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Nanocoatings in modern construction

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ABSTRACT: The review analyzes the state of the nanocoating market, shows main types of nanocoatings, as well as drivers and barriers to their development and application. Modern progress in the field of nanotechnology allows us to attribute nanocoating to high performance materials, the structure and properties of which can be "designed" according to specific functional criteria and the level of environmental impact. They present unique remarkable characteristics compared to conventional coating materials in construction industry. The government's grandiose plans to commission new housing and road infrastructure, as well as ambitious projects to develop the Arctic and ensure national security, should lead to the growth of the industry as a whole, as well as to an increase in demand for more efficient, innovative building materials, including nanocoatings and nanopaints.

KEYWORDS: construction, nanomaterials and nanotechnologies, functional coatings, world market, drivers and barriers, sustainable development.

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INTRODUCTION

The industry of building materials and construction, despite of their obviously conservative character, quite often has to face so-called "industrial revolution of the XXI century". New trends, new methods of experiments and researches are becoming perspective foundation for creation of high-tech products and processes characterized by guaranteed reliability index, developing principles of manufacturing up-to-date "supermaterials" and are marking the start of the sixth technological wave [1].

Along documents of the International Union of Laboratories and Experts in Construction Materials, Systems and Structures (RILEM) developed by TC 197-NCM, a special place among high-tech products is occupied by functional coatings, which increase material properties manifold, for example, their optical and thermal properties, durability, wearing capacity, resistance to different exposures, provide self-cleaning and prevent walls from being painted, etc. [2].

According to the standard ISO 4618:2014 [3], the term "coating" means layer formed from a single or multiple application of a coating material to a substrate. Coating material is a product in liquid, paste or powder state which when being applied on substrate forms a layer possessing protective, decorative and/or other specific properties. At this, "nanocoating" can be determined as a coating which either possesses nanosize thickness or contains as second phase of nanosize particles which are dispersed in matrix, or it is a coating with nanosize grains/phases etc. [4].

According scientific and analytical literature, paints are a part of coatings [5]. GOST 9.072-2017 [6] defines "paint coating" as a continuous coating formed as a result of applying one or several layers of paint material on painted surface and defines "nanocoating" as a coating with dried layers which thickness is from 1 to 10 nm. Scientific and analytical literature includes paints in the family of coatings [5].

Thus, summarizing the above material, we can say that nanocoatings by their nature, as a rule, belong in very thin layers of chemical matters (polymers, metals, composites, etc.) which are used to add specific chemical or physical characteristics to substrate surface: hydrophobic and/or oleophobic properties, corrosion resistance, resistance to abrasion and scratches, hardness, lubricity, transparency, plasticity et al.

MARKET OF NANOCOATINGS. DRIVERS AND BARRIERS

The world analytical agencies state that the volume of world market of nanocoatings in 2019 is estimated of 6101,8 million US dollars; according to prognoses, it will be of 22,96 billion US dollars by 2027 when compound annual growth rate (CAGR) is 18,4% per year. Nanocoating market is dramatically growing related to increased demand in such areas of end consumer as health care, automobile engineering, building materials and construction, electronics, shipbuilding, power industry, water treatment and packing [7–9].

Due to properties inherent in nanolevel, nanocoatings are usually multifunctional, demonstrating one or combination of the following properties: self-healing, self-cleaning, antibacterial and antivirus activity, catalytic activity, antistatic characteristic, sensor perception et al. Innovative nanocoatings have shape memory, are sensible to fingerprints as well as are energy-efficient.

Nanocoatings provide resistance to temperature variations, due to that application of them is rapidly increasing in products and structures exposed to temperature drop and severe climate: ceramic tile, glass windows, cryogenic storage vessels et al.

Efficient fire-proof nanocoatings are obtained by using nanosize double magnesium-aluminium hydroxides (LDHs), titanium nanodioxide (TiO_2) and silica nanodioxide (SiO_2) [10–12].

Nanocoatings create transparent, colorless protection which cannot being seen by eye, that provides esthetic appearance and preserve natural gloss and transparency. Moreover, the products with nanocoatings practically don't accumulate dust. In the rare cases where foreign contaminants, such as dust and dirt, stick to the surface, they can be easily removed by flushing.

Nanocoatings can provide protection from ultraviolet light (UV) and resistance to abrasion. This property significantly increases the service life of the products and makes them ideal for preserving paint surfaces. Nanoparticles of silica dioxide (SiO_2), titanium dioxide (TiO_2), aluminium oxide (Al_2O_3) and zirconium oxide (ZrO_2) are widely used to increase hardness and mechanical characteristics of coatings, rising by that their wear-resistance and resistance to scratches. One of the application areas for them is maintenance of surface appearance and durability of parquet floors or window glasses [13].

