# Surface Engineering Terminology and Description

*The deposition of a metallic coating onto a metallic or non-metallic substrate, or the application of an organic coating to a metallic or non-metallic substrate, or the treatment of a metallic substrate by the use of a physical, chemical or mechanical process, to enhance the appearance, function or performance of a product and to give added value and promote marketability.*

## INTRODUCTION

The term Metal Finishing is of long standing acceptance and remains in common use despite some inaccuracy. Metal is no longer the dominating Material of engineering construction and metal is no longer the main coating material used in finishing operations. Finishing is appropriate because the last operation applied to an engineering component, with only a few exceptions often involving heat treatment, is that to the surface relating to its appearance or performance. A definition might be:
*The deposition of a coating (metallic or non-metallic) on to a substrate (metallic or non-metallic), or a surface treatment yielding a thin film, to enhance the appearance, function or performance of a product and to give added-value and increased marketability.*
A generic name has become common, as a consequence, and Surface Engineering has come to imply the design and manufacture of a surface for engineering property advantage. Equally valid is the use of Surface Technology for the means by which the manufacture is achieved or Surface Science for the study of the structure and properties of the surface. Name change has been slow and not yet fully accepted.

## SURFACE PREPARATION

An old axiom is as true today as when it was first stated:
A coating is only as good as the surface on which it is laid.
While it is widely believed that a coating is a disguise or a shield for a poor surface this is not true despite it working in a few cases. The substrate surface should always be clean, free of corrosion product, free of old coating, blemish-free, smooth, level and preferably bright. To achieve this surface preparation may include operations such as the following.
Cleaning by organic solvent degreasing or by aqueous alkali detergent treatment, both processes aided by higher temperatures and scrubbing actions including ultra-sonic agitation to remove physically attached soils.
Pickling, usually, but not exclusively, by acids, to remove chemically attached soils such as tarnish, hot scale and corrosion products. If degraded coating is present the pickle process may involve several stages as a universal solution is unlikely to exist.
In situations where such chemical processes are unacceptable, typically re-coating large engineering assemblies other physical and mechanical methods can be used.
Flame cleaning where an oxy-acetylene flame utilises heat and jetting to expand and 'blow-off' soil. While useful it is not a superior technique.
Shot blasting, with air or water medium, to remove gross scale. Widely used for bridges, buildings etc to good effect. Wire power tool abrasion is an easy DIY technique allowing continual inspection of the surface but is generally regarded as a poor technique and is likely to leave the surface damaged.
In every case the preferred technique and solution used must be carefully selected or designed. There is no universal process in existence!

## SURFACE PRETREATMENT

When the surface is clean a second step must be taken as soon as possible because surface deterioration, especially by polluted atmospheres, can be rapid. Because the substrate surface does affect the final properties, this is the stage to commence that influence. Pretreatments come in several categories.

Corrosion control requires chemical treatments to stabilise the surface against deterioration before the first real coating layer is applied. Conversion coatings or etch-primer types of treatment are used but which are primarily exploited for subsequent organic or paint finishes. The commonest conversion coatings are Phosphating and Chromating but others such as Oxalating have found specialist uses.

Chemical Etching can be employed to develop various levels of matt finish which are then perpetuated through thin overlay coatings. With thicker coatings the etch profile of roughness is gradually lost. Such matt finish production is probably most effective on aluminium and is widely used for internal and architectural applications of anodised finish.

Polishing was traditionally carried out manually as a labour-intensive operation. Nowadays chemical and electrochemical polishing is preferred but because the chemicals used are generally strong acids the fume and effluent disposal considerations are significant.

Mechanical modification, usually to develop ‘brushed’ finishes, can be achieved using steel wire brushes and roll embossing where the rolls have been brushed or shot-blasted. An attractive appearance can be produced through thinner coatings but the surface will be in compressive stress which may be a consideration. Heavy shotblasting can be employed as a means of promoting keying for paint or adhesion for polymer lamination and cladding; here the role of any adhesive must be recognised.

