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Review Paper

Comprehensive Review of Nanoparticles Dispersion Technology for Automotive Surfaces

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Abstract

Many innovations arose from the continual and thorough monitoring of overlooked characteristics of materials found in the environment. Automotive paints are always constantly exposed to a broad range of ambient temperature conditions, which reduces their longevity and encourages algae development. Through the effective incorporation of nanotechnology with this lotus effect, it has become possible to provide self-cleaning ability along with air purification and antibacterial performance to automotive surfaces like paint and coating. The addition of nanoparticles such as Titanium dioxide (TiO_2) and Silicon dioxide (SiO_2) helps to improve functionalities like water or stain resistance, ultra-violet protection, and scratch resistance. When the nanoparticles were added into paint, they degraded the polluting compounds on the material's surface by photo catalysis. Multiple photocatalytic functions and self-cleaning properties were observed in nanoparticles added to polyester acrylic paint. Therefore, this paper discussed the history of automotive painting, nanopaint technology, previous research on the method preparation, development, and current progress, the environmental health aspects of nanotechnology, as well as the performance in terms of automotive surfaces. The study discovered the requirements for nanoparticle dispersion and coating uniformity and appearance on automotive surfaces, which will serve as a benchmark for dispersion and coating methods for automotive surfaces.

Keywords: Nanopaint; Titanium oxide; Silicon oxide; Automotive paint; Nanotechnology

1. Introduction

Nanotechnology primarily deals with particles of a size in the nanometer range, which helps to improve their material capabilities. Nanoparticles are not just simple molecules themselves, but are composed of three layers [1]. The first layer is the surface layer, which is functionalized with various small molecules, metal ions, surfactants, and polymers; the second layer is the shell layer, which is chemically distinct from the core in every way; and the third layer is the core, which refers to the nanoparticles themselves [2]. Besides, nanoparticles can be classified into carbon-based nanoparticles, metal nanoparticles, ceramic nanoparticles, semiconductor nanoparticles, polymeric nanoparticles, and liquid-based nanoparticles according to their morphology, size, and chemical properties [1]. The methods for the synthesis of nanoparticles can be divided into two main groups, which are the bottom-up approach and the top-down approach [3]. The synthesis process of nanomaterials and nanostructures is an essential part of nanoscience and nanotechnology. The nanomaterial is a material with any internal or external structures on the nanoscale dimension. The possibility of new physical properties and applications of nanomaterials exists only when nanostructured materials are made available with the desired size, shape, morphology, crystal structure, and chemical composition [4], [5]. Nanostructures are structures that range between 1 nm (molecular scale) and 100 nm in at least one dimension. Most are synthetic and can be engineered to wide range of physical properties. Nano surfaces, cylindrical nanotubes, and nanospheres are common nanostructures. Nanoparticles can be used in variety of applications due to its relatively smaller size and the ratio of surface area to volume becomes much higher [6]. These features of nanomaterials have greatly influenced scientists and engineers, which paved the way for the usage of nanoparticles in various industries such as automotive industry, biomedical industry, oil and gas industry, and aircraft industry.

The automotive industry has been experiencing a continuous change in technology, especially in automotive painting and coatings. In fact, over the last decades, this industry has undergone greater than a 95% changeover in the composition of the paint and coatings applied to their products [7]. Various nanomaterials like Titanium Oxide (TiO_2), Carbon Nanotube (CNT), Silicon Dioxide (SiO_2), and others are added to paint so that its properties and strength are enhanced further [8]. Dirt absorption by paint coating is one of the problems faced in the automotive industry, as it raises maintenance costs and reduces surface aesthetics. By combining TiO_2 nanoparticles with paint, bio mimicking and nanotechnology are brought together to solve this problem. It can act as a hydrophilic material and by the process of photocatalysis in TiO_2 nanoparticles. According to (IRL) [9], the most desirable properties of organic coatings that are considered by paint manufacturers are scratch resistance, self-cleaning ability, high durability, water repellence, UV and microbial resistance. For customers, the quality of automotive coatings is defined by their appearance, and the most preferable is a new car appearance with high gloss. This paper discusses nanoparticle dispersion and its application in coatings for the automotive industry, with the goal of gaining a better understanding of nanoparticle dispersion in coatings and future research in the field of nanocoating, particularly in the area of automotive painting.

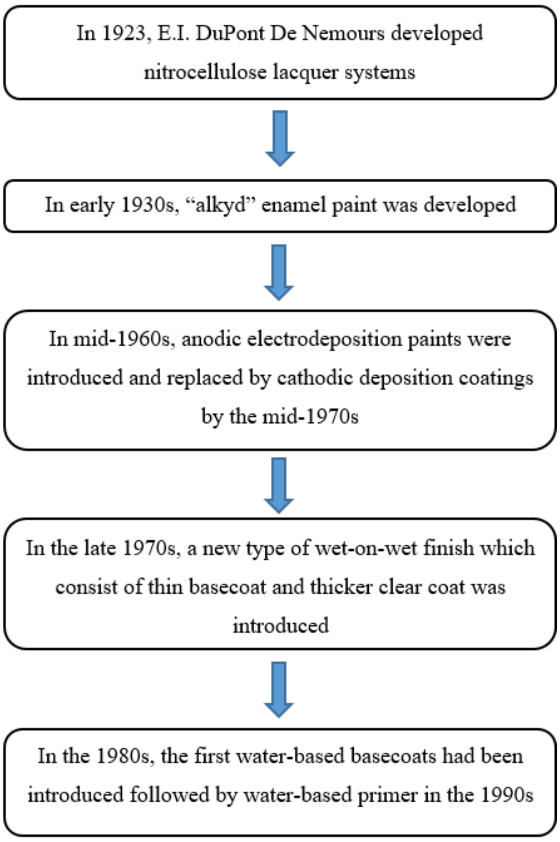
2. Historical Development of Automotive Paint

The history of automotive paint started at the age of about 1910, which is roughly 6 years after Henry Ford founded the Ford Motor Company. The coatings in question belonged to the varnish category. The painting of a car takes a long time to complete. A vehicle's paint job can take up to 40 days to complete. The painting procedure is similar to that of antique wood coats. The method was based on the same air-dry varnish system used for horse-drawn carriages with wooden furnishings. They were brushed onto the car's surface and then allowed to dry. After that, the coating was sanded smooth and refinished in the same way. The surface was polished clean once it had reached the proper thickness. The system was used until the mid-1920's, but the drawback of the system is that the only color that can be used for painting the automobile is black.

The summary of painting technology began in 1923, with the development of a nitrocellulose lacquer system, which offers many colour options and easier application, as shown in **Figure 1**. To achieve the desired properties, the lacquer systems required a spray gun that was invented by a dentist, and to achieve the desired properties, the vehicle required spray application of three to four coats of paint. The spray gun application is much faster than the brush method. It minimized sanding between coatings and applied the product evenly. But the lacquer also has a drawback, as it has poor resistance to a certain chemical solvent like gasoline. Continued exposure to gasoline spills could stain and damage the lacquer finishes. Then a major development in paint technology, using "stoving enamels" based on alkyd resins, was developed. The product was selected because of its higher gloss yield than varnish. Enamels formed a very durable film through chemical reaction after they were sprayed on the vehicle and baked in an oven. It is resistant to chemicals and solvents and can be applied much more quickly. It added many different choices of color to the consumer's palette. However, the paint oxidized in sunlight quickly.

The color begins to fade and dull when exposed to sunlight for several weeks.

The lacquer system was used on most vehicles until about 1957, when solution acrylic lacquers were introduced to improve the durability of enamel finishes. It offered much improved durability and a wider range of bright and pleasing colors, especially metallic. Later in the decade, manufacturers were looking for harder paint and more resilient elements that could dry faster. They found a way to achieve that by including a cross linking free radical additive in the formula. A catalyst is added to the paint. The product is sprayed on, and the process of curing begins. This process has become more popular for larger vehicles like airplanes. It is still in use today in both acrylic enamels and newer polyurethane products. However, the price was too costly for automotive applications.



