteristics of chalk as one of the natural fillers found that, due to the properties of chalk in the manufacture of modern coatings, it is used to increase corrosion resistance, increase adhesion, maintain weather resistance and hiding power of paint coatings, regulate their rheological properties, correct color and gloss in matte paints, as well as to reduce the cost of paint. So, the advantages of chalk are its following characteristics:

- Improved mechanical properties of the paintwork;
- Improved resistance to wet abrasion;
- Increases the shelf life of the paintwork. This is due to the fact that there are no soluble salts and various impurities in the chalk that cause damage to the paint. Consequently, there are fewer losses for processing and disposal;
- Chalk can be used as a rheological additive (anti-sludge additive), instead of aerosil and bentonite.
- Ease of use and convenient packaging to easily adapt to any production process.

Thus, after analyzing the properties of both samples studied by us, a significant advantage of the physicochemical, mechanical, adhesive, rheological properties of chalk was established in comparison with talc.

The third chapter is devoted to the experimental justification of the use of nanofillers in ship paint materials and the study of the features of the process of preparing finely dispersed talc and calcite powders.

It is indicated that with the use of nanofillers, new opportunities are opened for improving the technology of preparation and improving the quality of paint materials. Therefore, the development of optimal paint compositions using high-quality nanofill materials is of important scientific and practical importance.

The possibility of practical use of powders and nanopowders largely depends on their structure and exhibited physicochemical properties, and therefore their research is important.

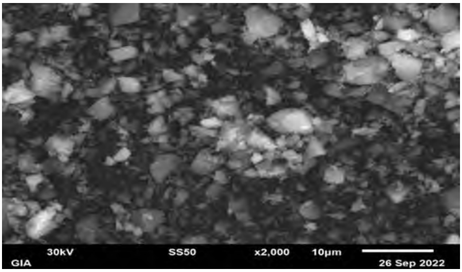
The Institute of Geology and Geophysics under the Ministry of Science and Education of the Republic of Azerbaijan analyzed the relationship between the technological, physical and chemical properties of paints and varnishes and the properties of mineral fillers.

The studies were carried out on a software hardware complex for studying the morphological, phase, elemental composition and molecular structure of materials and substances, which consists of a JEOL JSM 6610lv electron scanning microscope with a built-in Oxford X-Max (S1XMX1002) energy dispersive analysis module, equipped with the latest generation software complex with output to the Internet, and also equipped with a desktop installation for spraying a thin layer of metal JEOL JFC-1600 (pic.1).

a) b) c)

Picture 1. Software hardware complex:
a) electron scanning microscope JEOL JSM 6610lv;
b) desktop installation JEOL JFC-1600;
c) Oxford X-Max (S1XMX1002) energy dispersive analysis module

Chalk and talc were taken as filler samples. The morphological image of dry chalk is shown in picture 2.



Picture 2. Morphological image of dry chalk (2000x magnification)

Microscopic analysis of chalk showed that chalk is a sedimentary rock of organic (zoogenic) origin. Chalk has the chemical formula $CaCO_3$ and is close to limestone in its mineral composition, consists mainly of calcite and has a finely dispersed morphological structure (pic.2).

Based on the percentage of the chemical composition of chalk, it was revealed that chalk consists of 96.89% calcium oxide (CaO) and 3.11% magnesium oxide (MgO) (table 1).

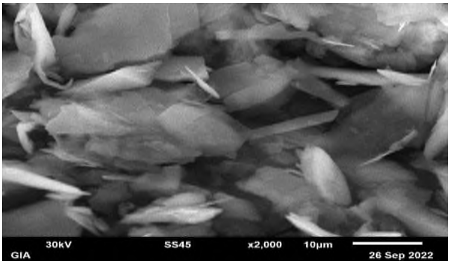
Table 1

Percentage of the chemical composition of pure chalk

Element	**Weight, %**	**Atomic,%**	**Connective, %**	**Formula**
Mg K	1.88	2.14	3.11	MgO
Ca K	69.25	47.86	96.89	CaO
O	28.88	50.00		
Total	100.00			

From the analysis of the chalk, it was concluded that the chalk does not contain impurities in its composition and has a microscopic particle size.

According to the results of chemical analysis of talc, it was revealed that it has a coarse structure. Morphological features of talc are represented by needle-like clusters, scaly and foliar aggregates, dense hidden and fine-scaly rocks, tabular crystals or fibrous masses, poorly faceted and hardly split into thin leaves and plates (pic.3).



Picture 3. Morphological image of dry talc (2000x magnification)

From the analysis of talc, it was concluded that talc is presented almost in pure form and has a microscopic particle size.

A percentage analysis of the composition of talc was carried out, which showed that talc consists of 65.57% silicon oxide SiO2 and 33.25% magnesium oxide MgO, and the remainder consists of impurities, as can be seen from table 2.