## DESIGNING A COATING SYSTEM

There are up to five stages in the design of a coating system once the purpose has been defined and the anticipated life decided. Those stages are:

1. Surface preparation for cleanliness
2. Surface pre-treatment
3. Application of a first ‘strike’ or ‘primer’ layer on the substrate
4. Application of the main underlayer to influence long term service
5. Application of the final topcoat giving the full surface properties

A product specification should consider all these stages, although not necessarily specify all. It should specify thickness of each layer and acceptable variability, roughness or brightness or opacity, any other special requirement such as lubricity, solderability, contact resistance etc. Use of International Standards is an obvious starting point and it is common to cite these wholly or partly in commercial contracts.

The specification should also specify a preferred coating method or name acceptable alternatives if this is feasible. In practice so many other considerations including cost may have already pre-decided the probable preferred method and choice is not appropriate.

## ELECTRODEPOSITION

In commercial terms electrodeposition or electroplating (or just plating) commenced in 1839-1840 in the UK and Russia using gold and silver on copper or brass for tableware, ornaments etc. Within ten years other metals (eg. zinc and cadmium) were depositable joined later by copper and nickel. Of the major metals, chromium was perhaps the last to be widely used (from 1930 onwards). In terms of area covered tin is the most used largely through its use on steel as tinplate for the canning industry, but because its average thickness is 1-2μm only the tonnage may not be greatest. Since 1950 the changes which have been experienced relate to the rise of electronic plating and contacts and connectors, the drop in automotive trim plating (ie. Ni, Cr), introduction of new alloys beyond brass, bronze and solder, and some specialist metals (eg. indium, palladium). There is also the fall of

cadmium and lead for environmental/toxicity reasons with some other metals under attack. The thickness range usually specified is 1-20µm; below that range the porosity is too great, above that range other technologies may be more cost-effective. (Exceptions can be found of course including hard chromium up to 500µm, electroformed nickel, gravure copper etc).The applications common come in a number of categories:
Decorative/aesthetic cosmetic marketable appearance
Functional/engineering corrosion and wear resistant
Electronic circuitry Printed Circuit Boards, Connectors and contacts
Repair/reclamation refurbishment of worn parts, recovery of tolerance
Manufacturing Electroforming
Economic Cheaper (eg. steel) substrates, expensive coating (eg. tin)

Advances are in constant study and review. Amongst present interest are new alloys, composite deposits in which particles are embedded in the metal deposit, use of pulsed currents to enhance deposition and deposit properties.

The process of electrodeposition requires a number of critical items of equipment each of which must be carefully selected, installed and used.
Solution choice relates to the ability to dissolve the metal to be deposited and the use of conductivity and pH salts to optimise its character, the addition of organic additives to improve metal distribution, appearance and stress. Each metal’s requirement is different.
The cathode (negative electrode) is the workpiece which must be conductive.
The anode (positive electrode) may be soluble to replenish the solution with metal ions, or insoluble to allow current to be passed while oxygen is evolved.
The direct current is supplied by a transformer-rectifier set, typically at 12V up to 1000A. Current control is necessary; current and amp-hours are measured and recorded.
The tank must be inert. It is traditionally mild steel lined with rubber or polypropylene but nowadays more commonly PVC or solid polypropylene. It is filled with an inert immersion heater and cooling coils. Agitation is traditionally by air sparging or cathode movement but enhanced agitation can be achieved by directed jetting using flow eductors.
Solution is circulated through a filter to remove insoluble particles and incipient sludges. An effluent routing is required for overspill and dragouts.
Workpieces are suspended from busbars on jigs which are carefully designed to ensure easy mounting and good deposit coverage. Large numbers of small components can be placed in rotating barrels with cathodic connection, the walls of which are permeable to solution from its submerged position and in which the cathode contactor is dangled in the work and anodes placed outside.
Fume extraction is mandatory and usually from the tank edge.

## IMMERSION DEPOSITION.

In electrodeposition ion reduction is ensured by delivery of electrons by the current. An alternative source of electrons could be a dissolving/corroding substrate. Thus immersion deposition is driven by substrate dissolution but limited by the deposit slowly covering the substrate. Consequently, immersion deposition yields thin layers, typically not one atom thick but not above 1µm, which are like precipitates, ie. amorphous, non-adherent and generally poor for engineering purposes.