In 1923, E.I. DuPont De Nemours developed nitrocellulose lacquer systems

In early 1930s, “alkyd” enamel paint was developed

In mid-1960s, anodic electrodeposition paints were introduced and replaced by cathodic deposition coatings by the mid-1970s

In the late 1970s, a new type of wet-on-wet finish which consist of thin basecoat and thicker clear coat was introduced

In the 1980s, the first water-based basecoats had been introduced followed by water-based primer in the 1990s

Figure 1. History of Automotive Coating System [10]

3. Automotive Paint

Generally, automotive paint is developed to produce advanced functionality, protection, and innovative decoration purposes [11]. Over the last decades, the automotive industry has been experiencing a continuous change in technology and has undergone greater than a 95% changeover in the paint composition and coatings applied to their products according to Weiss [12]. The changeover started at the beginning of the twentieth century and has been made recent by the general process of manufacturing technology that is encompassed by the continuation of the progress of materials and process development. Advancement in technology is one of the reasons for the rapid progress in process development. Establishment of mass production will require faster curing paints, better film performance in terms of durability of colors and corrosion, fully automated processes for better reliability, and improved environmental compatibility. These are the important driving forces that characterize the important milestones in this field, as shown in **Table 1**.

The automotive paint industry has developed enormously starting from the 1940s until the year 2000. Previously, in the 1920s, the painting process still took weeks to complete. However, after enamels have been introduced, the coating process, including all the important preparation such as sanding, cleaning, drying, repairing, and so on, can be finished in a day. Besides, the number of coatings has also been reduced to four or five layers during this time, as seen in **Figure 2** [13]**.** Each layer has a different type of function, which will be explained in detail in the next section. Later, in the 1950s, the primer process was replaced by the dip coating process (a more automated process) but was then changed to electro-deposition paint and water-borne paint due to hazardous solvent emissions. The process is much better in terms of material transfer as well as throwing power, which is necessary for impro-

Table 1. Driving forces that characterize the important milestones in many aspects [14]

Year	Topics/ Driving forces	Aspects
1920	Manual painting	Time-consuming process: weeks
1940	Mass production	Enamels/ oven/ time: day
1970	Improved film performance	CED/ 2-layer topcoat/ new material
1980	Environmental compliance	Waterborne coatings/ powders/ transfer efficiency
2000	Automated processes	First time capability/ time: hours

ved corrosion protection of the inner parts of the car body [14].

In the 1970s, the raw materials used were changed from melanized polybutadiene resins to modified reactive polyurethane-based and epoxy resin backbone crosslinkers, which resulted in anodic deposition to a cathodic deposition coating method. This method has been shown to produce better results, increased process reliability, and increasedspraying process. Alongside, two-layer topcoats, which consist of a thin base coat, gradually replaced the thicker clear coat and single layer top coats were applied wet-on-wet. Today, most of the clear coats in Europe are based on two-component (2K-) formulations, which consist of melamine crosslinkers and acrylic resins. An interesting one-component technology based on carbamate functionality was introduced in the United States [14]. The developments contributed to better film performance, resulting in longer top-coat durability and improved corrosion protection – i.e., gloss retention for up to 5-7 years as observed in Florida [14].

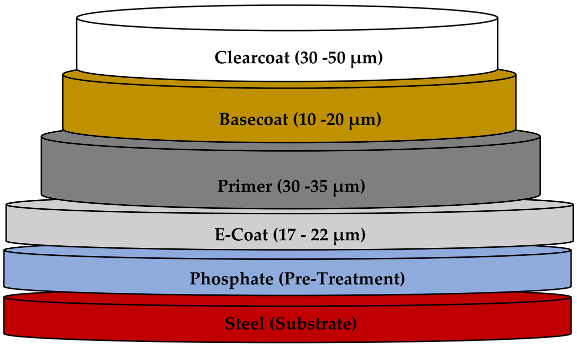


Figure 2. Paint Film demographic [13]

Today, automobile painting processes have been standardized better than ever due to the benefits of inorganic pre-treatments, liquid or powder primer surfaces, cathodic electrodeposition, liquid base coats, and one or two-component solvent-borne clear coats. In addition, the development and the rise of nanotechnology for coating has attained a point where limitless opportunities can be found to solve or improve paint performance. In short, in the brief history of automotive body painting, it suggested the new trends in automotive coating processes and gave a snapshot of possible future developments. Similarly, a comprehensive overview of the processes and methods of modern automotive coating will be described in more detail, followed by an examination of the paint components and tools used.

3.1. *Painting Process*

Most of the painting processes were performed with the use of specialized equipment and robots. Manual painting is only used in the vehicle cab interior and some hard-to-access places. The first step of the painting process is transporting the vehicle to the painting place, which is usually called the paint shop. Moreover, protection is applied against corrosion, dust, water, moisture, and mechanical damage. The first stage of the paint shop process is the pretreatment of the metal body. This activity is a multiple-stage process consisting of 11 zones where the body is progressively cleaned before a phosphate coating is applied. The phosphate line has several chemical mixing tanks, heat exchangers, and pumps associated with the process. Chemicals that are used in the process include phosphate and nitrite solutions, activating salt, caustic soda, nitric and sulphuric acids, fluoride, and degreaser. Waste products from this stage of the process are hazardous due to the high concentrations of zinc, phosphate, and nickel, and the low pH of the liquid.

Figure 3 clearly shows the detailed processes of car body paint that are used nowadays in almost every modern manufacturing plant (paint shop), starting from body-in-white (a joint component of the car body using different techniques) to washer until it goes to waxing and back to the assembly line. All the steps involved inside the paint shops are crucial to imparting various properties to it. Aesthetic characteristics, corrosion protection, ease of mass production, cost and environmental requirements, durability and appearance are the crucial factors of performance in automotive painting [10].

3.2. *Layer of Coating and Its Characteristics*

Modern automotive painting processes mainly consist of five layers, which include pre-treatment, electro deposition, a sealer, a primer and finally the topcoats (basecoat and clear coat). Each coating layer is applied to perform certain specific functions, as shown in **Figure 4**, though its activities are affected by other layers in the system. The interfacial phenomenon and the interactions between the different layers play a vital role in the overall performance of the multi-

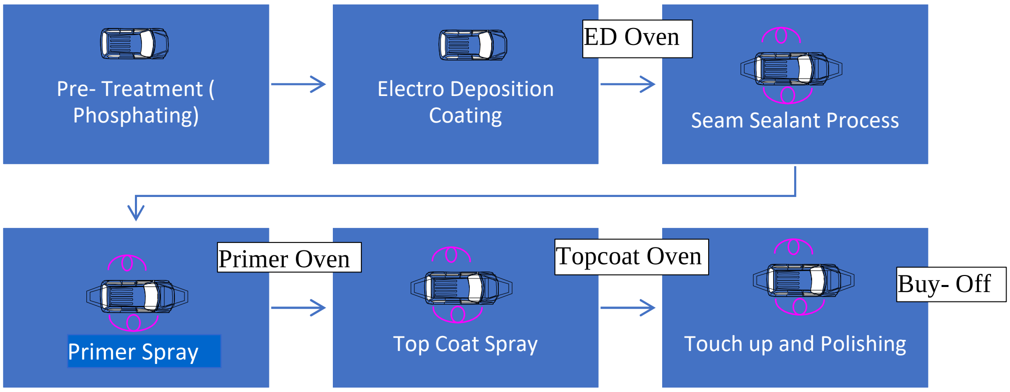


Figure 3. Detail Process for Automotive Paint

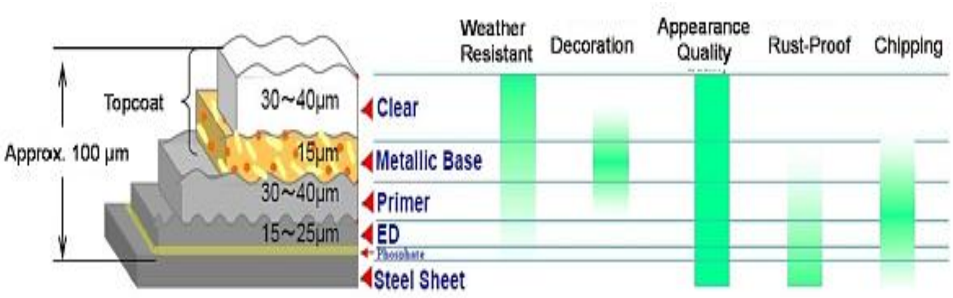


Figure 4. Layers of coating and its properties [10]

coat systems [15], [16]. Different properties of coatings are typically associated with specific parts of a coating system [17].