Table 2

Percentage of the chemical composition of pure talc

Element	**Weight, %**	**Atomic,%**	**Connective, %**	**Formula**
Mg K	20.05	16.60	33.25	MgO
Al K	0.33	0.25	0.63	Al_2O_3
Si K	30.65	21.96	65.57	SiO_2
Fe K	0.43	0.15	0.55	FeO
O	48.53	61.04		
Total	100.00			

The most common and productive way to obtain nanopowders is the mechanical grinding (dispersion) of materials. Grinding is carried out for uniform distribution of particles and for uniformity of mass [133][3].

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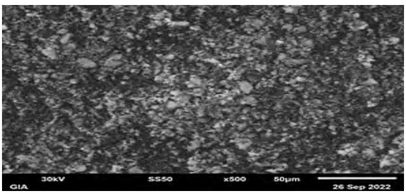
[3] Фатьянова Н.В. Особенности процесса подготовки высокодисперсных порошков талька // Сб. ст. Межд. науч. техн. конф. «Техническая эксплуатация Водного транспорта: Проблемы и пути развития», –Петропавловск-Камчатский: – 2020, – с. 70-72.

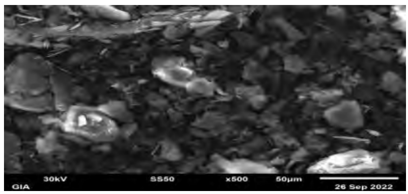
Both samples were sent to the Institute of Polymer Materials under the Ministry of Science and Education of the Republic of Azerbaijan for grinding in a universal cutting mill (pic.4) [138][4].

Picture 4. Universal cutting vertical mill VLM-2

After milling, both obtained samples of nanochalk and nanotalc were examined with an electron microscope. It was found that nanotalc is much smaller than nanochalk in size. Even after grinding the talc, it was still not possible to achieve a significant reduction in particles and get rid of the needle shape. While chalk in a significantly short time has greatly decreased in the size of its particles (pic.5 and pic.6) [140][5].



Picture 5. Morphological image of nanochalk

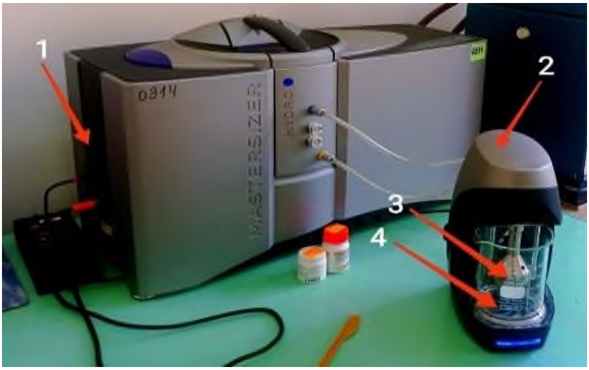


Picture 6. Morphological image of nanotalk

[4] Фатьянова Н.В. Исследование процесса получения высокодисперсных порошков талька и кальцита // Сб. межд. научно-технической конференции «Современные проблемы и перспективы развития электроэнергетики», – Баку: – 2022, – с. 154-162.
[5] Фатьянова Н.В. Применение наполнителей на основе наномела и нанотtalька в судовых ЛКМ как один из способов повышения коррозионной стойкости корпуса судна // – Баку: Socar Proccedings, серия техн.науки, –2023, №2, – с.136-144.

It has been established that a rational mode of dry grinding lasting about an hour provides sufficient dispersion, high exchange capacity and colloidality of chalk. While talc must be ground for several hours with the addition of surfactants.

Using a Mastersizer 3000 laser granulometer operating based on the laser diffraction method, the particle size of each sample was determined.



Picture 7. Laser granulometer Mastersizer 3000:
1 - single measuring unit; 2 – Hydro EV module;
3 – dispersion block; 4 – glass

Picture 8 presents data on the granulometric analysis of nanochalk. For the experiment:

a) used: 5 g nanochalk powder

b) determination time: 5 min

c) specific surface area of nanochalk: 5.876 m^2/kg

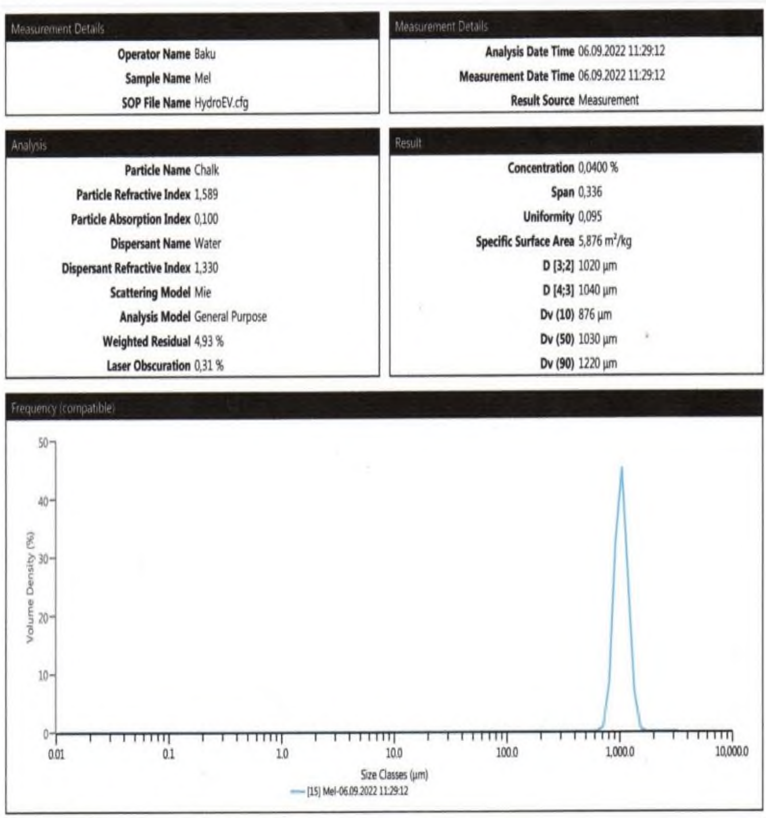
d) weighted balance: 4.93%

e) laser dimming: 0.31%

f) grinding quality: satisfactory (average volumetric diameter of nanochalk particles: 1020 μm)

g) total volume: 1040 μm

h) it has been established that: 90% of nanochalk powder consists of particles with a size of 1220 μm; 50% - 1030 μm; 10% - 876 μm or more.



Picture 8. Granulometric analysis of nanochalk

Picture 9 presents data on the granulometric analysis of nanotalc. For the experiment:

a) used: 5 g nanotalc powder

b) determination time: 5 min

c) specific surface area of nanochalk: 6.143 m^2/kg

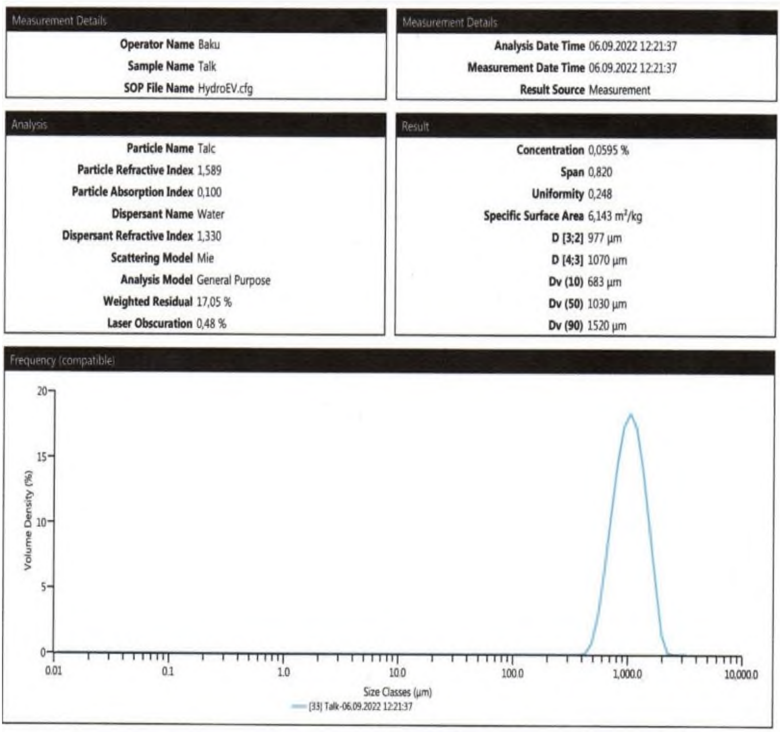
d) weighted balance: 17.05%

e) laser dimming: 0.48%

f) grinding quality: average (average volumetric diameter of nanotalc particles: 977 μm)

g) total volume: 1040 μm

h) it was established that 90% of the powder consists of particles with a size of 1520 μm; 50% - 1030 μm; 10% - 683 μm or more.



Picture 9. Granulometric analysis of nanotalc

To study the compositions and properties of paints and varnishes at the Bibi-Heybat shipyard in the paint shop, 3 samples of shipbuilding enamel PF-115 (manufactured in accordance with QOST 6465-76) based on talc, nanochalk and nanotalc were created.

Table 3 shows the recipe for the manufacture of 1 kg of each sample of the resulting PF-115 enamel with different fillers (nanochalk, nanotalc, talc).

