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PROTECTIVE COATINGS

Tutorial

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Наведено відомості про основні види корозії, методи і засоби захисту поверхонь деталей від впливу агресивних середовищ. Описано технологічні процеси нанесення металічних і неметалічних, лакофарбових покриттів, характерні дефекти покриттів. Подано основні поняття, які використовуються в дисципліні " Технологія захисних покриттів". Визначено методи і засоби контролю якості захисних покриттів у виробничих умовах.

Для студентів спеціальностей 134 «Авіаційна і ракетно-космічна техніка», 274 «Автомобільний транспорт», 101 «Екологія».

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Basic information about the main types of corrosion, basic methods and means of protecting the surfaces of parts from the effects of corrosive media are given. The technological processes of applying metallic and non-metallic, paint and varnish coatings, characteristic defects of coatings are described. The basic concepts used in the discipline "Technology of protective coatings" are presented. Methods and means of quality control of protective coatings in production conditions are determined.

For students of specialties 134 "Aviation and space-rocket technology", 274 "Automobile transport", 101 "Ecology".

Fig. 21. Tables 7. Bibliogr. : 7 names

INTRODUCTION

After a part is manufactured, it is common that the surface of the part will have additional processes done to it to ensure and enhance certain properties and characteristics. These include the following:

– improving resistance to wear, erosion, and indentation;

– reducing or control surface friction;

– reducing adhesion;

– improving lubrication;

– improving resistance to corrosion and oxidations;

– improving fatigue resistance;

– rebuilding surfaces on worn components;

– modifying surface texture;

– imparting decorative features.

Protective coatings are the most widely used products for corrosion protection. They are used to provide long-term protection under a broad range of corrosive conditions, extending from atmospheric exposure to the most demanding chemical processing conditions. Protective coatings in themselves provide little or no structural strength, yet they protect other materials to preserve their strength and integrity. The main function of a protective coating is to isolate structural reactive elements from environmental corrosives. The fact that protective coatings occupy only a very small fraction of the total volume of a system is quite telling of the strict requirements imposed on these materials.

A coating must provide a continuous barrier to a substrate, and any imperfection can become the focal point for degradation and corrosion of the substrate.

Metal finishing comprises a wide range of processes that are practiced by most industries engaged in manufacturing operations using metal parts. Typically, metal finishing is performed on manufactured parts after they have been shaped, formed, forged, drilled, turned, wrought, cast, and so forth. A"finish" can be defined as any final operation applied to the surface of a metal article to alter its surface properties and achieve various goals. The quality of a coating depends on many factors besides the nature of the materials involved. Metal finishing operations are intended to increase corrosion or abrasion resistance, alter appearance, serve as an improved base for the adhesion of other materials, enhance frictional characteristics, add hardness, improve solderability, add specific electrical properties, or improve the utility of the product in some other way.

1 CORROSION

Corrosion can be viewed as a universal phenomenon, omnipresent and omnipotent. It is there everywhere, air, water, soil and in every environment, we encounter. There is no single figure for loss to the nation due to corrosion. Corrosion has a huge economic and environmental impact on all facets of national infrastructure; from highways, bridges, buildings, oil and gas, chemical processing, water and waste water treatment and virtually on all metallic objects in use. Other than material loss, corrosion interferes with human safety, disrupts industrial operations and poses danger to environment. Awareness to corrosion and adaptation of timely and appropriate control measures hold the key in the abatement of corrosion failures.

1.1 Heterogeneities in metal

The effective use of metals as materials of construction must be based on an understanding of their physical, mechanical, and chemical properties. The last, as pointed out earlier, cannot be divorced from the environmental conditions prevailing. Any fundamental approach to the phenomena of corrosion must therefore involve a consideration of the structural features of the metal, the nature of the environment, and the reactions that occur at the metal–environment interface. The more important factors involved may be summarized as follows:

1. *Metal* – composition, detailed atomic structure, microscopic and macroscopic heterogeneities, stress (tensile, compressive, cyclic), etc.

2. *Environment* – chemical nature, concentrations of reactive species and deleterious impurities, pressure, temperature, velocity, impingement, etc.

3. *Metal-environment interface* – kinetics of metal oxidation and dissolution, kinetics of the reduction of species in solution, nature and location of corrosion products, film growth and film dissolution, etc.

Heterogeneities associated with a metal (Table 1.1).

The corrosion behavior of different constituents of an alloy is well known, since the etching techniques used in metallography are essentially corrosion processes that take advantage of the different corrosion rates of phases as a means of identification, for example, the grain boundaries are usually etched more rapidly than the rest of the grain owing to the greater reactivity of the disarrayed metal.

Macroscopic heterogeneities, for example, crevices, discontinuities in surface films, bimetallic contacts, etc. have a pronounced effect on the location and the kinetics of the corrosion reaction and are considered in various sections throughout this work. Practical environments are shown schematically in Figure 1.2, which also serves to emphasize the relationship between the detailed structure of the metal, the environment, and external factors such as stress, fatigue, velocity, impingement, etc.

Table 1.1 – Heterogeneities in metal

| Atomic (see Figure 1.1)	a) sites within a given surface layer ('normal' sites); these vary according to the particular crystal plane; b) sites at edges of partially complete layers; c) point defects in the surface layer: vacancies (molecules missing in surface layer), kink sites (molecules missing at edge of layer), molecules adsorbed on top of complete layer; d) disordered molecules at point of emergence of dislocations (screw or edge) in metal surface
Microscopic	a) grain boundaries – usually, but not invariably, more reactive than grain interior; b) phases – metallic (single metals, solid solutions, intermetallic compounds), nonmetallic, metal compounds, impurities, etc. – heterogeneities due to thermal or mechanical causes
Macroscopic	a) grain boundaries; b) discontinuities on metal surface – cut edges, scratches, discontinuities in oxide films (or other chemical films) or in applied metallic or nonmetallic coatings; c) bimetallic couples of dissimilar metals; d) geometrical factors – general design, crevices, contact with nonmetallic materials, etc.
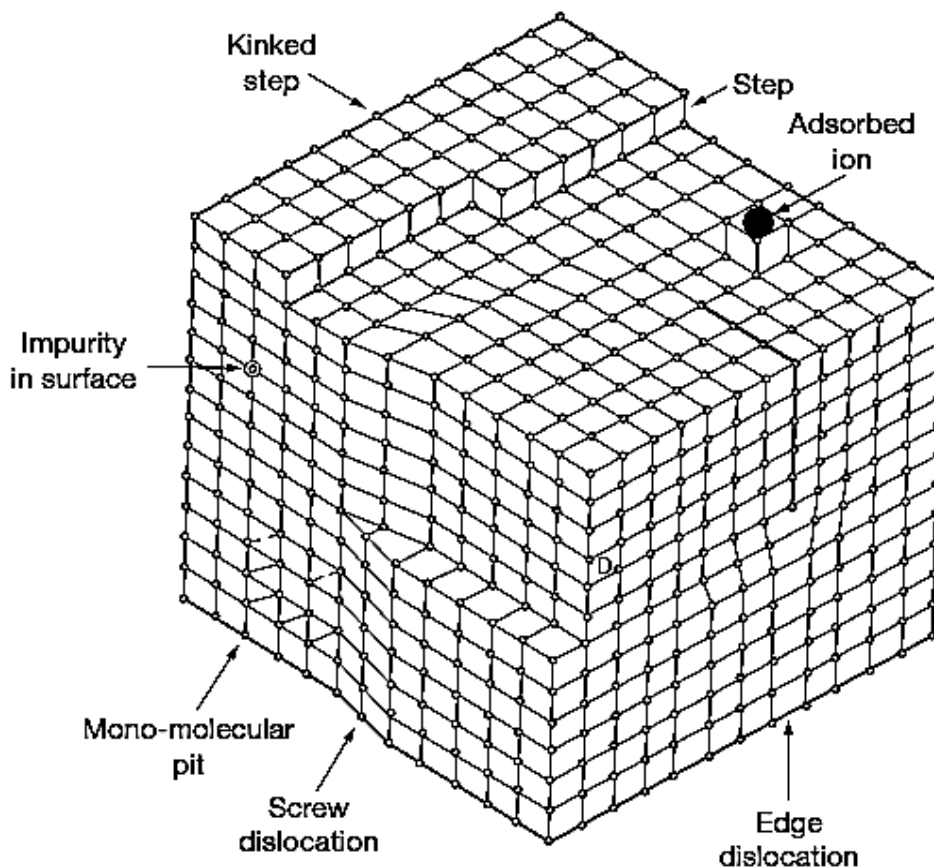
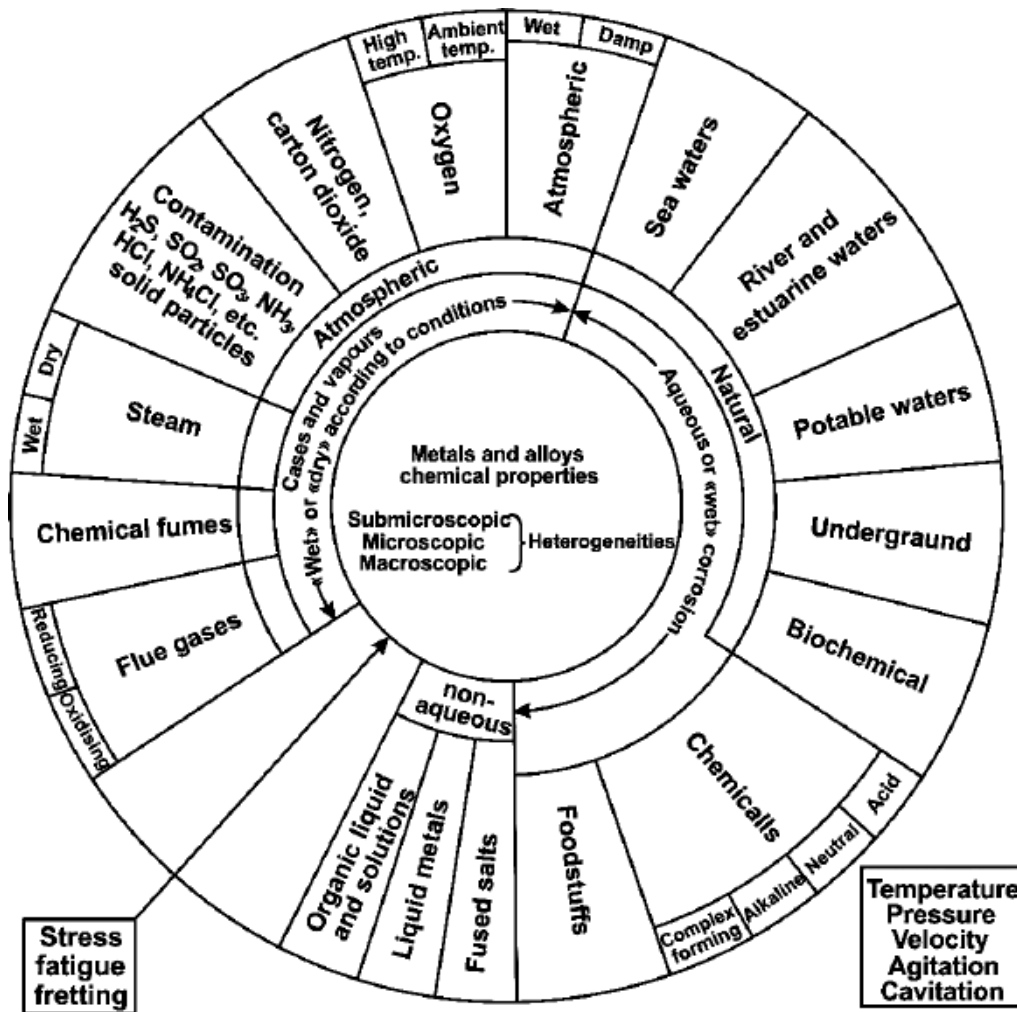Figure 1.1 – Surface imperfections in a crystal

Figure 1.2 – Environments in corrosion

1.2 Corrosion phenomena

Corrosion can affect the metal in a variety of ways, which depend on its nature and the precise environmental conditions prevailing, and a broad classification of the various forms of corrosion.

Ideally, the metal selected, or the protective system applied to the metal, should be such that no corrosion occurs at all, but this is seldom technologically or economically feasible. It is necessary, therefore, to tolerate a rate and a form of corrosion that will not be significantly detrimental to the properties of the metal during its anticipated life. Thus, provided the corrosion rate is known, the slow uniform corrosion of a metal can often be allowed for in the design of the structure; for example, in the case of a metal that shows an active–passive transition, the rate of corrosion in the passive region is usually acceptable, whereas the rate in the active region is not. It follows that certain forms of corrosion can be tolerated and that corrosion control is possible, provided that the rate and the form of the corrosion reaction are predictable and can be allowed for in the design of the structure.

Pitting is regarded as one of the most insidious forms of corrosion, since it often leads to perforation and to a consequent corrosion failure. In other cases,

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pitting may result in a loss of appearance, which is of major importance when the metal concerned is used for decorative architectural purposes. However, aluminum saucepans that have been in service for some time are invariably pitted, although the pits seldom penetrate the metal, that is, the saucepan remains functional and the pitted appearance is of no significance in that particular application.

These considerations lead to the conclusion that the relationship between corrosion and the deterioration of properties of a metal is highly complex and involves a consideration of a variety of factors such as the rate and the form of corrosion and the specific function of the metal concerned; certain forms of corrosion such as uniform attack can be tolerated, whereas others such as pitting and stress corrosion cracking that ultimately lead to complete loss of function cannot be.

The implications of the terms predictable and unpredictable used in the context of corrosion require further consideration, since they are clearly dependent on the knowledge and expertise of the engineer, designer, or corrosion designer who takes the decision on the metal or alloy to be used, or the procedure to be adopted, to control corrosion in a specific environmental situation.

1.3 Definitions and Types

Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. In simple terminology, corrosion processes involve reaction of metals with environmental species.

Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment which results in its consumption or dissolution into the material of a component of the environment. Often, but not necessarily, corrosion results in effects detrimental to the usage of the material considered. Exclusively physical or mechanical processes such as melting and evaporation, abrasion or mechanical fracture are not included in the term corrosion.

Corrosion can be classified:
– chemical and electrochemical;
– high temperature and low temperature;
– wet corrosion and dry corrosion.

Dry corrosion occurs in the absence of aqueous environment, usually in the presence of gases and vapours, mainly at high temperatures.

Electrochemical nature of corrosion can be understood by examining zinc dissolution in dilute hydrochloric acid:

$$Zn + 2HCl = ZnCl_2 + H_2.$$
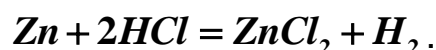
Anodic reaction is $Zn = Zn^{++} + 2e$ with the reduction of $2H^+ + 2e = H_2$ at cathodic areas on the surface of zinc metal. There are two half reactions constituting the net cell reaction.

Environmental effects such as those of presence of oxygen and other oxidizers, changes in flow rates (velocity), temperature, reactant concentrations and pH would influence rates of anodic and cathodic reactions.

Even though the fundamental mechanism of corrosion involves creation or existence of corrosion cells, there are several types or forms of corrosion that can occur. It should however be borne in mind that for corrosion to occur, there is no need for discrete (physically independent) anodes and cathodes. Innumerable micro level anodic and cathodic areas can be generated at the same (single) surface on which anodic (corrosion) and cathodic (reduction) reactions occur.

Each form of corrosion has a specific arrangement of anodes and cathodes and specific patterns and locations depending on the type can exist.

The most important *types* are:
– uniform corrosion;
– galvanic corrosion, concentration cells, water line attack;
– pitting;
– dezincification, dealloying (selective leaching);
– atmospheric corrosion;
– erosion corrosion;
– fretting;
– crevice corrosion; cavitation;
– stress corrosion, intergranular and transgranular corrosion, hydrogen cracking and embrittlement;
– corrosion fatigue.

Table 1.2 shows the classification of corrosion types by the nature of the destruction.

Table 1.2 – Classifications of corrosion types

General Corrosion	Localized Corrosion	Metallurgically Influenced Corrosion	Mechanically Assisted Degradation	Environmentally Induced Cracking
Corrosive attack dominated by uniform thinning: – atmospheric corrosion; – galvanic corrosion; – stray-current corrosion; – general biological corrosion; – molten salt corrosion; – corrosion in liquid metals; – high – temperature corrosion	High rates of metal penetration at specific sites: – crevice corrosion; – filiform corrosion; – pitting corrosion; – localized biological corrosion	Affected by alloy chemistry & heat treatment: – intergranular corrosion; – dealloying corrosion	Corrosion with a mechanical component: – erosion corrosion; – fretting corrosion; – cavitation and water drop impingement; – corrosion fatigue	Cracking produced by corrosion, in the presence of stress: – stress–corrosion cracking (scc); – hydrogen damage; – liquid metal embrittlement; – solid metal induced embrittlement

Crevice corrosion is a localized attack on a metal adjacent to the crevice between two joining surfaces (two metals or metal-nonmetal crevices). The corrosion is generally confined to one localized area to one metal. This type of corrosion can be initiated by concentration gradients (due to ions or oxygen). Accumulation of chlorides inside crevice will aggravate damage. Various factors influence crevice corrosion, such as:

– materials: alloy composition, metallographic structure;

– environmental conditions such as ph, oxygen concentration, halide concentrations, temperature;

– metal to metal or metal to nonmetal type.

Filiform corrosion is a special type of crevice corrosion.

Pitting corrosion is a localized phenomenon confined to smaller areas. Formation of micro-pits can be very damaging. Pitting factor (ratio of deepest pit to average penetration) can be used to evaluate severity of pitting corrosion which is usually observed in passive metals and alloys. Concentration cells involving oxygen gradients or ion gradients can initiate pitting through generation of anodic and cathodic areas. Chloride ions are damaging to the passive films and can make pit formation auto-catalytic. Pitting tendency can be predicted through measurement of pitting potentials. Similarly critical pitting temperature is also a useful parameter.

Uniform corrosion is a very common form found in ferrous metals and alloys that are not protected by surface coating or inhibitors. A uniform layer of „rust" on the surface is formed when exposed to corrosive environments Atmospheric corrosion is a typical example of this type.

Galvanic corrosion often referred to as dissimilar metal corrosion occurs in galvanic couples where the active one corrodes. EMF (Electromotive force series) series (thermodynamic) and galvanic series (kinetic) could be used for prediction of this type of corrosion. Galvanic corrosion can occur in multiphase alloys.

For example: Copper containing precipitates in aluminium alloys. Impurities such as iron and copper in metallic zinc.

Selective leaching (*Dealloying*) refers to selective dissolution of active metal phase from an alloy in a corrosive environment.

Examples:

a) brass containing copper and zinc. since zinc is anodic to copper, selective dezincification occurs in a corrosive medium, enriching the cathodic copper in the matrix (colour of brass turns red from yellow);

b) graphitization of grey cast iron-graphite being cathodic enhances dissolution of iron in the matrix, leaving behind a graphite network;

c) tin bronzes in hot brine or steam – destannification;

d) precious metal alloys such as gold containing copper or silver – strong acids, sulfide environment - preferential dissolution of copper or silver;

i) cupro-nickel alloys in condenser tubes-denickelisation.

Differential aeration (oxygen concentration cell) and ion concentration (salt concentration) cells create dissimilar polarities (anodic and cathodic areas) For example: Pitting of metals. Rusting of iron (Figure 1.3).
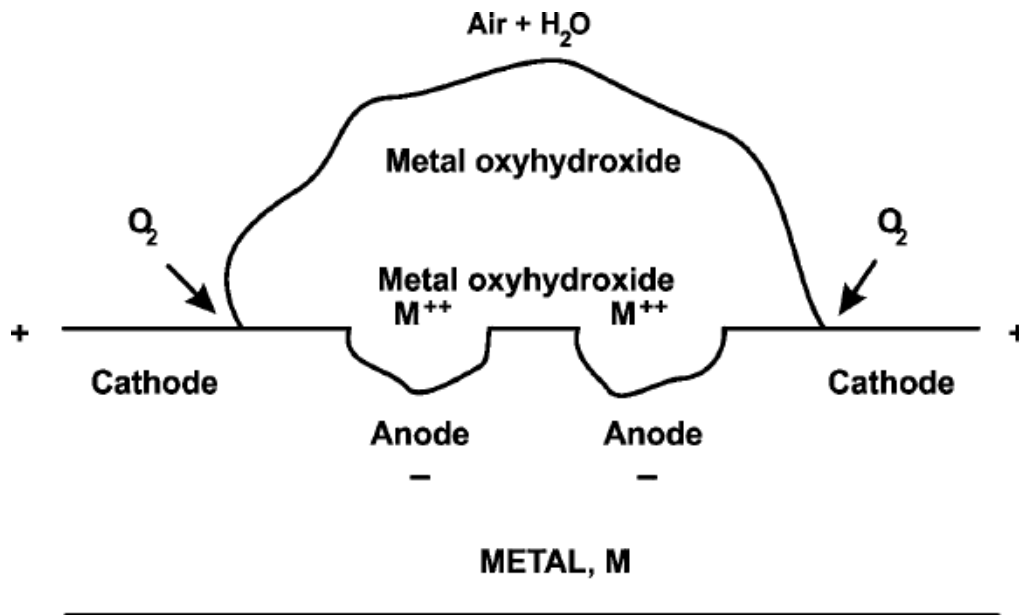
Figure 1.3 – Differential oxygen cells in rusting of iron

Localised attack at or nearer to grain boundaries in a metal or alloy can be termed as *intergranular corrosion*. Generally the following factors contribute to intergranular corrosion:

– impurities and precipitation at grain boundaries;
– depletion of an alloying element (added to resist corrosion) in the grain-boundary area.

A typical example is sensitized 18–8 stainless steels when chromium carbide is precipitated along grain boundaries. Lowered chromium content in the area adjacent to grain boundaries, leads to formation of anodic and cathodic areas.

Such intergranular corrosion is common in stainless steel welded structures and is referred to as weld decay. Intergranular attack can occur in other alloys as well.

For example, Duralumin-type alloys $(Al - Cu)$ due to precipitation of $CuAl_2$.

