CHAPTER

12

CLAYS AND ASSOCIATED MATERIALS IN SURFACE COATINGS AND PIGMENTS

12.1 PURPOSE OF SURFACE COATINGS

Coating indicates a covering applied to the surface of an object. In many cases, coatings are applied to improve surface properties of the substrate, such as appearance, adhesion and resistance against any type of corrosion or weathering. In other cases, coating forms an essential part of the finished product. Coatings may be applied as liquids, gases or solids. Surface coating—any mixture of film-forming materials plus pigments, solvents and other additives—when applied to a surface and cured or dried, yields a thin film that is functional and often decorative. Surface coatings include paints, drying oils and varnishes, synthetic clear coatings, and other products whose primary function is to protect the surface of an object from the environment. These products can also enhance the aesthetic appeal of an object by accentuating its surface features or even by concealing them from view. Most surface coatings employed in industry and by consumers are based on synthetic polymers, that is, industrially produced substances composed of extremely large, often interconnected, molecules that form tough, flexible, adhesive films when applied to surfaces. The other component materials of surface coatings are pigments, which provide colour, opacity, gloss and other properties; solvents or carrier liquids which provide a liquid medium for applying the film-forming ingredients; and additives which provide a number of special properties.

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Table 12.1: Functions of surface coatings

Properties	*Functions*
Melt-adhesive properties	For vacuum seal and heat seal applications
"Release" coatings	The liner of a double-sided tape or vinyl stickers
Low surface energy coatings	To act as a non-stick surface
Photo-sensitivity	For photographic film and paper
Water proofing coatings	For fabrics or paper, or on wood surfaces such as outdoor furniture, patio decks, yacht hulls and decks
Self adhesive properties	For tape, labels and packaging
Optical properties	Tint, colour, anti-reflection and holographic
Electronic properties	Passivity or conduction as with flexible circuits
Magnetic properties	For magnetic media like cassette tapes and floppy disks

12.2 CHEMICAL VAPOUR DEPOSITION

The chemical vapour deposition is discussed here as Metalorganic vapour phase epitaxy and Electrostatic spray assisted vapour deposition.

Metalorganic Vapour Phase Epitaxy

Metalorganic vapour phase epitaxy (MOVPE), also known as organometallic vapour phase epitaxy (OMVPE) or metalorganic chemical vapour deposition (MOCVD), is a chemical vapour deposition method of epitaxial growth of materials, especially compound semiconductors, from the surface reaction of organic compounds or metalorganics and metal hydrides containing the required chemical elements. For example, indium phosphide could be grown in a reactor on a substrate by introducing trimethylindium ($(CH_3)_3In$) and phosphine (PH_3). Formation of the epitaxial layer occurs by final pyrolysis of the constituent chemicals at the substrate surface.

Electrostatic Spray Assisted Vapour Deposition

Electrostatic spray assisted vapour deposition (ESAVD) is a technique to deposit both thin and thick layers of a coating on to various substrates. In simple terms when chemical precursors are sprayed across an electrostatic field towards a heated substrate, the chemicals undergo a controlled chemical reaction and are deposited on the substrate as the required coating. Electrostatic spraying techniques were developed in the 1950s for the spraying of ionized particles on charged or heated substrates.

ESAVD (branded by IMPT as Layatec) is used for various applications in many markets including:

- Thermal barrier coatings for jet engine turbine blades
- Electronic components

- Glass coatings (such as self cleaning)
- Corrosion protection coatings

12.3 PHYSICAL VAPOUR DEPOSITION

Physical vapour deposition (PVD) is a variety of vacuum deposition and is a general term used to describe any of a variety of methods to deposit thin films by the condensation of a vapourized form of the desired film material on to various workpiece surfaces (e.g., on to semiconductor wafers). The coating method involves purely physical processes such as high temperature vacuum evaporation with subsequent condensation, or plasma sputter bombardment rather than involving a chemical reaction at the surface to be coated as in chemical vapour deposition.

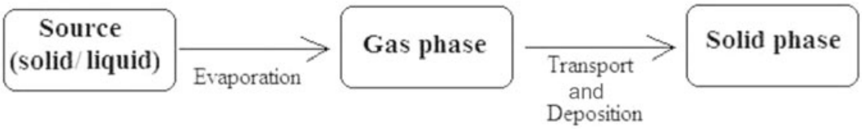

Fig. 12.1: Process flow diagram.