Table 3

Formulation of ship paints and varnishes based on various fillers

Components	Component weight
The composition of the paint based on nanochalk filler	
Varnish PF-60	0,455
Titanium dioxide (TiO_2)	0,083
Filler (nanochalk)	0,30
Solvent	0,145
Catalyst	0,017
The composition of the paint based on nanotalc filler	
Varnish PF-60	0,435
Titanium dioxide (TiO_2)	0,092
Filler (nanotalc)	0,343
Solvent	0,114
Catalyst	0,016
The composition of the paint based on talc filler	
Varnish PF-60	0,435
Titanium dioxide (TiO_2)	0,092
Filler (talc)	0,343
Solvent	0,114
Catalyst	0,016

After making samples of enamel PF-115, to test its quality, samples of shipbuilding steel RSD-32 [145][6] were taken and painted with all 4 enamels (one made at the Bibi-Heybat plant on the basis of chalk, which is a control sample and three obtained enamel samples) [146][7].

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[6] Шарифов З.З. Коррозионное поведение сварных соединений стали РСД32 и РСД32Ш в каспийской морской воде / З. З. Шарифов, И. А. Ханкишиев // Водний транспорт, – Украина: – 2016. – № 2. – с. 37-44.

[7] Шешуков А.В. ЛКМ для судовых покрытий / Э.Ф. Ицко, М.Б. Симанович, В.П. Кырпичев // ЛКМ и их применение, – Москва: – 1992. № 4, – с.24-29.

Thus, for comparison, we received 4 enamel samples:

1st sample - control sample;

2nd sample - with filler - talc;

3rd sample - with nanochalk filler;

4th sample - with filler - nanotalc.

Further, the following were determined: the degree and time of drying of paint and varnish films, a visual characteristic was given to the appearance of the films of each of the samples, a visual comparison of color was carried out, hiding power, conditional viscosity, and adhesion of the obtained enamel samples were determined. According to the results of the analysis, the advantages of enamel with a filler based on nanochalk were identified.

The results of visual tests of PF-115 paints with various fillers are presented in table 4.

Table 4

Results of visual tests of PF-115 paints with various fillers

Filler name	Chalk	Talk	Nanochalk	Nanotalk
Drying degree	20 h 54 min	20 h 16 min	18 h	19 h 23 min
Covering power	81 g/m^2	83 g/m^2	91 g/m^2	85 g/m^2
Conditional viscosity	90 s	95 s	105 s	103 s
Adhesion degree	4 points	3 points	2 points	3 points

The chemical compositions of PF-115 paints based on chalk and talc, nanochalk and nanotalc were also studied. Chemical analysis data is presented in tables 5, 6, 7 and 8.

Table 5

Chemical analysis of chalk-based enamel PF-115

Element	**Weight, %**	**Atomic,%**	**Connective, %**	**Formula**
Mg K	1.36	1.52	2.26	MgO
Al K	0.71	0.72	1.34	Al_2O_3
CaK	44.11	29.89	61.71	CaO
Ti K	20.79	11.79	34.68	TiO_2
O	33.03	56.07		
Total	100.00			

Table 6

Chemical analysis of PF-115 enamel based on talc

Element	**Weight, %**	**Atomic,%**	**Connective, %**	**Formula**
Mg K	9.28	8.73	15.39	MgO
Al K	1.36	1.15	2.57	Al_2O_3
Si K	17.03	13.87	36.43	SiO_2
Ti K	26.33	12.57	43.92	TiO_2
Pb L	1.56	0.17	1.68	PbO
O	44.43	63.51		
Total	100.00			

Table 7

Chemical analysis of PF-115 enamel based on nanochalk

Element	**Weight, %**	**Atomic,%**	**Connective, %**	**Formula**
Al K	0.93	0.96	1.76	Al_2O_3
Si K	0.85	0.84	1.81	SiO_2
Ca K	39.15	27.10	54.78	CaO
Ti K	23.08	13.37	38.50	TiO_2
Pb L	2.92	0.39	3.15	PbO
O	33.07	57.34		
Total	100.00			

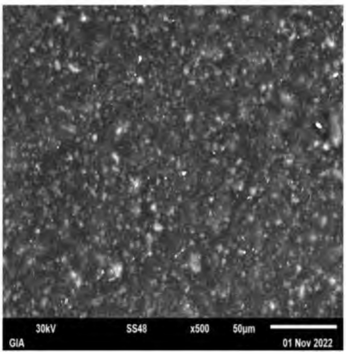
Table 8

Chemical analysis of PF-115 enamel based on nanotalc

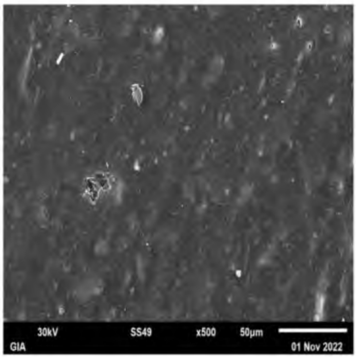
Element	Weight, %	Atomic,%	Connective, %	Formula
Mg K	10.50	9.61	17.40	MgO
Al K	1.44	1.19	2.72	Al_2O_3
Si K	21.40	16.95	45.78	SiO_2
Ti K	19.02	8.83	31.72	TiO_2
Pb L	2.22	0.24	2.39	PbO
O	45.44	63.19		
Total	100.00			

60-day, 120-day and 180-day surface samples painted with chalk, talc, nanochalk and nanotalc based enamels were also examined.