The first step of the automotive painting process involves pre-treatment, which includes removing the remaining oils from welding residues and stamping processes by cleaning the body surface through three primary liquid dip processes: degreasing, surface conditioning (also called activation), and phosphate washing [18], [19]. Pre-treatment helps in preparing the surface for the primer layer and improves primer adhesion. The second layer of coating is electro-deposition (ED) coating, which includes dipping vehicle bodies into the coating solution and passing an electric current through the body and the liquid ED paint solution. Due to the charged nature of this coating process, the ED paint penetrates places a spray would not reach. The ED paint is promoted to bond with the metal substrate, and a uniform coating thickness is produced. Then it will result in an insoluble and deposited layer that has firm adherence and very high solid content to the pre-treated body.

The third coating step is the application of a primer surface. It can be a powder, water-borne or solvent-borne. The application of primer until 1990 was to improve the appearance of chipping and weather resistance [10]. As the second paint layer on the body, it also protects the cathodic e-coat, the undermost paint layer, from UV radiation and improves adhesion between the e-coat and the topcoat. The primer itself is grey in color. Later, however, it is not visible on the car. The grey color helps the employees at the paint line identify the potential surface irregularities better during quality check. The defect will be easier to detect by human eyes on the light substrate. In addition, this will bring out the best features of the basecoat. However, the primer is visible in some places. Sometimes, on the customer's demand, the interior of the car is colored. For instance, there is no clearcoat or basecoat applied to the trunk. The primer is the final paint layer in these areas.

Application of the topcoat is the final step in the body coating process, which consists of two layers: the clearcoat and the basecoat. The third layer added to the car after the primer and before the clearcoat is the base coat, which contains the primary color pigment. Usually, it is applied using the wet-on-wet process, which means the clearcoat is applied onto the basecoat after a short flash-off and then cured in an oven. In the absence of a wet-on-wet process, the basecoat is cured before the clearcoat is applied. Originally, the basecoat was primarily responsible for determining the visual impression and had the opposite effect as the clear coat [19]. This is the final stage, similar to that of the primer, but consisting of a series of spray booths and Electrostatic spray guns. These colors are mixed in the paint mixing room from which the various paints are pumped to the spray booths. It is common practice to prepare batches of the same color utilizing an automatic color changing system whereby the guns are flushed with solvent (DI-water) and the new color pumped through. The waste paint/solvent may be collected and discharged to the paint sludge removal plant. This process utilizes two-coat metallic. In this case the first "color" coat is applied followed by a "clear" coat. This adds to the depth of the color and the gloss level. Chemicals used in the process include base coat, clear coat, clear coat hardener, spot repair, flushing solution and solvent, cleaning solution, coagulant, flocculation aid and antifoam agents with waste being discharged as paint sludge and wastewater, and exhaust air vented to the atmosphere.

Before the base coat is applied to the vehicle, the body is once again cleaned and "blow-dried". Paint is applied manually; however, there are 2 flash-off zones before the vehicle passes through the intermediate dryer's oven and cooling area. The topcoat process also includes manual and electrostatic gun paint applications used to apply the clear coat. The first flash off is before clear coat application and the second flash off is after clear coat application. However, for this project, the prepared basecoat with the addition of nanoparticles offers a new opportunity to further improve its physical/chemical properties. That will promote protective coating against environmental effects, corrosion, and UV light degradation, and will promote unmatched color retention, and provide a smooth, unblemished, and even finish. Moreover, this also supports the new development of paints and coatings soon, where the topcoats (basecoat and clear coat) are applied in one layer.

4. Nanoparticle Dispersion in Paint

A nanopaint is a material that contains the nano meter scale in at least one dimension, in which the major component is called a matrix, in which nanostructured fillers are dispersed [20]. The classification of nanopaint is based on several methods dealing with the type of nanoparticles and the type of matrix where the nanostructured fillers are dispersed. There are three main types of nano-composite paint groups [20]. The first group is 0D nano composite coatings, in which the fillers are nanoparticles (3D at the nanometre scale). The second group is 1D nanocomposite coatings in which the fillers are whiskers or nanotubes (2D at the nanometer scale). Third and lastly, is 2D nano composite coatings, in which the fillers are nano layers (1D at the nanometer scale).

There are two types of matrixes that can be found: organic and inorganic. Thus, nano composite coating has four main groups as follows (nano filler/matrix). The first group is the combination of organic and inorganic nanocomposite coatings (O/I nanocomposite coatings). The second group is the combination of organic and organic nanocomposite coatings (O/O nanocomposite coatings). The third group is the combination of inorganic and organic nanocomposite coatings (I/O nanocomposite coatings), and the fourth and last group is the combination of inorganic and inorganic nanocomposite coatings (I/I nanocomposite coatings). Chinglenthoiba, Ramkumar [5] reviewed the methods of nanocoating, including physical vapour deposition (PVD), chemical vapour deposition (CVD) and atomic layer deposition (ALD).

4.1. *Nanoparticle Dispersion Method*

In the past decade, researchers have paid much attention to the preparation of nanoparticles [21]–[25]. According to Zhou et al. [26] due to the effect of quantum, small size, high specific area, and macroscopic quantum tunnel of nanoparticles, they can be used to improve the electric, magnetic, mechanical, and optical properties of traditional materials, including organic coatings. There are a lot of methods that have been reported on ways to prepare nanoparticles, such as the hydrothermal method [27], [28], sol gel technique [29], chemical vapor deposition [30], [31] and physical vapor deposition [32], [33], electrochemical approaches [34], [35], solvothermal [36], [37], sonochemical reaction [38], and etc. However, the focus or main problem of organic coatings (resins, solvents, fillers, dispersants, and additives) is to obtain a good dispersion of nanoparticles since they can easily aggregate [26]. Hence, the dispersion of nanoparticles becomes a critical problem for their application.

As stated by Warrier et al. [39], nanofluids are stable nanoparticle dispersions in liquids such as oil, water, alcohol, paint, lubricant, or ethylene glycol. Despite the nanofluid comprising two components, according to Rea et al. [40], the nanofluid can be viewed as a single phase since very small solid particles are scattered in a base fluid. Thus, it is permissible to define nanofluids with low volumetric concentrations of nanoparticles as single-phase fluids. The single-step approach and the two-step method, often known as the dispersion method, are the two most common ways of preparing nanofluids [41]–[45].

4.1.1. *Single Step Method*

The single-step method combines the dispersion of nanoparticles into base fluid and the production of nanoparticles in a single step. Akoh et al. [46] have developed the VEROS (Vacuum Evaporation on a Running Oil Substrate) technique. The method involves condensing nano powders from the vapor phase directly into low pressure fluid that is flowing. Eastman et al. [47] developed a one-step physical method to rectify the difficulties faced by Wagener et al. [48] and obtain uniformly distributed nanoparticles into a base fluid. Zhu et al. [49] developed a single-step chemical method for preparing stable Cu in ethylene glycol-based nanofluids. It was synthesized by reducing copper sulphate pentahydrate with sodium hypophosphite in ethylene glycol under microwave irradiation. After that, Lo et al. [50] developed another single-step method, which is called the submerged arc nanoparticles synthesis System (SANSS), to prepare the metal nanofluids. In this method, a metal electrode is heated by means of arc sparking and condensed into liquid in a vacuum chamber to produce the nanoparticles. It is a good method to prepare high thermal conductivity metals. However, Singh [51] presented in a review paper that agglomeration is the common difficulty encountered during the preparation of the nanofluid. Thus, the researchers added the surfactant to the base fluids to counter this problem while preparing the nanofluid. According to Zhu et al. [49], the single-step method has two drawbacks that are only valid for low-pressure base fluids and the bulk preparation of nanofluids. Thus, it is not very suitable for high-pressure base fluids like paint [52].

