NANOTECHNOLOGY APPLICATION TO AUTOMOTIVE COATING MANUFACTURING

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Abstract

The last decade showed very fast growing of worldwide interest in nanotechnologies and nanomaterials. These trends can also be observed in high performance automotive coating formulations. Coating industry was one of the first branches that applied nanoscience and nanotechnology. Application of nanotechnology in organic coatings consists, mainly, in coating formulation using nanomaterials. Such obtained "nanocomposite coatings" consist of polymer matrix containing nano-scale particles. At this scale, properties of materials can be very different from those at a larger scale. Coating properties can be greatly affected by the size of filler particles; the smaller the filler particles the larger the effect. The effect of nanofillers depends on many factors, among others: chemical nature of nanofillers, their concentration and level of dispersion in the coating, as well as interaction between filler particles and organic matrix.

Protective and decorative automotive coatings are exposed to the action of such factors as: ultraviolet radiation, erosive particles, humidity and heat. The presence of nanofillers allows increasing coatings resistance to these factors. Resistance to erosive wear and scratch are very important features of automotive clearcoats. Pigments which particles are smaller than the wavelength of visible light may be applied in formulations of such coatings to increase their phisico-chemical properties. Application of nanofillers to clearcoats requires complete dispersion of their particles in polymer matrix. Complete dispersion of nanofillers in polymer matrix enables preparation of high performance clearcoats showing high transparency and resistance to erosive wear and scratch. Alumina and silica nanoparticles are very often used in such applications. The paper presents literature review on nanofiller application in automotive coating formulations.

Keywords: *automotive coating, nanotechnology, clearcoat, silica nanoparticles*

1. Introduction

Very fast growing of worldwide interest in nanotechnologies and nanomaterials can be observed last years [1]. Automobile manufacturing is one of the leading world industry sectors in nanoscience applications. In 1989, Toyota launched cars equipped with timing belt covers manufactured from polymer-clay nanocomposite NCH (Nylon 6-Clay Hybrid) [2]. Nanotechnology is already in mass production for automobile components (powertrain and chassis components, body panels, exhaust-catalyst substrates, fuel-system components, air condition equipment etc.) [3].

Nanotechnology research is showing great promise in numerous areas, among others in high performance coating formulations [4]. Coating industry was one of the first branches (together with plastic and cosmetic industries) that applied nanoscience and nanotechnology.

There is still a need for the introduction of new and innovative technologies into the automotive market. The development of nanotechnology in automotive coatings formulation results mainly from [3, 5]:

- efforts to reduce VOC emissions (most of industrial VOC emissions come from the car body paint shops in final assembly plants) to comply with more and more stringent regulations;

- possible advantages of multifunctional coatings (e.g. having high scratch resistance and dirt-repellence);
- demand for thin-film technology;
- development of sophisticated pigment systems (e.g. for special optical effects);
- product substitution.

Application of nanotechnology in organic coatings consists, mainly, in coating formulation using nanomaterials. Such obtained “nanocomposite coatings” consist of polymer matrix containing nano-scale constituents. According to the common definition, nanoparticles have at least one characteristic size between 1 and 100 nm (a human hair for instance is about 80 000 nanometres in diameter). At this scale, properties of materials can be very different from those at a larger scale. Nanofillers for coating application may be inorganic or organic materials, such as: colloidal silica, fumed silica, silicates, titanium, alumina, zinc oxide, carbon black, organo-clay, acrylics, uretanes and other.

Coating properties can be greatly affected by the size of filler particles; the smaller the filler particles the larger the effect. Many studies dedicated to nanotechnology in coatings have been published; e.g. [6-8]. The effect of nanofillers depends on many factors, among others: chemical nature of nanofillers, their concentration and level of dispersion in the coating, as well as interaction between filler particles and organic matrix.

The most desirable properties of organic coatings, according to the IRL report [5], are: scratch resistance, self-cleaning, high durability, water repellency, UV and microbial resistance (table 1).

Tab. 1. Paint manufacturers’ objectives in nanocoating applications (in 2005) according to the IRL report [5]

Coating property	Share in the market [%]
Scratch resistance	18
Self-cleaning	12
Improved durability	7
Water repellency	6
UV resistance/non-yellowing	6
Antimicrobial properties	6
Others	45

2. Application of nanotechnology to automotive coating formulations

There is continued customer demand for better quality and more durable automotive coatings. For customers, the quality of automotive coatings is determined predominantly by their appearance. The most desirable is new car appearance with high gloss.