The morphological structure and chemical analysis of a 180-day sample of a surface painted with PF-115 enamel based on nanochalk and nanotalc are presented in pic. 10 and 11 and in tables 9 and 10, respectively.



Picture 10. Morphological structure of PF-115 enamel based on nanochalk



Picture 11. Morphological structure of PF-115 enamel based on nanotalc

Table 9

Percentage of the chemical composition of a 180-day sample of a surface painted with PF-115 enamel based on nanochalk

Element	**Weight, %**	**Atomic,%**	**Connective, %**	**Formula**
Mg K	4.46	4.66	7.39	MgO
Al K	1.21	1.14	2.29	Al_2O_3
Si K	5.44	4.92	11.65	SiO_2
CaK	26.05	16.50	36.45	CaO
Ti K	24.91	13.20	41.55	TiO_2
Fe K	0.30	0.24	0.67	Fe_2O_3
O	37.40	59.35		
Total	100.00			

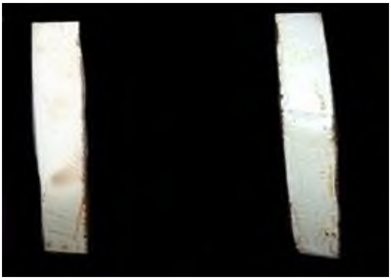
Table 10

Percentage of the chemical composition of a 180-day sample of a surface painted with PF-115 enamel based on nanotalc

Element	**Weight, %**	**Atomic,%**	**Connective, %**	**Formula**
Mg K	9.29	8.72	15.40	MgO
Al K	1.53	1.29	2.89	Al_2O_3
Si K	17.49	14.22	37.43	SiO_2
Ca К	1.85	1.05	2.59	CaO
Ti K	23.36	11.13	38.60	TiO_2
Fe K	1.10	0.39	1.60	Fe_2O_3
Pb L	1.39	0.15	1.50	PbO
O	44.19	63.05		
Total	100.00			

Chemical analysis of each sample of the painted surface proved that the corrosion process on a surface coated with talc-based enamel proceeds much faster than on a surface painted with chalk-based enamel.

According to the computer chemical, microscopic analysis, it was concluded that the technological, physical and chemical properties of local chalk and talc indicate that local chalk and talc can be used as a filler in the composition of ship paints and varnishes and paint and varnish coatings. However, chalk and nanochalk, unlike talc and nanotalc, fully meet the requirements that apply to paints and varnishes and are at the level of properties of calcite, widely used in various industries (pic.12 and pic. 13) [141][8].



Picture 12. Photograph of 180-day-old talc-based (left) and chalk-based (right) enamel surface samples

Picture 13. Photograph of 180-day-old nanotalc-based (left) and nanochalk-based (right) enamel surface samples

A positive effect of nanochalk additives on the regulation of paint gloss and an increase in cracking resistance has been established. Nanochalk also improves the rheological properties of the paint, increases the mechanical strength of paints and varnishes.

The weather resistance and moisture resistance of paints and varnishes are improved by nanochalk additives. It has been established that with small additions of nanochalk, the chemical and corrosion resistance of paints and varnishes increases.

The most important properties of nanochalk are high whiteness and softness, hydrophobicity and organophilicity, high heat resistance, chemical inertness and low electrical conductivity.

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[8] Фатьянова Н.В. Методы получения и применения нанонаполнителей в производстве судовых ЛКМ // – Баку: Научные труды АГМА, серия техн. науки, – 2023, №2, – с. 29-34.

Due to the softness of chalk nanoparticles, good sandability is imparted to paintwork materials and low abrasive wear of the surface is ensured.

The hydrophobicity and chemical resistance of nanochalk provides durability, anti-corrosion resistance, and also improves the appearance of the ship's hull surface.

The plasticity of chalk nanoparticles provides low water resistance, good hiding power and high strength characteristics of paints and varnishes.

The fourth chapter is devoted to calculating the environmental safety and economic efficiency of using nanofillers in the production of marine coatings.

Since production practice shows that most paints and varnishes contain components that can have a detrimental effect on the environment and the human body, we calculated the pollutants from the production of our samples.

1. When preparing paint, solvent vapors are released from solvents [81][9].

$$П^{п}=M_{\delta}\cdot\varphi_{v}\cdot\delta_{s}\cdot 10^{-4} \qquad (4.1.1)$$

M_{δ}- the number of components used in the preparation of paint;

φ_{v} - sum of volatile parts of paints and varnishes, 7%;

δ_{s} - amount of solvent released from the mixer, 3%;

Release of substances in the form of solvent vapors in a second

$$П^{п} =0{,}00058 \text{ g/s}$$

Solvent vapors:

Xylene	0,00029 g/s
White Spirit	0,00029 g/s

[9] «Методики расчета выделений (выбросов) загрязняющих веществ в атмосферу при нанесении лакокрасочных материалов (по величинам удельных показателей)» – Санкт-Петербург: Гидрометиоиздат. – 2021, – с.36.