PVD is used in the manufacture of items including semiconductor devices, aluminized PET film for balloons and snack bags, and coated cutting tools for metalworking. Besides PVD tools for fabrication, special smaller tools mainly for scientific purposes have been developed. They mainly serve the purpose of extreme thin films like atomic layers and are used mostly for small substrates. A good example are mini e-beam evaporators which can deposit monolayers of virtually all materials with melting points up to 3500°C. The source material is unavoidably also deposited on most other surfaces interior to the vacuum chamber, including the workholders.

Table 12.2: Some techniques to measure the physical properties of PVD coatings

Techniques	*Purpose*
Calo tester	Coating thickness test
Pin on disc tester	Wear and friction coefficient test
Nanoindentation	Hardness test for thin-film coatings
Scratch tester	Coating adhesion test

12.4 CHEMICAL AND ELECTROCHEMICAL TECHNIQUES

Anodizing

Anodizing, or anodizing, is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts. The process is called “anodizing” because the part to be treated forms the anode electrode of an electrical circuit. Anodizing increases corrosion resistance and wear resistance, and provides better adhesion for paint primers and glues than does bare metal. Anodic films can also be used for a number of cosmetic effects, either with thick porous coatings that can absorb dyes or with thin transparent coatings that add interference effects to reflected light. Anodizing is also used to prevent galling of threaded components and to make dielectric films for electrolytic capacitors. Anodic films are most commonly applied to protect aluminium alloys, although processes also exist for titanium, zinc, magnesium, niobium and tantalum. Iron or carbon steel metal exfoliates when oxidized under neutral or alkaline microelectrolytic conditions; i.e., the iron oxide (actually “ferric hydroxide” or hydrated iron oxide, also known as rust) is formed by anoxic anodic pits and large cathodic surface. These pits concentrate anions such as sulfate and chloride accelerating the underlying metal to corrosion. Carbon flakes or nodules in iron or steel with high carbon content (high carbon steel, cast iron) may cause an electrolytic potential and interfere with coating or plating. Ferrous metals are commonly anodized electrolytically in nitric acid, or by treatment with red fuming nitric acid, to form hard black ferric oxide. This oxide remains conformal even when plated on wire and the wire is bent. Anodization changes the microscopic texture of the surface and changes the crystal structure of the metal near the surface. Thick coatings are normally porous, so a sealing process is often needed to achieve corrosion resistance.

Conversion Coatings

Conversion coatings are coatings for metals where the part surface is converted into the coating with a chemical or electro-chemical process. Examples include chromate conversion coatings, phosphate conversion coatings, bluing, black oxide coatings on steel, and anodizing. They are used for corrosion protection, increased surface hardness, to add decorative colour and as paint primers. Conversion coatings may be very thin, of the order of 0.00001″. Thick coatings, up to 0.002″, are usually built up on aluminium alloys, either by anodizing or chromate conversion.

Ion Beam Mixing

It is a process for adhering two multilayers, especially a substrate and deposited surface layer. The process involves bombarding layered samples with doses of ion radiation in order to promote mixing at the interface, and generally serves as a means of preparing electrical junctions, especially between non-equilibrium or metastable alloys and intermetallic compounds. Ion implantation equipment can be used to achieve ion beam mixing.

Tarnision

It is a metal surface treatment used to remove impurities, such as stains, inorganic contaminants, rust or scale from ferrous metals, copper and aluminum alloys. A solution called tarnision liquor, which contains strong acids, is used to remove the surface impurities. It is commonly used to descale or clean steel in various steelmaking processes.

Plating

It is a surface covering in which a metal is deposited on a conductive surface. Plating has been done for hundreds of years, but it is also critical for modern technology. Plating is used to decorate objects, for corrosion inhibition, to improve solderability, to harden, to improve wearability, to reduce friction, to improve paint adhesion, to alter conductivity, for radiation shielding, and for other purposes. Jewellery typically uses plating to give a silver or gold finish. Thin-film deposition has plated objects as small as an atom; therefore plating finds uses in nanotechnology. There are several plating methods, and many variations. In one method, a solid surface is covered with a metal sheet, and then heat and pressure are applied to fuse them (a version of this is Sheffield plate). Other plating techniques include vapour deposition under vacuum and sputter deposition. Recently, plating often refers to using liquids. Metallizing refers to coating metal on non-metallic objects.

Sol-gel

The sol-gel process is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically metal oxides) starting from a colloidal solution (sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal salts (such as chlorides, nitrates and acetates), which undergo various forms of hydrolysis and polycondensation reactions.