4.1.2. *Two Step Method*

The two-step method, also known as the dispersion method, is the most common method for the preparation of nanofluid. In this method, the dry nanoparticles are either purchased or synthesized. The two step method is prepared when nanomaterials are converted to the powder form and directly dispersed in to the base fluid according to Azmi et al. [53]. By adding dispersants, nanoparticles are diluted into base fluids using mechanical stirring or ultrasonic agitation, by adjusting the pH value of nanofluids, or by adding dispersants. The purpose of mechanical stirring and ultra-sonification is to break down the nanoparticles’ aggregation. The addition of dispersants or adjusting the viscosity is to avoid the reaggregation of the nanoparticles and obtain a stable nanofluid. Most researchers use a two-step method to prepare the nanofluids without adding any kind of dispersant or surfactant. Only a few investigators used a dispersant to avoid agglomeration. In order to improve the stability of Cu nanoparticles in Cu/transformer oil-based nanofluid, Xuan and Roetzel [54] and Hwang et al. [55] have added oleic acid and salt as surfactants. Das et al. [56] have revealed that metal oxide particles are the first materials tried for the preparation of nanofluids. This is mainly because they are chemically stable in base fluids and easy to prepare. The use of instruments that rely on the use of mechanical energy, surface chemistry, or both is critical to the effective creation of nanofluids using the two-step technique. This approach, according to Manna [57], is excellent for the synthesis of oxide nanofluids. The two-step technique is the most commonly used method to prepare the nanofluids, and the nanofluids are usually metal oxide nanofluids [58]–[60].

4.2. *Nanopaint Dispersion Method*

In consonance with Loza et al. [61] who studied the stability of nanoparticle dispersions and particle agglomeration, the term "colloids" refers to the particles in the dispersed phase with a range of 1–500 nm. The larger surface area of nanoparticles results in low thermodynamic stability and tends to agglomerate over time because there is higher free surface energy compared to a system with larger particles. Moreover, the few parameters such as morphology, size, density, and surface state of the system will affect the physicochemical properties of nanomaterials. Consequently, in-depth characterization techniques are required to predict the degree of variation in properties. Steric stabilization or electrostatic stabilization (variation of pH, salt concentration, ion type) are used to improve and prevent the colloidal system from changing, thereby ensuring its long-term stability. During the middle of the 19th century, in which the advent of colloid chemistry started, it was also present with the synthesis and use of micro and nanoparticle dispersion other than for inks and paints [62]. A few parameters or variables, such as material, concentration, shape, size, mixing technique applied, temperature, and nature of the solvent, were the significant functions for suspension and stabilization of nanoparticles in a liquid. As mentioned earlier, the shape and structure of nanoparticles can be classified into 0D, 1D, and 2D. The properties of the dispersion of nanoparticles depend on the shape of nanoparticles.

5. Nanoparticle Dispersion Technology in Automotive Surfaces Studies of TiO_2, SiO_2 and Hybrid Nanoparticle

Kotnarowska and Wojtyniak [63] reviewed that there are some important factors that leads to the development of nanotechnology in automotive paints formulation, including the efforts to decrease VOC emissions to meet more stringent environmental regulations, potential of multifunctional paints, increasing demand in thin-film technology and development of complex pigment systems. The properties of materials at nano-scale might be very different with the materials at larger scale. The nanofillers that used for paint application can be inorganic or organic materials, including fumed silica, colloidal silica, silicate, titanium, carbon black and zinc oxide [63].

The dispersion of the nanoparticles in the paint is very important in the production of the nanopaint no matter the nanoparticles are spherical, fibrous or lamellar. Schincariol et al. [64] stated that the main aim is to disperse the nanofillers uniformly in the matrix structure to make sure every single nano-element is separated from each other. **Table 2** shows the components of the nanoparticle and their advantage in paint.

5.1. *Application of TiO_2 Nanoparticles*

Mathiazhagan and Joseph [16] stated that self-cleaning coatings have been developed using photocatalytic titanium dioxide (TiO_2), especially in the anatase crystalline form, in both academic and industrial sectors. TiO_2 also shows super hydrophilic behaviour, which is known as the "water sheathing effect". This behaviour helps wash away the contaminants with water or rainfall easily when the coatings are applied onto the external surfaces. They also stated that nano TiO_2 nanoparticles have been used in developing UV-resistant, anti-bacterial, and self-cleaning paints. These properties allow water droplets to slide over a fully cured surface and wash away the dirt and surface contaminants along the way. According to Schincariol et al. [64], TiO_2 nanoparticles bring some advantages, including colour effects, self-cleaning effects, photocatalytic effects, antimicrobial effects, protection against corrosion, and UV protection. Sangermano and Messori [65] stated that TiO_2 nanoparticles have been incorporated into curable resins to enhance the scratch and abrasion resistance of the coatings. The literature review about TiO_2 nanoparticles is summarised in **Table 3**.

Allen et al. [66] studied the photochemical activities of nanoparticle grade anatase and rutile titanium dioxide pigments. The nanoparticles and UV stabilizers were dispersed into the paint systems at 1, 2 and 5% by weight of total resin, together with 0, 0.5 and 1.0% hindered amine light stabilizers (HALS). The paints used in this experiment were alkyd and acrylic based paint films. The weathering of the paint films was conducted using the Atlas Ci65 weatherometer, and the durability was measured by mass loss and gloss loss. The UV absorption analysis shows that nanocoating with titanium dioxide absorbs more in the near UV below 350 nm. Researchers found that rutile titanium dioxide is an effective stabilizer with greater performance as compared to organic absorbers. Meanwhile, Maggos, Bartzis [68] carried out research to study the photocatalytic degradation of Nitrogen oxide, NO_x gases using TiO_2 containing paint. Researchers carried out the depollution tests in an artificially closed space that was polluted by car exhaust during the testing period. The ceiling

Table 2. Components of the nanopaint and their purposes [64]

Function	Nanoparticles	Advantage
Colour brilliance, shade, colour effects (flip-flop effect)	Oxides (TiO_2, Fe_2O_3, Fe_3O_4, SiO_2, Cr_2O_3) (on mica flakes or SiO_2 spheres, with metal pigments)	Intensify effects of metal pigments, positive effects in dispersion, prevent crack formation, improve resistance to fading
Self-cleaning ("easy-to-clean")	Nano-silica/colloidal silica embedded in resin particles following polymerization, TiO_2	Dirt and water repellant, protection against algae and fungi, easy removal of unwanted paint
Scratch resistance	Oxide (synthetic amorphous silica), SiO_2, Al_2O_3	Improved scratch resistance
Optimized flow characteristics	Oxide (synthetic amorphous silica)	Generate new rheological properties (elasticity, flow characteristics)
Photocatalytic effect, antimicrobial effect	TiO_2, ZnO_6, Ag	Removal of grease, dirt, algae, bacteria, fungi and pollutants
Corrosion protection	Zinc or aluminum coated with nano-TiO_2	Nano-clay coatings delay the fading (which is a result of the bleeding
UV protection, IR reflective or IR absorbing	TiO_2, ZnO, CeO_2, (needle-shaped particles with a length of 50-100 nm and width of 2 nm)	Enhanced UV resistance, blocking of IR and visible light

Table 3. Summary of TiO_2 nanoparticle application in automotive coating surfaces

Author	Based Paint	Finding
Allen et al. [66]	Isocyanate water-based acrylic	Nanoparticle rutile titanium dioxide pigments absorb UV more strongly compared to anatase titanium dioxide pigments.
Maggos et al. [67]	Acrylic	The experiment results showed the photocatalytic degradation of NO and NO_2 gases by ceiling surface painted with TiO_2 containing paint were 19% and 20%.
Veronovski et al. [68]	Geminis and SDS surfactants	Treatment in 5.0 mg/mL aqueous TiO_2 P25 dispersions in the presence of 250 x 10-6 mol/L Gemini surfactant in 5.0 x 10-3 mol/LKBr at 25ºC formed superior dense coatings on the fibre surfaces.
Mirabedini et al. [69]	Polyurethane	Addition of 0.5 to 1.0 wt.% APS treated TiO_2 nanoparticles reduces photocatalytic activity and improves the weathering performance of polyurethane nanocomposite coatings.
Subbiah et al. [70]	Alkyd resin	TiO_2 nanopaint coated surface reduced 70%, 72% and 59% of viable cells against Pseudomonas aeruginosa, Staphylococcus aureus and MRSA respectively after 24 hours of incubation.
Dijy and Divya [71]	-	Results showed that higher amount of TiO_2 in the paint increase the rate of reaction of NO_x gases with the paint.
Lysonkova et al. [72]	Polytertafluoroethylene	Due to the measurements maybe distorted by different pre-treatment of the surface, the roughness measurement visible results are not reported.

surface of the closed space was painted with white acrylic TiO_2 containing paint. The car park was filled with car exhaust gases. When the system reached a steady state, the UV lamps were turned on for five hours. The experiment results showed the photocatalytic degradation of NO and NO_2 gases by a ceiling surface painted with TiO_2 containing paint was 19% and 20%, respectively. Veronovski et al. [68] examined the preparation and characterization of titanium coated self-cleaning cellulose materials developed from TiO_2 P25 powder. In this experiment, TiO_2

nanoparticles used had an average diameter of 21 nm and concentrations of 0.5, 2.5, and 5.0 mg/mL. The TiO_2 P25 nanoparticles were dispersed in alkylammonium Geminis and sodium dodecyl sulphate (SDS) surfactants. Researchers found that when TiO_2 nanoparticles are optimally separated into smaller particles, they will show the best properties in the coating system. The results showed that the treatment of 5.0 mg/mL aqueous TiO_2 P25 dispersions in the presence of 250 x 10^{-6} mol/L Gemini surfactant in 5.0 x 10^{-3} mol/LKBr at 25℃ formed superior dense coatings on the fiber surfaces.