## ELECTROLESS DEPOSITION.

The name electroless arises from the discoveries of Brenner in 1945 in the USA: it really means electrodeposition less a current. As in Immersion Deposition an alternative reduction reaction must be sought and in this case it is a reducing agent in solution. A few such chemicals have been identified and include formaldehyde, hydrazine, and sodium hypophosphite. The deposition is not so spontaneous that it will take place throughout the tank but is catalysed by the metallic surface to be coated after which it is autocatalytic. Appreciation of this feature led to the development of plating on to plastic and glass surfaces a vital part of which is impregnation of an etched surface with catalyst atoms, usually palladium for rapid response.

Deposition is slow (eg. 1-10µm/hr) and can only be accelerated by use of high temperature. The deposit may contain reduction agent residues such as phosphorus from hypophosphite: this can be exploited by post-deposition heat treatment to substantially improve hardness and wear resistance through precipitation of phosphides in nickel.

The development of electroless copper solutions has been important in the rise of additive printed circuit board processing.

## ‘PHORETIC’ PAINT DEPOSITION

### Electrophoretic Deposition.

Electrodeposition uses current to reduce ions from solution to the metallic state as a deposit. Electrophoresis uses charged particles, the charges carrying the particles with them to the electrode surface. Consequently, the deposit builds up as consolidated particles and is self limiting at 5-20 particles thick, typically based on a particle size of 1-5µm. The particles are in suspension in a covalent medium (eg. organic solvent) and the charge is provided by traces of metal salt. The particles move slowly (cathodic or anodic depending on the charge) under high dc voltage, eg. 200-500V, but very low current, eg, 5-50mA.

The best known commercial success is so-called e-paint or electropaint which as a primer layer on car bodies can access crevices and box sections with large protection capability.

### Autodeposition

Autodeposition, often miscalled autophoretic, is becoming more widespread, in particular where the absence of external power source is a cost advantage. Only ferrous substrates can be treated. The process is simple and requires only four basic steps – clean, coat, rinse and bake (stove). The baths are mildly acidic and the iron released from the steel substrate immersed in the bath destabilises the paint in the vicinity of the steel surface and causes coagulation and deposition of paint onto the articles being processed. Similar to electrophoretic deposition, the process 'deposits where it wets’ thus throwing power is not a problem. Giving thicknesses in the range of 15 – 25 microns.

## ANODIZING

Anodizing was developed in the 1920s for aluminium by recognising that the protective oxide film needed to be formed under processing conditions, not natural exposure, whereby with sealing it could offer excellent guaranteed corrosion protection. The process is electrolytic (anodic) using sulphuric, chromic, oxalic or phosphoric acids depending on product requirements and yields a porous film which may be dyed or impregnated with wax, oil etc prior to sealing in a dip process which could be simply boiling water. An expansion in cold ‘chemical’ sealing using nickel fluoride salts has been encouraged by energy considerations but is generally limited to architectural; finishes. The natural film colour is grey and thicknesses of 1-50µm are normal. By using low temperature processing (eg. <0°C) less porosity is present and harder films result. At high temperatures (eg. >60°C) film formation becomes negligible and anodic dissolution dominates.

It is often claimed that over half of all aluminium is anodised for one purpose or another in the fields of decorative/coloured work, architectural, functional engineering. A separate application is for electronic capacitors where, with anodizing in boric acid, a pore-free film is formed giving highly predictable capacitance values.

Recent interest has been related to superior hard surfaces for which a Plasma Anodizing process has been developed notably as Keronite.

## CONVERSION COATING

A conversion coating process converts an active corroding surface into a passive film-protected surface by formation of an oxide-type film using an oxidising acidic solution. Hence Chemical Conversion and Phosphating and Chromating.

The processing is usually dip or spray but can be accelerated with chemical additives, high temperature and application of a current. The process is slow but simple, the film formed rather thin (eg. 0.1-5μm), and the protection offered not great. But in combination with a primer paint considerable synergy can be achieved.

Several variants exist but it is most widely used on steel and zinc notably galvanised steel and zinc and zinc alloys used on components notably fasteners.