Erosion corrosion is the deterioration of metals and alloys due to relative movement between surfaces and corrosive fluids. Depending on the rate of this movement, abrasion takes place. This type of corrosion is characterized by grooves and surface patterns having directionality. Typical examples are:

– stainless alloy pump impeller;
– condenser tube walls.

All equipment types exposed to moving fluids are prone to erosion corrosion.

Many failures can be attributed to impingement (impingement attack). Erosion corrosion due to high velocity impingement occurs in steam condenser tubes, slide valves in petroleum refinery at high temperature, inlet pipes, cyclones and steam turbine blades.

Cavitation damage can be classified as a special form of erosion corrosion. This is usually caused by formation and collapse of vapour bubbles in liquids closer to a metal surface. Typical examples include ship"s propellers, pump impellers and hydraulic turbines. Surface damage similar to that of pitting can occur and both corrosion and mechanical factors are involved.

Corrosion occurring at contact regions between materials under load subjected to slip and vibration can be termed Fretting. Such friction oxidation can occur in engine and automotive parts. Fretting is known to occur at bolted tie plates on rails. Parameters promoting fretting include:
– relative motion between two surfaces;
– interface under load.

Both the above produce slip and deformation of surfaces. Wear-oxidation and oxidation-wear theories are proposed to explain fretting corrosion.

Stress corrosion cracking (SCC) refers to failure under simultaneous presence of a corrosive medium and tensile stress. Two classic examples of SCC are caustic embrittlement of steels occurring in riveted boilers of steam-driven locomotives and season cracking of brasses observed in brass cartridge cases due to ammonia in environment. Stress cracking of different alloys does occur depending on the type of corrosive environment. Stainless steels crack in chloride atmosphere. Major variables influencing SCC include solution composition, metal/alloy composition and structure, stress and temperature. Crack morphology for SCC failures consists of brittle fracture and inter - or trans-granular cracking could be observed. Higher stresses decrease time before crack initiation. Tensile stresses of sufficient threshold levels are involved (applied, residual or thermal stresses).

Hydrogen embrittlement although many a time classified under stress corrosion, need be considered separately since the two types respond very differently to environmental factors.

Fracture of metals and alloys under repeated cyclic stresses is termed fatigue and corrosion under such circumstances is *corrosion fatigue* (reduction of fatigue resistance).

Electrochemical factors come into play in many of the above corrosion forms with respect to both corrosion mechanisms and corrosion protection.

2 COATINGS AND COATING PROCESSES

Coating fundamentals makes reference to a multitude of concepts and properties. A critical property of antifouling paint is, for example, the inhibition of living organism growth on the coating. A fire-resistant coating, on the other hand, should resist or retard the burning of the substrate. From a corrosion point of view a coating is rated on the resistance it provides against corrosion in

a specific environment, and because there are many variations in environment corrosivity, there is also a great variety of corrosion protective coatings. These can be broadly divided into metallic, inorganic, and organic coatings (Table 2.1).

Table 2.1 – Types of Protective Coatings

Type of Coatings	Examples
Metallic coatings	Hot-dip galvanizing, electroplating, electroless plating, anodizing, thermal spraying or metallizing, cladding, diffusion coating
Inorganic coatings	Porcelain coating, glass-lining
Organic coatings	Paints, vanishes, lacquers and numerous other polymeric materials that readily form durable dry films

2.1 Metallic coatings

Metallic coatings provide a layer that changes the surface properties of the workpiece to those of the metal being applied. The workpiece becomes a composite material exhibiting properties generally not achievable by either material if used alone. The coatings provide a durable, corrosion-resistant layer, and the core material provides the load-bearing capability.

The deposition of metal coatings, such as chromium, nickel, copper, and cadmium, is usually achieved by wet chemical processes that have inherent pollution control problems. Alternative metal deposition methods have replaced some of the wet processes and may play a greater role in metal coating in the future. Metallic coatings are deposited by electroplating, electroless plating, spraying, hot dipping, chemical vapor deposition, and ion vapor deposition. Some important coatings are cadmium, chromium, nickel, aluminum, and zinc. Copper, gold, and silver are also used in electrical equipment and occasionally for specialty fastener applications. Copper is used as a base layer in multiple-plate electroplating, silver is used for antifretting purposes, and both silver and gold are sometimes used to provide electrical conductivity in waveguides and at contacts.

Aluminum coatings can be applied to steel by hot dipping, cementation, ion vapor deposition, and spraying. Ion vapor deposition is a relatively new process, and spraying is the only process that has been used extensively over a long period of time. Pack cementation is widely used for gas turbine components. In soft waters aluminum is cathodic with respect to steel; however, in seawater or some fresh waters containing chloride ions or sulfate ions, aluminum may become anodic to steel, and aluminum coatings should therefore corrode sacrificially and provide cathodic protection to steel. However, as noted below, this may not always be the case.

Sprayed aluminum coatings provide an adherent, somewhat absorbent film about 100 to 150 μm thick. They provide very good protection to steel, and they may be sealed with organic lacquers or paints to provide further protection and delay the formation of visible surface rust. The surface of the steel must first be grit-blasted to provide a rough surface to aid adhesion. Unfortunately the thickness and relative roughness of the coatings make them unsuitable for close tolerance parts.

Ion vapor-deposited aluminum coatings have been used on a variety of parts including steel and titanium fasteners, electrical connectors, engine mounts and stator vanes, landing gear components, integrally machined wing skins, and a large number of miscellaneous components. These coatings are soft and ductile and are prepared using commercially available aluminum feed wire that is melted, vaporized, and ionized in a glow discharge created by an inert gas. The process is applied in a batch mode, where parts to be coated are held at a high negative potential relative to the evaporation source. The positively charged gas ions bombard the surface of the part and perform a final cleaning action. When this is done the aluminum is vaporized and ionized, and the ionized aluminum is accelerated toward the part surface where it plates as a dense, tightly adherent coating.

Minimum coating thickness are in the range 8 to 25 μm, and coatings may be used as prepared or with a supplementary chromate treatment. The thinner coatings are used when close tolerances are required such as on threads, intermediate thickness coatings (> 13 μm) are used on interior parts or where only mildly corrosive environments are expected, and the thicker coatings (> 25 μm) are used for exterior parts operating in highly corrosive environments and for engine parts. Ion vapor-deposited aluminum has been considered as a replacement for diffused nickel cadmium and aluminum pigmented paints for use in the cooler sections of gas turbines, where temperatures are less than 454°C. The process has also been considered as an alternative to pack cementation for the preparation of aluminide coatings on hot-section components. In this case the ion vapor-deposited aluminum is diffused into the nickel-based superalloy substrates to form the nickel aluminide coating.

Ion vapor deposition of aluminum is attractive because it avoids the environmental and toxicological problems associated with cadmium. It does not cause hydrogen embrittlement of steel or solid metal embrittlement of steel or titanium, and it should be more galvanically compatible with aluminum alloy structure and avoid the exfoliation corrosion of sensitive aluminum alloy structure. However, views on the ability of aluminum to protect steel fasteners appear to vary. A view is that the presently available pure aluminum coatings are not able to provide adequate sacrificial protection to steel in a chloride ion environment, and for this reason a recommendation is made for the development of aluminum coatings containing small amounts of zinc or other elements for improved protection.

Cadmium is widely used by the aircraft industry for electroplating steel fasteners and bearing assemblies because it provides a galvanically acceptable couple with aluminum. Cadmium is also anodic to steel and will cathodically protect the substrate at scratches or gaps in the coating and at cut edges. It also exhibits surface lubricity and conductivity and resists fretting and fatigue, and its corrosion products do not cause binding. Platings are usually deposited from cyanide baths, but baths containing fluoroborates or sulfamates are also used. The baths may contain special additives to reduce hydrogen penetration, and the coatings are usually 5 to 25 μm thick.

The use of cadmium introduces four problems. The first problem is that it is highly toxic, and environmental protection agencies have been concerned about its release into the environment. Disposal of wastes from cyanide baths is therefore a problem, as is the eventual disposal of the finished coated part. The second problem is that the electroplating process also exposes parts to cathodically produced hydrogen, and because many of the high-strength steels involved are highly susceptible to hydrogen embrittlement, stringent requirements exist to bake parts immediately after plating to remove this hydrogen. Most process specifications for cadmium plating include requirements for baking and subsequent testing of coupons to demonstrate absence of embrittlement. The problem of hydrogen embrittlement can be avoided by applying cadmium coatings by an ion vapor deposition process, which does not produce hydrogen. This process is sometimes used on very high strength steels where hydrogen would be difficult to remove by baking. Once deposited, these coatings are essentially similar to electrodeposited coatings and should receive the same type of additional paint protection. The third problem is that cadmium has been reported to cause solid metal embrittlement of steel and titanium alloys. Finally, cadmium has also been reported to cause exfoliation corrosion of susceptible aluminum alloys when used on fasteners in contact with these alloys in a riveted or bolted structure.

Many alternatives to cadmium plating exist, with no single universal substitute available. Some cadmium plating alternatives are zinc plating, tin or tin alloy plating, cobalt-zinc plating, zinc-nickel plating, zinc-iron plating, zinc-flake dispersion coating, metallic ceramic coating, and ion vapor deposition of aluminum. The most successful of these alternatives has been zinc-nickel plating, which has a long history in the electroplating industry. Generally, for alternatives to be successful, they must provide sufficient corrosion resistance, as measured by standard tests. For certain military and aerospace applications, the alternative deposits must also provide other desired characteristics, such as lubricity. Many electroplating job shops have eliminated cadmium plating because of a reduced market and the enforcement of local discharge standards.

Chromium is used as a protective coating, providing resistance to wear, abrasion, and corrosion. It has hardness in the range 900 to 1100 HV, low-friction characteristics, and high reflectivity. It is used as a thin coating, usually in the range 0.2 to 1 μm thick, as the final layer in a multipleplate copper-nickel-

chromium electroplating or as a thick coating up to 300 µm to provide wear resistance. When used as a constituent of a multiple-plate coating, chromium provides hardness, reflectivity, and tarnish resistance. The corrosion resistance is derived primarily from the barrier effect of the thick nickel plate under the chromium. However, copper, nickel, and chromium are all cathodic with respect to steel, and corrosion can be accelerated once the coating is breached and the underlying steel is exposed. For this reason these coatings are not chosen where corrosion protection is the primary concern.

Hard chromium plating is usually applied directly to steel parts in thickness up to about 300 µm to provide resistance to wear, abrasion, and corrosion. It is also used to build up worn or undersized parts. In the thicker applications it may be impervious but is subject to microcracks. Chromium is a metal with low cathode efficiency, and substantial amounts of hydrogen are deposited on the part along with the metal being plated. Because of this, parts must be baked as soon as possible after plating to drive off the hydrogen and prevent embrittlement.

Chromium plating is traditionally performed with a hexavalent chromium bath, but trivalent chromium plating has increased in use. With either process, an undercoat of nickel/copper or nickel is usually applied. Trivalent chromium plating is an economically attractive alternative to hexavalent plating for some applications. However, its use has been limited due to a difference in appearance from the standard hexavalent bath. The trivalent bath chemistry is more expensive to purchase than the hexavalent bath. The cost savings are a result of reduced metal loading on the treatment system (the trivalent bath contains less total chromium) and the avoidance of the hexavalent chromium reduction step during treatment. The total cost of trivalent chromium plating is about one-third of the costs for hexavalent solution.

Hard chromium plating is applied to tools, hydraulic cylinders, and other metal surfaces that require wear resistance. It is widely used in the mining industry. The major difference between the hard chromium and decorative deposits is their thickness. The hard chromium deposit is typically hundreds of times thicker than decorative ones. Although research efforts have aimed at a trivalent chromium substitute for hard chromium plating, no solutions are available commercially. Input material changes for hard chromium have focused on alternative deposits. Alternative processes have also been used. The most successful alternative input material is electroless nickel. Other alternative input materials under investigation are electroplated nickel alloys and nickel alloy composites. Alternative processes to hard chromium plating include brush plating, vacuum coating, and metal sprays.

Chromium use with aluminum finishing is perhaps most common in the aerospace industry. Chromium combines with aluminum on the surface of parts to provide corrosion and wear resistance and a chemically active surface for painting or coloring. The two most common processes are chromic acid anodizing and chromate conversion coating. Both processes are presently performed

in hexavalent chromium baths. The anodizing process is electrolytically performed, and the conversion coating process involves simple immersion. Significant research efforts have been undertaken to find alternatives to these processes. For many applications, alternatives have been identified and implemented. For example, chromic acid anodizing has been partially replaced by common sulfuric acid anodizing and sulfuric/boric acid anodizing, and chromium baths have been replaced to a lesser extent by nonchromium conversion coatings (e.g., permanganate, rare earth metals, and zirconium oxide).

Another use of chromium during aluminum finishing is for deoxidizing/desmutting. These preliminary processes (sometimes a combined single step) remove oxides and other inorganics that would interfere with aluminum processing (e.g., anodizing). Alternatives to the chromium-based products include iron and ammonium salts and amines mixed with various oxidizers and/or etchants. Owing to the extent of research for nonchromium aluminum finishing and the success rate of these efforts, it is possible that chromium use will eventually be eliminated from the aluminum finishing area. One would expect to see large-scale substitutions during the next 10 years. However, total elimination will take considerable longer because of small residual uses of chromium for which no satisfactory substitute exists.

Nickel. By far the greatest use of nickel plating is on steel in conjunction with copper and chromium as described above. However, nickel can also be deposited, both on metals and nonmetals by an electroless or nonelectrolytic process. The metal is deposited spontaneously on the surface of a catalytic substrate immersed in an aqueous solution containing the metal ion and a reducing agent together with a compound (frequently the salt of an organic acid) that acts as a buffer and a complexing agent for the metallic ion.

The baths often contain phosphorous or boron, and they provide coatings of uniform thickness even over sharp corners and into deep recesses. The coatings have low internal stress and are less magnetic than electrodeposited nickel platings, and they have hardness values of about 500 HV. The coatings can be heat treated to higher hardness of about 1000 HV, which provides wear and abrasion resistance. This increase in hardness is achieved by a precipitation hardening process involving the phosphorous, which is usually present in amounts of 5 to 10%. The heat treatment is carried out at temperatures of about 400°C.

Electroless nickel coatings about 25 µm thick are often used after baking to remove hydrogen and to provide protection against stress corrosion cracking of precipitation hardenable stainless steels.

Zinc coatings may be applied either by electroplating or spraying. Electroplatings are normally less than 25 µm thick and may be as thin as 5 µm on threaded parts. However, although they provide good protection to steel in rural atmospheres, they do not perform as well in marine or industrial environments. Zinc coatings 30 µm thick last about 11 years or longer in rural or suburban lo-

cations, about 8 years in marine locations, and only 4 years in industrial atmospheres. The short life in industrial atmospheres was attributed to attack by sulfuric acid in polluted atmospheres. Zinc plating does not perform as well as cadmium in tropical and marine atmospheres, and therefore cadmium is preferred for aircraft use. Where thicker coatings are permissible, zinc may be deposited by spraying but must compete with aluminum, which is usually the preferred material.

2.1.1 Plating

Plating and surface treatment processes are typically batch operations, in which metal objects are dipped into and then removed from baths containing various reagents to achieve the desired surface condition. The processes involve moving the object being coated through a series of baths designed to produce the desired end product. These processes can be manual or highly automated operations, depending on the level of sophistication and modernization of the facility and the application. Plating operations can generally be categorized as electroplating and electroless plating processes.

Electroplating. Electroplating is achieved by passing an electrical current through a solution containing dissolved metal ions and the metal object to be plated. The metal object serves as the cathode in an electrochemical cell, attracting metal ions from the solution. Ferrous and nonferrous metal objects are plated with a variety of metals, including aluminum, brass, bronze, cadmium, copper, chromium, iron, lead, nickel, tin, and zinc, as well as precious metals, such as gold, platinum, and silver. The process is regulated by controlling a variety of parameters, including the voltage and amperage, temperature, residence times, and the purity of bath solutions. Plating baths are almost always aqueous solutions; therefore, only those metals that can be reduced from aqueous solutions of their salts can be electrodeposited. The only major exception is aluminum, which can be plated from organic electrolytes. The sequence of unit operations in an electroplating operation typically involves various cleaning steps, stripping of old plating or paint, electroplating steps, and rinsing between and after each of these operations. Electroless plating uses similar steps but involves the deposition of metal on a substrate without the use of external electrical energy.

Electroless plating. Electroless nickel (EN) plating is a chemical reduction process that depends upon the catalytic reduction process of nickel ions in an aqueous solution (containing a chemical reducing agent) and the subsequent deposition of nickel metal without the use of electrical energy. Thus in the EN plating process, the driving force for the reduction of nickel metal ions and their deposition is supplied by a chemical reducing agent in solution. This driving potential is essentially constant at all points of the surface of the component, provided the agitation is sufficient to ensure a uniform concentration of metal ions and reducing agents. The electroless deposits are therefore very uniform in thickness all over the part's shape and size. The process thus offers distinct

advantages when plating irregularly shaped objects, holes, recesses, internal surfaces, valves, threaded parts, and so forth.

Electroless (autocatalytic) nickel coating provides a hard, uniform, corrosion-, abrasion-, and wear-resistant surface to protect machine components in many industrial environments. EN is chemically deposited, making the coating exceptionally uniform in thickness. Careful process control can faithfully reproduce the surface finish, eliminating the need for costly machining after plating.

In a true electroless plating process, reduction of metal ions occurs only on the surface of a catalytic substrate in contact with the platingsolution. Once the catalytic substrate is covered by the deposited metal, the plating continues because the deposited metal is also catalytic. As a result, electroless plating processes are widely used in industry to meet the end-use functional requirements and are only rarely used for decorative purposes. Distinct advantages of EN plating are:

– uniformity of the deposits, even on complex shapes. The electroplated coatings are thinner in recessed areas and thicker on projecting areas;

– deposits are often less porous and thus provide barrier corrosion protection to steel substrates that is much superior to that of electroplated nickel and hard chrome;

– deposits cause about one-fifth as much hydrogen absorption as electrolytic nickel and about one-tenth as much as hard chrome.

– deposits can be plated with zero or compressive stress. Fatigue strength debit on the substrate material is thus zero or positive;

– deposits have inherent lubricity and nongalling characteristics, unlike electrolytic nickel;

– deposits have good wetability for oils;

– deposits have good solderability, braze weldability, and weldability;

– deposits are much harder with as-plated microhardness of 450 to 600 HV, which can be increased to 1000 to 1100 HV by a suitable heat treatment, the increase being due to the precipitation of Ni3P,which causes general hardening of the alloy.

Deposits have unique magnetic properties. EN deposits containing more than 8% P are generally considered to be essentially nonmagnetic in the as-plated condition. In Ni-P coatings, phosphorus is present as supersaturated solution in fine microcrystalline solid solution, bordering on amorphous or liquid-like (glasslike) metastable structure, and is responsible for nonferromagnetic behavior of as-plated Ni-P deposits (with P > 8%).

A second generation of EN plating has been developed by codepositing micrometer-sized particles of silicon carbide with the nickel, thereby creating an extremely wear- and corrosion-resistant coating. The nickel alloy matrix provides corrosion resistance, and the silicon carbide particles, which are actually the contacting surface, add wear resistance.

2.1.2 Hot dip galvanizing

Hot dip galvanizing is the process of applying a zinc coating to fabricated iron or steel material by immersing the material in a bath consisting primarily of molten zinc. The simplicity of the galvanizing process is a distinct advantage over other methods of providing corrosion protection.

Galvanizing can be found in almost every major application and industry where iron or mild steel is used. The utilities, chemical process, pulp and paper, automotive, and transportation industries, to name just a few, have historically made extensive use of galvanizing for corrosion control. They continue to do so today. For over 140 years, galvanizing has had a proven history of commercial success as a method of corrosion protection in a myriad of applications world-wide.

The electrochemical protection provided to steel by zinc coatings is a vital element in the effectiveness of galvanized coatings in protecting steel from cor-rosion. All pregalvanized products rely on the cathodic protection provided by zinc to prevent corrosion of exposed steel at cut edges. While the potential dif-ference between metals is the prime driving force providing the corrosion cur-rent, it is not a reliable guide to the rate and type of corrosion occurring at a particular point. The severity of galvanic corrosion also depends on the ratio of the areas of metals in contact, the duration of wetness (galvanic corrosion can only occur in the presence of a conductive solution), and the conductivity of the electrolyte. The presence of oxide films on the surface of one or both of the metals can greatly inhibit galvanic corrosion.

In any situation where zinc is corroded sacrificially to protect exposed steel, the mass of available zinc will determine the corrosion protection perfor-mance. Corrosion rates of zinc coatings required to cathodically protect un-coated steel in aggressive environments (saltwater/ marine) may be 25 times higher than the normal zinc corrosion rate.

2.1.3 Pack cementation

Diffusion coatings are formed by depositing a layer of aluminum on the metal surface and then heating the component in a furnace for a period of time. During this heat treatment, the aluminum and metal atoms migrate, or diffuse, into each other, which is the reason these coatings are called diffusion coat-ings. This processing is usually performed by a pack cementation process in which the aluminum deposition and the heat treatment occur simultaneously.

Pack cementation is widely used to confer oxidation resistance on ferrous alloys. Usually relatively expensive aluminum or binary alloys grade reagent is used during the pack process with aluminum as a source. Pack cementation processes include aluminizing, chromizing, and siliconizing. Components are packed in metal powders in sealed heat-resistant retorts and heated inside a furnace to precisely controlled temperature-time profiles. In the aluminizing process, a source of aluminum reacts with a chemical activator on heating to form a gaseous compound (e.g., pure Al with NaF to form AlF). This gas is the

transfer medium that carries aluminum to the component surface. The gas decomposes at the substrate surface, depositing aluminum and releasing the halogen activator. The halogen activator returns to the pack and reacts with the aluminum again. Thus, the transfer process continues until all of the aluminum in the pack is used or until the process is stopped by cooling. The coating forms at temperatures ranging from 700 to 1100°C over a period of several hours.