Mirabedini et al. [69] carried out research work to evaluate the dispersion of nanoparticles and surface morphology of the nano-filled polyurethane coatings. Rutile form titania nanoparticles with an average particle size of 20 nm were used in this work. The coating used in this experiment was 2K polyurethane refinish clearcoat based on hydroxyl functional acrylic resin. The surface modification of TiO_2 nanoparticles was carried out by using an γ-aminopropyltriethoxy silane (APS) coupling agent with Et_3N as a reaction catalyst. The experimental results showed that surface modification of TiO_2 nanoparticles can control the photocatalytic activity of nanoparticles and can enhance the weathering performance of polyurethane nanocomposite coatings. However, unmodified nanoparticles cannot be directly added into the coating because it results in poor dispersion and poor weathering performance. Results revealed that modified nanoparticles improved the mechanical properties of the coating. Subbiah et al. [70] carried out an experiment to evaluate the antibacterial properties of TiO_2 nanopaint coatings. Researchers obtain TiO_2 nanoparticles by implementing a size reduction method that uses high-energy ball milling for nine hours. Alkyd resin was used as a binder. TiO2 nanoparticles were used as a pigment source. The crystallite size of synthesized TiO_2 nanoparticles was found to be 23 nm. The surface coated with TiO_2 nanopaint diminished 70%, 72%, and 59% of feasible cells against Pseudomonas aeruginosa, Staphylococcus aureus, and Methicillin-resistant S. aureus (MRSA) individually after incubation for 24 hours. Due to its photocatalytic properties, TiO_2 nanoparticles have been found to be a good antibacterial agent.

Dijy and Divya [71] investigated the reduction of air pollution from vehicles using titanium dioxide. An experiment setup that showed the photocatalytic effect of TiO_2 on reducing air pollution has been demonstrated. The wooden box is fitted with titanium dioxide coated tiles, a pipe carrying smoke to the wooden box, a UV light source and a gas analyzer. A leakage test has been carried out to study the percentage leakage during the experiment. Results showed that a higher amount of TiO_2 in the paint increases the rate of reaction of NOx gases with the paint. Besides, the reduction rate of NOx gases will reach a saturation point after a time period, which depends on the amount of TiO_2 in the paint. Lysonkova et al. [72] studied the possibility of extending the lifetime of working surface molds with the addition of TiO_2 nanoparticles into the PTFE coating. The substrate used is an aluminum alloy of type Al-Si-Cu. The samples were prepared by coating nano powder titanium dioxide with a concentration of 0%, 2%, 5%, and 9% into the polytetrafluoroethylene (PTFE) coating. However, due to the measurements' being distorted by different pretreatments of the surface, the roughness measurement visible results are not reported. Hardness testing using the instrument ERNST Härteprüfer is not suitable for nanomaterials and should be replaced by other testing instruments such as DSI.

5.2. *Application of SiO2 Nanoparticles*

Mathiazhagan and Joseph [16] showed the use of siloxane encapsulated SiO_2 nanoparticles for developing scratch and abrasion resistant coatings. Scratch resistant coatings have been developed by incorporating SiO_2 nanoparticles into an organic matrix. The enrichment of the nanoparticles near to the coating surface leads to an enhancement in the scratch resistance of the coating. Mohseni et al. [73] also stated that the incorporation of SiO_2 into a clearcoat matrix can improve its scratch resistance. According to Schincariol et al. [64], SiO_2 nanoparticles can improve the color effects and scratch resistance of the coatings. Moreover, Sangermano and Messori [65] stated that nanoparticles such as SiO_2 had been incorporated into curable resins and showed improved scratch and abrasion resistance of the obtained coatings.

Lörinczová and Decker [74] carried out the work to study the influence of various factors on the scratch resistance of UV-cured acrylic coatings. Colloidal silica acrylate was used as an additive in UV-cured polyester arcylate coating at concentrations up to 50 wt.%. The results from the Scotch-Brite test showed that the incorporation of SiO_2 nanoparticles enhanced the mar resistance of the surface and the transparency of the polyesteramides (PEA) coating after the test showed no losses observed. However, increasing the content of SiO_2 nanoparticles from 7.5 to 15 wt.% showed a decrease in the ductile/brittle transition value. Jwo et al. [75], researched and produced water-base nano-polyurethane paint with energy conservation, environmental awareness, and high efficiency heat insulation. The SiO_2/W-PU nanocomposite paint was prepared at 4 wt.% and 8 wt.%. The results demonstrated that the dispersion of SiO_2 powder in the water-based polyurethane paint is very even. The water absorption of a sample prepared by adding SiO_2 powder at 8% wt. to the commercial water-base polyurethane is improved around 10.1 times, and its weak acid erosion rate is increased by 3.3 times.

Rosero-Navarro et al. [76] developed a hybrid organic-inorganic self-healing coating to provide anticorrosive protection for AA2024 (Al, 4.4% Cu, 1.5% Mg, 0.6% Mn). Three different samples were prepared from tetraethoxysilane (TEOS) and 3-methacryloxypropyl trimethoxysilane (MPS) with SiO_2 nanoparticles incorporated. Researchers found that the hybrid coatings reinforced with SiO_2 nanoparticles can produce self-healing effects. This also helps in enhancing the corrosion protection of aluminum alloys. Floryancic et al. [77] studied the effects of silica nanoparticles on automotive refinish polyurethane clearcoats. The base formulation used in all experiments is an ambient-cured, two-component polyurethane automotive refinish coating. The silica nanoparticles were added to the coating formulation with methoxy propyl acetate/methoxy propanol as the medium under agitation for ten minutes. The nanoparticles dispersed rapidly and evenly into the resin. Each sample was applied to cold-rolled steel panels. Results showed that silica nanoparticles made slight improvements in scratch resistance.

Findings from the research by Scrinzi et al. [78] found the influence of nano-silica particles on the clearcoat properties. The research used three different two-component isocyanate/polyol clear coats were used; one without any fillers and two with nano-silica particles dispersed in the coating surface layer. The results from the Taber tests done during the studies and the falling abrasive tests indicated the positive role of nano-silica particles in the surface layer of the coating that increase the mar resistance of the clear coat by increasing the surface hardness. The abrasion and erosion resistance were increased further with an enhanced crosslinking level. After 1000 hours of UVA exposure, mar resistance increases slightly due to an increased crosslinking level of the coating caused by the interaction of ultraviolet radiation with the polymer bonds.

Dolatzadeh et al. [79] investigated the influence of surface modification and silica content on the electrochemical behavior of the resultant nanocoating. Three different types of hydrophobic silica nanoparticles were used. Each type of silica nanoparticle with a 4, 6, and 8 wt.% was dispersed into the acrylic polyol by the pearl milling method. According to morphological studies, all organ silane-modified SiO_2 nanoparticles dispersed well in the polyurethane matrix at 6 wt.%, which delivered particle sizes of less than 50 nm. The presence of more hydrophobic groups and longer-lengthened hydrophobic chains on the surface layer of the nanoparticles greatly improves the interactions at the polymer/filler interfaces. Khelifa et al. [80] carried out experiments to synthesize new hybrid polymeric nanocomposites to be used as coating materials through the sol-gel method. The silica nanoparticles were dispersed into the acrylate-based coatings by in situ acid hydrolysis and condensation of tetrathoxysilane (TEOS). An aluminum alloy was used as a substrate. Results showed that a ratio of 75:25 between TEOS and 3-glycidoxypropyltrimethoxysilane (GPTS) leads to excellent morphology and other properties. To achieve the best mechanical properties performance, the presence of nanoparticles must be controlled in terms of amount and distribution. Small silica particles like morphology with good dispersion within the matrix permit excellent mechanical reinforcement of the coating and also preserve the excellent barrier properties of the acrylate coating.