In recent years, "anti-graffiti" nanostructured coatings on the basis of polyurethane modified with nanoparticles of silica and titanium dioxide have been widely used [14–17]. They are particularly promising on the historical and stone surfaces as they help to keep cultural heritage.

Nanocoatings significantly increase corrosion resistance of structures (reinforced concrete, stone structures, metals, etc.) that prolong their service life and durability. The most recent technical solutions for the use of self-healing and smart coatings to improve corrosion protection are discussed in [18].

Nanocoatings are antiadhesive and more hygienic compared to common coatings. They prevent from growth of bacteria and micro organisms. Structures and details with nano-coating does not require waxing to maintain its luster. In addition, they are also eco-friendly, non-toxic and breathable, which allows them to be used effectively on a variety of products, as they suppress dampness and mold.

Since the end of 90s some German and Spanish companies have been manufacturing nanotechnology-based products, among which were coatings for total water-repellent treatment, coatings for protection from graffiti, coatings for elimination of biodeterioration sources such as mildew, fungus, mosses, lichen, and coatings for efflorescence prevention.

Hydrophobic coatings [19–23] are used mainly to make coatings water-proof and corrosion resistant. In this way, hydrophobic system on the basis of silica nanodioxide (SiO_2) for water creates contact angle exceeding 150°, and angle of inclination is less than 10° [24]. Up-to-date, organosilicone compounds (OSC) can visibly improve these values [25].

In fact, OSC with their active groups can react with mineral (nonorganic) substrates which contain silanol groups (Si–OH), such as concrete, cement, stone, brick, reinforced concrete with siloxane bonds (Si–O–Si) formation between substrate and modifier molecules that leads to stable hydrophobization of the surface. Another positive property to be noted is that OSC penetrate substrate at the depth from ~0,5 mm to 1 mm. Emersed alkylsiloxane surface, apart from stable hydrophobic effect, prevents from exfoliation. Moreover, modified surface becomes resistant to weather impact and ultraviolet radiation [5].

Today, hydrophobization is actively used to increase efficiency of mineral insulators ("mineral cotton") that minimizes their hydro- and vapour absorbtion. The application areas of hydrophobizated insulators are petrochemical facilities, shipbuilding, civil buildings (walls, floors and ceilings), thermal stations, oil refineries, electric power plants, recording studios, conference halls, airports and metro systems, air conditioning systems, manufacture of sandwich panels, etc. [5].

Significant changes have taken place in the area of development and application of new generation of self-cleaning coatings. It is important that such coatings are being considered today within the framework of scramble for dramatic decrease of costs and operation time required for service, repairs and restoration of the structures in complex objects.

As it is known, under the influence of ultraviolet light, modified TiO_2 acts as a photocatalyst, releasing atomic oxygen from water vapor or atmospheric oxygen. It is enough to have disengaged active oxygen to oxidize and decompose organic pollutants, deodorize rooms and to destroy bacteria.

For now, TiO_2-nanoparticles are being widely applied in cement paints, special cements, cement mortars, road pavements, both concrete and bitumen self-cleaning materials and structures, air purification materials and structures, antibacterial materials and structures, compositions and finishing materials for external and internal works [26].

These photosensitive catalysts are especially used for formation of concrete self-cleaning surfaces due to discovered super hydrophobic property, that makes it possible to maintain aesthetic appearance of built objects unchangeable for a long time.

The first scaled application of photocatalytic self-cleaning materials dates back 1996 when the company Italcementi took part in construction of Dives in Misericordia Church in Rome. According to the design, this complex structure would be constructed in the form of three gigantic sails assembled from precast reinforced concrete. For that purpose, a concrete with unique properties was required. Such concrete not only should have high strength and durability but also should keep white color due to self-cleaning properties of the surface for a long time.

Photocatalytic cements were also used in other prestigious European architectural projects, first of all, in France – Cité de la Musique in Chamberi (2003), Hotel de Police in Bordeux, as well as in Saint John Court in Monte Carlo (Monaco), schools in Mortara, Italy (1999), and multi-storey dwelling buildings in Ostend, Belgium. Moreover, compositions of cement paints and plasters with photocatalysts were formulated. These paints and plasters are widely used in Italy in construction of residential buildings in megapolises and in city environment to increase eco-friendly properties of tunnels, underground parkings, petrol stations, etc.