Pack cementation is the most widely used process for making diffusion aluminide coatings. Diffusion coatings are primarily aluminide coatings composed of aluminum and the base metal. A nickel-based superalloy forms a nickel-aluminide, which is a chemical compound with the formula NiAl. A cobalt-based superalloy forms a cobalt-aluminide, which is a chemical compound with the formula CoAl. It is common to incorporate platinum into the coating to improve the corrosion and oxidation resistance. This is called a platinum-aluminide coating. Diffusion chrome coatings are also available.

Diffusion aluminide coatings protect the base metal by forming a continuous, aluminum oxide layer, Al_2O_3, which prevents further oxidation of the coating. (Actually, oxidation continues but at much slower rates than without a continuous aluminum oxide scale.) When part of the Al_2O_3 scale spalls off, the underlying aluminide layer is exposed to form a new Al_2O_3 scale. Thus, the coating is self-healing.

Pack cementation can also be used to produce chromium-modified aluminide coatings. The addition of chromium is known to improve the hot corrosion resistance of nickel-based alloys. Although chromium can be codeposited with aluminum in a single-step process, a duplex process is frequently used to form the chromium-modified aluminide. The component is first chromized using either pack cementation or a gas phase process, and this is then followed by a standard aluminizing treatment. The final distribution of the chromium in the coating will depend on whether a low- or high-activity aluminizing process is employed.

For a platinum-aluminide coating, a thin (typically 8-µm) layer of platinum is first deposited onto the substrate, usually by a plating process. The second step involves aluminizing for several hours using the conventional packed cementation process to form the platinum-aluminide coating.

Conventional pack cementation processes are unable to effectively coat internal surfaces such as cooling holes. The coating thickness on these internal surfaces is usually less than on the surface due to limited access by the carrier gas. Access can be improved by pulsing the carrier gas, or by use of a vapor phase coating process.

Another method of coating both the internal and external surfaces involves generating the coating gases in a reactor that is separate from the vessel the parts are in. The coating gases are pumped around the outside and through the inside of the parts by two different distribution networks. Internal passages can be coated by filling them with the powder used in the pack (actually a variation of this powder).4 Slurry processes can also be used to deposit

the aluminum or the aluminum and other alloying elements. The slurry is usually sprayed on the component. The component is then given a heat treatment, which burns off the binder in the slurry and melts the remaining slurry, which reacts with the base metal to form the diffusion coating. After coating, it is usually necessary to heat treat the coated component to restore the mechanical properties of the base metal.

2.1.4 Cladding

Corrosion resistance can be improved by metallurgically bonding to the susceptible core alloy a surface layer of a metal or an alloy with good corrosion resistance. The cladding is selected not only to have good corrosion resistance but also to be anodic to the core alloy by about 80 to 100 mV. Thus if the cladding becomes damaged by scratches, or if the core alloy is exposed at drilled fastener holes, the cladding will provide cathodic protection by corroding sacrificially.

Cladding is usually applied at the mill stage by the manufacturers of sheet, plate, or tubing. Cladding by pressing, rolling, or extrusion can produce a coating in which the thickness and distribution can be controlled over wide ranges, and the coatings produced are free of porosity. Although there is almost no practical limit to the thickness of coatings that can be produced by cladding, the application of the process is limited to simple-shaped articles that do not require much subsequent mechanical deformation. Among the principal uses are lead and cadmium sheathing for cables, lead-sheathed sheets for architectural applications, and composite extruded tubes for heat exchangers. Because of the cathodic protection provided by the cladding, corrosion progresses only to the core/cladding interface and then spreads laterally, thus helping to prevent perforations in thin sheet. The cut edges of the clad product should be protected by the normal finish or by jointing-compound squeezed out during wet assembly.

The thickness of the cladding is usually between 2 and 5% of the total sheet or plate thickness, and because the cladding is usually a softer and lower-strength alloy, the presence of the cladding can lower the fatigue strength and abrasion resistance of the product. In the case of thick plate where substantial amounts of material may be removed from one side by machining so that the cladding becomes a larger fraction of the total thickness, the decrease in strength of the product may be substantial.

2.1.5 Thermal spraying

Energy surface treatment involves adding energy into the surface of the work piece for adhesion to take place. Conventional surface finishing methods involve heating an entire part. The methods described in this section usually add energy and material into the surface, keeping the bulk of the object relatively cool and unchanged. This allows surface properties to be modified with minimal effect on the structure and properties of the underlying material. Plas-

mas are used to reduce process temperatures by adding energy to the surface in the form of kinetic energy of ions rather than thermal energy.

Advanced surface treatments often require the use of vacuum chambers to ensure proper cleanliness and control. Vacuum processes are generally more expensive and difficult to use than liquid or air processes.

Facilities can expect to see less-complicated vacuum systems appearing on the market in the future. In general, use of the advanced surface treatments is more appropriate for treating small components (e.g., ion beam implantation, thermal spray) because the treatment time for these processes is proportional to the surface areas being covered.

Coatings can be sprayed from rod or wire stock or from powdered materials. The material (e.g., wire) is fed into a flame, where it is melted. The molten stock is then stripped from the end of the wire and atomized by a high-velocity stream of compressed air or other gas, which propels the material onto a prepared substrate or workpiece. Depending on the substrate, bonding occurs either due to mechanical interlock with a roughened surface, due to localized diffusion and alloying, and/or by means of Van der Waals forces (i.e., mutual attraction and cohesion between two surfaces).

The basic steps involved in any thermal coating process are substrate preparation, masking and fixturing, coating, finishing, inspection, and stripping (when necessary). Substrate preparation usually involves scale and oil and grease removal, as well as surface roughening.

Roughening is necessary for most of the thermal spray processes to ensure adequate bonding of the coating to the substrate. The most common method is grit blasting, usually with alumina. Masking and fixturing limit the amount of coating applied to the workpiece to remove overspray through time-consuming grinding and stripping after deposition. The basic parameters in thermal spray deposition are particle temperature, velocity, angle of impact, and extent of reaction with gases during the deposition process. The geometry of the part being coated affects the surface coating because the specific properties vary from point to point on each piece. In many applications, workpieces must be finished after the deposition process, the most common technique being grinding followed by lapping. The final inspection of thermal spray coatings involves verification of dimensions, a visual examination for pits, cracks, and so forth. Nondestructive testing has largely proven unsuccessful.

There are three basic categories of thermal spray technologies: combustion torch (flame spray, high velocity oxy-fuel, and detonation gun), electric (wire) arc, and plasma arc. Thermal spray processes are maturing, and the technology is readily available. Environmental concerns with thermal spraying techniques include the generation of dust, fumes, overspray, noise, and intense light. The metal spray process is usually performed in front of a "water curtain" or dry filter exhaust hood, which captures the overspray and fumes.

Water curtain systems periodically discharge contaminated wastewaters. Noise generated can vary from approximately 80 dB to more than 140 dB. With

the higher noise-level processes, robotics are usually required for spray application. The use of metal spray processes may eliminate some of the pollution associated with conventional tank plating. In most cases, however, wet processes, such as cleaning, are necessary in addition to the metal coating process. Therefore, complete elimination of tanks may not be possible. Waste streams resulting from flame spray techniques may include overspray, waste-waters, spent exhaust filters, rejected parts, spent gas cylinders, air emissions (dust, fumes), and wastes associated with the grinding and finishing phases.

2.1.6 Physical vapor deposition

Vapor deposition refers to any process in which materials in a vapor state are condensed through condensation, chemical reaction, or conversion to form a solid material. These processes are used to form coatings to alter the mechanical, electrical, thermal, optical, corrosion-resistance, and wear properties of the substrates.

They are also used to form free-standing bodies, films, and fibers and to infiltrate fabric to form composite materials. Vapor deposition processes usually take place within a vacuum chamber.

There are two categories of vapor deposition processes: physical vapor deposition (PVD) and chemical vapor deposition (CVD). In PVD processes, the workpiece is subjected to plasma bombardment. In CVD processes, thermal energy heats the gases in the coating chamber and drives the deposition reaction.

Physical vapor deposition methods are clean, dry vacuum deposition methods in which the coating is deposited over the entire object Physical vapor deposition. Vapor deposition refers to any process in which materials in a vapor state are condensed through condensation, chemical reaction, or conversion to form a solid material. These processes are used to form coatings to alter the mechanical, electrical, thermal, optical, corrosion-resistance, and wear properties of the substrates. They are also used to form free-standing bodies, films, and fibers and to infiltrate fabric to form composite materials. Vapor deposition processes usually take place within a vacuum chamber.

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Physical vapor deposition methods are clean, dry vacuum deposition methods in which the coating is deposited over the entire object simultaneously, rather than in localized areas. All reactive PVD hard coating processes combine:

– a method for depositing the metal;
– combination with an active gas, such as nitrogen, oxygen, or methane;
– plasma bombardment of the substrate to ensure a dense, hard coating.

PVD methods differ in the means for producing the metal vapor and the details of plasma creation. The primary PVD methods are ion plating, ion implantation, sputtering, and laser surface alloying.

Waste streams resulting from laser cladding are similar to those resulting from high-velocity oxy-fuels and other physical deposition techniques: blasting media and solvents, bounce and overspray particles, and grinding particles. Generally speaking, none of these waste streams are toxic.

CVD is a subset of the general surface treatment process, vapor deposition. Over time, the distinction between the terms physical vapor deposition and chemical vapor deposition has blurred as new technologies have been developed and the two terms overlap. CVD includes sputtering, ion plating, plasma-enhanced chemical vapor deposition, low-pressure chemical vapor deposition, laser-enhanced chemical vapor deposition, active-reactive evaporation, ion beam, laser evaporation, and many other variations. These variants are distinguished by the manner in which precursor gases are converted into the reactive gas mixtures. In CVD processes, a reactant gas mixture impinges on the substrate upon which the deposit is to be made. Gas precursors are heated to form a reactive gas mixture. The coating species is delivered by a precursor material, otherwise known as a reactive vapor. It is usually in the form of a metal halide, metal carbonyl, a hydride, or an organometallic compound. The precursor may be in gas, liquid, or solid form. Gases are delivered to the chamber under normal temperatures and pressures, whereas solids and liquids require high temperatures and/or low pressures in conjunction with a carrier gas. Once in the chamber, energy is applied to the substrate to facilitate the reaction of the precursor material upon impact. The ligand species is liberated from the metal species to be deposited upon the substrate to form the coating. Because most CVD reactions are endothermic, the reaction may be controlled by regulating the amount of energy input. The steps in the generic CVD process are:

– formation of the reactive gas mixture;

– mass transport of the reactant gases through a boundary layer to the substrate;

– adsorption of the reactants on the substrate;

– reaction of the adsorbents to form the deposit;

– description of the gaseous decomposition products of the deposition process.

The precursor chemicals should be selected with care because potentially hazardous or toxic vapors may result. The exhaust system should be designed to handle any reacted and unreacted vapors that remain after the coating process is complete. Other waste effluents from the process must be managed appropriately. Retrieval, recycle, and disposal methods are dictated by the nature of the chemical. For example, auxiliary chemical reactions must be performed to render toxic or corrosive materials harmless, condensates must be collected, and flammable materials must be either combusted, absorbed, or

dissolved. The extent of these efforts is determined by the efficiency of the process.

2.2 Inorganic coatings

Inorganic coatings can be produced by chemical action, with or without electrical assistance. The treatments change the immediate surface layer of metal into a film of metallic oxide or compound that has better corrosion resistance than the natural oxide film and provides an effective base or key for supplementary protection such as paints. In some instances, these treatments can also be a preparatory step prior to painting.

2.2.1 Anodizing

Anodizing involves the electrolytic oxidation of a surface to produce a tightly adherent oxide scale that is thicker than the naturally occurring film. Anodizing is an electrochemical process during which aluminum is the anode. The electric current passing through an electrolyte converts the metal surface to a durable aluminum oxide. The difference between plating and anodizing is that the oxide coating is integral with the metal substrate as opposed to being a metallic coating deposition. The oxidized surface is hard and abrasion resistant, and it provides some degree of corrosion resistance.

However, anodizing cannot be relied upon to provide corrosion resistance to corrosion-prone alloys, and further protection by painting is usually required. Fortunately the anodic coating provides an excellent surface both for painting and for adhesive bonding. Anodic coatings break down chemically in highly alkaline solutions (pH > 8.5) and highly acid solutions (pH < 4.0). They are also relatively brittle and may crack under stress, and therefore supplementary protection, such as painting, is particularly important with stress corrosion-prone alloys.

Anodic coatings can be formed in chromic, sulfuric, phosphoric, or oxalic acid solutions. Chromic acid anodizing is widely used with 7000 series alloys to improve corrosion resistance and paint adhesion, and unsealed coatings provide a good base for structural adhesives. However these coatings are often discolored, and where cosmetic appearance is important, sulfuric acid anodizing may be preferred.

The Al_2O_3 coating produced by anodizing is typically 2 to 25 μm thick and consists of a thin nonporous barrier layer next to the metal a porous outer layer that can be sealed by hydrothermal treatment in steam or hot water for several minutes. This produces a hydrated oxide layer with improved protective properties. Figure 2.1 illustrates a porous anodic film and its evolution during the sealing process. Improved corrosion resistance is obtained if the sealing is done in a hot metal salt solution such as a chromate or dichromate solution.
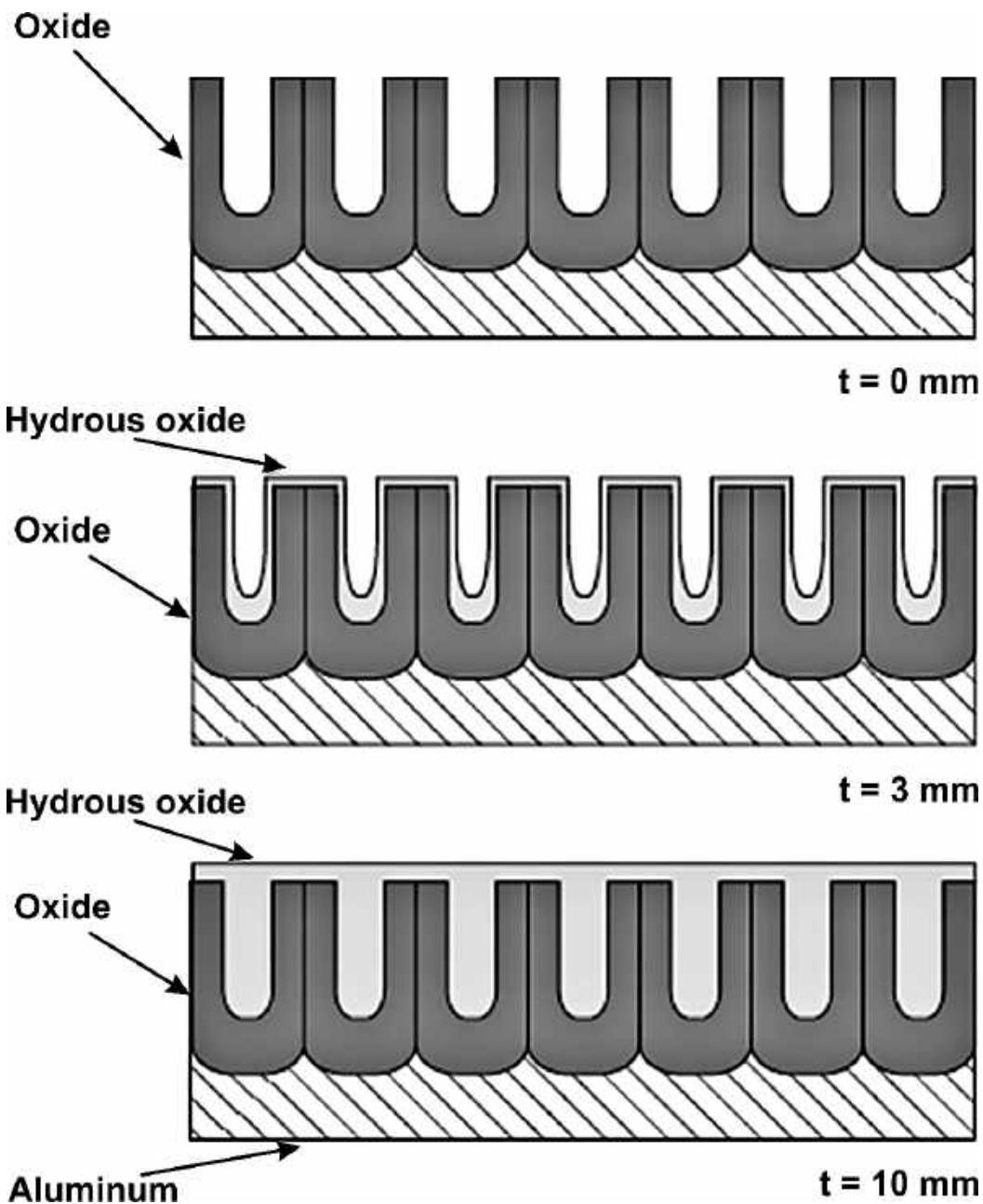
Figure 2.1 – The evolution of a porous anodic film on aluminum as a function of the sealing time at 85°C

The oxide coatings may also be dyed to provide surface coloration for decorative purposes, and this can be performed either in the anodizing bath or afterward. International standards for anodic treatment of aluminum alloys have been published by the International Standards Organization and cover dyed and undyed coatings. There are many reasons to anodize a part. Following are a few considerations and the industries that employ them:

1. *Appearance*. Products look finished, cleaner, and better, and this appearance lasts longer. Color enhances metal and promotes a solid, well-built appearance while removing the harsh metal look. Any aluminum product can be color anodized.

2. *Corrosion resistance*. A smooth surface is retained and weathering is retarded. Useful for food handling and marine products.

3. *Ease in cleaning.* Any anodized product will stay cleaner longer and is easier to clean when it does get dirty.

4. *Abrasion resistance.* The treated metal is tough, harder than many abrasives, and is ideal for caul plates, tooling, and air cylinder applications.

5. *Nongalling.* Screws and other moving parts will not seize, drag, or jam, and wear in these areas is diminished. Gun sights, instruments, and screw threads are typical applications.

6. *Heat absorption.* This can provide uniform or selective heatabsorption properties to aluminum for the food processing industry.

7. *Heat radiation.* This is used as a method to finish electronic heat sinks and radiators. Further, anodizing will not rub off, is an excellent paint base, removes minor scuffs, and is sanitary and tasteless.

Anodizing treatments are also available for magnesium and titanium alloys. The treatments commonly used with magnesium alloys involve several processing options to produce either thin coatings of about 5-μm thickness for flexibility and surfaces suitable for paint adhesion, or thick coatings, up to about 30 μm for maximum corrosion and abrasion resistance. When anodizing is used for the treatment of titanium and titanium alloys, it can provide limited protection to the less noble metals against galvanic corrosion, and when used together with solid film lubricants, it helps to prevent galling. The process produces a smooth coating with a uniform texture and appearance and a uniform blue-toviolet color.

2.2.2 Chromate filming

A number of proprietary chromate filming treatments are available for aluminum, magnesium, cadmium, and zinc alloys. The treatments usually involve short-time immersion in strongly acid chromate solutions, but spraying or application by brushing or swabbing can also be used for touchup of parts. The resulting films are usually about 5 μm thick and are colored depending on the base alloy, being golden yellow on aluminum, dull gold on cadmium and zinc, and brown or black on magnesium. The films contain soluble chromates that act as corrosion inhibitors, and they provide a modest improvement in corrosion resistance of the base metal. However, their main purpose is to provide a suitable surface for sealing resins or paints. Epoxy primer, for example, which does not adhere well to bare aluminum, adheres very well to chemical conversion coatings.

A process for zinc alloys has been described to consist of immersion for a few seconds in a sodium dichromate solution at a concentration of 200 g/L and acidified with sulfuric acid at 8 ml/L. The treatment is performed at room temperature and is followed by rinsing and drying to produce a dull yellow zinc chromate coating.

2.2.3 Phosphate coatings

A number of proprietary treatments such as Parkerizing and Bonderizing are available for use on steel. They are applied by brushing, spraying, or prolonged immersion in an acid orthophosphate solution containing iron, zinc, or manganese. For example a solution might contain $Zn(H_2PO_4)_2$ $2H_2O$ with added H_3PO_4. The coatings consist of a thick porous layer of fine phosphate crystals, tightly bonded to the steel. The coatings do not provide significant corrosion resistance when used alone, but they provide an excellent base for oils, waxes, or paints, and they help to prevent the spreading of rust under layers of paint. Phosphating should not be applied to nitrided or finish-machined steel, and steel parts containing aluminum, magnesium, or zinc are subject to pitting in the bath. Some restrictions apply also to heat-treated stainless and high-strength steels.

2.2.4 Nitriding

Steels containing nitride-forming elements such as chromium, molybdenum, aluminum, and vanadium can be treated to produce hard surface layers, providing improved wear resistance. Many of the processes employed are proprietary, but typically they involve exposure of cleaned surfaces to anhydrous ammonia at elevated temperatures. The nitrides formed are not only hard but also more voluminous than the original steel, and therefore they create compressive residual surface stresses. Therefore, nitrided steels usually exhibit improved fatigue and corrosion fatigue resistance. Similar beneficial effects can be achieved by shot peening.

2.2.5 Passive films

Austenitic stainless steels and hardenable stainless steels such as martensitic, precipitation hardening, and maraging stainless steels are seldom coated, but their corrosion resistance depends on the formation of naturally occurring transparent oxide films. These films may be impaired by surface contaminants such as organic compounds or metallic or inorganic materials. Treatments are available for these materials to clean and degrease surfaces and produce uniform protective oxide films under controlled conditions. These usually involve immersion in an aqueous solution of nitric acid and a dichromate solution.

2.3 Organic coatings

Paints, coatings, and high-performance organic coatings were developed to protect equipment from environmental damage. Of prime importance in the development of protective coatings was the petroleum industry which produced most of the basic ingredients from which most synthetic resins were developed. The cracking of petroleum produced a multitude of unsaturated workable compounds that are important in the building of large resin polymers such as vinyls and acrylics. The solvents necessary for the solution of the resins were also de-

rived from petroleum or natural gas. The building blocks for epoxies and modern polyurethane coatings are other derivatives produced by refining petroleum products.