Zhang et al. [81] studied the dispersion level of nanoparticles, filler-matrix interface, and abrasive wear tests. The materials used in this experiment were pyrogenic silica nanoparticles (R7200 and R9200) with a primary particle size of 12 nm and the colloidal nano silica sol "C150" consisting of 50 wt.% colloidal silica nanoparticles and 50% trimethylolpropane triacrylate (TMPTA). Researchers found that both colloidal and pyrogenic silica nanoparticles improved the abrasive wear resistance of polymeric coatings at various testing conditions. The addition of silica nanoparticles to polymeric coatings improved the coating's load-carrying ability and crack resistance. When the nanoparticles having similar morphology are compared, the filler-matrix interface becomes important in wear resistance. The stronger interface will lead to higher wear resistance. Yari et al. [82] summarized the effect of weathering on various properties of a typical acrylic melamine clearcoat containing various loads of nano silica. Different acrylic melamine clearcoat formulations containing nano silica particles at 0 wt.%, 2.5 wt.%, and 3.75 wt.% were applied to such a basecoat by the wet-on-wet procedure. The nanoparticle used in this experiment was a hydrophobic nano-silica surface treated with a nonpolar silane coupling agent, and its particle size was about 20 nm. The results from gloss retention, surface topology, and chemical structure investigations showed that nano silica particles improved the weathering performance of clearcoats.

Sadreddini and Afshar [83] investigated the influence of different concentrations of SiO_2 nano-sized particles in the bath on the deposition rate, surface morphology, and corrosion behavior of Ni-P-SiO_2 composite coatings. In this experiment, various concentrations of amorphous spherical SiO_2 nanoparticles ranging from 5 to 15 g/l with a diameter of 15-20 nm and 99.5 % purity were added to the bath. The amount of SiO_2 nanoparticles co-deposited reached a maximum value of 4.5 wt.%. The results showed that the corrosion rate decreases (6.5-0.6 $\mu A/cm^2$) and the corrosion potential increases (-0.64 to -0.3) with increasing the quantity of SiO_2 nanoparticles in the bath. Wang and Bhushan [84] developed superoleophobicity surfaces exhibiting high wear resistance, anti-smudge properties, and optical transparency for industrial applications. A double-layer coating was fabricated on a polyethylene terephthalate (PET) substrate. In this study, methylphenyl silicone resin and hydrophobic SiO_2 nanoparticles with a diameter of 55 nm were selected. The coated surfaces were found to be able to preserve the superoleophobicity after wear. The coating produced was transparent, but some transparency was lost due to the plasma treatment and a thicker coating. With the anti-smudge properties combined with wear resistance, the coating has great potential for industrial applications.

Bahreini et al. [85] investigated the mechanical and chemical properties of an acrylic-melamine clear coat with different percentages of well-dispersed nano-layered sodium montmorillonite (Na-MMT) silicate particles. Thick mild steel panels of 0.8 mm were used for spraying the clearcoat. Results showed that samples containing 1 and 2 wt.% nano-layered silicate showed the best results in hardness, cupping, and gloss tests as compared with unmodified clear coat. The results showed that nano-silica additives improve the tribological and mechanical properties of the examined coatings. According to Malaki et al. [86], a precipitated type of nano-silica clearcoat is hard, tough, and has good resistance to wear and environmental conditions. They also found that the scratch and abrasion resistance of the acrylic-based polyurethane nano-particulate clearcoats is reinforced by the two types of fumed and precipitated nano-silica reinforcements. The fumed and precipitated silica nanoparticles were added to an acrylic-based polyurethane clearcoat as a filler. Mora et al. [87] studied the impact of silica nanoparticles in terms of morphology and mechanical properties of sol gel derived coatings. A sample panel of mild steel type was used as the substrate. In this research, synthesized silica was functionalized and had a nanoparticle size of about 30 nm. The coating matrix was fabricated by the sol-gel method in the presence of an acidic catalyst of HCl (hydrogen chloride) with water and industrial methyl spirit as solvents. The results show that a sol-gel coating reinforced with silica nanoparticles improved the mechanical properties of the coating and increased the erosion impact resistance. The mechanical properties improved when silica nanoparticles were surface treated. Dispersion of silica nanoparticles also increased the hardness and rigidity of the coating, and no cracking or chipping was observed. **Table 4** shows the summary of literature review about SiO_2 nanoparticles.

5.3. *Application of Hybrid TiO_2/SiO_2 Nanoparticles*

According to Mathiazhagan and Joseph [16], the addition of SiO_2 to TiO_2 can improve the self-cleaning properties of the coating. However, since the TiO_2 particles will oxidize the polymer, photo-

Table 4. Summary of SiO_2 nanoparticle application in automotive coating surfaces

Author	Based Paint	Size (nm)	Finding
Lörinczová and Decker [74]	Water-based resins made of acrylate functionalised oligomers	13 and 50	The best performance for mar resistance was achieved by the addition of relatively large amount (30 wt.%) of acrylate-functionalised silica nanoparticles.
Jwo et al. [75]	Waterborne polyurethane	-	The dispersion of SiO_2 powder in the water-base polyurethane paint is very even.
Rosero-Navarro et al. [76]	Hybrid organic–inorganic sols developed from (TEOS) and (MPS)	20	The incorporation of cerium (III) to hybrid sol– gel coatings of TEOS – MPS – colloidal SiO_2 develop self-healing effect improving the corrosion protection of AA2024T3 alloy.
Floryancic et al. [77]	Polyurethane	30 to 40	By dispersing nanosilica in coating, the scratch resistance and adhesion of the coating had been improved.
Dolatzadeh et al. [79]	Polyurethane	<50	According to morphological studies, all organosilanemodified SiO_2 nanoparticles dispersed well in the polyurethane matrix at 6 wt.% which delivered particle sizes of less than 50 nm.
Scrinzi et al. [78]	Isocyanate/polyol	<50	The presence of nanosilica particles in the surface layer increases the surface hardness.
Khelifa et al. [80]	Acrylate-based	-	Small silica particles like morphology with a good dispersion within the matrix permits to obtain a good mechanical reinforcement of the coating.
Zhang et al. [81]	Urethane–acrylate	20	The colloidal silica nanoparticles showing excellent homogeneous dispersion level with mean size of 20 nm and narrow distribution of particle size.
Yari et al. [82]	Acrylic melamine	20	The clearcoats containing nanosilica had lower crosslinking density compared to the pristine clearcoat.
Sadreddini and Afshar [83]	Ni-P	15 to 20	Corrosion rate decreases (6.5-0.6μA/cm^2) and the corrosion potential increases (-0.64 to -0.3) with increasing the quantity of the SiO_2 nanoparticles in the bath.
Wang and Bhushan [84]	Methylphenyl silicone resin	55	The coated surfaces were found that it able to preserve the superoleophobicity after wear.
Bahreini et al. [85]	Acrylic-melamine-formaldehyde	-	Incorporation of 1 and 2 wt.% of nano-layered silicate make desired improvement in both mechanical and chemical properties of the acrylicmelamine clear coat.
Malaki et al. [86]	Acrylic Polyurethane	7 to 15	Nano-silica additives enhance tribological and mechanical properties of examined coatings. Precipitated type of nanosilica clearcoat is hard, tough and have good resistance against wear and environmental conditions.
Mora et al. [87]	Sol-gel chemistry with TES40 and GPTMS used as precursors	25	When silica nanoparticles were surface treated, the defect density of the coating decreased further and the mechanical properties improved. Silica nanoparticles reinforced with the sol-gel matrix increases the erosion resistance of the coatings and led to mass loss reduction of around 80%.