Automotive coatings are exposed not only to conventional weathering (the sun’s radiation, oxygen and humidity) but also to the action of other environmental factors (e.g. erosive particles, acid rains, salts). Automatic car wash operations are also significant contributors to scratch and mar damage. Therefore, resistance to erosive wear and scratch are very important features in the case of automotive topcoats [9, 10]. The presence of nanofillers allows increasing this resistance. Scratch resistance is also desired to prevent adverse results such as dirt pick up.

Mineral nanofillers such as alumina or silica show high hardness numerals (9 and 7, respectively, due to the Mohs’s scale). Pigments which particles are smaller than the wavelength of visible light may be applied in formulations of clearcoats to increase their phisico-chemical properties. The great advantage of inorganic-organic clearcoats is their high hardness combined with excellent transparency and additional functions (e.g. UV resistance, defined wettability, barrier or antistatic properties) what allows to extend coating, and in many cases – product life, reducing in this way waste and increasing sustainable use of resources.

Scratch resistance is the most commercialized property of nanoparticles. Among nanoparticles, silica (the first nanoparticle produced) and alumina are the most commonly used nanoparticles to achieve scratch resistance in all types of coating formulations. Often alumina particles are preferred in such applications for its higher hardness (Figs 1-3).

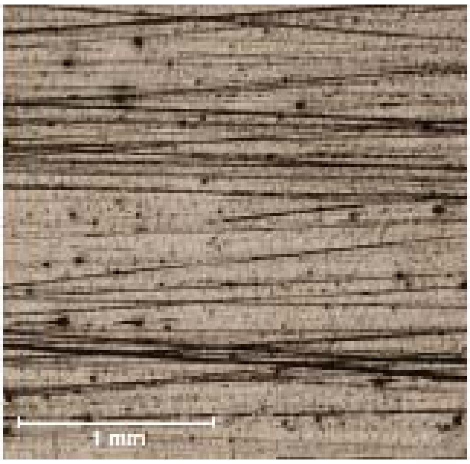


Fig. 1. Appearance of the clearcoat surface without nanoparticles after scratch test [11]

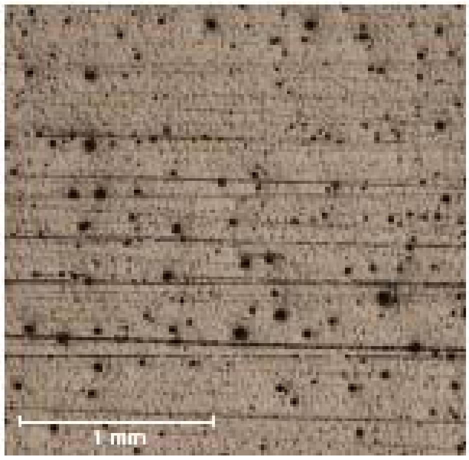


Fig. 2. Appearance of the clearcoat surface with 2% 40 nm alumina after scratch test [11]

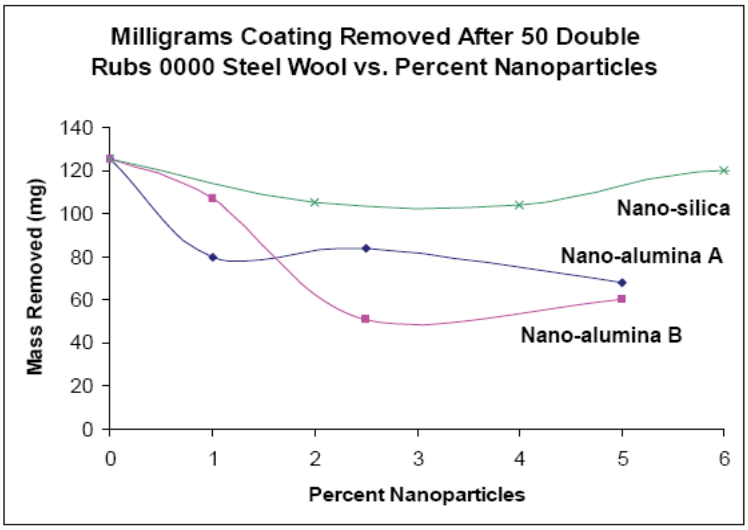


Fig. 3. Scratch resistance of 2K polyurethane automotive refinish coatings containing silica or alumina nanoparticles [12]

However, silica nanoparticles influence less transparency in clearcoat formulations. Such advantage results from a small difference between refractive indices of silica and most coating polymers (1.55 and ca. 1.5 respectively). Refractive index of alumina is 1.72. Statement, that alumina is better for scratch resistance improvement, and silica for highly transparent coatings applications, is true in the case of unmodified nanoparticles.