The Steel Structures Painting Council (SSPC) is the world's acknowledged resource and authority for protective coatings technology. SSPC's mission is to advance the technology and promote the use of protective coatings to preserve industrial marine and commercial structure components and substrates.

Components of Coatings – All organic coatings consist of three basic components: (1) solvent, (2) resin, and (3) pigment. Not all coatings contain solvent and pigmented components . There are solvent-free (100 percent solids) coatings and clear, pigment-free coatings, but not resin -free coatings.

Coating chemical formulators commonly group solvent, resin, and pigment components into two general categories. The first category combin es the solvent and the resin together.

The solvent portion is called the "volatile vehicle," and the resin portion is called the "non volatile vehicle." The combination of the solvent and the resin, where the resin is dissolved in the solvent, is called the "vehicle."

The second category is the pigment. Pigments are additives that impart specific properties to the coating and are subdivided into two general categories: (1) color and (2) inert and reinforced . Figure 2.2 illustrates the relationship of these components.

When a coating is applied , the solvent evaporates during the curing process, leaving only the resin and the pigment components on the substrate. The remaining resin and pigments are some times called the " coating solids," and they form the protective film for corrosion protection.
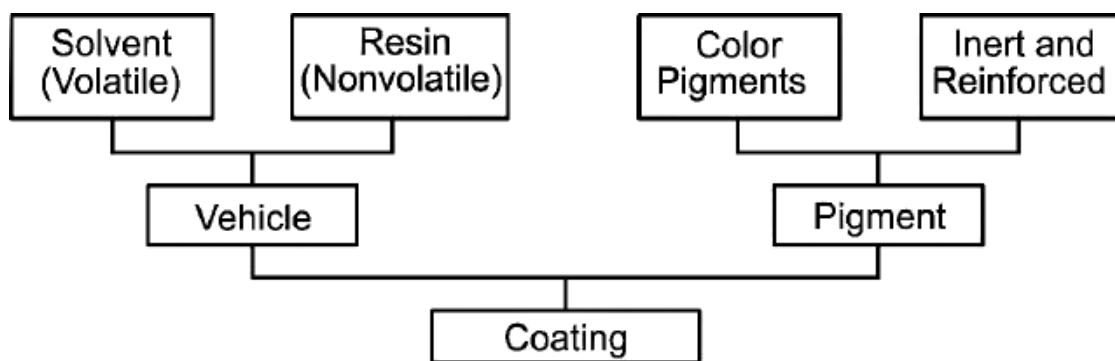

Figure 2.2 – Components of coatings

Some other concepts important for designing corrosion-resistant coatings include those of coating protection, component design, component function, and coating formulation. Many coatings contain as many as 15 to 20 ingredients with their own range of functionality. Some of the main variables used to design corrosion protective coatings are:

1. *Impermeability.* The ideal impermeable coating should be completely unaffected by the specific environment it is designed to block, be it most commonly humidity, water, or any other corrosive agent such as gases, ions, or

electrons. This ideal impermeable coating should have a high dielectric constant and also have perfect adhesion to the underlying surface to avoid any entrapment of corrosive agents. Good impermeability has been the successful ingredient of many anticorrosion coatings.

2. *Inhibition*. In contrast with coatings developed on the basis of impermeability, inhibitive coatings function by reacting with a certain environment to provide a protective film or barrier on the metallic surface. The concept of adding an inhibitor to a primer has been applied to coatings of steel vessels since these vessels were first constructed. Such coatings were originally oil based and heavily loaded with red lead.

3. *Cathodically protective pigments*. As with inhibition, cathodic protection in coatings is mostly provided by additives in the primer. The main function of these additives is to shift the potential of the environment to a less-corrosive cathodic potential. Inorganic zinc-based primers are good examples of this concept.

The coating system approach. For serious corrosion situations, the coating system approach (primer, intermediate coat, and topcoat) provides all the ingredients for a long-lasting solution.

Primers. The primer is a universal component of all anticorrosive coatings and is considered to be one of the most important element of a protective system. A good primer generally provides the ability to stifle or retard the spread of corrosion discontinuities such as pinholes, holidays, or breaks in the film. To perform satisfactorily they must themselves adhere well to the base metal or any surface conversion coating that might be present. They should also contain an adequate concentration of a leachable inhibitor, where this is considered an important feature of the protection system, and this is usually a chromate pigment. The primary functions of a primer are:
– adhesion or strong bond to the substrate;
– cohesion or internal strength;
– inertness to the environment;
– high bond to intermediate coat;
– appropriate flexibility.

Intermediate or body coats. Intermediate or body coats are usually used in coating systems designed for specific applications where coating thickness and structure are advantageous. Intermediate coats with red lead and inert pigments have been giving coatings a heavy body that is impervious to the most demanding applications. The primary purposes of an intermediate coat are to provide:
– thickness to a protective coating;
– strong chemical resistance;
– resistance to moisture vapor transfer;
– increased coating electrical resistance;
– strong cohesion;
– strong bond to primer and topcoat.

Topcoats. In the coating system approach, the topcoat provides a resinous seal over the intermediate coats and the primer. The first topcoat may in fact penetrate into the intermediate coat, thus providing the coating system with an impervious top surface. The topcoat is the first line of defense of many coatings against aggressive chemicals, water, or the environment. It is generally more dense than intermediate coats because topcoats are formulated with a lower pigment-tovehicle (solvent) ratio. The topcoats commonly used include air-drying paints and oil-based varnishes which harden by oxidation; acrylics and other lacquers, which dry by solvent evaporation; and polyurethane and epoxy paints, which dry by cold curing chemical reactions. Hightemperature curing or stoving can also be used with certain types of epoxy to produce a harder finish, but this also makes them more difficult to remove.

Polyurethane paints have been widely used in marine applications worldwide. However, these paints are quite brittle and tend to chip and crack, and for these reasons many prefer solvent-drying acrylic paints for the exterior finish. These paints can be removed locally by chemical solvents down to the primer and are reported to be easier to touch up. Whichever paint system is selected for exterior use, it is usual to qualify the system on the basis of its ability to prevent filiform corrosion. Topcoats main functions are to provide:
– a resistant seal for the coating system;
– an initial barrier to the environment;
– resistance to chemicals, water, and weather;
– toughness and wear resistance to the surface;
– a pleasant appearance.

However, there are a number of situations where the intermediate coats provide the primary barrier to the environment, and the finish coat is applied for entirely different purposes. The topcoat can be used, for example, to provide a nonskid surface, and the intermediate coat and the primer provide the barrier to the environment, as in a marine environment.

2.4 Plating on plastics

Electroplating on plastic
When you need to give plastic materials the ability to conduct electricity, then an effective solution is to "metalize" these materials by adding a metal coating via a process known as electroplating on plastic.

While electroplating is typically viewed as a "metal on metal" manufacturing technique, it is possible to electrodeposit metals onto other non-metallic objects as well. The process of plating metal onto plastic is now a widely accepted industrial practice that offers a number of crucial benefits for manufacturers everywhere.

Tracing the Development of Plating on Plastic
The first commercial metal plating plastic process was developed in the early 1960s, primarily for use in the automotive industry. Automobile manufacturers were seeking ways to make their vehicles more fuel efficient, which led

to the increased use of lightweight plastic parts and components. Electroplating served the purpose of "metallizing" these parts to give them the gleaming appearance that appealed to most car buyers of the era. A key advancement was the development of a reliable chemical process for the surface preparation of acrylonitrile butadiene styrene (ABS), a thermoplastic polymer that offers the toughness and impact resistance required for automotive manufacturing applications. The new process provided sufficient adhesion between the ABS substrate and the metal coating.

In recent years, there has been a resurgence in the demand for plating on plastic in a wide range of industries, specifically in the North American and European markets. This can be attributed to a renewed desire for bright trim among purchasers of vehicles and other products. Additionally, improvements in quality and environmental compliance have made the plastic plating process a more viable manufacturing technique than before.

Process of Electroplating on Plastic

Special preparation is necessary prior to plating on plastic. The material is initially etched in a chromic acid-based solution to enhance its adhesive capabilities. Any excess chromic acid that is produced must then be neutralized. A solution consisting of palladium and tin salts is then applied to the material. Next, the surface of the material is coated with either nickel or copper from an electroless plating solution. The palladium and tin salt solution serves as catalyst when combined with the nickel or copper. The material is now ready for electroplating using standard plating technology.

Another option is to apply a conductive paint to the plastic surface prior to commencing the electroplating process.

The increasing popularity of the use of plastics and plastic composites in a wide variety of manufacturing processes has also led to a greater demand for plating on plastic. Plating plastic with a metal surface enhances the appearance of the material and creates the impression of higher quality. As a result, it is often selected when a highly decorative look is desired.

Additionally, plating on plastic can be an effective means of protecting a substrate against the forces of corrosion and make it more resistant to damage from chemicals used in the manufacturing process. In some instances, plating on plastic can increase the strength and wear resistance of the substrate.

An important benefit of plating on plastic is that it can significantly enhance the appearance of the substrate. Most industrial plastics tend to have a dull finish. While colorizing the plastic can make it more visually appealing, it still will not produce the bright, shiny appearance that many product owners desire. While plating with chrome has long been a popular technique, the potential health hazards posed by the hexavalent chromium plating process has led many metal finishing providers to employ safer alternatives, particularly nickel plating.

Electroplating can also give a non-conductive plastic surface the ability to conduct electricity, a property that is invaluable to the manufacturers of elec-

tronic parts and components used in automobiles, aircraft and a multitude of other products. A metal coating can also reflect potentially damaging light away from the surface of a plastic substrate and serve as a protective barrier against harmful gases and corrosion. Additionally, metallization can help to control the dissipation of energy.

The Best Metals to Plate Onto Plastic Substrates

Plating on plastics can be achieved with various metals. Copper is the obvious choice when there is a need to enhance the electrical conductivity of the substrate. Gold or silver plating plastic can also be used to add aesthetic appeal to a plastic product. Nickel plating on plastic is also a widely implemented metal finishing industry practice.

It is possible to plate a variety of metals onto plastic including:

Gold. Gold plating plastic parts will obviously improve their appearance. Gold also offers a number of additional benefits. Gold provides protection against corrosion and is such a good conductor of electricity that it is frequently used to provide a conductive coating on electronic parts and components. Additionally, gold's excellent heat shielding properties make it suitable for high-temperature applications.

Nickel. Because of nickel's bright, metallic appearance, it can serve as a suitable – and less toxic – substitute for chrome when plating plastic automotive parts. Nickel also provides protection against corrosion and wear. Alloying nickel with other metals such as tin and tungsten can increase the hardness of the nickel deposit and enhance its corrosion and wear resistance capabilities.

Copper. Copper is perhaps best known for its excellent electrical conductivity, which is why copper plating is such as popular choice for metallizing non-conductive metal surfaces. Copper plating can also be used as a heat stop-off for masking. A major benefit of copper plating is its relatively low cost, especially when compared to precious metals such as gold and silver.

Chrome. Despite the fact that hexavalent chromium is a known carcinogen and is listed as a hazardous air pollutant by the U.S. Environmental Protection Agency, many metal finishing shops still use chrome.

In many plastic plating applications, it is necessary to deposit an undercoat onto the plastic substrate prior to electroplating in order to build thickness and promote coating adhesion. A process known as electroless plating is typically used to accomplish the task. Electroless plating differs from electroplating in that no electrical current is used to deposit the coating. Instead, deposition occurs via an autocatalytic chemical reaction. Nickel and copper are the two most commonly used metals for electroless plating, although techniques for gold and tin have also been developed.

Plastic Plating Process

The process of plating on plastic is somewhat different than traditional electroplating. There are a number of additional steps that must occur prior to the application of the metal coating. It's essential to thoroughly clean the surface of the substrate to remove any dirt and debris that could negatively affect

coating adhesion. The next step is etching the plastic substrate in a chromic acid solution to promote adhesion and then neutralizing any excess chromic acid.

After that, it is necessary to activate the substrate surface with a palladium and tin salt solution, which is followed by the application of the electroless nickel or copper coating. At this point, the metal coating can be applied using standard electroplating techniques.

Because of the difficulty involved with plating on plastic, it is necessary to closely monitor the process and perform troubleshooting steps as needed.

2.5 Basic coating components

2.5.1 Binders

To perform in a practical environment, a coating must convert, after its application, into a dense, solid, and adherent membrane that has all the properties discussed previously. The binder is the material that makes this possible. It provides uniformity and coherence to the coating system. Not all binders are corrosion resistant, so only a few serve in the formulation of protective coatings. The binder's ability to form a dense, tight film is directly related to its molecular size and complexity. Binders that have the highest molecular weight will form films by the evaporation of the vehicle, whereas binders with smaller molecular weight will generally be reacted in situ. Binders can be classified according to their essential chemical reactions.

Oxygen-reactive binders. Oxygen-reactive binders are generally low molecular weight resins that are only capable of producing coatings through an intermolecular reaction with oxygen. This reaction is often catalyzed by metallic salts of cobalt or lead.

Alkyds. Alkyds are produced by chemically reacting natural drying oils to form a synthetic resin with good film curability, chemical resistance, and weather resistance.

Epoxy esters. Epoxy resins react chemically with drying oils to form epoxy esters. The drying oils' part of the molecule determines the basic properties of the epoxy ester coatings. The coating dries by oxidation in the same manner as an alkyd.

Urethane alkyds. Epoxy resins are also chemically combined with drying oils as part of the molecule that further reacts with isocyanates to produce urethane alkyds. Upon application as a liquid coating, the resin-oil combination converts by oxidation to a solid.

Silicone alkyds. Alkyd resins are combined with silicone molecules to form an excellent weather-resistant combination known as silicone alkyds.

Lacquers. Lacquers are coatings that are converted from a liquid material to a solid film by the evaporation of solvents alone. Lacquers have generally a low volume of solids.

Polyvinyl chloride polymers. This principal corrosion-resistant lacquer is made from polyvinyl chloride copolymers. The vinyl molecule is relatively large and will effectively dissolve in solvent in the 20% range.

Chlorinated rubbers. To be effective, chlorinated rubbers have to be modified by other resistant resins to obtain higher solids, decreased brittleness, and increased adhesion.

Acrylics. Acrylics are also of high molecular weight and may be combined with vinyls to improve exterior weatherability and color retention.

Bituminous materials. Bituminous asphalts and coal tars are often combined with solvents to form lacquer-type films. They can provide good corrosion resistance but can only be applied where appearance is not a factor.

Heat-conversion binders

Hot melts. Hot melts normally involve asphalt or coal tar and are melted and applied as 100% solids in the hot-liquid condition.

Organisols and plastisols. These are high molecular resins (organisols) or vinyl materials (plastisols) that are dispersed in a solvent or plasticizer to solvate them into a filming material upon heating.

Powder coatings. Powder coatings are high molecular weight thermoplastic resins or semithermoset resins applied to a substrate as a very fine powder that is melted to form a coating. Powder coatings can be applied by using an electrostatic field with the coating and substrate charged with opposing polarities. Such an application method is very efficient because the coated section of a substrate becomes insulating, therefore making the uncoated section the only one electrostatically attractive to the powder being applied.

Coreactive binders

Coreactive binders are formed from two low molecular weight resins that are combined prior to the application to the substrate, where they react to form a very adherent and solid film.

Epoxies. Epoxy binders are made of relatively low molecular weight resins in which the epoxy group is at the end of each molecule. The epoxy resins are then reacted with amines of various molecular weight and cured to form high molecular weight binders with good solvent and chemical resistance.

Polyurethanes. Polyurethanes are coreactive binders in which low molecular weight resins containing alcohol or amine groups are reacted with diisocynates into an intermediate resin prepolymer that is then capable of reacting with other groups containing amines, alcohol, or even water.

Condensation binders

Condensation binders are based primarily on resins that interact to form cross-linked polymers when subject to sufficient thermal energy. These binders are also called high-baked materials and are commonly used as tank and pipe linings. Condensation is essentially the release of water during the polymerization process.

Coalescent binders

Coalescent binders are coatings where binders of various resin types are emulsified to form a liquid binder. They are primarily emulsified with water or less commonly with some other solvent dispersions. When applied to the surface, the medium evaporates, leaving the coating in such a way that the binder resin gradually flows into itself, or coalesces, to form a continuous film.

Inorganic binders. Inorganic binders are mostly inorganic silicates dissolved in water or solvent that react with moisture in the air after their application to a surface. The type of inorganic binder depends on the form of the silicate during the curing period.

Postcured silicates. Soluble silicates are combined with zinc dust to form very hard rocklike films that are further stabilized by reacting them with an acidic curing agent.

Self-curing water silicates. In this case, the soluble alkali silicates are combined with colloidal silica to improve the curing speed. Once applied to a surface they develop water insolubility by reacting with carbon dioxide and moisture from the air.

Self-curing solvent-based silicates. These binders are organic esters of silica that are converted from a liquid form to a solid by reaction with moisture from the air, forming a very hard and corrosion-resistant binder. A major advantage of these materials is their conversion to rain- or moisture-resistant form shortly after their application.

2.5.2 Pigments

Pigments are essentially dry powders that are insoluble in the paint medium and that consequently need to be mixed in it by a dispersion technique. They range from naturally occurring minerals to artificial organic compounds. Pigments contribute several properties essential to the effective use of protective coatings. Several different pigments may be used within the same coating, all of them contributing to the coating's general characteristics to perform important functions such as providing:
– color;
– protection to resin binder;
– corrosion inhibition;
– corrosion resistance;
– film reinforcement;
– nonskid properties;
– sag control;
– increased coverage;
– hide and gloss control;
– adhesion.

Zinc phosphates are now probably the most important pigments in anticorrosive paints. The selection of the correct binder for use with these pigments is very important and can dramatically affect their performance. Red lead is likely to accelerate the corrosion of nonferrous metals, but calcium plumbate is unique in providing adhesion to newly galvanized surfaces in the absence of any pretreatment and is claimed to behave similarly on other metals.

2.5.3 Solvents

Most coatings are made with multiple solvents and rarely with a single solvent. The choice of solvents influences viscosity, flow properties, drying speed, spraying and brushing characteristics, and gloss. There is no universal solvent for protective coatings, the best solvent in one system being often impractical for another. Asphalts, for example, can be readily dissolved by hydrocarbons but are insoluble in alcohols. One of the most serious problems associated with coatings is the wrong choice of solvent because it can severely affect the curing and adhesion characteristics of the final coating. One convenient way to describe solvents is to regroup them into the following categories:

1. *Aliphatic hydrocarbons.* Aliphatic hydrocarbons or paraffins such as naphtha or mineral spirits are typically used with asphalt-, oil-, and vinyl-based coatings.

2. *Aromatic hydrocarbons.* Aromatic hydrocarbons, such as toluene, xylene, or some of the higher-boiling homologs, are typically used with chlorinated rubbers, coal tars, and certain alkyds.

3. *Ketones.* Ketones such as acetone, methyl ethyl ketone, methyl isobutyl or amyl ketone, and many others, are very effectively used with vinyls, some epoxies, and other resin formulations.

4. *Esters.* Esters such as ethyl, n-propyl, n-butyl, and amyl acetates are used commonly as latent solvents (a type of solvent that just swells the binder at room temperature) with epoxy and polyurethane formulations.

5. *Alcohols.* Alcohols such as methyl, propyl, iso-propyl or butyl alcohols, and cyclo-hexanol are good solvents for highly polar binders such as phenolics. Some alcohols are used in connection with epoxies.

6. *Ethers and alcohol ethers.* Ethers such as ethyl ether are excellent solvents for some of the natural resins, oils, and fats. The usual forms of ether used in protective coatings are alcohol ethers such as ethylene glycol mono methyl ether, known commonly as cellosolve. Cellosolve is a good solvent for many oils, gums, natural resins, and synthetic resins such as alkyds, ethyl-cellulose, nitro-cellulose, polyvinyl acetate, polyvinyl butyryl, and phenolics. Cellosolve is a slow solvent that is used in many lacquers to improve flow-out and gloss.

7. *Water.* The recent regulations to reduce the emission of volatile organic compounds (VOCs) produced by organic solvents are forcing the coating industry to reconsider the applicability of water as a solvent. The most common water-borne coatings used for application to metals are air dried or force dried at temperatures below 90°C. A wide range of coating formulations falls into this category. The most commonly available technologies are water-reducible alkyds and modified alkyds, acrylic latexes, and acrylic epoxy hybrids.

2.5.4 Nonstick coatings

Nonstick coatings for industrial, architectural, automotive, aeronautical industry and marine use are widespread. Hull coatings that resist the formation of

strong bonds to marine organisms keep ships free from marine growth without needing heavy metal toxins that accumulate in the environment. Maintaining sanitation in health-care facilities and food processing plants is eased by surfaces that resist microbial attachment.

Investigations of nonstick surfaces have usually focused on the surface and overlooked the adherent. The free energy of a surface or its critical surface tension has long been believed to be the dominant factor in adhesion.

Surface free energy is the excess energy of the groups, atoms, or molecules on the surface compared with their counterparts in the bulk material. The size of the free energy represents the capability of the surface to interact spontaneously with other materials. Organic polymers possess surface free energies typically between 11 and 80 $mJ \cdot m^{-2}$. Many commercial polymers with surface energies at the lower end of this range have been studied in the search for nonstick coatings.

Hydrocarbons such as polyethylene and polypropylene are readily available and inexpensive, but they are not sufficiently soluble to cast as films. Unsubstituted hydrocarbons are easily oxidized and their nonstick properties rapidly deteriorate in exterior usage. Halogenated polymers containing chlorine and especially fluorine have also received a great deal of attention. There are at least half a dozen commodity homopolymers and copolymers containing vinyl fluoride, vinylidene fluoride, tetra-fluoroethylene, hexa-fluoropropylene or chlorotrifluoroethylene. All of these have surface energies between 15 and 31 $mJ \cdot m^{-2}$ and show excellent resistance to chemicals.

Fluorinated precursors are now commercially available to help overcome the obstacles of solubility and adhesion to the substrate. These oligomers have molecular weights of 2000 to 7000 and contain fluorine to impart low surface energy and hydroxyl groups to confer reactivity and adhesion. They are formulated with polyisocyanates to produce urethane coatings. The dominant fluorinated polyols used today are copolymers of chlorotrifluoroethylene and assorted nonhalogenated vinyl ethers. The latter are functionalized to provide reactivity, adhesion, and solubility, and their structure and proportions vary widely. The materials are known generically as *fluorinated ethylene vinyl ether* (FEVE) resins.