In terms of the degree of impact on the body, xylene belongs to the 3rd hazard class (moderately hazardous substances), white spirit belongs to the 4th hazard class (low-hazardous substances) according to QOST 12.1.007-76 [32][10].

2. Dust emissions are calculated as follows:

When various powdery substances (chalk, talc, etc.) are added to the paint mixer, this zone is taken as a source of intense non-volatile dust formation.

To calculate dust-like emissions of powdery substances (chalk, talc, etc.), the data taken for calculating dust is used.

Dust volume:

Secondary release of pollutant

$$q = \frac{k_1 \cdot k_2 \cdot k_3 \cdot k_4 \cdot k_5 \cdot k_7 \cdot B \cdot G \cdot 10^6}{3600} \quad g/s \qquad (4.1.2)$$

$к_1$ = 0,09 - weight fraction of dust fraction;

$к_2$ = 0,06 - the proportion of dust (of all dust by weight) that turns into an aerosol;

$к_3$ = 1 - coefficient taking into account meteorological conditions (wind speed);

$к_4$ = 0,1 - coefficient of the degree of protection of the workplace from external influences (dust formation conditions);

$к_5$ = 0,7 - material moisture coefficient;

$к_7$ = 0,8 - material size coefficient;

B = 0,4 - coefficient of filling height;

G = 0,451 - total amount of processed material.

q = 0,015 g/s

[10] ГОСТ 12.1.007-76 ССБТ. Вредные вещества. Классификация и общие требования безопасности, – Москва, Стандартинформ, –2007, – 7с.

According to the degree of impact on the body, dust-like emissions belong to the 3rd hazard class (moderately dangerous substances).

As calculations have shown, emissions into the environment and harm to the human body are insignificant, and the paint is moderately toxic.

Next, a comparison was made of the economic efficiency of obtaining nanochalk and nanotalc samples. Using the calculated characteristics of the Tesca company, the productivity of nanotalc was calculated and compared with the productivity of nanochalk, and the specific energy consumption spent on grinding each of the materials was compared and the obtained values were compared.

According to the obtained values, it was concluded that with practically the same specific energy consumption for grinding nanotalc and nanochalk, the productivity of nanochalk is more than 2 times higher than the productivity of nanotalc. This is due to the structure of chalk, as well as the shorter time spent on obtaining nanochalk.

At the next stage the chemical and physical characteristics of the foreign paint Jotun and PF-115 paint based on nanochalk were analyzed. The data obtained showed that both materials have similar properties, including high adhesion, corrosion resistance and a high degree of surface protection. These results suggest that nanochalk paint PF-115 could be a successful alternative to Jotun paint.

One of the key points was to compare the cost-effectiveness of both staining options. This includes analysis of theoretical and practical material consumption, as well as accounting for losses associated with various aspects of the dyeing process. Practical calculations showed that the second painting option, which involves replacing the first layer of Jotun paint with PF-115 paint, turned out to be more economically profitable. A comparison of the total material costs for painting the underwater part of the ship with three layers of paint showed that using Jotun paint requires 66,524 manats, while the second option with PF-115 paint costs 44,753 manats. Savings of AZN 21,771 using the second option indicate a significant economic benefit and make it preferable. This method reduces overall material costs and plays a key role in increasing the profitability of projects in the marine industry.

An important aspect of the study is also the need to take into account additional factors, such as losses from surface roughness, painting methods, working conditions and inevitable losses of material. These aspects influence the overall material consumption and therefore the economic efficiency of the process. Taking them into account when developing a strategy for painting underwater parts of ships can lead to significant savings in resources.

Based on the results of our research, it is recommended to introduce a second painting option, replacing the first layer of Jotun paint with nanochalk-based PF-115 paint, as preferable for practical use in the marine industry. This approach meets modern quality requirements, provides reliable protection for the underwater part of the vessel, and is at the same time economically profitable.

Thus, based on the experimental studies carried out, we can conclude that the use of nanochalk as a filler for paints and varnishes, in addition to the physicochemical properties that chalk and nanochalk have, is also beneficial from the point of view of economic efficiency, achieved due to higher productivity and lower price per kg of raw materials, as well as by painting the underwater part of the vessel with the replacement of the first layer of Jotun paint with PF-115 paint based on nanochalk.

GENERAL CONCLUSIONS

In the course of achieving the goal and solving the tasks in the dissertation work, the following scientific and practical results were obtained:

1. The insufficient effectiveness of existing methods for protecting steel hull structures of ships in sea water from corrosion damage has been revealed. The expediency of applying ship paintwork to the hull as one of the methods of protection is substantiated.