A key aspect of nanofillers is their surface activity. They have high surface area (Fig. 4) what produces lots of interfaces between particles and binder. Nanofillers show strong tendency to agglomerate and it is difficult to obtain their uniform dispersion throughout the binder. However, application of nanofillers to transparent coatings requires complete dispersion of their particles in polymer matrix because the presence of aggregates deteriorates coating transparency. The best properties show coatings containing well-dispersed (or single-dispersed) inorganic constituents. Poor dispersibility of nanofillers is one of the major hurdles in the rapid development of nanocoatings sector. This is the main reason why nanocoatings are not yet very much commercially significant.

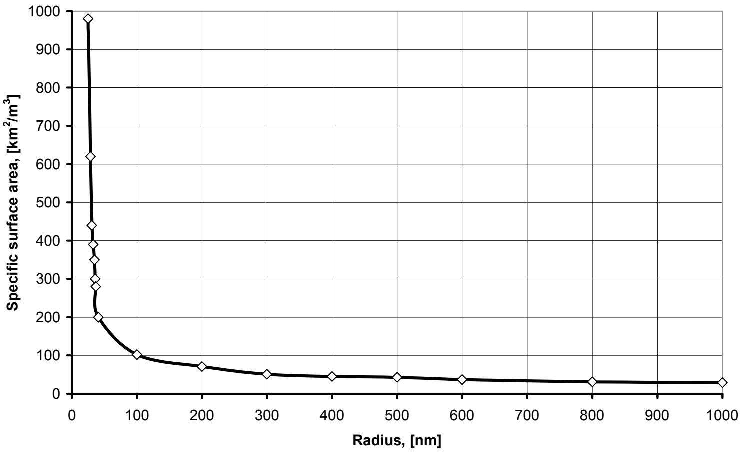
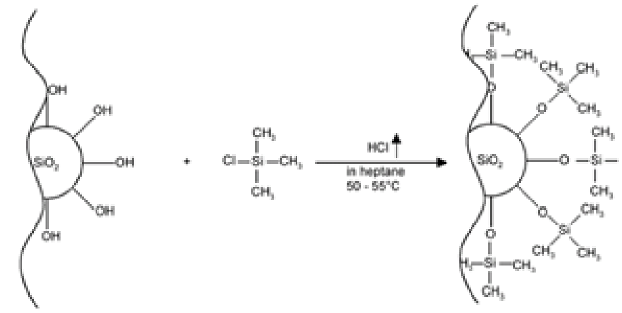


Fig. 4. Variation of specific surface area with particle size [8]

To prevent agglomeration in order to fully utilize the potential of nanofillers, various methods are applied in the formulation process; from simple mixing, through ultrasonic radiation, emulsion polymerization and in situ polymerization in the presence of nanofillers, up to chemical modification of the nanofiller surface. Chemical modification (usually with organosilanes - Fig. 5) of most inorganic nanoparticles (e.g. SiO_2, Al_2O_3, AlOOH or ZnO_2) surfaces changes their hydrophilic character and renders them hydrophobic promoting in this way physical bonding with polymer as well as making easier their distribution in the matrix. Another way of chemical treatment of nanofillers is functionalization of their particles by attaching certain molecules or functional groups to their surface (Fig. 6). The attached groups react with coating polymer what allows better cross-linking of the matrix.



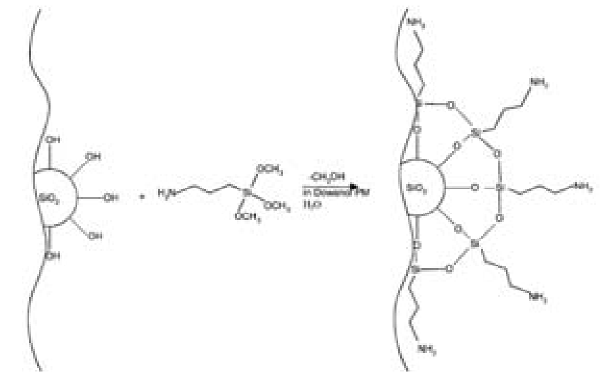


Fig. 5. Schematic of modification of silica nanoparticles with trimethylchlorosilane [13]

Fig. 6. Schematic of modification of silica nano- particles with 3-aminopropyltrimethoxysilane [13]

Chemical modification of silica surface renders it high efficient in scratch resistance improvement as showed by unmodified alumina (Figs 7 and 8). So, in automotive coating applications, where both extreme transparency and excellent scratch resistance are required, using modified silica nanoparticles is very good solution.