Fluorinated polyols derived from hexafluoroacetone (HFA) are also produced for surface coatings. The surface energy of these polyols is close to that of poly(tetrafluoroethylene) (PTFE), and PTFE can be dispersed in the resin as any conventional paint pigment. Flakes of PTFE overlap in the dry film, improving the barrier properties of the coating. These coatings are used as interior linings in large fuel storage tanks and have been used as anticorrosion coatings for ship bilges and tanks and as nontoxic fouling release coatings on small boats.

Industrial and marine coatings containing either FEVE- or HFAbased fluoropolyurethanes are applied as a topcoat over a urethane or epoxy primer.

When topcoating is done before the basecoat has fully cured, chemical reaction between the two coats takes place and ensures good adhesion and durability. Fluorinated groups preferentially migrate to the upper surface, where they demonstrate their nonstick behavior.

However, some drawbacks to fluorocarbon surfaces persist. For example, pure PTFE is quite porous and accumulates marine fouling rapidly, in spite of its low surface free energy, because marine organisms inject their adhesive and achieve a mechanical interlock. In addition, fluorine atoms impart stiffness to fluoropolymer chains by raising the barrier to rotation about the backbone bond. In addition, fluorourethane coatings are highly cross-linked thermosets with little or no significant molecular mobility.

2.6 Supplementary Protection Systems

Supplementary protection is provided to surfaces that already have some form of permanent or semipermanent protection such as cladding or conversion coating. The supplementary protection may be in the form of a material that can be easily applied and removed and that will be replaced periodically during the life of the system. Jointing compounds and sealants are examples of this type.

2.6.1 Jointing compounds and sealants

Jointing compounds are used for protection at joints where they act by excluding dirt and moisture and by providing a reservoir of soluble passivators that act as inhibitors. Sealants are applied to joints to prevent the escape of fluids, such as fuel, but they also exclude moisture. Jointing compounds must remain flexible to allow easy disassembly of parts. Various synthetic resins are used for this purpose. The compounds harden sufficiently at edges to take paint, but they remain tacky within the joint so that flexure does not cause cracking. Sealants of the type now being specified are also elastomeric, and the most popular are polysulphide sealants containing corrosion inhibitors. The inhibitive sealants are very effective when used in faying surfaces and butt joints, for wet installation of fasteners, and over fastener patterns. They are also effective in insulating dissimilar metals.

2.6.2 Water-displacing compounds

Water-displacing compounds may be useful in providing supplementary protection for paint systems that have deteriorated or become damaged in service. They are applied as fluids by wiping, brushing, spraying, or dipping, and they are usually immiscible with water and displace water from surfaces and crevices. A number of fluids used are based on lanolin and contain various solvents and inhibitors. The evaporation of the solvents leaves either thin soft films, semihard films, or hard resin films that provide varying degrees of protection. Some of these fluids may be used to provide short-term protection. They should then exhibit excellent water-displacing characteristics and leave a thin oily film, providing short-term corrosion protection.

Two typical water displacement products used by aircraft maintainers are AML-350 and AMLGUARD. AML350 is a petroleum sulfonate in a mineral spirit solvent. When applied to a metal surface, it spreads over the surface and under water droplets, and as the solvent evaporates, it leaves a soft oillike film of sulfonate, which isolates the metal from the environment and acts as a corrosion inhibitor. The film is built up to a thickness of 2 to 5 μm.

AMLGUARD is a water-displacing compound containing solvents, silicone and silicone alkyd resins, barium petroleum sulfonate, and several other additives. It dries to the touch in about 18 h, but continues to cure for 1 to 3 months to form a hard, dry, but flexible finish between 25 and 50 μm thick. It not only displaces water, but it also leaves a protective barrier coating containing barium petroleum sulfonate and alkyl ammonium organic phosphate as inhibitors. AML350 is intended for use on internal metallic parts and electrical connectors. AMLGUARD is intended for temporary use on external aircraft parts, such as wheels, wheel wells, cables, landing gear parts, wing leading edges, and helicopter blades.

2.7 Surface Preparation

It is well recognized that you can make a poor coating perform with excellent pretreatment, but you cannot make an excellent coating perform with poor pretreatment. Surface pretreatment by chemical or mechanical means is also important in painting, and the methods used are designed to ensure good adhesion of the paint to the alloy surface. Surface engineering for increased material performance is one important element in the world of metal finishing. Most metal surface treatment and plating operations have three basic steps:

1. Surface cleaning or preparation, which involves the use of solvents, alkaline cleaners, acid cleaners, abrasive materials, and/or water.

2. Surface modification, which involves some change in surface properties, such as application of a metal layer or hardening.

3. Rinsing or other workpiece finishing operations to produce the final product.

3 PAINT COATINGS

Paints are stable mechanical mixtures of one or more pigments which impart desired colour and to protect the film from penetrating radiation, such U. V. rays.

The purpose of paint may be protective or decorative or both and can be applied on a metal or wood surface. It is applied by brushing, dipping, spraying, or roller coating.

The important varieties of paints are emulsion paints, latex paints, metallic paints, epoxy resin paints, oil paints, water paints or distempers etc.

3.1 Classification of paint

On the basis of their applications, paints can be classified as:

1. Exterior house paints.

Generally have constituents such as pigment (ZnO, TiO2, white lead etc.), extenders (talc, barytes, clay etc), vehicle (e.g. boiled linseed oil) and

thinners (e.g. mineral spirit, naphtha etc.) Coloured pigments for light tint are also added in varying amount.

2. Interior wall paints.

It is prepared by mixing pigments (e.g. white and colored pigments), vehicle (e.g. varnish or bodied linseed oil) and resins (e.g. emulsified phenol formaldehyde resins and casein)

3. Marine paints.

Also known as antifouling paint and can be prepared by mixing various ingredients such as pigments (ZnO and venetian red), resin (shellac), driers (manganese lineolate), vehicle (coal tar), diluents (pine oil), toxic components(cuprous oxide and mercuric oxide) and small amount of bees wax.

4. Emulsion paints.

These paints are highly durable, impermeable to dirt, resistant to washing, rapidly drying, contain water as thinner and can be easily cleaned. It contain an emulsion of alkyds, phenol formaldehyde etc.(vehicle) in water pigments and extenders are also added to get other desirable properties.

5. Chemical resistant paints.

Consist of baked oleo resinous varnishes, chlorinated rubber compositions, bituminous varnishes and phenolic dispersion as chemical resistant materials in paint formulations.

6. Fire resistant paints.

These paints impart a protective action on the article being coated through easy fusion of the pigments and other paint ingredients giving off fume on heating, they do not support combustion. It consist of borax, zinc borate, ammonium phosphate synthetic resins etc as anti-fire chemicals.

7. Luminous paints.

Consist of phosphorescent paint compositions such as pigment (sulfides of Ca, Cd and Zn dispersed in spirit varnish), vehicle (chlorinated rubber, styrol etc.) and sensitizer for activation in UV region.

8. Latex paints.

These paints usually contain:

– protein dispersion. Prepared by soyabean proteins or casein in aqueous ammonia solution for about an hour at room temperature;

– pigments (ZnS,TiO2 etc dispersed in water);

– extenders (clay, talc, MgSiO3, BaSO4 etc.);

– preservatives (Penta chlorophenol);

– antifoaming agent (Pine oil);

– plasticizer (Tributylphosphate);

– latex. Prepared from a butadiene styrene copolymer in water.

All these ingredients well stirred in water, screened, again stirred and packed.

9. Aluminum paints.

Used as heat reflecting paints and consist of pigment (aluminum powder) and vehicle (spirit varnishes) and cellulose nitrate lacquers.

10. Metal paints.

Applied on the metal surfaces or bodies for protection and decoration and are of two types: barrier coating, galvanic coating.

Barrier coating

Protective barrier is formed between the surface coated and its surroundings. These consist of pigment, vehicle, anticorrosive agents (e.g. zinc or chrome yellow), resins (e.g. alkyds, epoxy, polyamides, chlorinated rubbers and silicones) etc. Alkyd resists weathering of metals, epoxy and polyamides form tough film resistant to chemicals. Chlorinated rubbers resist action of soaps, detergents and strong chemicals and silicons are added as heat resistant and water repellents.

Galvanic coating

Protection is provided by self-undergoing of galvanic corrosion e.g. Zinc coating (Galvanization) on steel.

Before applying metal paints it is important to clean thoroughly the surface to be coated. Moreover, paint should be applied over a primer such as red lead by a high pressure spray gun.

11. Cement paints.

It is prepared by mixing white cement with colouring matter or pigments, hydrated lime and fine sand as inert filler. They are available in the form of powder of particular colour.

The dispersion medium may be water or oil, depending upon the purpose of coating. Water and linseed oil are used as dispersion medium for stone/brick structure and for coating of corrugated metal surfaces respectively. Before applying cement paint a primer coat is applied which consist of a dilute solution of sodium silicate and zinc sulfate.

Cement paints have marked water proofing capacity, give a stable and decorative film and do not require fresh application even in four to five years, if coated even on rough surface.

12. Distempers.

Distempers are water paints consisting of pigments which may be white as well as coloured (e.g. Reimann's green), extenders (e.g. chalk powder, talc), binders (e.g. casien or glue) and dispersion medium water. These water paints have good covering power, easy applicability, and smooth, pleasant looking durable film. The major disadvantage of these is the porous nature of the film which is not moisture proof.

In general the paints are known for their gloss, adhesion as well as chemical and mechanical properties. They are suitable for the interior decoration as well as painting.

3.2 The components of paint

The composition of a paint is indicated in Table 3.1 which also indicates the function of the main components.

Table 3.1 – The composlition of paints

	Components	Typical function
Vehicle (continuous phase)	Polymer or resin (Binder)	Provides the basis of continuous film, sealing or otherwise protecting the surface to which the paint is applied.Varies in chemical composition according to the end use.
	Solvent or diluent	The means by which the paint may be applied. Avoided in a small number of compositions such as powder coatings and 100% polymerizable systems.
Pigment (discontinuous phase)	Additives	Minor components, wide in variety and effect, e.g. catalysts, driers, flow agents.
	Primary pigment (fine particle organic or inorganic)	Provides opacity, colour, and other optical or visual effects. Is thus most frequently used for aesthetic reasons. In primers the pigment may be included for anti-corrosive properties.
	Extender (coarse particle inorganic matter)	Used for a wide range of purposes including opacity/obliteration (as an adjunct to primary pigment); to facilitate sanding, e.g. in primer surfacers.

Not all paints have every ingredient, as will be indicated in subsequent specialist chapters. For example gloss paints will not contain extenders which are coarse particle inorganic materials. These are used in matt paints such as the surfacers or primer surfacers used in the motor industry.

Major differences occur between the polymers or resins that are used in paints formulated for different purposes. This is because of differences between the methods of application and cure, the nature of the substrate, and the conditions of use. Thus architectural ('decorative' or 'household') paints will be required to be applied in situ at ambient temperatures (which may be between 7 and 30 °C depending on climate and geographical location). They will 'dry' or 'cure' by one of two mechanisms: (i) atmospheric oxidation or (ii) the evaporation of diluent (water) accompanied by the coalescence of latex particles comprising the binder. Many industrial finishing processes will require the use of heat or other forms of radiation (UV, IR, electron beam) to induce chemical reactions, such as free radical or condensation polymerization, to convert liquid polymers to highly crosslinked solids. The most common of these processing

methods uses 'thermosetting' polymers which will frequently be admixtures of two quite different chemical types of material, e.g. alkyd combined with amino resin. There is a similarity between both the oxidative drying and industrial thermosetting processes in so far that in both cases the polymers used are initially of low molecular weight and the curing process leads to crosslinking of these polymers to yield highly complex extremely high molecular weight products. In contrast, it is possible to produce coatings without the need for crosslinking, for use in both of these distinctive markets. In the case of decorative or architectural paints this is exemplified by the emulsion paint, in which the binder is in the form of high molecular weight polymer particles suspended in an aqueous medium. Lacquers used in the motor industry may be based upon high molecular weight polymer in solution. Both systems avoid the need for crosslinking to achieve satisfactory film properties, but recent technological developments suggest that improved film properties can be achieved by the introduction of crosslinking in some form, e.g. by the use of microgels.

3.2.1 Polymer or resin film formers

The organic chemistry of film formers is will be useful to indicate here some of the range of polymers and resins that have come to be used as film formers, and to indicate their general areas of application.

Film formers or binders may be classified according to their molecular weight.Thus low molecular weight polymers that will not form solid films normally without further chemical reaction form one class. High molecular weight polymers that will form useful films without further chemical reaction form the second class. Examples of polymers and resins classified by this means are shown in Table 3.2.

Table 3.2 – Examples of polymers and resins classified

Low molecular weight	High molecular weight	
Oleoresinous binders	Nitrocellulose	
Alkyds	Solution vinyls	
Polyurethanes	Solution acrylics	
Urethane oils	Non-aqueous dispersion polymers (NADs)	
Amino resins	Polylvinyl acetate (PVA)	
Phenolic resins	Acrylic	latexes
Epoxide resins	Styrene/butadiene	
Unsaturated polyesters		
Chlorinated rubber		

Low molecular weight film formers

Oleoresinous binders
These are prepared by heating vegetable oils with naturally occurring resins such as wood rosin, fossil resins such as Congo Copal and Kauri gum. They would also include oil-modified phenolics.To a large extent these types of

resinous binder have been displaced by alkyd resins and the like, but many are capable of providing products that in performance are the equal of their successors, particularly in specific applications such as in architectural undercoat paint.They are less reproducible than condensation polymers like alkyds and are less attractive in terms of modern manufacturing processes.

Alkyds

Alkyds are polyesters derived as the reaction products of vegetable oil triglycerides, polyols (e.g. glycerol), and dibasic acids or their anhydrides (e.g. phthalic anhydride). They are generally formulated with very different end uses in mind, and classified according to vegetable oil content (described by the term 'oil length') in three broad categories: short oil, medium oil, and long oil, roughly corresponding to <45%, 45–60%, >60% respectively. The variation in oil length is usually coincident with changes in the nature of the vegetable oil used and consequently the end use.Thus, for architectural gloss paint of maximum exterior durability, the alkyd binder will be a long oil alkyd based upon a drying oil such as linseed or soya bean oils (i.e. an unsaturated triglyceride oil). The drying oil provides the means by which the film former dries. In this case the conversion from a low molecular weight liquid polymer to a highly crosslinked solid arises as a result of oxidation. One characteristic of the long oil alkyd is that it is soluble in aliphatic hydrocarbons. In contrast the short oil alkyd is likely to be based on a saturated triglyceride (such as coconut oil). It will not be soluble in aliphatic hydrocarbons and will normally be dissolved in a high boiling aromatic. Although the short oil alkyd may be capable of forming a lacquerlike film it would have a low softening point, and it is necessary to crosslink it in order to achieve a satisfactory film. In this case it is usually combined with an amino resin and crosslinked by condensation in a heat-curing process. It is debatable in this type of system whether the amino resin is crosslinking the alkyd or the alkyd is plasticizing the highly crosslinked amino resin. The former explanation is usually preferred because the proportion of the alkyd is invariably greater than that of the amino resin. The alkyd/amino resin ratio usually falls between 2 : 1 and 4 : 1 by weight. These types of system are used in industrial finishing. Alkyd/melamine formaldehyde compositions have found use in the automotive market for many years. Alkyd/urea formaldehyde compositions have found use in the domestic appliance market, although in both cases there have been new products developed that have displaced these materials to some extent, particularly when more stringent performance requirements have to be met.

Polyurethanes, urethane alkyds, and urethane oils.

Structurally, these materials resemble alkyds in which polyester linkages are replaced partially or totally by urethane linkages:

$$-NH-\underset{\underset{O}{\|}}{C}-O-$$

45
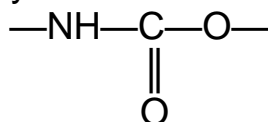
Polyurethanes also include two-pack compositions for the industrial and refinish markets in which the curing is achieved by reaction between free isocyanate groups in one component and hydroxyl groups in the second component. The advantages of urethane oils and urethane alkyds are derived from the resistance of the urethane link to hydrolysis. In decorative (architectural) paints it is common practice to use binders which are a mixture of a long oil alkyd and urethane alkyd for maximum durability.

Amino resins

The most common types of amino resin are reaction products of urea or melamine (1:3:5 triamino triazine) and formaldehyde. The resins are prepared in alcoholic media, which enables the molecular weight and degree of branching to be controlled within practically determined limits related to the end use of the resin. The effect of this modification is shown in the solubility and reactivity of the resins so produced. The polymers produced are generally regarded as being derived from the hydroxymethyl derivatives of melamine and urea respectively; subsequent addition condensation and etherification reactions lead to complex, highly branched polymeric species. Curing or crosslinking to solid films (usually in combination with an alkyd or other polymer) can be achieved thermally (oven-curing) or at room temperature. In both cases the presence of an acid catalyst is essential if adequate and rapid cure is to be obtained.

The crosslinking capability of amino resins may also be utilized as a means of curing acrylic resins. In this type of film former a minor proportion (usually a few percent) of a monomer such as N-butoxymethyl acrylamide is incorporated into the polymer. This provides reactive sites which enable the acrylic copolymer to be crosslinked. A suitable choice of monomers allows the acrylic resin to be plasticized internally, so that the use of added plasticizers is avoided. These resins are of particular interest where high levels of performance and particularly good adherence and flexibility are required.

Phenolic resins

The reaction of formaldehyde with a phenol gives rise to a range of resins that, in combination with other resins or drying oils, find use in industrial coatings. Broadly two main types of phenolic are produced, novolacs and resoles. Novolacs are low molecular weight linear condensation products of formaldehyde and phenols that are alkyl substituted in the para position. If the substituent alkyl group contains four or more carbon atoms (i.e. butyl or above – in the homologous series) the resin is likely to be oil-soluble. Resoles are products of the reaction of unsubstituted phenols with formaldehyde. Since the para position on the phenolic ring is available for reaction as well as the ortho position these resins are highly branched and can with continued reaction be converted into hard intractable glassy solids. Phenolics tend to confer chemical resistance to the compositions in which they are used.

They are always used in combination with other resinous film formers. In some cases they may be prereacted with the other resin components, or they

may be simply blended together. Thus a phenolic resin (e.g. a novolac) may be reacted with rosin or ester gum and then blended with a bodied (heat-treated) drying oil to form the binder in an architectural paint primer, or used simply in an unpigmented form as an oleoresinous varnish. Phenolic-based compositions find use in chemically resistant systems such as are required for pipes and tank linings.

Epoxide resins

The use of the epoxide or oxirane group:

$$—CHCH_2$$
$$\backslash\ /$$
$$O$$
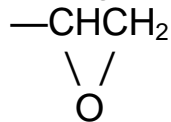
as a means of synthesizing resins and as a means of crosslinking binders is now well established. A large group of epoxide resins is based upon the reaction products of epichlorhydrin and bisphenol A (diphenylolpropane). These resins may be esterified with unsaturated fatty acids to give epoxy esters. These are film formers in their own right and resemble air-drying alkyds. They exhibit better chemical resistance than alkyds but are less durable than long oil alkyds in some circumstances.

The way in which they break down may, however, be turned to good use, for example when used as 'self-cleaning' coatings. In this case the films may be pigmented with uncoated titania in the anatase form so that degradation in ultraviolet radiation causes erosion of the surface layers of the film, otherwise known as chalking. Such films gradually weather away, always presenting a white surface to the elements.

Epoxide resins may also be used in conjunction with melamine formaldehyde (MF) or phenolics, or they may be formulated into epoxy-alkyds, i.e. where they are effectively being used as polyols in admixture with less functional polyols such as glycerol. The epoxide group offers great versatility in curing, and a wide range of two-pack compositions are possible. One of the most popular methods of crosslinking uses the reaction with polyamides. This is the same method of cure as used in epoxy adhesive compositions. The crosslinking occurs as an addition of terminal amino groups of the polyamide to the epoxy group. This reaction occurs slowly at room temperature. Crosslinking through the epoxide group can also arise from the use of polyamines or by means of the acid-catalysed polymerization to give ether crosslinks. It will be apparent that most of these products will be used in industrial applications.

Unsaturated polyesters

Unlike the previously described binders, unsaturated polyesters offer the benefit of totally polymerizable systems because the solvent in which they are dissolved is a polymerizable monomer. The simplest and most common polyesters are prepared from maleic anhydride/phthalic anhydride mixtures esterified with glycols such as propyleneglycol. The resins so produced are dissolved in styrene or vinyl toluene. The free radical copolymerization of the vinyl mo-

nomer and the maleic unsaturation in the polyester is usually initiated by a transition metal/organic hydroperoxide system at ambient temperature or by the use of the thermal scission of a diacyl peroxide at higher temperatures. Unsaturated polyesters have found extensive use both pigmented and as clears in the wood finish market.They are capable of widely divergent uses depending on their composition. Chemically resistant finishes for tank linings, for example, can be formulated on polyesters derived from isophthalic and terephthalic acids. Another class of chemically resistant finish is based upon chlorinated polyesters. In this case the polyester incorporates chlorendic anhydride in place of the more common phthalic anhydride.

Chlorinated rubber

Chlorinated rubber is a film-forming resin that is available in a wide range of molecular weights, from 3500 to about 20 000. It is prepared by chlorinating rubber in solution, the commercial product containing about 65% of chlorine. It is used as the main binder in air-drying paints which are to be used in situations requiring a chemically resistant product of great durability. Because the polymer is a brittle solid, in paint applications chlorinated rubber requires plasticization. Chlorinated rubbers are also used in conjunction with other resins with which they are compatible, such as alkyds. Paints based on chlorinated rubber have been used for building, masonry, swimming pools, road marking, and marine purposes.

