ISSN 1070-3632, Russian Journal of General Chemistry, 2021, Vol. 91, No. 3, pp. 540–545. © Pleiades Publishing, Ltd., 2021.
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Waterborne Polyurethane Paints and Varnishes for Metal Surfaces: Patent Review

D. M. Nikalin[a],*, A. S. Serdtselyubova[a], Yu. I. Merkulova[a], and A. A. Kozlova[a]

[a] *All-Russian Research Institute of Aviation Materials, Moscow, 105005 Russia*
**e-mail: lab15@viam.ru*

Received January 1, 2019; revised January 10, 2019; accepted January 10, 2019

Abstract—Patent literature of the past 15 years dealing with waterborne coatings used for painting metal surfaces was reviewed. Based on the physicomechanical testing results reported in the patents surveyed, a comparative analysis of the physicomechanical characteristics of the waterborne coating materials proposed was carried out, current trends in their development were identified, and a conclusion concerning the most promising development directions in this area was made. Selected for survey were patents relating to metal coatings with good resistance to corrosion and aggressive external factors.

Keywords: waterborne coatings, polyurethanes, aqueous dispersions, organofluorine polymers, anticorrosion pigments

DOI: 10.1134/S1070363221030233

The ever-toughening requirements for aviation materials, including paints and varnishes, have actualized the service life extension for the paint coatings as one of the strategic objectives in this sphere [1–3].

Waterborne paints and varnishes are compositions having water as the major (and sometimes the only) solvent component. Water, a liquid base for paints and varnishes, has its distinguishing features making water-soluble coatings unique in their own way. It appears that the main feature of water is that most polymers are either absolutely insoluble or very poorly soluble therein (it should be noted at the outset that fully water-soluble organic polymers forming transparent aqueous solutions fall beyond the scope of this review). Producing good durable water-based coatings requires preparing stable aqueous dispersions of polymer binders and inorganic fillers, which generally presents a more difficult task compared to the case of solvent-based compositions.

Progressively more stringent standards have been recently established for paints and varnishes, specifically concerning the reduction of emissions of harmful volatile organic compounds (VOCs) in production of both paints and varnishes and coatings thereof. Against this background, waterborne paint compositions are gaining increasing importance and widening application. These systems have undeniable advantages of noncombustibility and nontoxicity, which allow them to ideally occupy the niche of products fulfilling the principles of green chemistry. In fact, traditional solvent-based paint systems of various designations are being gradually replaced now by safer and more environmentally friendly water-based coating.

This is particularly true of paintwork materials intended for building applications, where only waterborne versions are now permitted for some enamel types. It should also be noted that environmental requirements for reducing harmful emissions generated during the production process were extended as to cover mass production sector such as automotive industry. Accordingly, multilayer painting systems for car parts and assemblies are now being actively studied and implemented at large production facilities. These systems comprise either exclusively waterborne paints (wet-on-wet, 3C1B technologies for thermally cured materials, etc.) or those whose painting operation generates minimal emission of volatile compounds (low VOC refers to <100 g VOC per liter of finished paint or enamel coating).

Polyurethane (PU) coatings represent a widespread coating type which falls into categories of two- (2K) and one-component (1K) polyurethanes. Film formation in the case of a two-component coating requires a chemical reaction to occur between the polyol (or amine) component and the isocyanate type curing agent. 2K polyurethane coatings have an excellent film-forming temperature, high adhesion, good wear resistance, high hardness, and good chemical and weather resistance. Two-component waterborne polyurethane coatings combine high performance of 2K solventborne PU coatings with low VOC content. The problem of stabilization of very labile isocyanate groups in the aqueous phase, faced by chemists seeking to obtain urethane polymers in water, was solved by converting reactive tri- and diisocyanate species into partially polymerized biurets and allophanates in an organic solvent.

By contrast to 2K waterborne polyurethane paint compositions, 1K coatings are applied directly onto substrate (dilution with water to working consistency is acceptable), with the film being formed either due to physical drying (escape of water and volatile organic solvents) or due to a chemical curing reaction which can be initiated by raising the temperature [e.g., in the case of blocked isocyanates or for the purpose of accelerating slow reaction of alkoxysilane groups $Si(OAlk)_3$ with hydroxy groups] or by irradiation (UV light or electron bombardment). Physical drying of films typically requires no heating; the film is formed from pre-polymerized resins dispersed in water. The quality of the resultant coating will be strongly dependent on the dispersion of the polymer particles and inorganic fillers, as well as on the stability of particles of these components in the aqueous medium [4].