-catalytic TiO_2 particles cannot be dispersed into organic coatings. Ramezanzadeh and Mohseni [88] developed nanostructured hybrid clearcoats using sol-gel based organic and inorganic precursors. Farahmandjou and Khaili [89] studied the superhydrophobic self-cleaning surface of SiO_2/TiO_2 nanoparticles developed by the Sol-Gel approach. SiO_2 and TiO_2 nanoparticles were synthesized by a chemical method. The resulting powder was rinsed with distilled water and then dried at 75 °C for 24 hours. Finally, the samples were calcinated at 550 °C for 2 hours. The SiO_2/TiO_2 superhydrophobic layers were coated on glass. TEM images of the SiO_2 and TiO_2 showed uniform nanoparticles for self-cleaning processing purposes. The photography of the samples with SiO_2/TiO_2 self-cleaning coatings showed that the round water droplets roll down and pick up the dust on the surface.

Verma et al. [90] fabricated anti-scratch and anti-algal coating formulations with silica and silica-titania core-shell nanoparticles individually in a polyurethane binder. The silica nanoparticles were prepared by using tetraethyl ortho-silicate (TEOS) as a precursor through the sol-gel method, while titania nanoparticles were prepared through the peptization method by adding 2 mL of titanium isopropoxide into 50 mL of distilled water with continuous stirring. The silica-titania core shell nanoparticles were prepared through the peptization process by adding 2 mL of titanium tetra-isopropoxide into 50 mL of distilled water and continuous stirring in the presence of 1 g of silica nanoparticles, which were prepared by the sol-gel method. Then the polyurethane coating formulations were fabricated by mixing polyurethane binder, thinner and nanoparticles under sonication, and the nanoparticles were maintained at 4 wt.% in the liquid coating formulation. Results showed that the silica with high mechanical properties enhances the strength and anti-scratch property of the polyurethane coating, while titania with good photo-catalytic activity improves the anti-algal property of the polyurethane coating. The polyurethane with silica-titania core-shell formulation can bear a load of up to 5 N in an anti-scratch test and provides good anti-algal property. **Table 5** shown the literature review of previous research on hybrid TiO_2/SiO_2 nanopaint.

6. Automotive Coating Characterization and Performance

According to Akafuah et al. [10], the performance of an automotive coating can be evaluated from a variety of perspectives, including the coating's durability and aesthetic features. In fact, the automotive company needs to maintain good appearance standards to meet customer expectations. Ilenda et al. [91] stated that one of the desired properties for most coatings is damage resistance. Harsh environments cause wear and tear and may cause chipping, cracking, marring, or scratching of the coating surface. Researchers discovered that the damage-resistant coating can be created by using organic polymeric nanoparticles with a crosslinked structure and a diameter of less than 100 nm alone or in combination with inorganic nanoparticles. There are various properties of the coatings that are associated with specific functions, such as functional coatings, anticorrosive coatings, scratch and abrasion resistant coatings, and self-healing coatings [16]. Lörinczová and Decker [74] stated that one of the important properties for acrylic coatings is protection against mechanical damage, such as abrasion resistance and scratching resistance. Mar is a very small mark that is difficult to see by the human eye, but if it is present in a large volume, then it will become visible and it will result in loss of glossiness and transparency of clearcoats. A scratch refers to a mark caused by a hard and sharp moving object that will form a visible groove or damage on the surface.

Table 5. Summary of TiO_2/SiO_2 nanopaint application in automotive coating surfaces

Author	Nanoparticles	Finding
Farahmandjou and Khaili [89]	SiO_2/TiO_2	The photography of the samples with SiO_2/TiO_2 self-cleaning coatings showed that the round water droplets roll down and the dust drip off on the surface.
Verma et al. [90]	SiO_2/TiO_2	Polyurethane coating could not sustain 3N load for anti-scratch test; Silica-polyurethane coating can bear load up to 5 N and started crack after 5 N; Silica-Titania core-shell coating can sustain load of 3 N but started crack after 3 N.

The crucial procedure in the case of organic matrices is correct nanoparticle dispersion to achieve the necessary final characteristics. For this reason, nano-sized nanoparticles offer several benefits, including the ability to penetrate ultra-small pores, capillary regions in the polymer matrix, and indentation. The inclusion of nanoparticles into epoxy resins improved the endurance and integrity of coatings by filling microcavities and fissures [92], [93]. Additionally, nanoparticles may inhibit polymer disaggregation during curing, resulting in a uniform covering. Nanoparticles having a greater specific surface area are known to improve not only the epoxy-curing process but also the nanoparticle dispersion in the epoxy matrix [94], [95]. For polyester coatings, Golgoon et al. [96] found that the embedding nano clays created a more uniform and denser coating and fewer pores compared to the pure polyester coating. The presence of nanoparticles has an impact on polymer crystallization. In most cases, nanofillers increase crystallinity and lower the spherulites file of semi-crystallinity polymers. In the case of inorganic matrices, the creation of nanocomposite structures connects the segregation of one phase to the grain boundaries of the second phase, and this effect stops grain expansion.

According to Li et al. [97], the addition of nanoparticles (rutile nano-TiO_2 and anatase) decreased the grain size of the nickel matrix. The typical material, the grain size of monocrystals, ranges from around 100 nm to several hundred centimeters. In this situation, the number of atoms in the grains is substantially larger than in the border areas. The grain size of nanocrystalline materials is around 10 nm or smaller [98]. With the addition of the nanocrystal phase to the metal matrix, the volume percentage of grain boundaries may rise. Within a metal matrix, Mitterer et al. [99] created nitride nanocrystalline phases, such as TiN in Ni, ZrN in Ni, ZrN in Cu, and CrN in Cu. A metal can be transformed to nitride in the nanocrystalline phase of these coatings, while others are carried into the growing film unreacted. Furthermore, heat post treatment has a significant impact not only on dislocation density, nanoparticle-matrix interactions, and microstructural phase bonding, but also on grain size [100] crystallization, and morphology.

7. Approach to Evaluate Automotive Paint Characterization

The characterization of an automotive paint can be evaluated from a variety of perspectives, including the coating's durability and aesthetic features. In fact, the automotive company needs to maintain good appearance standards to meet customer expectations. Akafuah et al. [10] also stated that the qualities of automotive paint can be evaluated based on three main criteria, including protection against harsh environments, durability, and appearance. An excellent automotive paint must have good resistance against damage caused by falling objects, ultraviolet radiation, scratches, and rock hits. Paint durability is defined as having good rust proofing for more than 20 years while maintaining excellent gloss and color appearance. The parameters to judge the appearance quality are paint smoothness, color, and gloss. Bensalah et al. [101] studied the performance of the different coating systems over metallic substrates. Researchers aim to characterize the mechanical, tribological, and corrosion behaviors of commercial coating primers and commercial topcoats that are applied on different substrates. There are a few testing methods for this study, including the Persoz pendulum hardness test, impact resistance test, resistance of the coating against cupping test, degree of coating adhesion, friction test, abrasion resistance test, and corrosion test.

7.1. *Automotive Film Thickness*

Every automobile spray paint process aims to produce the desired film thickness with the least amount of waste and flaws possible while maintaining the highest level of consistency. Coating thickness variations can cause a variety of visual and flow-related problems. While most people are aware of the orange peel that can appear when film thickness is too low or sags when it is too high, today's high-performance vehicle coatings have standards that go much beyond these two qualities. Moore [102] discussed the basic concepts of film uniformity and film thickness control. These two principles are foundational for both design and continuous improvement efforts relating to a production line.

7.2. *Automotive Adhesion*

According to Valli [103], the most important property of a coating is its adhesion to the substrate. The development of standard techniques for adhesion evaluation is needed to promote the widespread use of coating methods and ensure user confidence. If the purpose of a coating is to fulfil its function of decorating or protecting a substrate, it must adhere to it for the expected service life. A substrate and its surface preparation have a drastic effect on the adhesion of coatings. A method to evaluate the adhesion of a coating to different substrates or surface treatments, or of different coatings to the same substrate and treatment, is of considerable benefit in the industry. An adhesion test for hard tribological coatings should be quick and easy to carry out with easy-to-interpret results. The test should also be practicable for real machine parts and tools. A special preparation of samples is not required. Adhesion assessments have at least nine different basic techniques, which are acceleration (body force) testing, pressure sensitive tape testing, shock wave testing, electromagnetic stressing, tensile and shear testing, acoustic imaging, laser techniques, scratch testing, and indentation tests.