## HOT DIP COATING

Use of a molten metal as coating material immediately places severe thermal limits on the substrate. Consequently, as steel is the commonest substrate and would be seriously softened by annealing if subjected to coating above 720°C, the technique is limited to tin, lead, zinc and aluminium. The first two are now much less used, the last has an important niche in high temperature erosion oxidation conditions (eg. ovens, fume extractors, exhaust pipes) leaving zinc as the major product. It is likely that as much as 20% of all steel is coated with zinc, at least half of which is hot dipped. The applications include steel structural work, bridges, oil rigs, industrial building, agricultural building etc. Coatings up to 100μm thick are possible giving structural lives of up to 50 years with paint. It should be noted that the act of hot dipping causes interdiffusion to take place, thereby providing superior adhesive bonding of coating to substrate, but the formation of a brittle intermetallic layer reduces its formability substantially. Thus steps must be taken to minimize diffusion for sheet and wire products required to be deformed during final fabrication.

Is there a cold dip coating process? Yes, but not using a metal. Notably paint processes still use dipping especially when a thick coating is required. But the analogy ends there because no diffusion is involved.

## THERMAL SPRAYING

Thermal or Metal Spraying utilizes metal in powder or wire form and feeds it into a hot spray gun from which it is fired at the cold substrate. On impact it rapidly solidifies forming a coherent coating. The gun is traditional energised by oxy-acetylene which uses the combustion gases as a flow medium. In this format it has long been used for zinc or aluminium coating of assembled structures for which the portable nature of the gun is advantageous if cumbersome.

The deposit character can be varied considerably by the coating variables of melt temperature, gun to target distance, time of solidification etc. But the greatest development has been the recognition that by using much higher gun temperatures coating can be achieved using high melting point metals and even ceramics such as carbides. Such guns use plasma melting or detonation technology to create melt zones at over 5000°C. In this format the main applications are not as a portable technique but for factory application of hard facings both on large components such as axles and selective coating of special shapes such as jets and nozzles, and cutting tools.

## MECHANICAL PLATING

Bonding energy need not come exclusively from high temperatures. The tumbling of small parts in a barrel has long been practiced for polishing and electroplating but the possibility of using not water or bran as a medium but metal powder was an important niche development in the period 1960-75. The metal powder could be almost any metal or alloy and the coating could be 5-20µm thick. However, its most favoured applications were for high tensile steel fasteners which were susceptible to hydrogen embrittlement during electroplating with cadmium or zinc. The absence of water ensured the absence of hydrogen, so no embrittlement will be experienced.

## CLADDING

. Evidence of the original clad processes can be found in the ancient civilizations where beating of silver or gold foils on to preformed substrates was a well-established art and craft for tableware and hollowware. In the UK its culmination was Sheffield Plate and Thomas Boulsover's tradition of applying silver to copper using a bed of lead for the hammering. The fact that hammering led to interfacial heating and hence bonding was well-known but its demise was due to economics so that when Elkingtons discovered electroplating as a faster and more economic use of silver (ie. thinner coating for better appearance) Sheffield Plate was doomed.
An exciting new development from Belfast has been explosion cladding and forming where a small charge of explosive in a confined chamber provides one intense energy shock which can shape and bond and offer some new opportunities.

## DIFFUSION COATING

Adhesion of a coating to a substrate usually depends upon either good mechanical keying or chemical bonding. But a third option is to create metallic covalent bonding by diffusing the coating and substrate together. This requires thermal energy provided by heat treatment typically of several hours at an elevated temperature which is often related to the melting point of one component metal, eg 0.5Tm where Tm is the melting temperature in degrees Kelvin. The depth of diffusion is dependent on time and the diffusion layer could consist of intermetallic compounds which are hard and relatively noble but brittle.
Such diffusion may be an integral part of the coating process as in hot dip coating of steel with zinc, aluminium, lead or tin, but may be a deliberate step to increase product performance, eg. chromising (chromium on steel) for high temperature oxidation resistance.