Building materials with TiO_2 are interesting not only due to their self-cleaning properties. The studies show, such materials possess promising opportunities in monitoring of city pollution. For example, photocatalytic system "TiO_2/cement" can destroy NO_x, SO_x, NH_3, CO, volatile organic hydrocarbons, such as benzene or toluene, organic chlorides, aldehydes, and condensed aroma compounds [27].

Doping of TiO_2 mesoporous film with small amount of nanosilver can strengthen its antibacterial effect, even without ultra-violet bombarding radiation.

Both hydrophilic and hydrophobic coatings can be used, first of all, for flat surfaces and basic construction materials, such as concrete and reinforced concrete, stone and wood.

In recent times, coatings with phase change (PCMs), used as hidden heat accumulating systems are becoming more common [28]. In general, they are applied in internal and external surfaces, for example, walls, windows, floors [29–31], to control temperature within specified range.

Nanochromic materials, for example, tungsten trioxide (WO_3) [32], nonstoichiometric nickel oxide (NiO_x), titanium dioxide (TiO_2) and vanadium dioxide (VO_2) [33, 34] can be applied in the form of thick film layers on the window glasses as energy-efficient coatings [35]. Electro chromic windows are the most promising solution to decrease cold stress, heat stress and to save consumption of lighting power in buildings in which they are capable to maintain transmission factor up to 68% of all solar spectrum.

Nanoporous films of titanium dioxide (TiO_2) on thin film of tin oxide (SnO_2) has been successfully implemented in photovoltaic (PV) systems to obtain more power [36]. Moreover, [37] describes a method of antireflection with the use of nanosize dot matrix as one of the most efficient method to achieve high efficiency in such systems.

High-strength, high-elastic and impact-resistant coatings make up a special group resistant to chemical impacts and at the same time effective to protect structures from corrosion.

A key concept of nanocoating performance mechanisms is its ability to self-healing through "self-assembly" process [38]. Self-assembly refers to the phenomenon in which the components of a system spontaneously assemble as a result of interaction, forming a larger functional unit. Such spontaneous organization can be caused by direct specific interactions and/or implemented indirectly through its environment [39].

A technology to obtain nanocomposite materials containing of interpenetrating polymer networks (IPN) on the basis of polyurethane, epoxy resins and acrylates modified in liquid phase with nanoparticles SiO_2, TiO_2 or other metal oxides is of great interest [40]. The basic element of this technology is branched (dendritic) aminosilanes which serve as a curing agent for many oligomers. They allow introducing of siloxane fragments into structure of epoxyamine composition; an additional hydrolysis of aminosilane oligomer makes it possible to obtain secondary nanostructured network polymer which significantly improves performance characteristics of compound. Such nanostructured polymer networks create unique capability to control micro- and nanostructured characteristics of new composite materials. Two-component compound combines high mechanical characteristics of polyurethane with a chemical resistance of epoxy binder. The developed branched dendroamine hardeners are a new direction in the chemical technology of cyclocarbonates, epoxy and acrylic resins [41]. Polymer nanocomposites of a new class are environmentally friendly materials that do not contain harmful or volatile components.

In [42], the properties of new composite materials and nanoheterogenic compounds based on the use of epoxy resins, liquid rubber, amine hardeners, and fluorine-containing surfactants were studied and developed. The resulting nanostructured epoxy rubber coatings for concrete and reinforced concrete structures dramatically reduce their deformability under short-term and long-term load action. Protective epoxy rubber coatings provide an increase in the tensile strength of concrete during bending by two to three times and, consequently, increase its crack resistance. They have good chemical resistance, high mechanical characteristics and heat resistance.

There are many market players at the market of paints and coatings. Two of them vis Akzo Nobel and PPG – have almost a quarter of the market. One should also note other large manufacturers Sherwin Williams, Dupont and BASF (from 7 to 4%). Almost all major manufacturers of paints and coatings develop nanoproducts, buying nanocomponents in different places and do not distribute them. The exception is Sherwin-Williams because this company possesses DIY store network. Among the numerous specific products, it is possible to distinguish the facade paint with dirt-repellent properties Herbol Symbiotec produced by Akzo Nobel; the product system based on Nanoguard technology (BEHR); the surface protection system with permanent graffiti protection effect based on nanostructured polyurethane-acrylate composites (MC Baishemie); a wide range of coatings, paints with high adhesion to metal, tiles, concrete, glass and unique energy-saving characteristics, dirt-repellent, fire and moisture protection by Nansulate (Nanotechnic) technology [43]. New trends that have a direct impact on the dynamics of the nanoindustry include nanostructured coating for the prevention of biofilm infections and the development of nanocoats for waterproof mobile devices.