12.5 SPRAYING

Thermal Spraying

Thermal spraying techniques are coating processes in which melted (or heated) materials are sprayed on to a surface. Thermal spraying can provide thick coatings (approx. thickness range is 20 micrometres to several mm, depending on the process and feedstock), over a large area at high deposition rate as compared to other coating processes such as electroplating, physical and chemical vapour deposition. Coating materials available for thermal spraying include metals, alloys, ceramics, plastics and composites. They are fed in powder or wire form, heated to a molten or semimolten state and accelerated towards substrates in the form of micrometre-size particles. Combustion or electrical arc discharge is usually used as the source of energy for thermal spraying. Resulting coatings are made by the accumulation of numerous sprayed particles. The surface may not heat up significantly, allowing the coating of flammable substances. Coating quality is usually assessed by measuring its porosity, oxide content, macro- and micro-hardness, bond strength and surface roughness. Generally, the coating quality increases with increasing particle velocities.

Several variations of thermal spraying are: Plasma spraying; Detonation spraying; Wire arc spraying; Flame spraying; High velocity oxy-fuel coating spraying (HVOF); Warm spraying; and Cold spraying.

Plasma Spraying

In plasma spraying process, the material to be deposited typically as a powder, sometimes as a liquid, suspension or wire, is introduced into the plasma jet, emanating from a plasma torch. In the jet, where the temperature is of the order of 10,000 K, the material is melted and propelled towards a substrate. There the molten droplets flatten, rapidly solidify and form a deposit. Commonly, the deposits remain adherent to the substrate as coatings; free-standing parts can also be produced by removing the substrate. There are a large number of technological parameters that influence the interaction of the particles with the plasma jet and the substrate and therefore the deposit properties. These parameters include feedstock type, plasma gas composition and flow rate, energy input, torch offset distance, substrate cooling, etc.

12.6 OPTICAL COATING

An optical coating is one or more thin layers of material deposited on an optical component such as a lens or mirror, which alters the way in which the optic reflects and transmits light. One type of optical coating is an antireflection coating, which reduces unwanted reflections from surfaces, and is commonly used on spectacle and photographic lenses. Another type is the high-reflector coating which can be used to produce mirrors which reflect greater than 99.99% of the light which falls on them. More complex optical coatings exhibit high reflection over some range of wavelengths, and anti-reflection over another range, allowing the production of dichroic thin-film optical filters.

12.7 CHARACTERISTICS OF PIGMENTS

A pigment is a material that changes the colour of reflected or transmitted light as a result of wavelength-selective absorption. This physical process differs from fluorescence, phosphorescence, and other forms of luminescence, in which a material emits light. Many materials selectively absorb certain wavelengths of light. Materials that humans have chosen and developed for use as pigments usually have special properties that make them ideal for colouring other materials. A pigment must have a high tinting strength relative to the materials it colours. It must be stable in solid form at ambient temperatures. Pigments are used for colouring paint, ink, plastic, fabric, cosmetics, food and other materials. Most pigments used in manufacturing and the visual arts are dry colourants, usually ground into a fine powder. This powder is added to a vehicle (or binder), a relatively neutral or colourless material that suspends the pigment and gives the paint its adhesion.

12.8 CONSTITUENTS OF PIGMENTS

The iron oxides minerals which form the major constituents of pigments are hematite, magnetite and goethite. Limonite, often used in the description of pigments, is a hydrated iron oxide of poor crystallinity and consists mainly of goethite or lepidocrocite.

Table 12.3: Physical properties of iron oxides and hydroxides minerals

Mineral	*Hardness*	*Specific gravity*	*Refractive index*	*Colour*
Hematite	5-6	5.25	2.87-3.22	Light red to dark violet
Goethite	5-5.50	4.3	2.26-2.51	Green yellow to brown yellow
Lepidocrocite	5	4.09	1.94-2.51	Yellow to orange
Magnetite	7.50-8	5.20	2.42	Black
Maghemite	7.50-8	4.88	2.52-2.74	Brown to orange brown

12.9 PHYSICAL BASIS

Pigments appear in the colours they are because they selectively reflect and absorb certain wavelengths of visible light. White light is a roughly equal mixture of the entire spectrum of visible light with a wavelength in a range from about 380 or 400 nanometres to about 760 or 780 nm. When this light encounters a pigment, parts of the spectrum are absorbed by the chemical bonds of conjugated systems and other components of the pigment. Some other

