3 Surface Modifications and Protective Coatings – Types and Approaches

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CONTENTS

3.1 INTRODUCTION

Surface engineering is the mother of almost all technologies and can be the first or final step of several industrial and day-to-day applications. Its range can start from a simple example of a glowing face to a sophisticated component of an aeroplane. A fashion-conscious person is always bothered about how long her makeup will look fresh, for which she explores not only a good make up foundation and top cream but also for a good cleansing solution, which needs to be applied before makeup, to clean any dust or grease on the face. This is very similar to the surface preparation of a steel part before application of coating for corrosion protection. Many industrial components require coatings for improving either aesthetics or corrosion protection, but their application requires, first, a good surface preparation using a suitable chemical cleaning or mechanical cleaning using a blast machine (TNEMEC, 2015). The final step in any component fabrication is its outer look and aesthetics. This requires a proper cleaning followed by a suitable coating. This is true for our several daily use items, such as many consumer durables, car body, our mobiles and electronic watch etc.

The term ‘surface engineering’ actually can alternatively be called ‘surface treatment’ or ‘surface modification’ or ‘creating an engineered surface using various surface modification methods.’ Surface treatment can be simply a change due to washing or cleaning by a chemical which can either remove dust or grease or a chemical reaction which can change the surface composition to a

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different chemical entity on the surface. In surface modification, it can be a combination of surface cleaning followed by application of a different material which protects it from many environmental pollutants. In surface engineering, it can be the role of some physical process which alters the properties of the surface. Surface treatment, using shot-blasting, shot-peening by high impact, or allowing accelerated particles to hit on the surface to create a new surface, can be examples of surface engineering to create clean and stress-free surfaces, respectively (Hutchings and Shipway, 2017). To simplify, it is better to classify surface engineering in three main categories, as discussed in what follows.

3.1.1 SURFACE MODIFICATION WITHOUT CHANGING THE MATERIAL CHEMICALLY

This type of surface modification can be achieved by thermal or mechanical means, altering metallurgy of the surface or surface texture.

- *Thermal processes*: Surface heat treatment, particularly those that undergo phase transformations like the martensitic reaction hardening of carbon steels, low-alloy steels, and cast irons – laser, flame, induction.
- *Mechanical processes*: Cold working – by shot-peening, shot blasting, explosive hardening, or other specialized machining processes induce compressive stresses, increasing hardness and fatigue resistance.
- *Changing surface texture using machining and blasting.*
- *Other processes*: Modification of surfaces by chemical/electro-etching, laser engraving, use of various chemical, solvent, and ultrasonic cleaning processes could also be included here.

3.1.2 SURFACE TREATMENT BY ALTERING SURFACE CHEMISTRY

These processes involves either [SVD], diffusion of elements from the coating material to the substrate, or result in a chemical reaction of the substrate with the coating material when exposed to a chemical liquid or vapour at high temperatures.

- *Thermochemical diffusion processes*
  a Carburizing
  b Carbonitriding
  c Nitriding/nitro-carburizing
  d Boronizing
- *Chemical vapour deposition*
  a Aluminizing (calorizing, alonizing)
  b Chromizing
  c Siliconizing
- *Electrochemical processes* (anodizing)
- *Chemical conversion coatings* (phosphating, chemical blacking, chromating, etc.)
- *Ion implantation processes* (impingement of accelerated ions on the surface entering up to depth of nano-dimension)

3.1.3 SURFACE MODIFICATION BY ALTERING SURFACE CHEMISTRY BY APPLYING A FOREIGN MATERIAL (COATINGS) ON THE SURFACE

The coated material usually has a mechanical bond with the substrate or can form a chemical bond with the surface. Examples include corrosion protection coatings using paints, thermal spray, physical vapour deposition, chemical vapour deposition, electroplating, dip coating, etc. (Tanya

Galvanizers, 2016). The following properties of the surface can be changed as a result of these surface modification processes:

- *Aesthetic*: Clean surface, free of dust, grease, salts, and corrosion products
- *Mechanical properties*: Hardness, impact, friction and wear, erosion, and abrasion
- *Chemical*: Corrosion, oxidation
- *Conductivity*: Conductive surfaces, anti-static surfaces
- *Smart surfaces*: Hydrophobic, dust free, textured, anti-bacterial

The next question is the basis of selecting various surface treatment/modification techniques.