Survey of the patents relating to waterborne polyurethane paints and varnishes for metal surfaces allowed several general conclusions. Over the past 20 years the greatest inventive activity in the field of interest has been shown by developers from China, Japan, the United States, and the Republic of Korea (in decreasing order), as well as by those from some other countries. It should be noted that selected for this review were patents dedicated to coatings on metals (ferrous and nonferrous). On analyzing these inventions it is becoming apparent that they are dominated by developments closely related to painting of car bodies and parts. To avoid overburdening of this patent review with too biased coverage of the developments proposed, many similar inventions were omitted from survey, while they are presented fairly widely in the literature, and some of them [5–10] are attributable directly to automotive sector. As regards the development of automotive paints, including waterborne polyurethane compositions, as well as of multilayer systems for wet-on-wet coating which are simultaneously thermally cured in multiple layers, the dominant positions are occupied by global giants of the paints and varnishes industry such as DU PONT, BASF, SIKA, PPG, KCC, ASAHI GLASS, and other.

Regarding the trends in development of waterborne protective coatings, it is essential to note that neat waterborne polyurethanes do not satisfy the actual needs in terms of many their properties such as surface hardness, water resistance, chemical resistance, tensile strength, and impact toughness, which limits their application scope. Therefore, modification of water-soluble polyurethanes has become an inevitable trend. Chemical modification of PU coatings with the aim to improve their durability implies increasing the water resistance of the polymer molecule via introducing hydrophilic functional groups (carboxy, ammonium, or nonionic hydrophilic groups such as glycide, hydrazine, etc.) and via modifying urethane moieties using other types of binders (acrylic, alkyd, epoxy, organosilicon, phosphate ester, and others). This yields additional linkages between the polymers, thereby improving their strength and stability.

It is a common knowledge that fluorinated moieties, when introduced into the polymer structure, can improve hydrophobicity, water resistance, corrosion resistance, and other properties of coatings [11]. However, use of fluorinated products in waterborne painting compositions requires dealing with the problem of dispersibility of these often highly hydrophobic molecules in water. The quality of the final coating strongly depends on the size of the particles to be dispersed (fluoropolymers and inorganic fillers, pigments) and on their stabilization in the aqueous phase. Methods of polyurethane modification with organofluorine compounds are well-established, but there exist some special aspects. Aqueous dispersions of small polymer particles in the case of perfluorinated polyolefins (PTFE, PTFCE, PHFP, and the like) are obtained after polymerization and are blended with urethane or acrylic latexes in water, often in a bead mill. Also, perfluoropolyolefins with modifications for waterborne materials, having acidic (carboxylic and sulfonic) groups incorporated into the perfluorinated carbon chain of the polymer (these materials are much more easily dispersed in water), are already being produced. Alternatively, modification with fluoropolymers can be effected via producing FEVE polymers (fluoroethylene/vinyl ethers) with hydrophilic (carboxy or alcohol) groups in the molecule or via obtaining polymers by polymerization of acrylic and vinyl esters of highly fluorinated alcohols.

Thus, the primary modification routes for waterborne polyurethane binders are blending (mixing) and chemical bonding with fluoropolymers; modern organosilicon [12–15] (epoxy/silane, acrylic/silane ethers, as well as some aminosilane crosslinking reagents) and phosphate ester reagents are also widely used for modification [16–18].

Extensive research is underway now to improve the overall performance of waterborne polyurethane coatings by introducing inorganic nanofillers. Among the latter, graphene has excellent mechanical strength, chemical stability, electrical and thermal conductivity, high specific surface area, and other useful characteristics. By combining graphene with aqueous polyurethane it is possible to improve the water, solvent, and heat resistance of aqueous polyurethanes. At the same time, bonding between the abundant surface hydroxy groups of nanosilica and the isocyanate groups will enable increasing the degree of crosslinking and improving the complex characteristics of waterborne polyurethane coatings. A challenging task with introduction of such nanofillers is to provide their uniform dispersing throughout the aqueous polyurethane systems. Examples of using chemically modified graphene and nanosilica gel for improving the anticorrosion performance of waterborne compositions can be found in [19, 20]. Earlier Chinese patents [21, 22] described the use of silane coupling agents for graphene modification.

Functional coating type such as conductive anticorrosion coating is also presented in several patents surveyed. Along with conducting current and neutralizing the static charge accumulated on the substrate surface, such coatings must exhibit satisfactory anticorrosion performance; they are primarily applied in the petroleum, chemical, construction, and aviation industries, as well as in the military field. A novel type of conducting polymers is represented by polyaniline. It exhibits good electrical conductivity and stability; its further advantages are ease and cheapness of synthesis and excellent anticorrosion properties. Therefore, much attention is being paid now to the production of polyaniline-based conductive anticorrosion coatings. For example, preparation of primer coatings with the use of polyanilines as functional pigments was reported in [20, 23]. Specifically, a single-component anticorrosion coating containing graphene and polyanilines as functional pigments, in which a polyurethane resin is blended with a polytetrafluoroethylene (PTFE)-based nanoscale dispersion, was described in [20]. Also, a double-component waterborne coating based on a nanodispersed mixture of polyaniline and epoxy/acrylic resin additionally crosslinked with urethane groups by isocyanates was proposed [23].