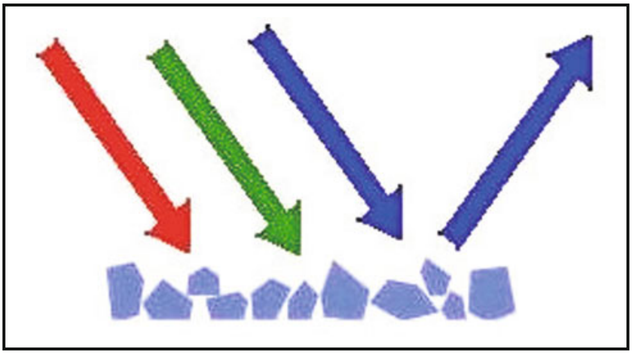

Fig. 12.2: A wide variety of wavelengths (colours) encounter a pigment. This pigment absorbs red and green lights, but reflects blue, creating the colour blue.

wavelengths or parts of the spectrum are reflected or scattered. Most pigments are charge transfer complexes, like transition metal compounds, with broad absorption bands that subtract most of the colours of the incident white light. The new reflected light spectrum creates the appearance of a colour. Ultramarine reflects blue light, and absorbs other colours. Pigments, unlike fluorescent or phosphorescent substances, can only subtract wavelengths from the source light, never add new ones. So a *blue pigment* is *blue* because it doesn't reflect *red* and *green* lights, or because it reflects all colours but the complementary of the *blue* one, which is *orange*. The appearance of pigments is intimately connected to the colour of the source light. Sunlight has a high colour temperature, and a fairly uniform spectrum, and is considered a standard for white light. Artificial light sources tend to have great peaks in some parts of their spectrum, and deep valleys in others. Viewed under these conditions, pigments will appear different colours.

Colour spaces used to represent colours numerically must specify their light source. Lab colour measurements, unless otherwise noted, assume that the measurement was taken under a D65 light source, or "Daylight 6500 K", which is roughly the colour temperature of sunlight.

Other properties of a colour, such as its saturation or lightness, may be determined by the other substances that accompany pigments. Binders and fillers added to pure pigment chemicals also have their own reflection and absorption patterns, which can affect the final spectrum. Likewise, in pigment/binder mixtures, individual rays of light may not encounter pigment molecules, and may be reflected as it is. These stray rays of source light contribute to the saturation of the colour. Pure pigment allows very little white light to escape, producing a highly saturated colour. A small quantity of pigment mixed with a lot of white binder, however, will appear desaturated and pale, due to the high quantity of escaping white light.

12.10 MANUFACTURING AND INDUSTRIAL STANDARDS

Before the development of synthetic pigments, and the refinement of techniques for extracting mineral pigments, batches of colour were often inconsistent. With the development of a modern colour industry, manufacturers and professionals have cooperated to create international standards for identifying, producing, measuring, and testing colours. First published in 1905, the Munsell Colour System became the foundation for a series of colour models, providing objective methods for the measurement of colour. The Munsell system describes a colour in three dimensions—hue, value (lightness) and chroma (colour purity)—where chroma is the difference from gray at a given hue and value. Many manufacturers of paints, inks, textiles, plastics, and colours have voluntarily adopted the Colour Index International (CII) as a standard for identifying the pigments that they use in manufacturing particular colours. First published in 1925, and now published jointly on the web by the Society of Dyers and Colourists (United Kingdom) and the American Association of Textile Chemists and Colorists (USA), this index is recognized internationally as the authoritative reference on colourants. It encompasses more than 27,000 products under more than 13,000 generic colour index names.

12.11 ATTRIBUTES OF PIGMENTS

The following are some of the attributes of pigments that determine their suitability for particular manufacturing processes and applications:

- Lightfastness and sensitivity for damage from ultra violet light
- Heat stability
- Toxicity
- Tinting strength
- Staining
- Dispersion
- Opacity or transparency
- Resistance to alkalis and acids
- Reactions and interactions between pigments

12.12 BIOLOGICAL PIGMENTS

In biology, a pigment is any coloured material of plant or animal cells. Many biological structures, such as skin, eyes, fur and hair contain pigments (such as melanin). Animal skin colouration is often achieved with specialized cells called chromatophores, which in animals such as the octopus and chameleon can be controlled to vary the animal's colour. Many conditions affect the levels or nature of pigments in plant, animal, some protista, or fungus cells. For instance, Albinism is a disorder affecting the level of melanin production in animals. Pigmentation is used in organisms for many biological purposes including camouflage, mimicry, aposematism (warning), sexual selection and other forms of signalling, photosynthesis (in plants), as well as basic physical purposes such as protection from sunburn. Pigment colour differs from structural colour in that it is the same for all viewing angles, whereas structural colour is the result of selective reflection or iridescence, usually because of multilayer structures. For example, butterfly wings typically contain structural colour, although many butterflies have cells that contain pigment as well.