- Based upon change in function property
- Substrate characteristics
- Thickness of the modified surface
- Throughput of the process (slow, fast)
- Requirement of vacuum
- Geometry of the component
- Economics of process

One of the simplest ways to select a technique or process is based on the thickness of change on the surface you are looking for. Figure 3.1 is a schematic of the range of various techniques based

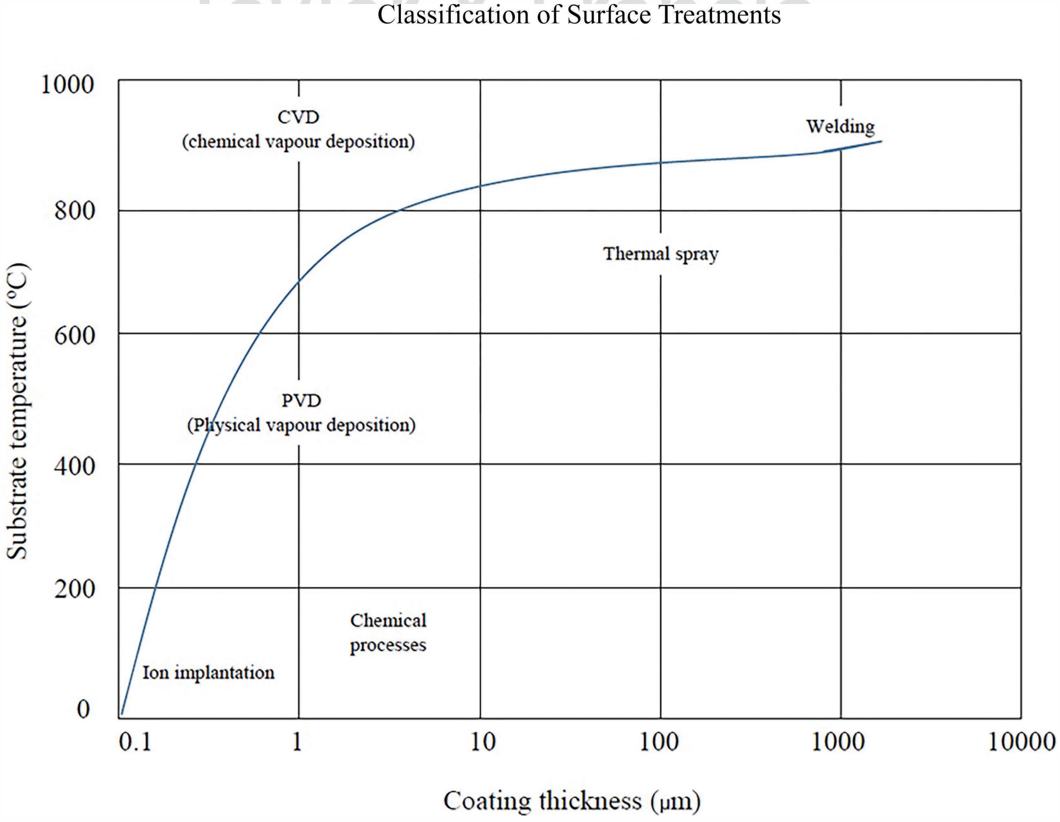


FIGURE 3.1 Schematic of various surface treatment techniques based upon the thickness of change on surface and the temperature of the process. *Modified after (Billard et al., 2018).*