Inventions reported in [18, 24] also relate to waterborne anticorrosive conductive coatings, though to those containing inorganic metallic pigments. The development described in [18] deals with the brilliant silver paint suitable both as a primer and as an individual coating. The paint preparation method proposed consists in dispersing waterborne polyacrylate resin with an aqueous paste of aluminum powder whose surface is modified by nanosilica deposition, so that the aluminum powder surface gets coated with a dense 50–100-nm thick protective film. In [24], adding zinc and aluminum metal powders to a waterborne polyacrylic or polyurethane resin in order to enhance its anticorrosion properties was proposed. The composition is cured by baking at 150–200°C for 10–20 min. The resultant formulation is suitable as a chromate-free primer for steel and aluminum surfaces. To reduce the zinc reactivity and suppress the formation of gaseous hydrogen in an aqueous medium, the zinc powder surface is passivated by treatment with tetraethoxysilane $Si(OEt)_4$. For better film adhesion to the metal surface a phosphate ester modifying additive is introduced into the composition. Both inventions describe coatings possessing remarkable anticorrosion properties.

Special mention should be made of inventions [15, 17, 25–28] concerning one-component UV-curable waterborne coatings irradiated with light at a wavelength of 250–450 nm [29]. In some developed countries of the world UV-curable coatings account for ~10% of the total finishing area, and in Japan this share reaches 50% of the entire area of paints and varnishes (water- and solventborne). UV-curable waterborne systems possess and further develop many advantages of waterborne coatings such as low production costs, low working viscosity of solutions, simple equipment, and nontoxic and noncombustible materials. Owing to benefits they offer, production technologies for waterborne UV-curable resins have been rapidly developed and found ever expanding application in recent years.

Some complexities involved in the production of waterborne UV-curable systems should not be left unmentioned, considering the fact that the corresponding method is underlain by the polymerization reaction proceeding by the radical mechanism, specifically, by polymerization of unsaturated compounds with a C=C bond. Therefore, the starting monomers and oligomers must have a double bond in their structure [(e.g., (meth) acrylates, vinyl esters, styrenes, etc.]. Moreover, such reactions require a water-soluble photoinitiator capable of triggering polymerization over a broad wavelength range. Another challenge consists in that the aqueous system of UV-curable coatings may contain a significant amount of water whose removal will require much energy. Fast drying and curing of coatings at room or at close to room temperatures is an issue of critical importance for development of UV-curable coatings. Notably, all the above-listed inventions involve a brief step of incomplete drying for water removal from the wet freshly applied coating before UV-induced polymerization. This is achievable either through air drying at room temperature or through incorporating into the production process a step of gentle heating (to 40–50°C) with air blowing of the coated material (sometimes, using a heat gun) for removing excess water before polymerization. Thus, creation of UV-curable coatings is not only of high scientific significance but also of great practical importance.

Two inventions relating to corrosion protection of parts of ships and marine equipment [30, 31] are of particular note. Development proposed in [30] describes 1K waterborne anticorrosion baking coating composition on phosphated steel, which withstands more than 2500 h of salt spray corrosion resistance test. Patent [31] concerns 2K waterborne epoxy resin-based marine anticorrosive coatings showing good resistance to various aggressive factors as well.

Patents [32, 33] describing water-based polyurethane paints for protecting windmill generator blades and wind generating sets are worth mentioning as a separate point. Though differing slightly in details, these systems have a common feature of being produced by successively depositing an aqueous epoxy-zinc primer to reinforced fiberglass and of having a waterborne epoxide basic layer and a finishing layer which can be transparent and based on polyfluoroacrylo/urethane latex. Along with passing all the necessary tests for resistance to various aggressive factors (chemical resistance, salt fog, UV aging, etc.), a remarkable no less than 20-year working life of the coating system was declared by both inventors.

Invention concerning 2K polyurethane waterborne composition for effecting minor repairs (elimination of chips, scratches, “craters”, etc.), so-called “conditioner,” is also noteworthy [34]. This is an easy to use composition which does not require temperature operation for curing, equally suitable for application over any substrate type (nonferrous and ferrous metals, old cleaned coating, including dusty areas).