The first automotive clearcoat to use nanoparticle technology was CeramiClear coating developed by the world's largest producer of transportation coatings – PPG Industries [14]. This is a clearcoat composition, containing nanoparticles of colourless, substantially spherical complex silicon oxides, designed to guarantee long-term gloss and durability. The particles do not contain hydroxyl groups and did not agglomerate during preparation of the paint. According to US Patent Applications 2003/0162876 and 2003/0162015, the presence of these nanoparticles gives to the coatings excellent chip and scratch resistance, outstanding appearance, superior sandability and resistance to water spotting and acid etch. The coating is compatible with existing waterborne basecoat, primer and electrocoat layers and can be applied using conventional equipment. CeramiClear does not increase emission levels.

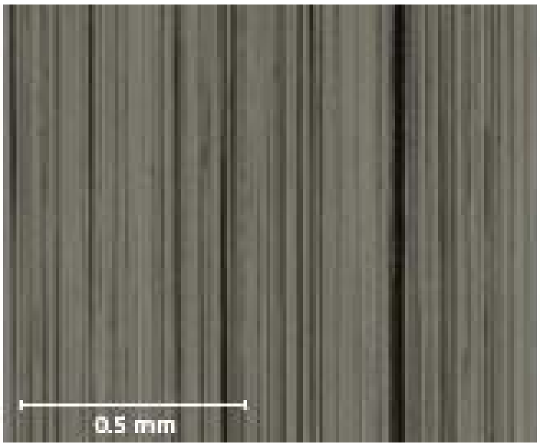


Fig. 7. Surface appearance of an automotive refinish clearcoat (2-pack acrylic/isocyanate) without nanoparticles, after dry abrasion test [11]

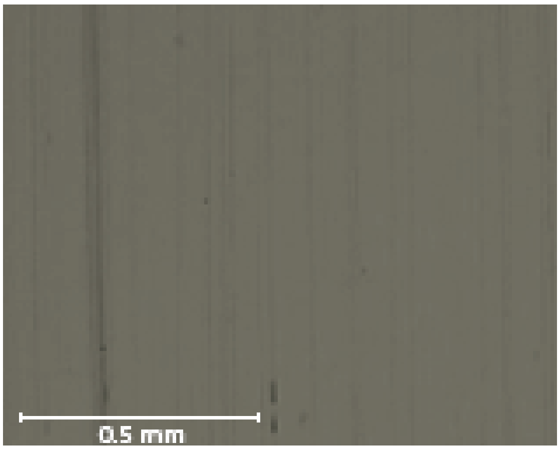


Fig. 8. Surface appearance of an automotive refinish clearcoat (2-pack acrylic/isocyanate) containing 2.2% surface-treated silica nanoparticles, after dry abrasion test [11]

CeramiClear is claimed to be the first clearcoat applied by OEM. Daimler-Chrysler used it for the first time at the end of 2003 on Mercedes-Benz passenger cars. Tests performed according to DIN standards in a laboratory car wash demonstrated high coating scratch resistance. After 10 wash cycles with a mixture of water and fine particulate matter – reproducing the wear-and-tear effect of some 50 to 100 regular car washes – the painted sheet metal showed around 40 percent higher gloss compared with the samples of conventional clearcoat [15]. The Mercedes-Benz C-, E-, S-, CL-, CLK-, SL- and SLK-Classes are the first vehicles worldwide having nanoparticle clearcoat as a standard feature. At the Automechanika Trade Show in 2004 they were named "Most Washable Cars of 2004". Ceramiclear can still be damaged by keys but most day-to-day use degradation is eliminated.

Due to environmental regulations there is a great effort of automotive industry and coating manufacturers to replace current VOC containing coating materials with more environmental friendly alternatives. The solutions may be: powder coatings, UV-cured coatings, high solid coatings and waterborne coatings. To improve phisico-chemical properties of such coatings, intensive research is carried on, also in the direction of nanofiller applications, mainly to waterborne coating formulations e.g. [16, 17].

3. Conclusions

Modern, high performance automotive coatings are challenged to meet a large number of properties. Intensive R&D work is carried on to develop new materials and technologies to produce such coatings. Among a variety of new approaches being researched nanotechnology seems to be very attractive solution.

Resistance to erosive wear and scratch as well as high gloss are the most desirable features of automotive clearcoats. In contrast to conventional clearcoats, “nanocomposite clearcoats” contain mineral particles that do not influence transparency and increase coating mechanical properties. The most widely used in such applications are alumina and silica nanoparticles due to their high hardness. Surface modification is essential for avoiding agglomeration and segregation of nanofiller particles in the matrix. The first automotive clearcoat to use nanoparticle technology was applied by Daimler-Chrysler on Mercedes-Benz in 2003.

A very important drawback of common application of nanocoatings is their high cost. Depending on the kind of nanomaterial and its level, coatings containing nanofillers can be from 15% up to 200% more expensive than “traditional” ones.

Development in the field of nanoparticle applications must also be oriented towards better understanding the potential environmental and human-health impact of such particles.

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