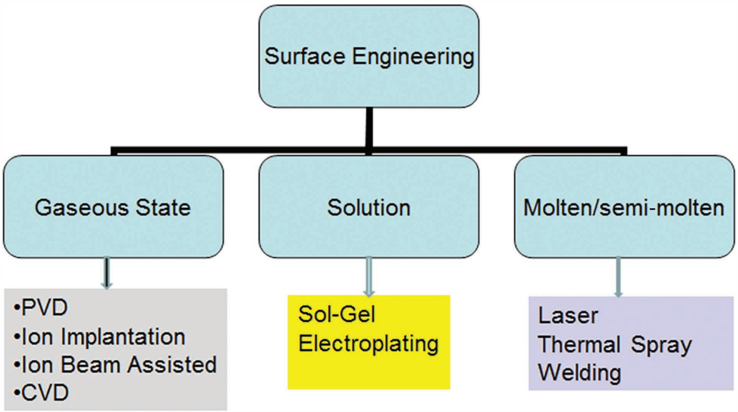


FIGURE 3.2 Classification of various surface modification techniques based upon the state of the coating material.

on thickness of the coating and the temperature up to which a process can reach during application (Billard et al., 2018).

Thus, based on **Figure 3.1**, it is clear that if one is interested in a surface modification by coating at a low thickness, lower than 10 µm, the physical vapour deposition (PVD) and chemical vapour deposition (CVD) are the only possibilities. If one is looking for larger thicknesses from a fraction of a mm to more than a mm, then thermal spray is perhaps the answer. Also, both PVD and CVD require vacuum for initiating the process, white thermal spray processes work in normal environments such as arc, flame, and atmospheric plasma. Further, PVD and CVD require costly equipment's, while thermal spray is relatively a cheaper technique.

There are several other techniques such as paint coating which requires a simple brush and roller for application, but for big areas, it requires spray guns. Electroplating is again simple but requires electrochemical baths, and the coating can form from very thin to thick coating. Dip coatings are very common, for example, galvanization zinc coating on steel, which is formed by dipping steel into molten zinc metal at temperatures above 450°C.

There are still sophisticated processes such as laser surface modification where the desired material is added through a laser radiation which melts the substrate and allows the desired material to react with the substrate, simultaneously creating a layer of the material to be coated.

There is another classification of various surface treatment processes based upon whether the process is in a gaseous/vapour state, solution, or solid/melt. This is given in **Figure 3.2.**

Another very powerful classification of various surface modification techniques is based upon their mechanism of bonding: whether it is mechanical bonding or chemical bonding. Table 3.1 classifies various techniques in these two categories:

Now we would discuss various coating processes.

3.2 METALLIC COATINGS

3.2.1 Hot-Dip Coatings

The metallic coating is one of the biggest sectors, where surfaces are coated with various metals or alloys using a host of different processes. The simplest one is the hot-dip method, which is a very old process and is based upon dipping the substrate in a molten metal for a few seconds, where it partially reacts with the substrate and forms a chemically bonded coating. The most common metallic coating is the zinc coating, which is applied by dipping steel sheets in liquid zinc melt, maintained at a temperature above its melting point for a few seconds. The dipping is done after the steel

TABLE 3.1

Classification of Coatings Based upon Their Bonding to Substrate

Mechanical-bonded	**Chemical-bonded (diffusion thru substrate)**
Paint coatings	Sol-gel coatings
PVD	Hot-dip galvanization
Thermal spray	CVD
	Laser alloying
	Nitriding, carburizing

surface is thoroughly cleaned and activated in several activation processes. The coating formed is a true metallic coating with a multilayer structure with pure zinc on top and another three layers with lower zinc alloyed with iron from steel. Galvanized coatings have the biggest market used for several day-to-day and industrial applications.

On the other hand, the aluminizing is carried out by an entirely different method of thermo-chemical diffusion process at high temperatures, typically in the range of 800°C to 1000°C with a prolonged soaking time to aid the diffusion potential. It is a chemical diffusion treatment wherein the surface layer of the material is impregnated with aluminium in the form of pack having aluminium and chromium in a matrix of aluminium oxide. This process is called the pack aluminizing process. It is primarily used on steels but also on nickel- and cobalt-based alloys to obtain greater creep resistance, hardness, and corrosion resistance (Total Materia, 2019).