Other participants of the market are the following fast growing companies: CTC Nanotechnology, Theta Chemicals, Advenira Enterprises, Inframat, Nanogate, AdMat Innovations, Nanophase Technologies, Tesla NanoCoatings [8].

Speaking of the Russian market, its leader in the segment of coatings and paints – Finnish Tikkurila – does not have a leading global position in nanotechnology products. The only world leader with significant positions in Russia is Akzo Nobel.

Nanocolouring can be performed with maximum accuracy by means of the process which comprises atomic building blocks, where atoms are precipitated in controlled mode to obtain a layer which evenly corresponds to each surface features.

Due to wider introduction of nanotechnological building materials into construction industry, as well as commoditization of nanocomponents production, in general, the segment of building materials and, in particularly, segment of coatings, will grow faster compared to other segments.

Generally speaking, the tightening of environmental regulations is the main driver of the popularization of new nanotechnological building materials. The increasing attention of the world community to the problem of sustainable development [44] determines the introduction of new regulatory requirements in the construction industry. At the same time, the main focus is on reducing CO_2 emissions, energy efficiency, and reducing air pollution. A significant role in commercialization is also played by economic factors – an increase in the service life of buildings and structures, the use of fewer building materials, easier maintenance, and shorter construction times. All this, in one degree or another, is ensured by the use of effective nano-coating.

Despite high initial investments into production, the necessity to follow principles of sustainable development [45] can cause dramatical increase of new materials use with respect to considerable decrease of consumption on the basis of entire building life cycle analysis. To preserve environment is the important driver for spreading of innovative materials.

Growth of demand for innovative products in recent years can be explained by changes in life style of people, tendencies towards more comfortability and functionality of residential buildings. Some groups of citizens of Europe and North America require increased sustainability of buildings and are ready to pay high cost for this.

Implementation of tighten environmental codes and energy efficiency standards can really support demand for nanotechnological building materials.

Disconcertingly, Russia still lacks this market, each part of it. First of all, this is due to low demand for nanoproducts by the state as well as by individual consumers. Builders, in general, are not aware about innovative materials and, as a rule, do not look for them on the market, and the manufacturers do not have enough special production capacities in the RF. As a result, despite existing drivers which are opportunities for market development, some negative factors block them.

To our opinion, development of nanotechnological building materials market will be promoted by accomplishing the National programs "Providing Russian Citizens with Affordable and Comfortable Housing and Communal Services", "Environmental Protection" and "Development of Transport System" as well as by setting tasks to increase energy efficiency of economy and commercialization of innovative activities.

Indeed, the government's large-scale plans to commission new housing and road infrastructure, ambitious projects to develop the Arctic and ensure national security should lead to the growth of the industry as a whole, as well as to an increase in demand for more efficient, innovative construction materials. Today, Russia is significantly behind the world's leading countries in terms of housing stock per capita: 2 times compared to the EU and 4 times compared to the United States. From this point of view, the use of new technologies to increase the full life cycle and improve the quality of life should allow us to significantly approach the announced targets.

At the same time, the growing use of nanomaterials raises certain concerns about their safety for human health and the environment. Currently, there are a number of serious uncertainties and knowledge gaps regarding the behavior, chemical and biological interactions, and toxicological properties of nanomaterials [46–49]. Unfortunately, it is unlikely that all of them will be resolved in the near future, since their elimination will require a large amount of complex experimental work and the development of new basic knowledge. It is of great importance to take into account the whole life cycle of nanoproducts to provide systematic detection of any impacts of them [50–51].

CONCLUSION

Today, the studies aimed to improve properties, functionality and application areas of nanocoatings are still being conducted all over the world. These researches are still in the phase of continuous evolution, if not revolution, although even today, through the use of nanocoats of various types and mechanisms of action, a significant modification of the properties of a surface or substance can be achieved in accordance with user-defined parameters. It should be expected that the most significant functionality of nanotechnology products in the near future in the segment of paints and coatings will be to increase their durability

Foundation and intensification of activities of Russian institutes of development that promote innovative nanoproducts, support the organization of their production and use in various industries, including construction, will definitely favor emerging of new building materials which facilitate achieving national targets. Up-to-date progress in the area of nanotechnologies allows us to hope that many tasks, which seem fantastic today, will be successfully solved in the near decade.

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