In conclusion, analysis of the patents reviewed allows several conclusions to be made about the development of the waterborne paint and varnish sector in general and of its most promising and demanded areas in particular. It is fair to say that the share of waterborne paints and varnishes among all the most mass-demanded paint materials, namely, those intended for application in the construction and automotive industries, will only increase relative to solventborne coatings, as evidenced by the current dynamics. However, it is also obvious that, today, waterborne paints and varnishes cannot entirely replace solventborne compositions which still surpass them generally in many technical areas, in many respects. The major weak points of waterborne coatings are their far from perfect characteristics such as water resistance, surface hardness, abrasion resistance, and corrosion resistance. All the patents reviewed herein address these problems, though in different ways.

Another indisputable trend observed in the development of the entire sector of paintwork materials, along with reduction of harmful emissions generated during the production process, is reduction of energy costs. Production of thermally cured compositions (especially at temperatures above 100°C) is known to be highly expensive. This places greater focus on coatings that do not require heating for curing (room temperature-cured coatings) or on those produced under gentle heating (to 40–80°C), including both 2K and 1K, in particular, UV-curable, formulations. Thermally cured, in particular waterborne, compositions are likely to retain their role in the future, especially for painting small-sized parts, but definitely will not be used on a massive scale.

Interestingly, the “chemical” part of the patents, discussing the chemical steps of the preparation of monomers and of the polymerization steps, in most cases implies that the production cycle, and the very process of coating preparation according to the inventions of interest, begin with the synthesis of the starting monomers, modifying additives, and the like [35]. Specifically, coatings are obtained using the starting materials

Table 1. Selected physicomechanical characteristics of the coatings proposed in the patents reviewed

Characteristic					References
Curing conditions[a]	Water resistance	Surface hardness	Salt spray test result	Adhesion, points	
1K, UV-curable	No changes in hardness observed after 7 days of exposure to moisture	8H	Less than 5% rust after 240 h of test (with notches)		[25]
1K, UV-curable		4H; 5H		0; 1	[27]
1K, UV-curable			Less than 5% rust after 72 h of test (with notches)	0	[17]
1K, UV-curable	2.7–3.45% water absorption (over 72 h)	6H			[15]
2K, *RT*		3H	1200 h		[23]
2K, *RT*	No externally observable effects after 7 days of exposure to moisture	HB; 2H		0; 1	[36]
1K, *RT*	1.1–1.9% water absorption (over 48 h)	4H; 5H	4500–5000 h	1	[20]
1K, *RT*		H	Less than 5% rust after 240 h of test (with notches)		[40]

[a] *RT* is room temperature; surface hardness is expressed by the pencil hardness grade.

Table 2. Trends in development of waterborne paints and varnishes Trends in development of waterborne paints and varnishes

Development trends identified	Technical solutions realizing the trends identified	References
Reduction of energy costs of thermal curing	1K UV-curable and physically drying coatings	[15, 19, 20, 23, 25, 27]
	2K coatings curable without heating (under gentle heating to 40–80°C)	[28, 36, 37]
Improvement of water resistance	Modification with organofluorine compounds	[5, 12, 38, 39]
	Modification with organosilicon compounds	[12, 39]
Enhancement of surface hardness	Modification with organosilicon compounds	[13, 15]
	Application of chemically modified nanosilica gel	[19, 20, 38]
Improvement of anticorrosion performance	Special organic and inorganic pigments	[18, 20, 23, 24]
	Modification with organofluorine compounds	[12, 20, 39]

synthesized from available reagents, rather than from off-the-shelf components. This applies especially to UV-cured waterborne coatings, where each successful coating is unique in its own way, being prepared with the use of monomers synthesized specially for a target application.

Based on the results from physicomechanical testing of the coatings proposed in the inventions reviewed, a comparative analysis of their physicomechanical characteristics was carried out (Table 1), and the following current trends in development of waterborne paint coatings were identified (Table 2):

– Reduction of energy costs through the use of materials obtained by least energy-intensive procedures, i.e., 1K UV-curable and physically drying coatings or 2K coatings produced without heating (“mix-apply-leave”). They represent, or will represent, the most promising directions in the field of waterborne paints and varnishes; hot-drying waterborne compositions will retain their value for painting small parts, which application does not belong to the most popular sector.

– Improvement of water resistance via modifying polyurethanes with organofluorine and organosilicon compounds.

– Enhancement of surface hardness, generally by means of additional crosslinking between the polymers and fillers via using some organosilicon compounds and chemically modified silica gel.

– Improvement of anticorrosion performance through the use of special pigments (organic and inorganic), organofluorine polymers.

FUNDING

This study was carried out within implementation of strategic direction no. 17 “Complex corrosion protection, hardening, wear-resistant protective, and heat-protective coatings” (“Strategic directions of development of materials and of their processing technologies for the period till 2030”).

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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