High molecular weight film formers

Almost all high molecular weight polymers are produced by the free radical initiated polymerization of mixtures of vinyl, acrylate, or methacrylate monomers.They may be polymerized in solution, in suspension or dispersion. Dispersion polymerization may be in hydrocarbon diluents (NAD) or in aqueous media ('emulsion polymers').

One major exception to the foregoing is nitrocellulose. This material is formed by the direct nitration of cellulose in the presence of sulphuric acid. It is available in grades determined by the degree of nitration which, in turn, determine its solubility in various solvents. The grades used in refinish paints, wood-finish lacquers, etc. require the molecular weight of the original cellulose to be reduced somewhat, to meet viscosity requirements in the solvents commonly used.

In most cases the high molecular weight polymers do not need to be crosslinked in order to develop adequate film properties.A small number of solution polymers of moderately high molecular weight are, however, crosslinked through reactive groups incorporated into the polymer chain. The physical properties of films produced from high polymers may be only marginally affected by the manner in which they were prepared or their physical form at the stage of film application.Thus automotive finishes derived from solution acrylics and NADs are virtually indistinguishable, albeit that the methods of application,

processing conditions, etc. may be significantly different. In most cases the product that is selected will be dependent on the economics of the process overall rather than the product cost alone.The need to meet end use specification is the main reason for the similarity in film properties and performance of alternative product formulations.

Aqueous latexes (emulsion polymers) as a group have been one of the fastestgrowing sectors of the paint market. Starting with the use of homopolymer PVA as a binder in matt and low-sheen decorative wall paints we have seen the development of more robust systems using internal plasticization (i.e. the incorporation of a plasticizing comonomer) and, more recently, the use of acrylic and methacrylic copolymer latexes. Improved performance has enabled the introduction of these paints into exterior masonry applications.

The most recent developments in this field have entailed preparing latex particles with specific morphologies, such as core/shell particles in which the particle cores may be crosslinked. These physical changes in the structure of the latex particles enable significant improvements to be achieved in the mechanical properties of the derived films, and in film integrity as measured by 'scrub resistance'.For industrial paint applications, functionalized polymers that will undergo crosslinking after coalescence have been developed. These compositions have low volatile organic content (VOC) and are thus 'environmentally friendly'.

3.2.2 Pigments

Primary pigments

Primary pigments comprise solid particulate material which is dispersed in the binder or film former described previously.We shall distinguish between them and supplementary pigments, extenders, fillers, etc. in that they contribute one or more of the principal functions, namely colour, opacification, and anti-corrosive properties. The supplementary pigments, extenders, although important, do not in general contribute to these properties to a major extent. Their function is related to reductions in cost, but they can contribute properties to a paint that may be less obvious than colour or opacity. Thus they may enhance opacity, control surface sheen, and facilitate ease of sanding.

The principal pigment in use is titanium dioxide. This is primarily because of reasons of fashion, e.g. in the decorative paint market there has been a tendency for white and pastel shades to gain greater acceptance over strong colours in recent years.The same is true to a lesser extent in other fields, such as the motor car industry. In this case early motor cars were painted black, and it was difficult to obtain cars in other colours. Nowadays it is the black car that is a comparative rarity. Titanium dioxide in its pigmentary form is a highly developed pigment.The high refractive index rutile form is most commonly used, and the pigment is manufactured within very close limits with respect to particle size and particle size distribution. Although normally regarded as being chemically inert the surface of the titanium dioxide crystal is photoactive, and the pigmen-

tary form is surface coated to minimize photochemical activity at the binder/pigment interface. Typical coatings contain silica and alumina in various proportions, and in addition to reducing photochemical activity they can improve the dispersibility of the pigment in the binder. Considerable research has been carried out into titanium dioxide pigments, and manufacturers are now able to offer a range of grades that are suitable for use in different types of paint media.

Coloured pigments fall into two main groups, inorganic pigments and organic pigments. As a result of legislation governing the handling and use of toxic materials, many of the inorganic pigments traditionally used by the paint industry have been replaced by other less toxic materials. Thus except in a few industrial compositions lead pigments of all types (e.g. chromate, oxide, carbonate) have to a large extent been replaced, and it is to be expected that lead in all of its forms and chromates will ultimately be eliminated from all paints. Their removal from the scene gives rise to problems if a coloured pigment is used for the dual purposes of providing colour and contributing positively to the anti-corrosive properties of the paint film.

Some commonly used pigments are shown in Table 3.3.

Table 3.3 – Some typical primary pigments

Colour	Inorganic	Organic
Black	Carbon black Copper carbonate Manganese dioxide	Aniline black
Yellow	Lead, zinc, and barium chromates Cadmium sulphide Iron oxides	Nickel azo yellow
Blue/violet	Ultramarine Prussian blue Cobalt blue	Phthalocyanin blue Indanthrone blue Carbazol violet
Green	Chromium oxide	Phthalocyanin green
Red	Red iron oxide Cadmium selenide Red lead Chrome red	Toluidine red Quinacridones
White	Titanium dioxide Zinc oxide Antimony oxide Lead carbonate (basic)	—

At one time colour matching was an art carried out visually by very skilful individuals.Whilst the skilled colour matcher has not been entirely replaced, there has been a gradual change to instrumental colour matching, a trend that has been accelerated by the development of sophisticated colorimeters and the use of the computer.

In automotive and aviation paints there has been a growth in the use of aluminium flake as a pigment to provide attractive metallic finishes. The dimensions of the flakes and their orientation within the paint film give rise to optical effects that cannot be achieved in other ways. Inevitably such paints are subject to problems in quality control, application, and colour matching that do not exist in solid colours. Nevertheless these problems are sufficiently well understood to be kept under control, and their continued use is amply justified aesthetically.

Extenders, fillers, and supplementary pigments

All three names have been applied to a wide range of materials that have been incorporated into paints for a variety of purposes. They tend to be relatively cheap materials, and for this reason may be used in conjunction with primary pigments to achieve a specific type of paint. For example it would be technically difficult and prohibitively expensive to produce satisfactory matt white emulsion paint using titanium dioxide as the only pigment.Titanium dioxide is not cost effective as a matting agent and indeed is not designed for this purpose. It is much more economic to use a coarse particle extender such as calcium carbonate in conjunction with TiO_2 to achieve whiteness and opacity in a matt or semi-matt product (e.g. a matt latex decorative paint, an undercoat or primer). Extenders do not normally contribute to colour, and in most cases it is essential that they be colourless. The particle sizes of extenders range from submicrometre to a few tens of micrometres; their refractive index is generally close to that of the organic binders in which they are used, and so they contribute little opacity from light scattering. Platelet type extenders such as wet-ground mica can influence the water permeability of films, and many therefore contribute to improved corrosion resistance. Talcs are often used (e.g. in automotive primer surfacers) to improve the sanding of the paint prior to the application of a topcoat. Many of the extenders in common use are naturally occurring materials that are refined to varying extents according to the use to which they are put.Whilst every attempt is made to ensure that they are reproducible they tend to be more variable and with a greater diversity of particle shape, size, and size distribution than primary pigments. A list of typical inorganic extenders is given in Table 3.4.

In recent years there have been several attempts to make synthetic (polymeric) extenders to meet special needs, in particular to replace some of the titanium dioxide in the paint film. One such material, 'Spindrift', originating from Australia, is in the form of polymer beads (spherical particles up to 30mm in diameter which incorporate submicrometre air bubbles and a small proportion of pigmentary titanium dioxide).

Table 3.4 – Some typical extenders

Chemical nature	Type
Barium sulphate	Barytes
	Blanc fixe
Calcium carbonate	Chalk
	Calcite
	Precipitated chalk
Calcium sulphate	Gypsum
	Anhydrite
	Precipitated calcium sulphate
Silicate	Silica
	Diatomaceous silica
	Clay
	Talc
	Mica

The introduction of air bubbles into the polymer that forms the beads influences the light-scattering power of the titanium dioxide in one of two ways. It can reduce the average effective refractive index of the polymer matrix and so enhance the light-scattering of the titanium dioxide, if the bubbles are very small (<0.1 mm). If the bubbles are large (~0.8 mm) they are able to scatter light in their own right. Other methods of introducing voids into paints in a systematic way to take advantage of the scattering of light by bubbles have included the emulsification of small droplets of a volatile fluid into aqueous latex paints which leave cavities within the film by evaporation after coalescence ('Pittment'); yet another is the use of non-coalescing latex particles in combination with coalescing latexes to give rise to cusp-like voids within the film (Glidden). All of these methods seek to achieve a cost-effective contribution to opacity without sacrifice of film integrity and other properties.These methods have received limited acceptance, mainly owing to economic reasons. Nevertheless, they do increase the opportunities open to the paint formulator to formulate a paint for a given purpose.

3.2.3 Solvents

Solvents are used in paint compositions for two main purposes. They enable the paint to be made, and they enable it to be applied to surfaces. This may seem to be stating the obvious, but it is important to appreciate that so far as the paint film performance is concerned the solvent plays no long-term role in this. This is not to say that in the early life of the film solvent retention does not affect hardness, flexibility, and other film properties.

The term solvent is used frequently to include liquids that do not dissolve the polymeric binder, and in these cases it is more properly called a diluent. The function of the diluent is the same as a solvent, as stated above. In water-based systems the water may act as a true solvent for some components, but

be a non-solvent for the main film former. This is the case in decorative emulsion paints. More often in these cases it is common to refer to the 'aqueous phase' of the composition, acknowledging that the water present, although not a solvent for the film former, is present as the major component of the liquid-dispersing phase.

A wide range of organic liquids are used as paint solvents, the type of solvent depending on the nature of the film former.

Considerable research effort has gone on into the study of the thermodynamics of solutions. This has provided the paint formulator with much more precise methods of solvent selection. The improved methods are based upon a better knowledge and understanding of molecular attractions in liquids and a recognition of the additivity of molecular attractions in mixed solvent systems. It is very rare for a single solvent to be acceptable in most situations, and the newer methods based upon solubility parameter concepts enable the more rational selection of solvent mixtures to meet a particular need.

Solvency alone is not the only criterion upon which solvent choice is made. Other important factors include evaporation rate, odour, toxicity, flammability, and cost.

These factors assume different degrees of importance depending on how the paint is used. If the paint is applied under industrial manufacturing conditions it is likely that problems associated with odour, toxicity, and flammability may be under control, but this is by no means certain. The need to install expensive extraction equipment or after-burners may preclude the use of some solvents and therefore some types of paint composition. Closely related to considerations of toxicity are those of pollution. Many countries have enacted legislation to protect the individual and the environment. This legislation has had a profound effect on the development of the paint industry and has influenced both the raw material supplier on the one hand and the paint user on the other.

Other alternatives to solvent-based paints are 100% polymerizable systems and powder coatings. In the former case a polymerizable monomer such as styrene fulfils the role of solvent for the composition, being converted into polymer in the curing reaction. With powder coatings, solvents may be used in the early stages of the paintmaking process, but they are removed and recycled, so do not provide a hazard or problem for the user.

3.2.4 Paint additives

The simplest paint composition comprising a pigment dispersed in a binder, carried in a solvent (or non-solvent liquid phase) is rarely satisfactory in practice. Defects are readily observed in a number of characteristics of the liquid paint and in the dry film. These defects arise through a number of limitations both in chemical and physical terms, and they must be eliminated or at least mitigated in some way before the paint can be considered a satisfactory article of commerce.

Some of the main defects worth mentioning are settlement of pigment and skinning in the can; aeration and bubble retention on application; cissing, sagging, and shrivelling of the paint film; pigment flotation; and flooding. These defects represent only a small number of defects that can be observed in various paints:

– "cissing" is the appearance of small, saucer-like depressions in the surface of the film;

– "shrivelling" is the development of a wrinkled surface in films that dry by oxidation;

– "sagging" is the development of an uneven coating as the result of excessive flow of a paint on a vertical surface;

– "floating" is the term used for the colour differences that can occur in a paint film because of the spontaneous separation of component pigments after application;

– "flooding" (also known as "brush disturbance") is the permanent colour change of a paint subject to shear after application.

To overcome these defects their cause requires to be understood and a remedy found. In some cases the defect may be overcome by minor reformulation. Shrivelling, for example, is commonly due to an imbalance between the surface oxidative crosslinking of a film and the rate of crosslinking within the film. This can usually be overcome by changing the drier combination, which consists of an active transition metal drier such as cobalt which promotes oxidation and a "through" drier such as lead or zirconium which influences crosslinking, but does not per se catalyse the oxidation process. In other cases simple reformulation will not provide a remedy, and specific additives have been developed to help in these cases. Thus anti-settling agents, anti-skinning agents, flow agents, etc. are available from specialist manufacturers for most defects and for most paint systems.

The problems of "floating" and "flooding" are associated with colloidal stability of the pigment dispersion and may arise from a number of different causes. The differential separation of pigment illustrated by floating occurs as a result of the differences in particle size of the component pigment and may be overcome by coflocculation of the pigments in the system. Another method of curing the condition may be to introduce a small proportion of a very fine particle extender such as alumina, of opposite surface charge to the fine particle pigment, to coflocculate with the latter.

The flooding (or brush disturbance) problem is indicative of flocculation occurring as a film dries. Under shear, as the brush disturbs the paint, the pigment is redispersed and the paint becomes paler in shade. This is because an

increase in the back-scattering of incident light occurs, owing to the white pigment becoming deflocculated.

Cissing and sagging are illustrative of other aspects of physical properties associated with surface chemistry and rheology. In the former case, the effect is caused by a localized change in the surface tension of the film. In extreme cases this can give rise to incomplete wetting of the substrate, often distinguished by the term "crawling". Sagging, on the other hand, is a bulk property of the film that may be influenced by the colloidal stability of the composition. Ideal, colloidally stable dispersions tend to exhibit Newtonian behavior, i.e. their viscosity is independent of shear rate. This means that on a vertical surface a Newtonian liquid that is of a suitable viscosity to be spread by a brush, i.e. with a viscosity of about 0.5 N sm^{-2}, will flow excessively unless the viscosity rises rapidly as a result of solvent loss. Alternatively, the paint formulator may aim to induce non-Newtonian behaviour such that the low shear viscosity of the product is very high. Thus, sagging may be avoided by either or a combination of these effects.

3.3 Paint making

Having considered briefly the most important constituents of paint, their function, and what they contribute to the final product, we need to consider the paint-making process. It is possible for a paint manufacturer to make almost all types of paint without any chemical processing. This is because each of the constituents can be purchased from a specialist manufacturer. Providing the paint manufacturer has certain basic plant capable of storing, mixing, dispersing, blending, and filling, he or she can be in business. Indeed some small volume or specialist manufacturers do just this, using basic formulations often provided by the resin or pigment supplier. However, the major paint manufacturers world-wide, seeking to capture a significant proportion of world markets, mount considerable research and development effort to produce products that are technically superior to those of their competitors or, if no better, can be produced more cheaply.

One of the most important parts of the paint-making process is the dispersion of pigment to prepare a stable and reproducible product. This is usually carried out in two stages, the dispersion of the pigment in part of the binder solution (or other dispersing medium) to form a "millbase", followed by blending ("second staging") with the remaining binder solution. Finally, minor components of the composition, such as driers, flow agents, solvent (to adjust the viscosity), and tinters (according to the requirements of colour matching) are added.

The dispersion process involves the wetting of the pigment with the dispersing medium, the separation of particles from their aggregated state and

their stabilization in suspension, either as individual particles or in a lightly flocculated condition. The millbase is prepared in one of a number of mills (depending on the type of paint to be prepared), ranging from ball mills to cavitation mixers and attritors.

3.4 Methods of application

There are four main methods of applying paint:
– by spreading, e.g. by brush, roller, paint pad, or doctor blade;
– by spraying, e.g. air-fed spray, airless spray, hot spray, and electrostatic spray;
– by flow coating, e.g. dipping, curtain coating, roller coating, and reverse roller coating;
– by electrodeposition.

The methods adopted depend on the market in which the paint is used, each type of paint being formulated to meet the needs of the application method. Spreading by brush or hand-held roller is the main method for applying decorative/architectural paints and the maintenance of structural steelwork and buildings generally. It is also important in marine maintenance, although other methods (e.g. airless spray) may be used during the construction of a ship.

Application by spraying is the most widely applicable method. It is used for painting motor cars in the factory and by refinishers following accident damage; it is used in the wood-finishing industries (e.g. furniture) and in general industrial paints (e.g. domestic appliances). The various forms of spray painting make it a particularly versatile method of application.The flow coating methods are limited essentially to flat stock (e.g. chipboard) and coil coating (aluminium or steel coil) where they are much valued because of the high rates of finishing that can be achieved.

Electrodeposition has become established as the main method of priming the steel body shells of motor cars. The total process which involves degreasing, phosphate treatment, electrodeposition of primer, and then spray application of surfacer and finishing coats has raised the standards of corrosion resistance and general appearance considerably during this period. Electrodeposition may take place with the car body acting as either the anode or the cathode. In recent years it has been claimed that cathodic forms of electropaint give the better corrosion protection.

Mainly because of environmental considerations, powder coating has been a major growth area in industrial finishing, particularly in Western Europe, which produced 53% of the total world market for powder coatings in 1993. Powder coatings are normally applied by electrostatic spray, with minimal overspray losses and without the emission of VOCs.

4 COATING SYSTEM SELECTION

4.1 Criteria for Selecting a Coating System

No single coating or coating system can satisfy every service condition or environment that may be encountered in a given works facility. Selecting candidate coating systems for an exposure environment depends on identifying and understanding how each of the environments impact various coatings. For example, chlorinated rubber or vinyl coatings, which are thermoplastics, would not be used in locations subjected to high heat or strong solvents because they would quickly dissolve or soften. If alkyd enamels were used in an environment with, for example, caustic conditions, they would soften, swell, and quickly disbond as a result of saponification. Chemistry, experience, and the coating system performance history have illustrated these facts. The Paint Systems and Painting Schedule section of CWGS 09940 and the Supplementary Application Instructions contained therein show paint systems that will provide satisfactory, cost-effective performance based on given service environments. Characteristics of the environment that the coating system will encounter must be well identified. Once the environmental exposure has been properly determined, the process to select coatings systems that have a known history and track record of successful use in these identified environments may begin.

4.1.1 Identifying the service environment(s)

Picking the correct coating for painting projects might be described as a process of elimination rather than one of selection. Probably the most important step in coating selection is to evaluate the conditions under which the coating must perform. This cannot be a superficial evaluation but must consider all the conditions that may exist. Even small and seemingly irrelevant factors may affect coating system performance. In most situations, a combination of two or more service environments act together to create a hostile environment:

1. Temperature extremes. Most applied coating systems are subject to temperature variances within their applied environments. For the most part, these fluctuations are moderate (normal atmosphere fluctuations). Even normal atmospheric temperature variations have an effect on coating performance. Additionally, in many instances, unique processes or system operations may generate adverse (cold or hot) temperatures outside the normal. Extreme cold or heat can cause brittleness, poor impact resistance, shrinkage, or loss of adhesion and may alter the corrosion-prevention characteristics of the coating system. High temperatures also tend to aggravate the corrosivity of the environment severely (i.e., many acids become increasingly aggressive with temperature increases). Curing mechanisms involved with conventional coatings frequently are temperature dependent. With high heat, the curing process may occur too rapidly or, conversely, in cold temperatures curing may not occur at all. Coatings to be applied in extremely cold environments must have excellent adhesion, resiliency, and plasticity. Likely candidates for heat-resistant coatings

are those modified with silicone and/or metal flake (i.e., aluminum, stainless steel). Some inorganic, zinc-rich coatings can be applied at temperatures as cold as –18 °C (0 °F) and provide excellent corrosion protection in the extreme cold.

2. High humidity. High humidity frequently is accompanied by condensation. Consequently, such a continuously wet, heavily moisture laden environment is often considered to be in a state of constant immersion. A water molecule is extremely small and can pass through the molecular network of even the most moisture-resistant protective films. Each coating and resin type has a unique moisture vapor transfer rate. Obvious coatings for such continuously moist environments should exhibit low moisture vapor permeability (MVP) and water absorption rates. Industry practice generally has found that, the lower the moisture vapor transfer rate, the better corrosion protection the coating provides. Commonly used coatings with typically low moisture vapor transfer rates are formulations of two-part epoxies, vinyls, coal tars, and respective modifications of these coatings. Coatings pigmented with metallic or glass flake have been found to improve moisture resistance and lower the MVP rate of some coatings.

3. Immersion. Immersion service coatings are exposed to water solutions ranging from highly pure deionized water to water containing high concentrations of various chemicals, acids, or alkali solutions. Specific immersion linings may be subject to the effects of storage of petroleum or solvents. Primarily though, water is the main exposure element in immersions. Coatings for immersion service must exhibit good adhesion, moisture resistance, vapor transfer, ionic penetration, cathodic disbondment, osmosis, and variances in temperature. Examples of coatings that traditionally have performed well in immersion are: coal tar epoxies (CTE), vinyls, untopcoated zinc-rich coatings, and modifications of epoxy coatings.

4. Oxidizing-reduction. Oxidizing environments – such as atmospheric service or areas of ozone generation and strong oxidizing agents such as bleach or nitric acid – are more common than reduction environments. Most coatings are more susceptible to oxidation than to reduction. Oxidation may cause coating film brittleness and loss of cohesive strength; a common example of this is an old, weathered alkyd that can oxidize to an almost powdery state after many years. Generic coating types that historically have performed well in oxidizing environments are: CTEs, chlorinated rubber, and formulations of epoxies and polyurethanes.

5. Extreme pH. Extremes of pH, such as strong acid or alkaline environments, can have a dramatic effect on coatings systems selection. The degree of impermeability of the chosen coating to the environment is of primary importance. The coating film essentially must be inert to prevent a reaction with the environment or permeation of the solution into the coating film. Alkali resistance is vitally important to a primer coating. Chemical reactions that take place in the corrosion process produce strong alkaline products that are deposited on the

substrate. Subsequently, any primer that is not resistant to these by-products will have a tendency to fail because of cathodic disbondment. This failure can result in additional undercutting of the coating and the spreading of underfilm corrosion. Substrates such as concrete typically have a high alkalinity; therefore, a coating system chosen for a concrete substrate also must exhibit good alkaline resistance. Formulations of coatings that have a good history of performance in extreme pH environments are vinyls, chlorinated rubbers, and epoxy modifications. However, alkyd or oil-containing coatings tend to have a poor resistance to alkalinity and should not be used in such an environment.