A comparative analysis of foreign and domestic marine paints and varnishes was carried out, the reasons for the low quality of domestic materials and the limited range of paints were identified. It was discovered that the capabilities of nanotechnology, local mineral resources, and environmentally anti-corrosion coatings on polyester, polyurethane and acrylate bases have not been developed.

A classification of methods for combating corrosion has been carried out, and ways to reduce economic losses from corrosion of ship hulls in the Caspian Sea have been indicated. The technological process of applying paints and varnishes, which meets the requirements of the register of shipping, and includes complete mechanization of painting operations while observing sanitary and hygienic standards, has been analyzed.

2. The physicochemical and mineralogical characteristics of fillers have been studied, and their comparative technological features have been emphasized. It has been revealed that these materials help to increase strength and thermal conductivity, resistance to environmental influences, and improve the appearance of the ship's hull. The effectiveness of using nanochalk in marine coatings due to its chemical composition and physical properties is emphasized. When nanochalk is added to paint and varnish materials, their thermochemical resistance in aggressive environments, strength, adhesion, resistance to temperature changes, resistance to mechanical stress increases, and defects on painted surfaces in aggressive environments are reduced.

3. An analysis of the technology for preparing coatings and the equipment used at the Bibi-Heybat shipyard was carried out. It is noted that pentaphthalic enamels are one of the most common and in demand coatings on the ships of the Caspian Shipping Company. Caspian Shipping Company is also actively working on developing its own coatings to reduce procurement costs. The use of nanofillers in paintwork materials provides new opportunities for improving the technology and quality of paintwork materials.

4. Gas emissions from different classes of marine paints and varnishes have been identified, as well as the compositions of volatile organic compounds characteristic of these materials. It was revealed that paintwork materials contain moderately toxic components that

meet environmental standards. Pollutants from the production of paints and varnishes have been calculated, and the results demonstrate compliance with sanitary and epidemiological standards.

5. The requirements for finding the optimal composition of ship paints and varnishes have been determined. A universal quality criterion for paint and varnish formulations has been developed. The process of managing the composition of paintwork materials includes several stages: creating a general model with restrictions, clarifying restrictions on the concentration of components and searching for a model formulation with an assessment of the impact on the quality of paintwork materials.

6. Experiments have been conducted on the use of nanofillers in marine paints and varnishes, including the process of producing highly dispersed chalk and talc powders. The grinding method is recognized as the most optimal for obtaining fine powders. After dry grinding, samples of chalk and talc nanoparticles were obtained. Research has shown that talc does not undergo a significant reduction in particle size when dry milled, unlike chalk. Thus, it has been experimentally confirmed that talc requires the addition of surfactants during wet grinding to achieve good results.

7. To study the compositions and properties of paintwork materials, 3 samples of shipbuilding paint based on talc, nanochalk and nanotalc were created at the Bibi-Heybat ship repair plant. Analyzes of the chemical composition of these enamels and computer analysis of chemical data were carried out. The results of the analysis showed that enamel based on chalk and nanochalk is superior to enamel based on talc and nanotalc in physicochemical parameters.

Based on the test results, the advantages of using nanochalk in marine paint and varnish coatings have been established: high weather and moisture resistance of coatings, improved protective properties, regulation of viscosity and haze, increased strength, effective use of pigment and high hiding power, prevention of cracking and low flow during application, improvement of rheological characteristics.

8. Based on data from Tecsa, a company specializing in grinding equipment, data on the performance and energy consumption of

samples with nanochalk-based fillers were analyzed. The specific energy consumption for grinding nanotalc and nanochalk was calculated and the data obtained were analyzed. The analysis showed that the productivity of nanochalk exceeds the productivity of nanotalc by more than 2 times with similar energy consumption for grinding. This justifies the use of nanochalk in paint and varnish materials, which proves the economic efficiency and feasibility of such a solution in terms of physical and chemical properties and economic benefits, providing significant savings in material resources and costs.

Technical and economic efficiency calculations also confirmed that using PF-115 paint with nanochalk instead of the first layer of Jotun paint to paint the underwater part of a project 11611A vessel is the best option. This provides the necessary protection and quality of the coating, which confirms the advantages of using nanochalk in paints and varnishes from a physicochemical and economic point of view, saving resources and reducing costs.

The expected economic efficiency from the implementation of research is 21,771 manats per painting of one vessel.

Thus, the effectiveness and feasibility of using nanofillers in paintwork materials to improve the corrosion resistance of the ship hull has been confirmed.