3.2.2 THERMAL SPRAY COATINGS

The other most frequent method of doing metallic coating is thermal spray. Thermal spray is a process in which either the powder of the said metal/alloy or metal in the form of wire is melted using a strong heat source, flame, arc, or plasma. Liquid drops so formed are forced at a very high speed on the surface to be coated, where they are splat cooled, resulting in a strong coating. Four different thermal spray processes differ in terms of their heat sources: heating the source by a flame called flame spray process, heating by an arc is known as arc spray process, and where heating is initiated by plasma, it is called plasma spray process. If the heating is carried out by detonation process in the gun, it is called detonation spray process. All four thermal spray processes give different morphology of the coating which differs in the density/porosity and hence in their effectiveness in preventing corrosion, oxidation, and wear and abrasion (**Figure 3.3**) (Kuroda et al., 2008).

Typical applications of thermal spray cover a huge range of components, either as part of the original manufacturing process or as a reclamation or re-engineering technique for a wide range of rotating and moving parts from machines of all kinds, including: road and rail vehicles, ships, aircraft, pumps, valves, printing presses, electric motors, paper making machines, chemical plants, food machinery, mining and quarrying machinery, earthmovers, machine tools, power generation and aerospace turbine repair, landing gear (chrome replacement), and virtually any equipment which is subject to wear, erosion, or corrosion. This is done using either arc spray, flame spray, or high-velocity oxygen fuel (HVOF) systems to spray steels, nickel alloys, carbides, stainless alloys, bronzes, copper. Hard coatings were made using the HVOF process (Khanna et al., 2009).

A few typical industrial applications which confirm increased durability, modified electrical properties, improved corrosion protection, higher hardness, and/or improved wear and abrasion properties:

- *Wind turbines*: To prevent atmospheric corrosion damage to wind turbines.
- *Oil & gas industry*: Pipes, shafts, which are often exposed to harsh environments.

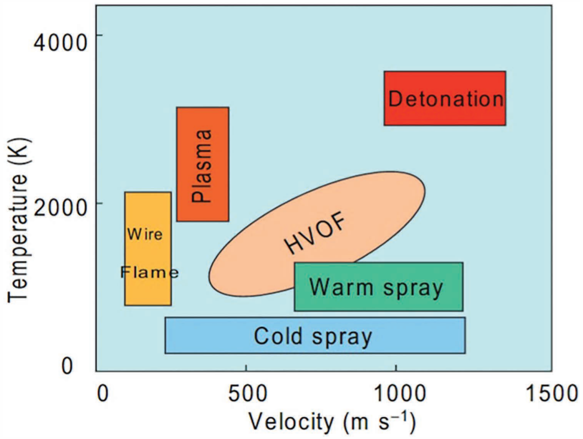


FIGURE 3.3 Thermal spray process – description in terms of the intensity of heat source and the velocity on substrate. *Reproduced with permission from (Kuroda et al., 2008) © 2008 National Institute for Materials Science.*

- *Bridges*: Metal (zinc or aluminium) spraying to increase its durability due to cathodic protection.
- *Petrochemical plants*: Proper metallic coating of pipes in the inner layer of these petrochemical pipes.
- *Infrastructural industry*: The structure of an infra project is build up by steel coated with metallic coatings to provide strength to the surface of a structure.
- *LPG cylinders*: Metal spraying is used to protect LPG, propane gas, or butane gas bottles against corrosion.
- *Architectural coatings:* Metal spraying is preferred to hot-dip galvanizing in some industries.
- *Film industry sets:* Artistic coatings for shooting the shots.

3.2.3 PHYSICAL VAPOUR DEPOSITION

Another method of applying thin metallic coatings is PVD. It includes a host of processes which have the basic principle to bring the desired material to be coated in vapour form and then allow it to fall on the substrate. Simple methods of vapour deposition to ion plating to sputter deposition and electron beam deposition are well known. The coating thickness ranges from fraction of a micron to a few microns. Most of the coatings made are usually to enhance wear and friction of the substrate. Electron beam deposition became one of the most important processes for thermal barrier coatings for turbine blade application.

In the electron beam evaporation method, the desired metal to be coated can be evaporated using high-energy electrons in the form of an intense beam. A hot filament is used to get thermionic emission of electrons, which can, after acceleration, provide sufficient energy for evaporating any material. In a typical case involving 1 A of emission accelerated through a 10 kV voltage drop, 10 kW is delivered upon impact (Wikipedia, PVD) (Green, 2022).