12.13 USING PIGMENTS

Add the pigment to the slip and sieve through a 120× mesh screen to ensure adequate dispersion. Depending on the use, pigments may be used straight and just mixed with water, but they are more commonly added as colourants in clay bodies and glazes. Some pigments are specifically formulated for clay bodies while some are not suitable at all. When used in clay, pigments are usually used in engobes and slips as a coating for clay rather than pigmenting the entire body.

When using pigments in glazes, usually in concentrations of 1-10%, a little more care must be taken because some pigment systems react with materials in a glaze. Some pigments are affected by the presence, or lack of, boron, zinc, calcium and magnesia. Manufacturers provide information on specific reactions. While most pigments can be used in both oxidation and reduction atmospheres, some are limited to certain maximum temperatures. Again, this information is available from manufacturer websites. To achieve a wider palette, most pigments can be mixed to achieve even more colours. The exception is that black pigments cannot be used to obtain shades of gray because blacks are made from a combination of several metallic oxides. If low percentages are used, the final colour is affected by the predominant oxide in the black pigment.

12.14 KAOLIN CLAY AND ITS FEATURES

Clay, mainly Kaolin is used in pigment to form it as a paste like material, by increasing its density. The important features of kaolin clay are its purity, high brightness, easy dispersion, accurate chemical composition and capacity to withstand high temperature.

Table 12.4: Physical properties of kaolin clay

Contents	*Percentage*
Moisture	1.37%
pH of 10% solution	7 to 8
Bulk density	0.47 g/cc
Oil absorption	35 to 40%
Water absorption	29.94%
Loss on ignition	12.10%

Table 12.5: Chemical composition of kaolin clay

Contents	*Percentage*
Al_2O_3	33.67%
SiO_2	50.40%
Fe_2O_3	1.28%
CaO	0.20%
TiO_2	1.50%
MgO	0.30%
Na_2O	0.12%
K_2O	3.00%

12.15 SOME TYPES OF PIGMENTS

Using clay some pigments are formed and they are differentiated according to their physical and chemical properties and uses. These are highlighted below.

Ultra Marine Blue Pigment

Kaolin clay acts as ingredients for forming ultramarine blue pigments, which has dark blue colour. Best quality ultramarine blue is used in all types of laundry while technical and industrial grades for applications in coating, cosmetic, ink and plastic pigments.

High Whiteness Pigment

Calcined kaolin clay acts as ingredients, used in formation of washing powder and liquid blue. It is composed of Fe_2O_3, Al_2O_3, TiO_2 and moisture content. Whiteness and fine particles are main two characteristic features of it. Percentage of physical property and chemical composition are listed in Table 12.6.

Table 12.6: Chemical composition and physical properties of high whiteness pigments

Chemical compositions (%)		*Physical property (%)*	
Al_2O_3	36	Particle size -2 μm	70-75
TiO_2	0.2	Particles >45 μm	0.05
Fe_2O_3	0.75	Whiteness (%)	85
pH	4.0-6.0	Moisture (%)	2

N0842, Kaolin Clay Powder for Pigment

Main ingredients of formation of this type of pigments are kaolin clay. It is the best pigment, extender and filler in water-based coating. It is used in paper formation.

Table 12.7: Chemical components and percentage of kaolin clay

Chemical component	*Percentage of component*
Al_2O_3 content	32-38%
Moisture content	7-27%
TiO_2 content	<0.5%
K_2O content	<0.05%
Whiteness	85

China Clay

It is produced with calcined kaolin having high and standard brightness kaolin. It is used for paints, paper, plastics, rubber, pigments, fertilizers, pesticides, pharmaceuticals, cosmetics and medical.

Table 12.8: Chemical components and percentage of China clay

Chemical component	*Percentage of component*
SiO_2 content	45.8%
Fe_2O_3 content	0.21%
Al_2O_3 content	37.8%
Moisture content	1%
TiO_2 content	0.8%
K_2O content	0.065%
Whiteness	84-86

12.16 APPLICATIONS OF KAOLIN CLAY

- Used in paints for lending excellent exterior durability and archeological improvement
- Acts as an essential ingredient of oil-based and water-based paints
- Used as a coating pigment in the manufacture of coated paper and boards
- Demanded by the rubber industry to improve the impact resistance, tensile strength, hardness and abrasion of rubber
- Extensively used in PVC wires, inks, adhesives, toothpaste, soaps, etc.

QUESTIONS

1. How does functions of surface coatings relate with their properties.
2. What is physical vapour deposition? Explain with the help of diagram.
3. What are anodizing and spraying?
4. Briefly explain: attributes and constituents of pigments.
5. What are the various types of constituting clay and their percentage?
6. How does wavelength of colour influence the pigment?

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