6. Solvent exposure. The function of solvents in coating formulation in relation to the application properties of the coating is well known. However, solvents often become an exposure environment to the dry-cured coating system. The effects of the solvent on the coating system generally will vary by solvent type and the resistance of the generic type of coating that has been applied. There are numerous types of solvents. Typical solvents frequently can be classified into two categories: hydrocarbons and oxygenated solvents. A less important group of solvents are called the terpenes. Hydrocarbons are so named because their molecules contain only hydrogen and carbon atoms.

The molecules of oxygenated solvents also contain oxygen atoms. But some commonly used oxygenated solvents may contain atoms of other chemical elements such as nitrogen. Hydrocarbon solvents more commonly are found than oxygenated solvents. Oxygenated solvents and hydrocarbon solvents frequently are blended for use in lacquers, catalyzed coatings, and synthetic resins solutions. As with many other exposures, a high degree of impermeability is necessary for the coatings to resist solvents. The coating system chosen must not be dissolved or softened by the solvent in the exposure environment. For example, USACE vinyl systems are resistant to solvents of the aliphatic variety and most often can tolerate spills from aromatic hydrocarbons. However, the stronger oxygenated solvents will readily attack, soften, and dissolve the vinyl film. Therefore, it is necessary to make a good system selection because the binder may be dissolved easily and softened by various levels of solvency strength. Historically, twocomponent highly crosslinked coatings, such as formulations of epoxy and urethane coatings, have exhibited good solvent resistance. Therefore, the blend and type of solvent in the exposure environment should be identified so the appropriate coating system can be chosen. When all pertinent factors have been identified, coating manufacturers can be consulted for system recommendations. The major manufacturers of high performance protective coatings have an excellent understanding of the temperature and chemical exposure limitations of their products. In fact, many publish tables of chemical resistance for various coatings and include some of this information in technical product data sheets. Specific facility coatings histories, manufacturers' performance history, and published coating system service life data are particularly helpful. When searching for such information, the exposure environment must be accurately assessed to select only those coating systems

with a high probability of success and/or a proven track record. When a process is new and the exposure environment is uncertain, field test patches of candidate products can be applied in that environment and evaluated. If a new environment can be identified and simulated, screening and testing of candidate materials can be performed by qualified laboratories using specially designed test apparatus. However, the key to success for any situation rests with thorough, accurate identification of the exposure environment:

*a)hydrocarbons.*There are two types of hydrocarbon solvents: aliphatic and aromatic. Special blends of these solvents have been developed to form solvents called semiaromatics. Aliphatic and aromatic hydrocarbons differ in the way in which the carbon atoms are connected in the molecule. This characteristic structural difference leads to a sharp difference in the chemical and toxicological properties. The aromatic hydrocarbons are the stronger solvents for coating film formers. They also are more irritating to humans in both liquid and vapor forms. Typical aromatic hydrocarbons are: benzene, toluene, and xylene. Typical aliphatic hydrocarbons are: hexane, heptane, and odorless mineral spirits. Ordinary mineral spirits are mostly aliphatic hydrocarbons. Aromatic and aliphatic hydrocarbons generally are derived from heat distillation of petroleum products. They generally are found as a blend of aliphatic and aromatic components and are readily available in an extensive range of solvent strengths and evaporation rates;

b)oxygenated solvents. Oxygenated solvents are manufactured by a variety of processes. Those most commonly known of these solvents are: alcohols, ethers, ketones, and glycol-ethers. Typically, there may be a blend or combination of these solvents in the exposure environment. Examples of alcohol solvents are: methanol, ethanol, isopropanol, and butanol. Examples of ether solvents are: ethyl acetate, isopropyl acetate, butyl acetate, and butyl cellusolve acetate. Examples of ketones are: acetone, methyl ethyl chloride, methyl isobutyl ketone, and cyclohexanone. Examples of glycol-ethers are: cellusolve and butyl cellusolve;

c)terpene solvents. These solvents are derived from the sap of pine trees; examples are terpene, dipentent, and pine oil.

7.Wet/dry cycling. Alternate wet and dry cycling, such as that associated with atmosphere and weather, may have a significant effect on the performance of a coating system. Coating subject to wet and dry cycling must exhibit strong adhesion, low moisture vapor transfer rates, and good corrosion and undercutting resistance. Although a significant number of coatings will perform satisfactorily in a cycling environment, coating system selection mainly will depend on other in-service elements that impact this environment.

8. Thermal cycling. Thermal cycling naturally generates the forces of expansion and contraction. For a coating system to provide maximum protection to the substrate, it must have the ability to expand and contract with the substrate. For the most part, thermal cycling is associated with normal atmospheric weathering. For example, a metallic substrate may heat up rapidly when ex-

posed to the sunlight; however, when the sun sets or if it becomes cloudy, the temperature can rapidly decrease. Such stresses must be withstood by the coating system without loss of adhesion or checking and cracking. Acrylics, vinyls, and inorganic zinc coatings have proven exceptionally resistant to fluctuations in temperature.

9. Ultraviolet exposure. Resistance to ultraviolet (UV) radiation is extremely important. Sunlight can rapidly degrade a coating and will cause a complete loss of film integrity, resulting in chalking, loss of gloss, fading, and brittleness in a rather short period of time. Such degradation may result in an aesthetically unacceptable coating appearance. Specific generic coating types exhibit better resistance to UV light than others. For example, a two-component epoxy coating will chalk rather rapidly under exposure to UV light, but formulations of acrylic aliphatic polyurethanes remain stable on UV light exposure.

Inherent in most alkyd and oil-based products is poor resistance to UV exposure, which results in chalking, loss of gloss, and loss of color. However, modifications with silicone (i.e., silicone alkyds) can greatly enhance the performance characteristics of surfaces exposed to UV light. Modifying alkyds with silicone combines the workability of the alkyds with the durability, gloss retention, general weather resistance, and heat resistance of the silicones. Silicone alkyds are widely used as a maintenance upgrade finish over conventional alkyd coatings because of these improved properties. Silicone alkyds are used rather extensively for stack coatings and similar areas where moderately high temperatures are involved. USACE structures at which alkyds are used and improved gloss retention, weather resistance, and durability are desired should be considered for upgrades with silicone alkyd products.

10. Impact/abrasion. Impact and abrasion resistance are extremely important characteristics in coating selection. Although impact and abrasion resistance frequently are discussed in the same breath, they can designate two different exposure environments. For example, a coating must resist rupturing from the rapid expansion of a metal as it is deformed from a sudden impact. To resist this type of impact, coatings must have a high degree of flexibility such as most formulations of a vinyl coating. Formulations of epoxies and polyurethane coatings are excellent choices for abrasion resistance, but the inherent brittle qualities of the coating would cause it to fracture easily on impact. These coatings perform best where abrasion may be in the form of heavy equipment movement, foot traffic, or even scouring by tools and equipment. Abrasion also may be a result of naturally occurring phenomena, such as windblown sand or sand carried by waves of water. Consequently, it is extremely important for the coating specifier to determine if the exposure environment necessitates a coating that will withstand constant abrasion, sudden impact, or a combination of the two.

11. Special exposures. Special exposure environments such as food processing and potable water may be subject to regulations of the Food and Drug Administration (FDA) and the National Sanitation Foundation (NSF). In

addition to mixed exposure conditions, there most certainly will be extraneous circumstances such as inaccessibility and limitations on surface preparation methods. These situations could have a significant effect on coating system selection and should be thoroughly investigated prior to choosing a coating system. Sources of help for making decisions about these situations are discussed in the ensuing paragraph.

5 COATING DEFECTS

Although the science and technology of continuous galvanizing have improved significantly over the years, it is still a challenge to produce defect-free coatings. Studies indicate that poor substrate surface quality, insufficient strip cleaning, mechanical damage to the substrate surface due to handling, and inadequate process control are the main causes of coating defects. The recent introduction of high strength steels makes the production of galvanized coatings for applications such as exposed autobody panels even more challenging. To produce high quality zinc-coated strip, galvanizers need to improve quality control of the incoming strip as well as the continuous galvanizing process.

The surface quality of continuously galvanized coatings has improved significantly in recent years. However, galvanizers capable of producing such coatings are limited in number because the requirement of coating surface quality is extremely stringent. Any tiny blemish on the coating surface is objectionable for exposed automotive applications. The origins of coating defects can vary widely. The strip travels along a production line comprised of various equipment and rolls and involves a number of chemical reactions in the process. Any slight negligence in the maintenance of the line machinery and its control system can easily induce defects in the coatings. Also, the relevant chemical reactions take place mostly at elevated temperatures where reaction kinetics is hard to predict and control. Insufficient cleaning of the strip could result in poor wetting of the molten zinc alloy to the substrate, leading to bare spots. Improper atmosphere or temperature control in the in-line heat-treatment section may introduce carbon deposits or thin oxide film on the substrate surface, leading to bare spots or poor adhesion of the coating. Pot chemistry, working condition of the submerged hardware, bath skimming practices and air-knife settings all affect coating quality. It has been shown that good bath management practices can reduce coating defects. However, good bath management alone cannot eliminate all the defects. As a matter of fact, the chemistry of the steel and the substrate surface quality is of paramount importance for producing a high quality coating. In this regard, galvanizers who do not produce their own strip are at a disadvantage. While IF steels and similar grades can be easily galvanized, newly developed steel grades possess a complex chemistry, resulting in poor galvanizability. These steels contain strengthening elements, such as silicon and manganese, which are surface-active and have a strong affinity for oxygen. In an atmosphere which is reducing for iron, these elements can easily segregate toward the substrate surface and be preferentially oxi-

dized. The galvanizability of these high-strength steels is currently the subject of intensive research.

5.1 Defects Related to Substrate Surface Quality

It is well known that defects and imperfections pre-existing on the substrate surface can be easily duplicated and magnified in the hot-dipping stage, resulting in defective coatings. The experience indicates that strip with a good surface quality is the pre-requisite for producing a good quality coating. In fact, many coating defects are caused by the poor surface quality of the incoming strip.

Rough Surface

A rough substrate surface containing iron fines and slivers is prone to the development of outbursts in the coating. The resultant coating is rough with numerous areas of localized thick coatings. After being flattened in temper rolling, these areas reflect light differently, appearing as either dark or bright spots depending on the lighting condition. A typical sample is shown in Figure 5.1. Studies indicate that the density of this kind of defect decreases with increasing coating weight, suggesting that such a defect can be masked by a thick coating.
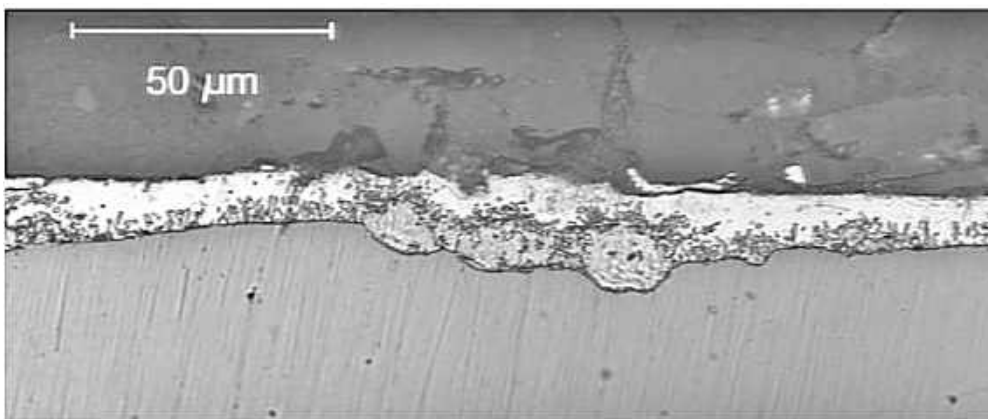
Figure 5.1 – A rough substrate surface results in Zn-Fe alloy outbursts in the coating

Mechanical Damage

Mechanical damage on the substrate surface, such as scratches and gouges, increases steel reactivity in galvanizing because iron atoms in these areas are in a high-energy state and can readily dissolve into the molten zinc alloy, resulting in an abnormally high iron solubility locally. If the bath effective aluminum level is relatively low and the extent of the damage is large, the reaction between the zinc and iron may not be inhibited. As a result, a Zn-Fe alloy layer forms at these gouges, resulting in a coating much thicker than the surrounding coating. Since the reaction kinetics is so fast, the Zn-Fe alloy layer can sometimes grow through the coating thickness and appear as dark spots. A typical sample is shown in Figure 5.2. Areas with a thick coating turned into so-called "abraded asperities" after skin pass and could appear as black spots as well.

| a | b | c |
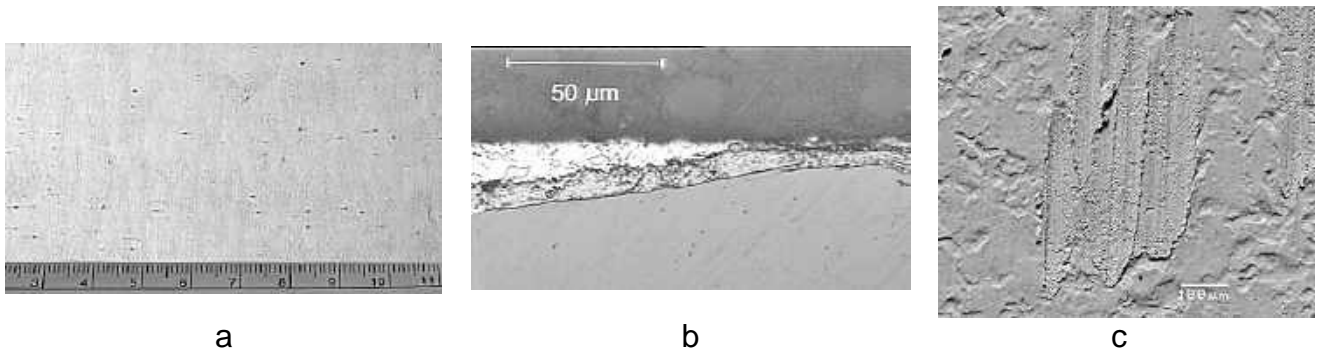
Figure 5.2 – coating defects induced by mechanical damage to the substrate:
a – numerous black spots exist on the coating surface; b – localized Zn-Fe alloy layers grew through the thickness, forming black spots in the coating; c – a large number of gouges were revealed after the coating was stripped off

Hot-Rolled Strip

The surface of hot-rolled strip is normally rougher than that of cold-rolled strip. However, the surface roughness can be mostly masked following the hot-dip process provided that the coating is thick enough. Such coated steels are mostly for construction applications. The quality requirement for these coated steels is by no means critical or stringent, and most surface imperfections can be tolerated by the users. A common defect that causes rejects is the peeling off of the coating due to poor adhesion. In addition to these factors which could also result in coating adhesion problems for cold-rolled strip, patches of residual surface oxide layer not totally removed in the de-scaling operation are a unique defect for hot-rolled substrate. The molten zinc alloy can wet the thin oxide layer well because the oxide reacts with aluminum in the molten zinc alloy to form a spinel-type product. The coating appears normal at first glance. However, the bonding between the substrate and the oxide layer is weak. The coating can be easily peeled off when subjected to forming operations. The remedy for this kind of defect is rather obvious – thorough de-scaling and pickling.

Hot-rolled strip is normally pickled to remove surface oxide and mill oil residue. If the pickling time is too long or the rinsing following the pickling is insufficient, residual pickling liquor can be entrapped at grain boundaries, which are always preferentially attacked in pickling. The residual pickling solution, containing mostly iron chlorides, is dried up during in-line heat-treatment. When the strip is being coated in the molten zinc pot, the iron chlorides at the grain boundaries react with aluminum in the molten zinc alloy, forming aluminum chloride ($AlCl3$), which vapourizes easily because of an extremely high vapour pressure at the galvanizing temperature. Numerous volcano-like craters will form on the coating surface. A typical sample is shown in Figure 5.3. Residual pickling solution reacts with aluminum in the molten zinc, releasing aluminum chloride ($AlCl3$) gas and forming numerous volcano-like craters in the coating.
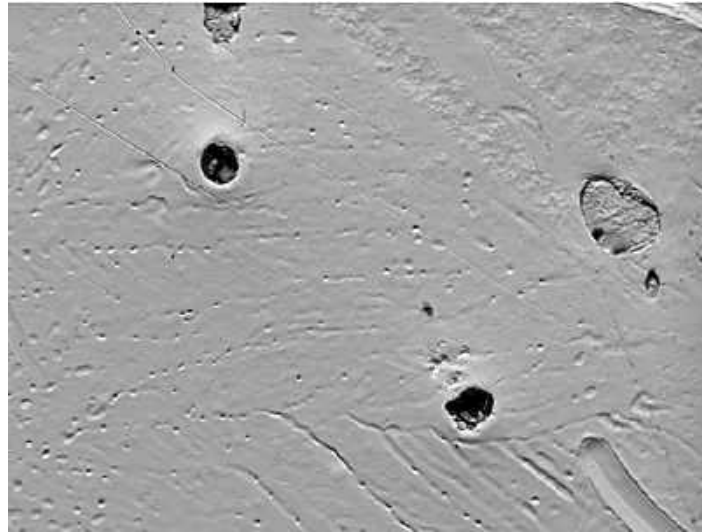
Figure 5.3 – Defects related to pickling and rinsing operations

5.2 Defects Related to Line Operation

Insufficient Cleaning

The strip must be thoroughly cleaned to remove all kinds of surface contaminants and to expose a chemically activated and metallically clean substrate surface. Failing to do so results in the formation of bare spots. It is a common practice to produce automotive-grade galvanized coatings in baths containing aluminum in excess of 0.2%. When the bath aluminum content is high, the cleanliness of the substrate surface becomes more critical to ensure a good wetting. Bare spots are frequently observed in automotive-grade coatings although these bare spots are too small to be noticed by the naked eye. A typical sample is shown in Figure 5.4.
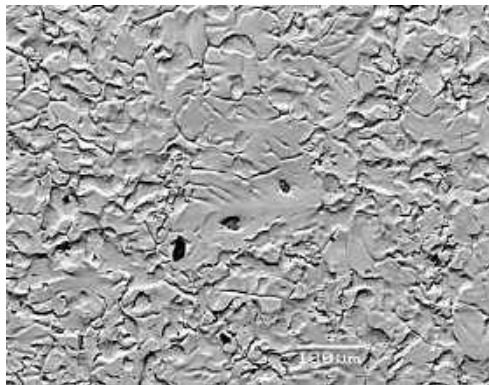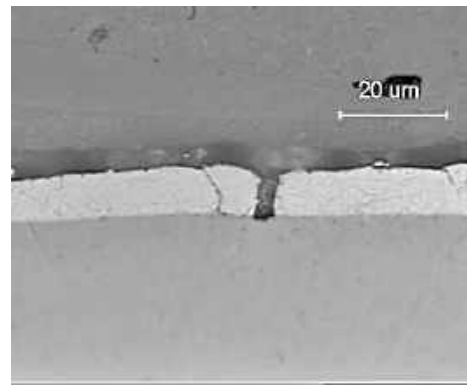
a   b

Figure 5.4 – Tiny bare spots in automotive-grade galvanized coating:
a – Optical image; b – SEM image

Improper Heat Treatment

An improper in-line heat treatment can result in a number of problems including carbon contamination and surface oxidation.

Carbon contamination of the strip can occur in direct-flame-fired furnaces if the temperature is lower than normal and an atmosphere of carbon monoxide occurs. Although carbon contamination is hard to detect using SEM-EDS only,

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its impact on coating structure is unmistakable. The inhibition layer on the affected areas is thin and ill-defined. Consequently, coating adhesion is poor. If the problem is severe, wetting becomes problematic, resulting in bare spots.

For high-strength steels under development, such as dual-phase and TRIP steels with a design tensile strength higher than 600 MPa, the chemistry is so complex that a heattreatment scheme to ensure good galvanizability has yet to be developed on existing galvanizing lines.

Poor Bath Management

Good bath management practices can not only reduce the severity of defects originated from a complex steel chemistry and inadequate substrate surface quality, but can also avoid defects originated in the hot-dipping stage, such as the entrapment of dross particles, the formation of Zn-Fe alloy crystallites in the coating, dents (localized thin coating), and line defects induced by dross growth on pot rolls.

Snout Dust If the atmosphere in the snout is too reducing, zinc evaporates quickly. The vapour condenses in the snout and the cooling section. When the zinc dust comes into contact with the substrate before it enters the molten zinc bath, it reacts with the steel to form Zn-Fe alloys. These areas appear as tiny black spots, resembling bare spots. The defect can be eliminated by introducing moisture to the snout, thereby minimizing zinc vapourization, and by periodical cleaning of the snout and the cooling section to physically remove the dust. If the snout immersion depth is insufficient, bath surface oxide can enter into the snout. The oxide will be dragged out by the strip, resulting in defective coatings.

Aluminum and Temperature Control

When the bath effective aluminum level is relatively low and the strip entry temperature is relatively high, Zn-Fe alloy crystallites form in coatings. These crystallites are metastable in nature and their formation mechanism has been explained by Tang. Normally, if the crystallites are small and discrete, they do not negatively affect coating quality in terms of both coating ductility and adhesion. However, the defect could be severe if the bath aluminum level and the strip entry temperature are out of control, or the substrate surface quality is poor. In this case, outbursts or a continuous alloy layer form, as shown in Figure 1, resulting in low ductility and poor adhesion of the coating.

Heavy coatings produced using a slow line speed may suffer from a line defect referred to as sag-lines and/or rippled coatings. Reducing the bath effective aluminum level and adding small amounts of antimony will generally alleviate the problem.