One of the very important applications of electron beam evaporation coatings (EBPVD) is turbine blades, which results in giving an elongated grain structure of coating instead of an equiaxed structure. The former helps in releasing stress in the coating and saves it from cracks and damages.

3.3 MODIFICATIONS BY PAINT COATINGS

Paint coating appears to be the most trivial method of surface modification. It is usually applied using a brush to give a barrier coating of paint, which is generally an insulating material, which helps in preventing corrosion by restricting the flow of electrons. However, paint coatings cannot be considered as a trivial technique when applied on industrial systems, where durability and its functionality become very important (Khanna, 2020). There are various varieties of paint coatings based upon its utility, purpose, and function. In a very simple classification, it can be divided into two main types: decorative and industrial. Decorative paints are usually applied to enhance the aesthetics of the structure/component, while industrial paints are mainly used for corrosion protection.

The second-best classification of paint coatings is based upon the type of resin (binder) it uses. Based upon the resin type, such as epoxy, urethane, vinyl, alkyd, or polyester, it is designated as epoxy coating, urethane coating, or vinyl-, alkyd-, or polyester-based coating, respectively. The main components of a paint coating are solvent, binder, pigment, and additives. A proper mixture of all these four makes a paint coating. The paint manufacturing is a simple mixing process where first the binder is added into the solvent and nicely dispersed. It is then followed by systematic addition of pigments and additives till a uniform mixture is obtained. The quality of paint depends upon the types of mixing methods used such as agitation, blending, attritions, ball, and bead mill, etc. (Made How, 2022).

The paint coatings are of a single component and of two components. Single-component paints are usually a mixture of solvent resin and some pigments and additives, while two-component paint systems have a resin part which is made using solvent, resin, pigments, and additives, and the second component is called catalyst or hardener, which is mixed with the resin part just before application. The role of catalyst/hardener is to harden the coating with time till it fully dries. This is achieved by chemical reaction between the resin and the hardener, leading to a high level of crosslinking, which provides superior anti-corrosion properties to the paint coating, especially low permeability and strong barrier protection. For example, for epoxy resins, amines or amides are used as hardeners. For two-component polyurethane coatings, cynates are used as hardeners.

3.3.1 GREEN COATINGS

Another important classification of paint coating is eco-friendliness of paint coatings. As discussed, the main components of paint coatings are solvent, binders, pigments, and additives. Based upon the amount of resin in the solvent and pigment and additive concentration, the paint has a volume solid percentage which decides the thickness of the coating after drying. As per the simplest mechanism of the paint drying process, the solvents, which are mostly volatile in nature, evaporate and leave the dried coating on the substrate. Since the most common solvents are benzene, xylene and toluene, which are toxic in nature, and hence, when they evaporate they pollute the environment and especially affect the health of applicators. Thus, a better paint system is that which either has very low quantity of solvent or has no solvent or uses alternative solvent such as water. This results in two additional types of classifications: solventless coatings and waterborne coatings. There are two additional advantages of solventless coatings: apart from eco-friendliness, they can give higher thickness from 500 to 2000 microns in one or more coat. Second, several high-performance and functional coatings used in industry are solventless with addition of several pigments such as fibres or glass flakes which enhance the durability of such coatings to a very long duration. **Figure 3.4** summarizes various paint coating classifications discussed here.

3.3.2 FUNCTIONAL/SMART COATINGS

Another classification of the coatings can be on its functional action and its smart behaviour. We have several coatings which come under the heading of smart coatings. These coatings, in addition