## CHEMICAL VAPOUR DEPOSITION

Coating metal can be delivered to a substrate surface through liquid or gaseous media. The former is typified by electroplating and the latter by chemical and physical vapour deposition. In the case of CVD the key to delivery is identification of a suitable vapour transport compound which can be formed and decomposed by use of temperature or pressure differences. The most famous example is the use of nickel tetracarbonyl which is a gas formed at 45C and decomposed at 180C at atmospheric pressure. Or alternatively, at ~120C it is formed at high pressure and decomposed at low pressure.
$Ni + 4CO = Ni(CO)_4$
Thus nickel can be transported through the vapour phase at modest temperatures. The success of CVD has been to enable high melting point metals to be applied as coatings (eg. Mo, W, Ta, Nb, Ti etc) at modest processing temperatures or to coat non-conducting substrates. Besides carbonyls, other convenient volatile compounds include chlorides and iodides. It is worth remembering that the classical processes of case-hardening, ie. carburising and nitriding, can be CVD processes where the

vapour transport compounds are carbon monoxide and ammonia respectively. The convenience of such processes is related to the ability to form the compound and the need to use multi-zone pressure vessels with rapid heating and rapid change of samples. By using mixed gases alloy or ceramic deposits can be easily produced, eg. carbides or nitrides.

## PHYSICAL VAPOUR DEPOSITION.

In PVD processes metal is vapourised in a low pressure or vacuum chamber and because no toxic chemicals are involved it is sometimes regarded as more environmentally-friendly than CVD but the chamber costs can be greater. Metal is vapourised by Evaporation from a filament or crucible or by Sputtering from a target which is bombarded by gaseous ions generated by an ion gun or plasma. The process is relatively slow thus enabling thin layers to be deposited in a controlled manner which has been a powerful technique in semi-conductor production.
A number of variations on the basic processes have been developed; eg. ion plating, and process enhancement has been possible through the use of plasma.

## VITREOUS ENAMELLING

Vitreous Enamelling (not to be confused with enamelling which is a lacquer process) involves the fusion of a glass or ceramic, applied by spray or dipping in the form of a frit, to a substrate to produce a hard surface with good bond strength. The disadvantage is brittleness typical of a glassy material and the difficulty of repairing cracks and chips that develop. In good condition the vitreous enamel can be very corrosion-resistant and by incorporating coloured minerals can be aesthetically attractive. The coating can be safely sterilized by chemical methods so is widely acceptable in the food processing and transport industries. While the fusing temperature may be as high as 800°C, which could cause thermal stresses to develop, low temperature enamels based on lead and other oxides are commonly employed especially as topcoat glazes. To obtain superior adhesion on cast irons and steel, a pre-treatment of thermal decarburization can be employed to yield a pure iron surface which can bond with the molten frit.

## ORGANIC COATINGS

The term Organic Coating covers a number of types and even more methods of application representing a substantial sector of industrial and domestic activity. The coatings can be more usefully named as Painting, Lacquering and Varnishing and the application processes include brushing, spraying, dipping, spinning, cladding and may take us into powder and electrophoresis technologies.
The three coating types have the presence of an organic binder or vehicle as the common feature and this is the components requiring stoving or curing to dry off solvents or set polymer resiuns.
A paint can have up to 60% pigmentation whose role is to add bulk, colour and opacity, corrosion and biological inhibition, light absorption etc. The amount of pigment will affect the gloss/matte appearance: >40% will be matte and 15-30% glossy after stoving. A lacquer may have <10% pigment and it is often purely colouration pigments. A varnish may be purely organic. The consequence is that the time and temperature of stoving varies considerably from a resin requiring polymerisation to a varnish requiring primarily evaporation of solvent. The final film may therefore be only 50% by weight of the applied coating for a paint. Current practice is to move away from organic solvents and vehicles to water-based systems. It is clearly environmentally driven but water-based paints can have other advantages including natural drying in reasonable times and adaptability to electrophoretic use in anodic or cathodic format.

Powder and clad coatings offer scope for thicker coatings and maybe thermoplastics or thermosets. The former are applied from a thermal gun using electrostatic fields which minimise the overspray at the earthed component and give excellent surface coverage. The latter are used as laminates or veneers with adhesive bonding to the substrate and must generally be organic polymers capable of being processed as sheet or calendared film. A substantial sector of industry is concerned with polymer laminating of wood for furniture as the laminate can carry patterns such as wood-grain finishes.