The main content of the dissertation is set forth in the following works:

1. Fatyanova N.V., Ismailov N.Sh., Sadygov V.B. Features of paints used in ship repair / Scientific works of ASMA, Baku, 2017, No. 2, p. 24-30

2. Fatyanova N.V., Sharifov Z.Z., Ismailov N.Sh. Paint and varnish materials - effective means of corrosion protection. // Scientific works of ASMA, Baku, 2018, No. 1, p. 24-28

3. Fatyanova N.V., Ismailov N.Sh. Comparative characteristics of paints of foreign manufacturers used by the "Azerbaijan Caspian Shipping Company "// "Ecology and water management" Baku, 2018, No. 1, p. 3-9

4. Fatyanova N.V. Methods and features of the study of the properties of ship paints // Scientific and practical journal "Young Researcher," Baku, 2018, p. 22-28

5. Fatyanova N.V. Methods of calculating the costs of ship paints // Scientific journal "Transport business of Russia," M., 2019, p. 156-157

6. Fatyanova N.V. Analysis of the composition and properties of paint materials manufactured at the Bibi-Eibat plant of ILC. Scientific and Technical Collection, St. Petersburg, 2019, p. 94-100

7. Fatyanova N.V. Determination of damage to the environment caused by ship paint materials. // Scientific works of ASMA, Baku, 2020, p. 15-22

8. Fatyanova N.V. Modern methods of increasing the corrosion resistance of metal structures using nanofillers in paint coatings in the ship and aircraft industry // Scientific journal "Bulletin of the Azerbaijan Engineering Academy," Baku.: 2020, p. 40-46

9. Fatyanova N.V. Stabilizing the properties of ship paint materials with additives of talc nanoparticles // Scientific works of ASMA, Baku, 2021, No. 2, p. 12-21

10. Fatyanova N.V., Ismailov N.Sh. Some characteristics of paints used in the Caspian Sea Shipping Company//Collection of the II International scientific and technical conference "Problems of Metallurgy and Materials Science," Baku, 2017, p. 244-246

11. Fatyanova N.V., Ismailov N.Sh. Features of the technology of painting at ship repair production. // Collection of the XIII international scientific and technical conference dedicated to the 95th anniversary of the birth of H. A. Aliyev, Baku, 2018, p. 13-20

12. Fatyanova N.V. Principles for the selection of ship paints and coating systems // Collection of the international scientific conference "Current problems and ways to solve them in the production of building materials," dedicated to the memory of prof. B.S. Sardarova. Baku, 2018, p. 147-151

13. Fatyanova N.V. Application of nanoparticles of mineral filler - talc in paints. Collection of articles of the XXIII Republican scientific conference. Baku, 2019, p. 198-201

14. Fatyanova N.V. Principles of selection of marine paint and coating materials and coating systems. Abstracts of the report of the XVI International conference of young scientists "Youth in Science 2019," Minsk, 2019, p. 240-242

15. Fatyanova N.V. Features of the process of preparing finely dispersed talc powders. Collection of articles of the International scientific and technical conference "Technical operation of water transport: Problems and ways of development." Petropavlovsk - Kamch., 2019, p. 70-72

16. Fatyanova N.V. Modern methods of using nanoparticles in the production of ship paints. // Collection of the XVI international scientific and technical conference dedicated to the 98th anniversary of the birth of H. A. Aliyev, Baku, 2021, p. 5-7

17. Fatyanova N.V. The method of searching for rational compositions of ship paints and varnishes // Scientific works of the ASMA, Baku, 2022, No. 2, -p.68-74.

18. Fatyanova N.V. Modern methods of application of nanoparticles in the production of ship paints and varnishes // Coll. XVII International Scientific and Technical Conference "Problems of Water Transport", Baku, 2022, p. 18-21.

19. Fatyanova N.V. Study of the process of obtaining highly dispersed powders of talc and calcite // Coll. of the international scientific and technical conference "Modern problems and prospects for the development of the electric power industry", Baku, 2022, p. 154-161

20. Fatyanova N.V. Innovative nanotechnology in paint and varnish materials in shipbuilding and aviation. Increase in corrosion resistance of metal due to the application of fillers based on nanochalk and nanotalc // Vestnik of the Azerbaijan Academy of Engineering, Baku: -2023, No.3, -p.15-27.

21. Fatyanova N.V. The use of fillers based on nanochalk and nanotalc in marine coatings as one of the ways to increase the corrosion resistance of the ship's hull // Socar Proceedings Scientific Journal, Baku, 2023, No. 2, - pp. 136-144

22. Fatyanova N.V. Methods for obtaining and using nanofillers in the production of marine coatings // Scientific works of the ASMA, Baku, 2023, No. 2, pp. 29-34.

Personal participation of the author in published works in co-authorship:

Works number [5, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22] were performed freely by the author.

Works number [1,2,3,4,6] the author performed the setting of research issues, theoretical studies, processing of results, making proposals, forming scientific provisions. The remaining parts were performed equally by the authors.

Works number [1,2,3,4,6] were written as a result of the joint discussion of the authors with the recommendation of the scientific supervisor in order to master the theoretical part of the problem.

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