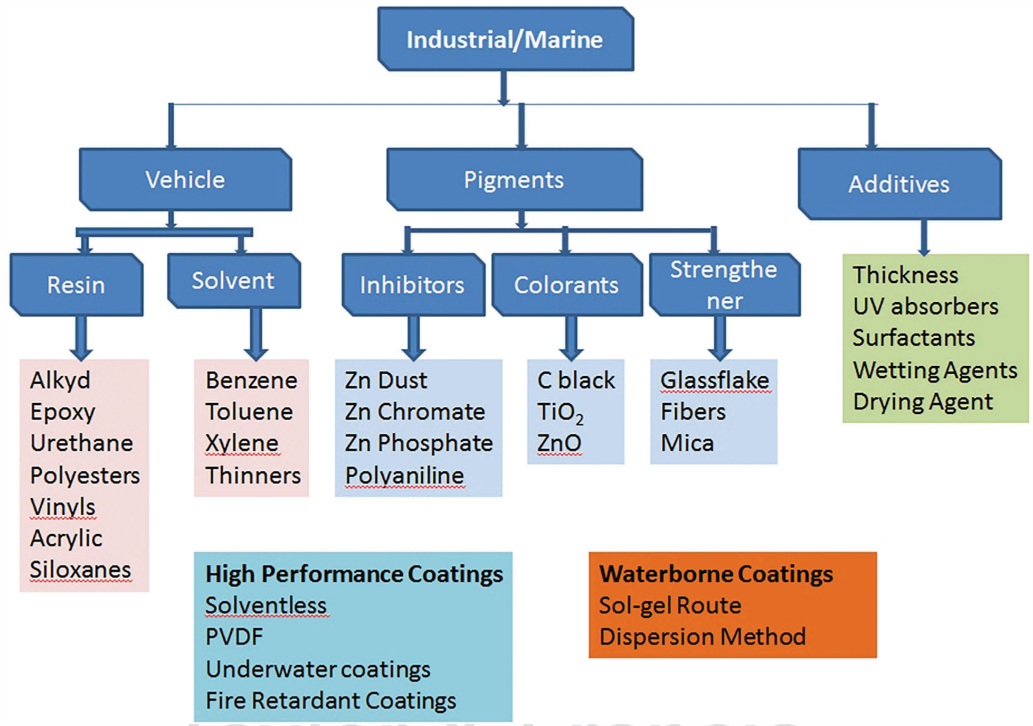


FIGURE 3.4 Classification of various paint coatings.

to doing the normal function of anti-corrosion, also do a specific function, such as self-cleaning (Verma et al., 2013), self-healing (Thanawala et al., 2014), or anti-graffiti (Adapala et al., 2015), creating a conducting surface and perhaps many more. The biggest role played to make a coating smart is by the addition of nanoparticles or to make a nano-coating by processes such as the sol-gel process.

3.3.3 Nano-Modified Coatings

The role of nanotechnology can be understood from **Figure 3.5**. As discussed, initial selection of coating is made based upon the chemistry of the resin, which decides how durable a coating is in a particular environment. Additional properties are decided by the choice of pigments and various additives. It is now established that as the particle size of the pigments/additives decreases, there is enhancement in the basic properties of the coating such as corrosion resistance, mechanical properties, and many specific properties such as fire resistance, waterproofing tendency, etc. It is now well established that size and shape of the nanoparticles is very important. The next important thing is the concentration of nanoparticles (Dhoke et al., 2009) (Gaur and Khanna, 2015).

Let us now first compare an epoxy coating where almost 10% micro-sized ZnO was added to take care of UV blocking resistance. Distribution of such particles in epoxy matrix is as shown in **Figure 3.6a**, which shows that even 10% of ZnO is unable to protect the epoxy matrix and it gets deteriorated when UV light falls on the matrix. Now consider the same case by taking now, 0.1% of nano ZnO particles with the achieved distribution as shown in **Figure 3.6b**. You would see that the matrix is almost covered by ZnO particles uniformly distributed in the resin matrix, so the chance of sunlight falling on the matrix is very low. Now take the third examples of 0.01% graphene particles (2D structure). They cover the whole surface in a still better way thus, showing that flat 2D graphene nanoparticles are even more effective, that too at a still lower concentration (**Figure 3.6c**).