The best adhesion between paint and substrate was obtained when a phosphatized steel substrate was used, compared to the poorest adhesion shown by phosphatized electronica steel. Tahmassebi and Moradian [104] investigated the possibility of using adhesion, scratch, and mar resistance measurements to predict the performance of basecoat and clearcoat automotive paint systems. Researchers found that the weathering performance of a basecoat/clearcoat automotive paint system can be compared by evaluating the abrasion and scratch resistance of the clearcoat and determining the adhesion between the clearcoat and basecoat. The scratch and abrasion resistance of the automotive paint systems can be evaluated correctly with this assessment procedure. Evaluation of the appearance changes, cupping tests, and hardness changes cannot be used to predict the long-term weathering performance of this coating system because it does not provide enough information for the anticipation.

Scrinzi et al. [78] carried out research to study the influence of silica nanoparticles on the properties of clearcoats. Color and gloss assessments were taken to determine the aesthetic changes. An FTIR analysis was carried out to evaluate the degradation of the polymer bonds. In order to simulate the coating abrasion and erosion, the Taber test and the falling adhesion test were carried out.

7.3. *Scratch Resistance*

According to Sangermano and Messori [65], there are various testing methods to determine the coating protection against scratch damage, such as the knife test and the pencil hardness test. Recently, scratch testing has been developed to overcome the shortage found in other test methods. The new scratch test uses different scratch testing modes combined with material science tools to objectively measure the scratch resistance of polymeric coatings. Scratch testing is usually carried out in three stages, which are an original profile, a scratch part, and a residual profile. Atomic force microscopy (AFM) is found to be not only used in determining surface topography but can also be used to examine scratch resistance. AFM has several modes that can perform detailed surface morphology analysis and surface property testing on a nano-scale. The scratch resistance of clearcoats can be determined using the Hoffmann test, the Clemen test, the Taber scratch tester, the needle test, single-pass pendulum sclerometer, the Taber haze test, the Revetest scratch tester, the Erichsen test, the Scotch-Brite test, the Rota Hub test, and the steel wool test [74]. The applied load and speed of scratch will become much smaller from macro-scratch testers to nano-scratch testers.

Bertrand-Lambotte et al. [105] studied the mechanical parameters determining the mar resistance of automotive clearcoats, especially the mar caused by car wash machines. Researchers carried out the indentation and scratching tests at room temperature on the automotive clearcoats. The data obtained from these tests is compared to the previous data obtained at room temperature. The transition in hardness results obeys an Arrhenius law and the activation energy of the visco-plastic process has been determined. Researchers found that the mar-resistance of the clearcoat is higher when the activation energy is higher. Gerlock et al. [106] carried out research to determine the hindered amine light stabilizer (HALS) additive distribution in the weathered basecoat and clearcoat paint systems. Researchers found that the analysis of clearcoat segments for "active HALS" does not need to provide enough information to determine the actual role of HALS to evaluate the long-term weathering performance of basecoat and clearcoat automotive paint systems. In the future, studies need to be carried out by combining photooxidation, "active HALS" and ultraviolet type A (UVA) profiles with fracture energy measurements of the mechanical repercussions to predict the long-term weathering performance of basecoat/clearcoat automotive paint systems with short-term exposure test specimens.

Seubert and Nichols [107] carried out an experiment to understand the scaling behaviour of various scratches produced by different sized scratch tips on automotive clearcoats. The findings of recent and previous studies revealed a complex relationship between scratch resistance and physical properties. The damage caused by scratching is not directly proportional to the various sizes of scratch tips. Therefore, researchers need to determine and understand the hidden differences between macro-scratching and nano-scratching in order to understand the scratch behaviour at various size scales.

7.4. Corrosion Resistance

Suay et al. [108] studied and investigated the different epoxy primer coatings for metal substrates by electrochemical impedance spectroscopy (EIS). EIS is believed to be an effective tool to study the effect of metal pre-treatment on corrosion protection of automobiles. The best properties of paint are obtained when applied to phosphatized steel. In addition, the best-behaved paint is the non-toxic paint, followed by the Pb paint cured at lower temperature (160 °C) and lastly, the Pb paint cured at a high temperature (180 °C).

Tahmassebi et al. [109] studied the possibility of using measurements of electrochemical properties to assess the weathering performance of basecoat and clearcoat automotive coating systems. Researchers tested the electrochemical properties of a basecoat and clearcoat automotive paint in a 3.5 percent NaCl solution in deionized water at various weathering exposure times in this study. Researchers found that the assessment of the electrochemical properties of coatings can provide sufficient information to compare the weathering performance of the basecoat and clearcoat automotive paint systems. It is possible to evaluate the water uptake, corrosion resistance, and weathering performance of the paint systems at the same time. Taha-Tijerina et al. [110] carried out research work to assess the anti-corrosion and tribological performance of coatings reinforced with montmorillonite nanoclay (MMT) nano clay at various filler fractions. Researchers carried out the salt spray fog corrosion test in a chamber to assess the coating performance in a salt solution environment. For further testing, the samples were exposed to salt spray for 1000 hours at 30 °C in a 5% sodium chloride vapor (NaCl) concentrated solution. The pin-on-disk tribometer was utilized to determine the tribological performance of the specimens. Researchers observe and compare the blister size and density to assess the corrosion performance.

Sánchez et al. [111] studied Al_2O_3–13% TiO_2 coatings that were produced from nano-sized and conventional powders with various spraying conditions. To carry out the characterization of the coating, SEM, TEM, and XRD, which are also called EDX methods, were used. With these methods, the surface morphology of the coatings can be studied and analyzed thoroughly. Besides, the microhardness, adhesion properties, and roughness were studied using the Vickers Microhardness test. The results showed that the coating deposited using nano-sized powder provided better performance in terms of hardness and abrasion resistance. Ramezanzadeh et al. [112] examined the impacts of biological materials on the properties of an automotive acrylic melamine clearcoat. Researchers carried out two different testing approaches, including pre-aging and post-aging, to evaluate the biological resistance. Results showed that important impacts of biological materials on visual performance and the appearance of the clear coat are due to the surface roughness produced by the harsh etching mechanism of these materials. In addition, the clear coat exposed to the post-aging testing process showed more serious biological degradation due to the effect of UV radiation as well as sunlight.

7.5. Non- Wetting Properties

Zimmermann et al. [113] introduced a new method to examine the wetting behaviour of superhydrophobic textiles that cannot be evaluated using classical contact angle measurement methods. With this new method, the water repellence of the superhydrophobic surface upon hitting the surface can be studied. The new method is easy and straightforward to carry out. This water shedding angle gives reliable results to evaluate the ability of superhydrophobic textiles to repel water. This method makes improvements to the existing method and is said to be a more reliable method to determine the wetting behavior of superhydrophobic textiles. Ramezanzadeh et al. [114] studied the possibility of using gonio-spectrophotometry as a new scratch testing method. The results of gonio-spectrophotometry showed that this new method is able to differentiate between plastic and fracture types of scratches. It is also suitable to analyses the self-healing abilities of the coatings. The results using gonio-spectrophotometry were checked with results from a scanning electron microscope (SEM) for its accuracy and reproducibility, and they showed great potential as a new approach

8. Conclusions

The technologies employed in automotive coatings have become much more sophisticated and efficient, and they are evolving rapidly. The pace of performance improvement over the past decade has been dramatic, and it will continue to accelerate. Surface damage to structures is a vital problem in automotive production. The surface defects that usually occur in the production line of after-sales service lead to the improvement of painting technology. When nanoparticles like TiO_2 nanoparticles are mixed with paint, it improves the durability of the surface. The size, shape, and greater surface area of these materials improve the existing properties of paint-coated surfaces due to their specific structural characteristics. This review paper has analyzed the possibilities of nanoparticles as nanopaint in automotive surface application. This paper provides comprehensive and up-to-date results of these new coating formulations that will be useful to researchers. It also offers a general overview of nano paint technology for the automotive industry with a hybrid of TiO_2 and SiO_2 nanoparticles. In the recommendation section, the new development trend in automotive coatings was chronicled and discussed. In summary, the paper presented herein demonstrates that this new technique has great promise in the automotive painting industry.

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Author's Declaration

Authors' contributions and responsibilities

The authors made substantial contributions to the conception and design of the study. The authors took responsibility for data analysis, interpretation and discussion of results. The authors read and approved the final manuscript.

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The authors declare no competing interest.

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