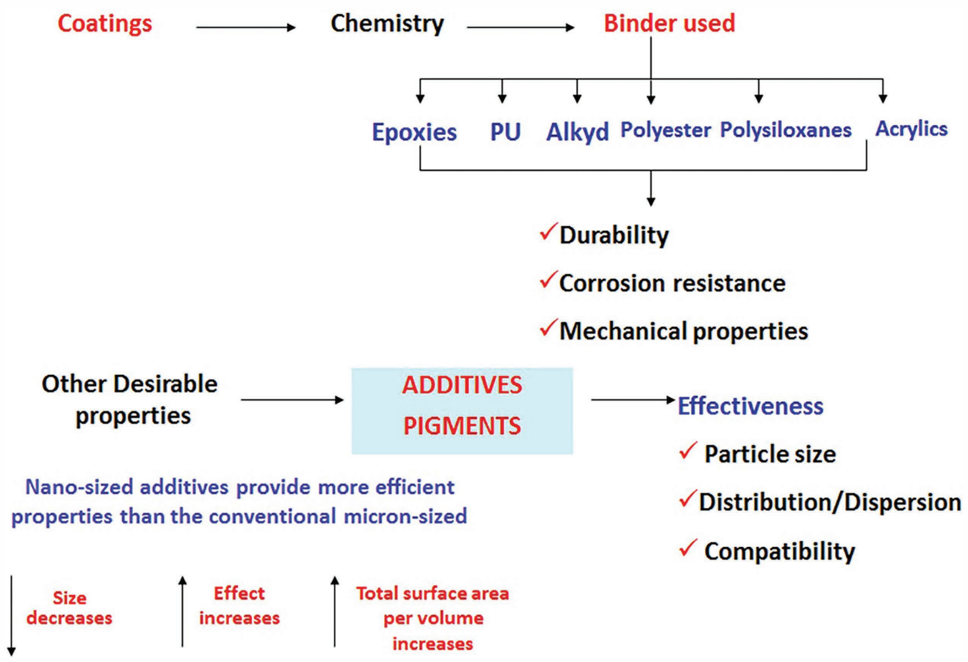
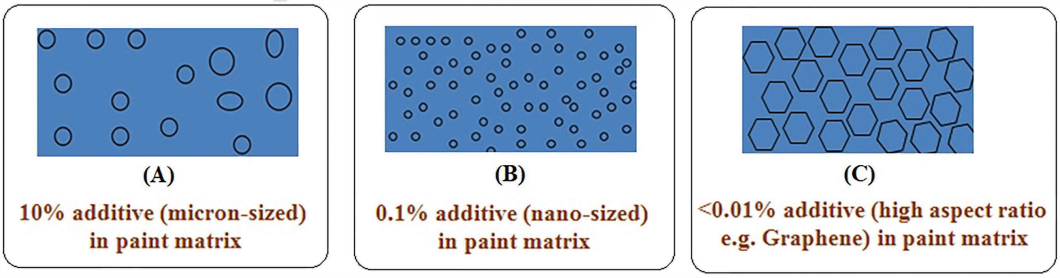


FIGURE 3.5 Concept of nanotechnology in paint coatings.


(A) 10% additive (micron-sized) in paint matrix

(B) 0.1% additive (nano-sized) in paint matrix

(C) <0.01% additive (high aspect ratio e.g. Graphene) in paint matrix

FIGURE 3.6 A simple way to show the effect of nanopigment additions, loading, and size effect.

Figure 3.7 shows some of the nanoparticles with different shapes and size, and **Figure 3.8** shows the effect of size and shape of nanoparticles in changing the effect of yellowness and % gloss due to UV light. It is very clear both size and shape and concentration affect the properties of the coating.

Another powerful method to develop high-performance coatings is to develop inorganic-organic thin coatings using the sol-gel method, which give excellent performance and functional applications such as water repellence, hydrophobicity, etc. (Pathak et al., 2006) (Wankhede et al., 2013).

3.4 CONCLUSIONS AND OUTLOOK

Surface engineering is the most powerful and essential branch of materials science, without which all material fabrications are incomplete. Its scope starts from cleaning to surface preparation and various kinds of surface treatments with and without changing the surface composition of the substrate. Various kinds of techniques are used for this purpose, starting from various cleaning

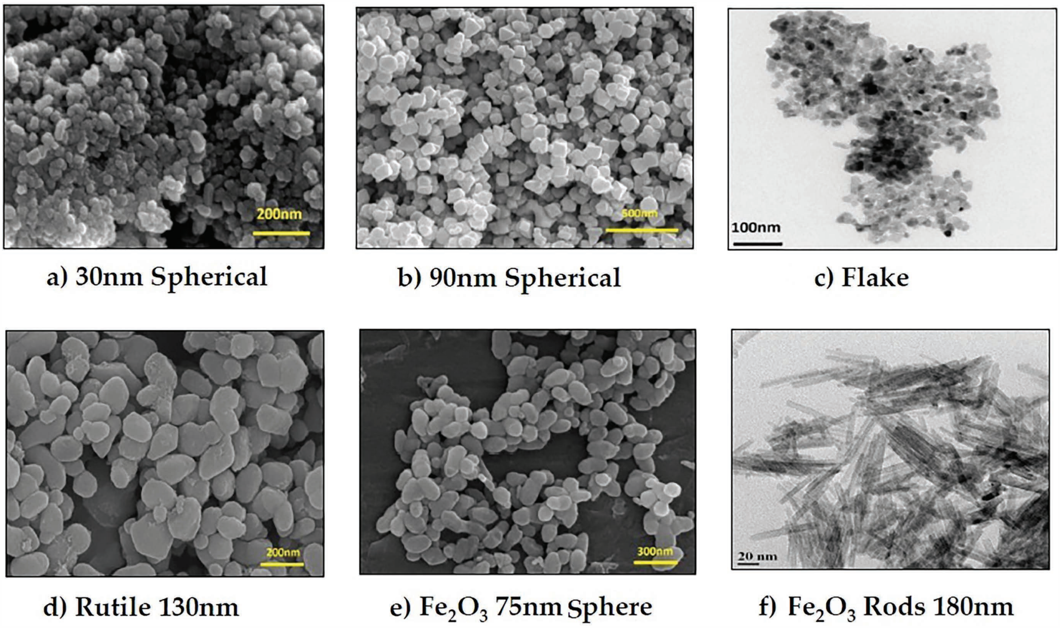


FIGURE 3.7 SEM images showing the size and shapes of different nanoparticles (Dolai and Khanna, 2021).

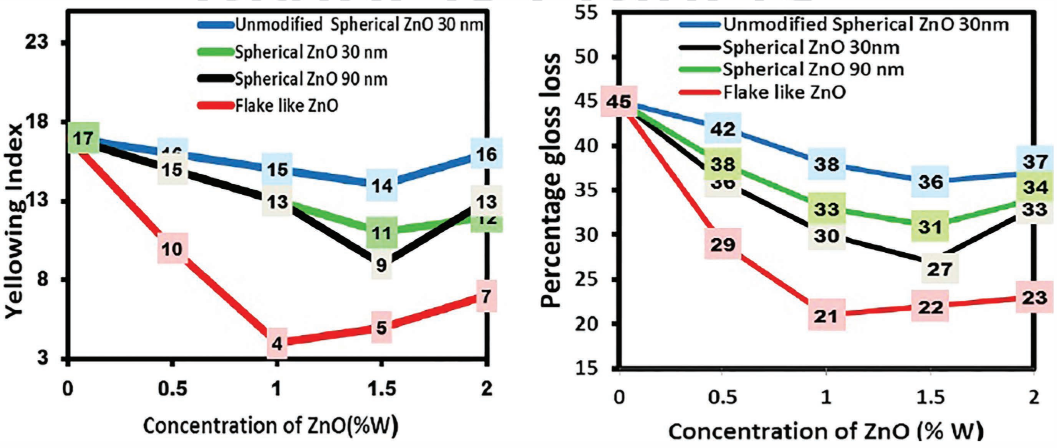


FIGURE 3.8 Effect of size, shape, and loading on the weathering properties of the paint coatings (Dolai and Khanna, 2021).

methods to surface treatments by heating, flame, lasers and all kinds of surface coating methods ranging from hot-dip to chemical conversion to PVD/CVD, thermal spray, and paint coatings.

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