Sink-Roll Growth

Growing on sink-roll grooves, intermetallic compounds can scratch the substrate, thereby inducing defects in the coating. The defects are easily recognizable because they distribute along lines with spacing matching that of the grooves. A typical sample is shown in Figure 5.5.
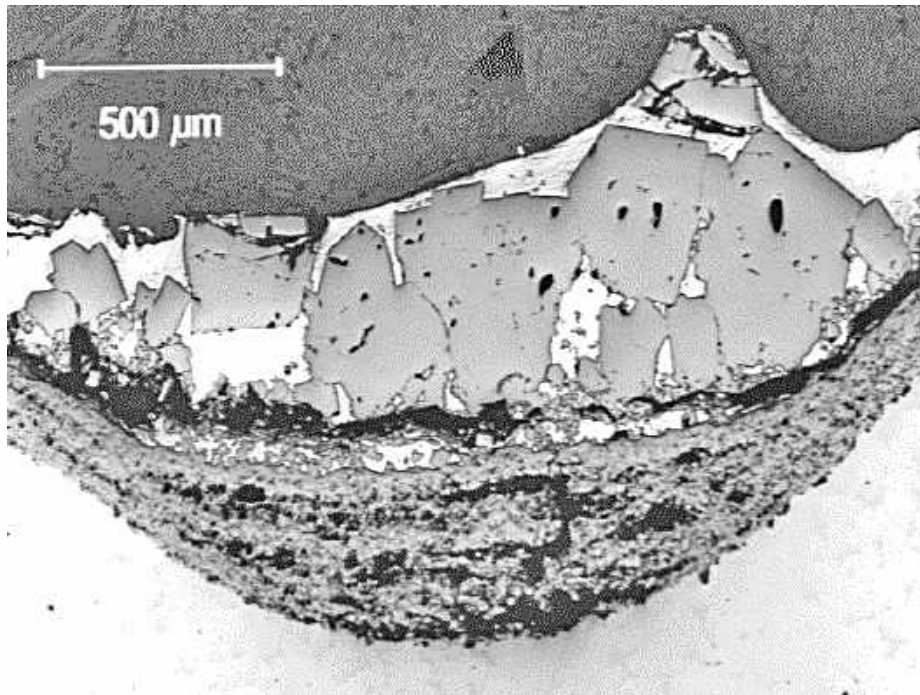
Figure 5.5 – Intermetallic growths in sink-roll grooves can scratch the substrate surface, resulting in line defects with spacing equal to that of grooves

Dross Entrapment

Top dross particles frequently coexist with the oxide film on the bath surface. These particles can enter the coating together with the oxide film picked up on the coating surface. A typical sample is shown in Figure 5.6. Maintaining a clean bath surface can avoid the entrapment of dross particles in coatings.
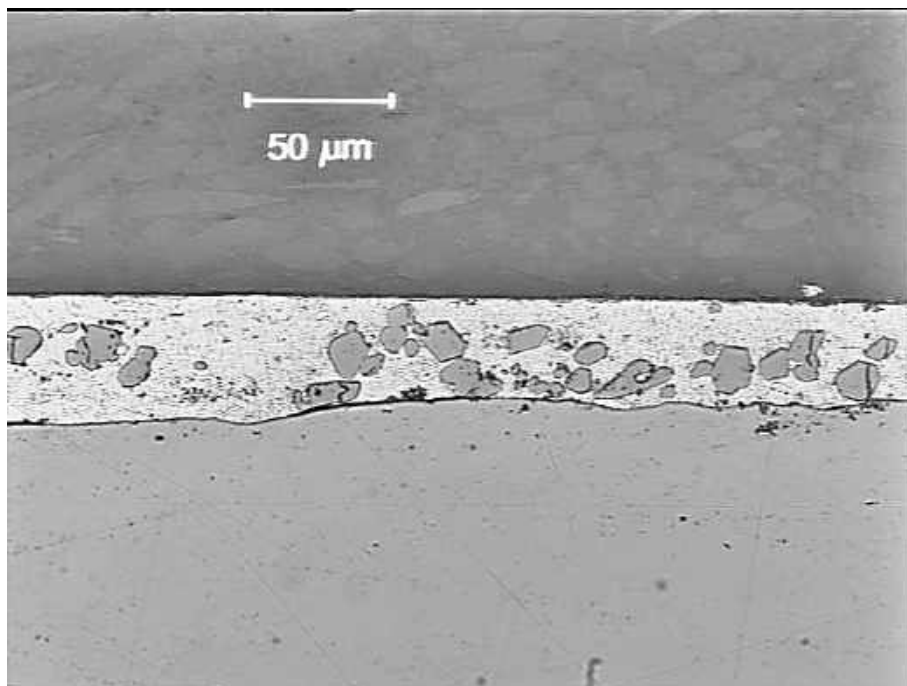
Figure 5.6 – Top dross particles entrapped in the coating due to pick-up of bath surface skimming by the coating

Dross entrapment in coatings occurs frequently during GA to GI production transition periods when brightener is used to speed up the transition. Due

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to a rapid increase in the bath aluminum level, iron solubility decreases correspondingly, resulting in the formation of dross particles. Also, bottom dross particles accumulated during the GA campaign start to convert to top dross particles, leading to a significant increase in the volume fraction of dross particles in the bath. Frequently, particles entrapped in coatings during the transition are larger in size. Such particles cause printing-through following temper rolling. A typical sample is shown in Figure 5.7. Recent studies indicated that a welldesigned GA to GI transition practice could minimize dross formation and conversion, thereby reducing the incidence of dross entrapment in coatings.
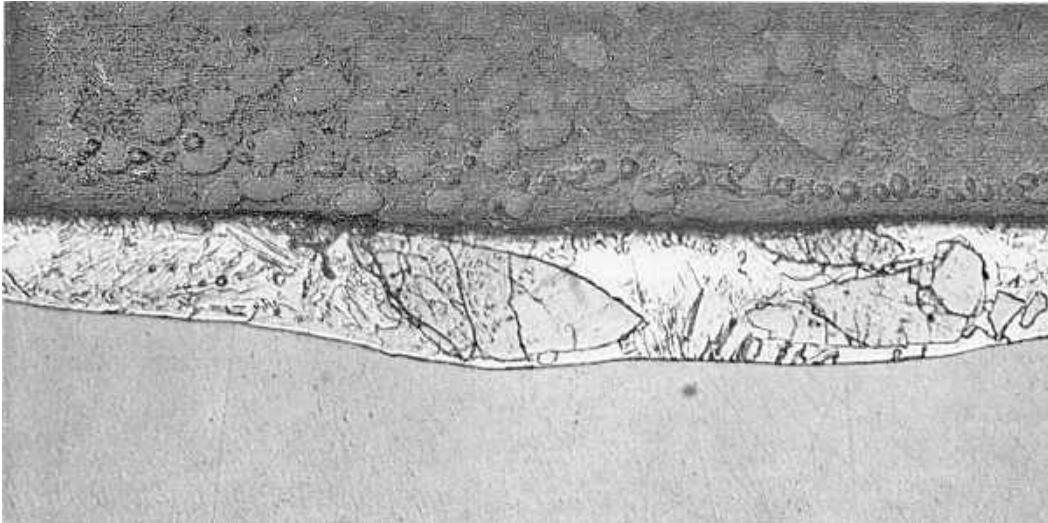
Figure 5.7 – Large dross particles picked up in coating during GA to GI transition

It should be mentioned here that the problem of dross particle entrapment in coatings is, in general, exaggerated by galvanizers because a number of defects, such as high or low points and surface contamination, resemble dross pick-up. Only less than 10% of all the defects, initially believed to be dross pick-up, were indeed dross particle entrapment in coatings. The majority of these coating defects was caused by problems of substrate surface quality.

Air Wiping

A number of defects can be generated when the coating passes air knives. Typical defects include dents, blow lines, sag-lines and peculiar features such as so-called "caterpillars". Localized thin spots, as shown in Figure 5.8, are frequently observed. This defect is referred to as white spots by one galvanizer and chip marks by another. The origin of this type of defect is not exactly known. Judging by the relatively straight edge on its topside and the associated flow lines on its flanks, the defect could be caused by the blowing away of entrapped dross particles. However, in some cases, the defect was so severe in nature and so large in size, yet no solid particles could be found in the coatings. Improper air-knife settings may also cause this type of defect. Indeed, reducing air-blowing pressure and increasing bath and strip entry temperatures will reduce the severity of the defect.
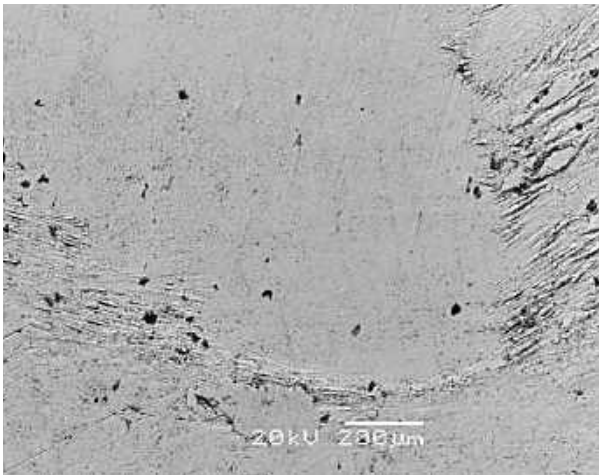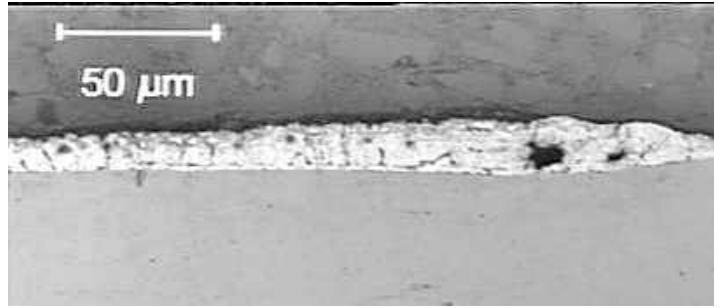
a   b

Figure 5.8 – A typical chip mark. The flow lines on its flanks:
a – SEM image; b – cross-sectional view of the chip mark

A type of defect referred to as "caterpillars" according to their morphology is encountered from time to time by producers of spangled coatings. A typical sample is shown in Figure 5.9. "Caterpillars" appear to nucleate along the solidification front of the coating. They run upwards from the edges toward the center of the strip, outlining an apparent isothermal line on the coating. Although its cause has not been clarified, the defect can be reduced or totally eliminated by lowering the bath temperature. Another type of line defect, referred to as "snaky coating", is shown in Figure 5.10. Instead of running upwards, these lines run downwards. This type of defect only occurs on heavy gauge steel with a heavy coating (>G90). Judging by its appearance, this defect is most likely caused by sagging of the coating during solidification. The sag-lines are stabilized by narrow bands of oxide film along these lines. Maintaining a clean oxide-free bath surface can alleviate this type of defect.
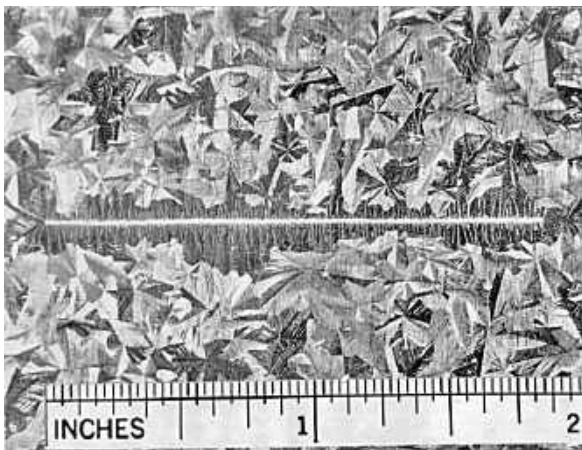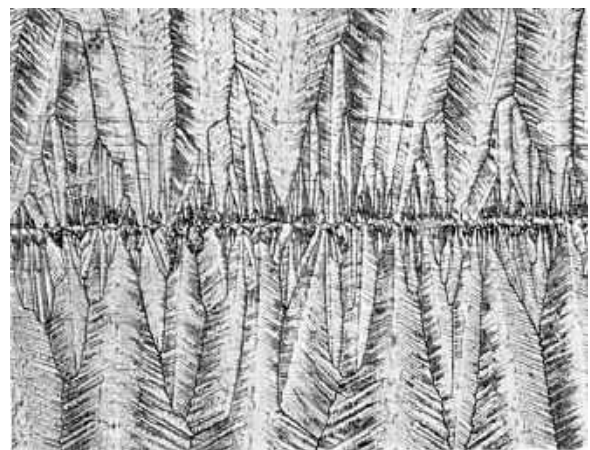
a   b

Figure 5.9 – "Caterpillars" form from time to time on spangled coatings:
a – the exact cause of this type of defect is still unknown;
b – reducing bath temperature can reduce this type of defect

The arrow indicates the strip moving direction (Figure 5.10). Close examinations suggested that these are sag-lines stabilized by patches of oxide films.
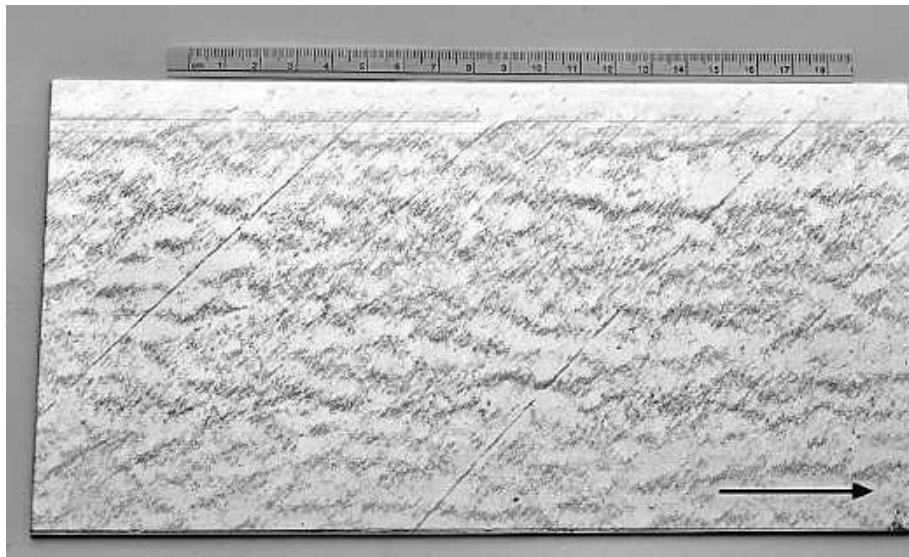
Figure 5.10 – Line defects referred to as "snaky coating" by the producer

Mini-Spanglizer

The operation of a mini-spanglizer may introduce coating defects. Shown in Figure 5.11 are circular dents apparently caused by the impingement of liquid droplets from the spanglizer. If spangles are minimized through the spray of zinc dust to the coating, residual zinc dust may accumulate on rolls down the stream, causing coating defects.

Post Hot-Dipping Treatment

Defects generated in post hot-dipping treatment include scratches, stains and zinc-dust pickup, etc. These defects are easily recognizable due to the periodicity in their distribution.
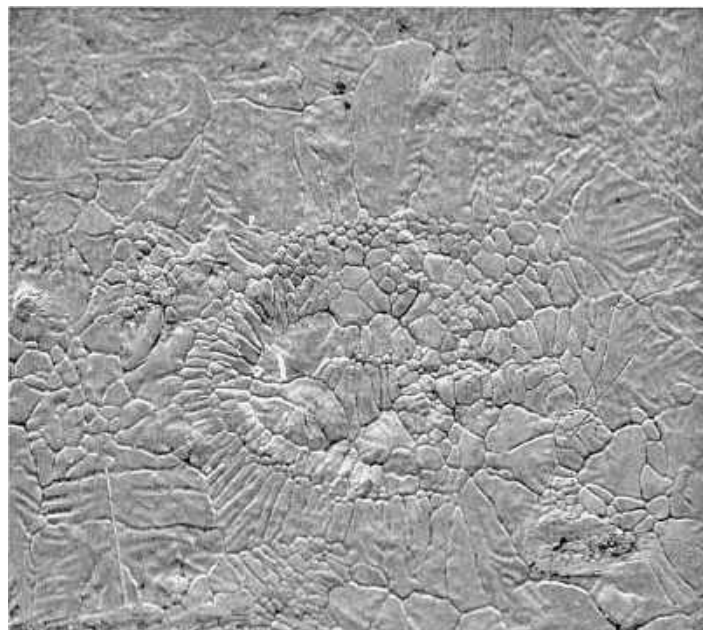
Figure 5.11 – Circular dents induced by the impingement of liquid droplets
from the spangle-minimizer

5.3 Defects in Galvanneal Coatings

Powdering and flaking of galvanneal coating on titanium-stabilized IF steels was a major problem at the beginning of the 1990s. Some researchers suggested that carbon-free grain boundaries serve as fast diffusion paths for zinc, resulting in outbursts at emerging grain boundaries. However, a number of studies produced evidence suggesting free titanium (titanium in solid solution) to be the main culprit. The problem has been largely resolved by partly replacing titanium with niobium, controlling the titanium/carbon ratio to reduce free titanium, increasing the bath effective aluminum level, and optimizing the in-line annealing scheme.

It has been well established that the optimum bath composition for producing galvanneal of IF steels is 0.135%Al, the knee-point of the iron solubility curve. This composition corresponds to the changeover of the d phase (bottom dross) to the h phase (top dross) as the equilibrium compound in the bath. Maintaining the bath aluminum at such a level can minimize the formation of bottom dross, thereby prolonging the GA campaign. The inhibition layer formed during the hot-dipping stage is thin. It becomes unstable and dissolves easily during the annealing treatment. In recent years, high-strength steels are replacing IF steels as the substrate for galvanneal coatings. Alloying elements in the steels, such as silicon and phosphorus, apparently stabilize the inhibition layer. Correspondingly, a much higher annealing temperature is employed to break down the inhibition layer. Preferably, the effective bath aluminum for producing galvanneal of high-strength steels should be lower than 0.135%. However, not all galvanizers are capable of controlling bath effective aluminum within a narrow range. From time to time, the bath aluminum level becomes too high, resulting in an inhibition layer too thick and stable. Correspondingly, galvanizers must resort to a much higher annealing temperature, producing galvanneal coatings with a thick G layer. Once again, powdering and flaking become a concern of galvanizers. Shown in Figure 5.12 is galvanneal coating of high-strength steel. Apparently, the G layer is quite thick. Powdering resistance of the coating deteriorates with increase in the thickness of the G layer.
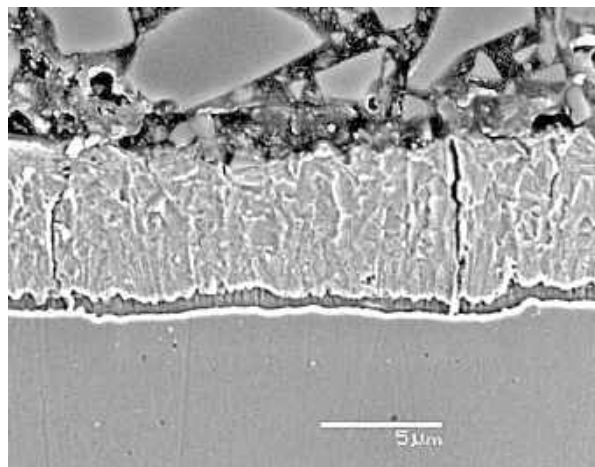
Figure 5.12 – Galvanneal coating with a relatively thick G layer

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Coated steels, considered to be good quality products for applications in the construction industry, could be objectionable from the viewpoint of the aircraft industry. Substrate surface quality is of paramount importance for the production of high-quality coatings. If the substrate quality is poor, defects are inevitable. Good bath management practices can reduce the severity of these substrate quality-related defects, but cannot totally eliminate them. However, good bath management procedures can avoid all the defects originating from the pot area.

6 QUALITY CONTROL OF COATINGS

To achieve the expected life for a coating on steel, the applicator and inspector must carefully control the coating application process. It is also generally understood that for a large structure 70% of the total cost of applying a protective coating lies in the access equipment and set-up required to bring the crew close enough to the structure to apply the coating. So getting the work right the first time is very important in controlling the cost as well as ensuring he quality of the completed work.

Many issues need to be addressed, from the quality of the coating material to the preparation of the surface and the monitoring of the conditions under which the coatings are applied. With the increasingly complex coating formulations created under the pressure to reduce the volatile organic compound (VOC) content, the care with which the processes are controlled also increases in significance for the longevity of the protective coating.

Monitoring and measuring techniques and instruments normally associated with the laboratory are constantly developing, but some of the techniques and instruments now available can be used on-site as well as in the lab. In addition, the instruments do not all require the expertise of a coating inspector. All this means that quality control can play an even greater role in the application process and is not just an add-on specifically for the coatings inspector.

6.1 Testing Paint as a Material

Many of the paint formulations that were in common use for many years have now been replaced by more environmentally friendly formulations.Some of these formulations have to be applied under more carefully controlled conditions. This makes the assessment of the paint as a material more significant in the achievement of a high quality finished coating.

Some of the paint testing methods that have been used in paint formulation can also be used on site for checking the paint in the cans before the work begins. For example, flow cups can be used with a stopwatch to establish that the viscosity of the coating material is correct, thus confirming that the chosen application process, e.g. spraying, rolling, brushing, etc., will work satisfactorily with the material supplied.

The viscosity is recorded by quoting the time in seconds and the type and cup size used. This can then be compared with the viscosity quoted in the

product data sheet to ensure that the paints meets the manufacturer's specification or that dilution has been carried out accurately in accordance with the specification.

The Hegman Gauge is used to determine the particle size in paint, and the Meier Gauge is used to check drying, shrinkage, and cracking of coatings. Both of these simple gauges allow assessment of the coating material supplied for a job against its specification.

The Hegman Gauge (Figure 6.1) is a precision instrument. The gauge and scraper are made of hardened stainless steel. A quantity of the paint is placed at the end of the gauge and then drawn along the sloping channel until the scrapper starts to drag the particles as their size matchesm the depth of the channel. The point where the pigment particles start to show is called the "fineness of grind" and is a measure of how well a paint has been made. The value obtained can be checked against that quoted in the product data sheet. This test, however, will also show whether a paint has been mixed properly before application because agglomerates of particles will be easily seen. It can also detect gelled particles from a partly cross-linked coating because these again would stand out on the gauge. In both cases, it could indicate whether a paint was fit to be applied.
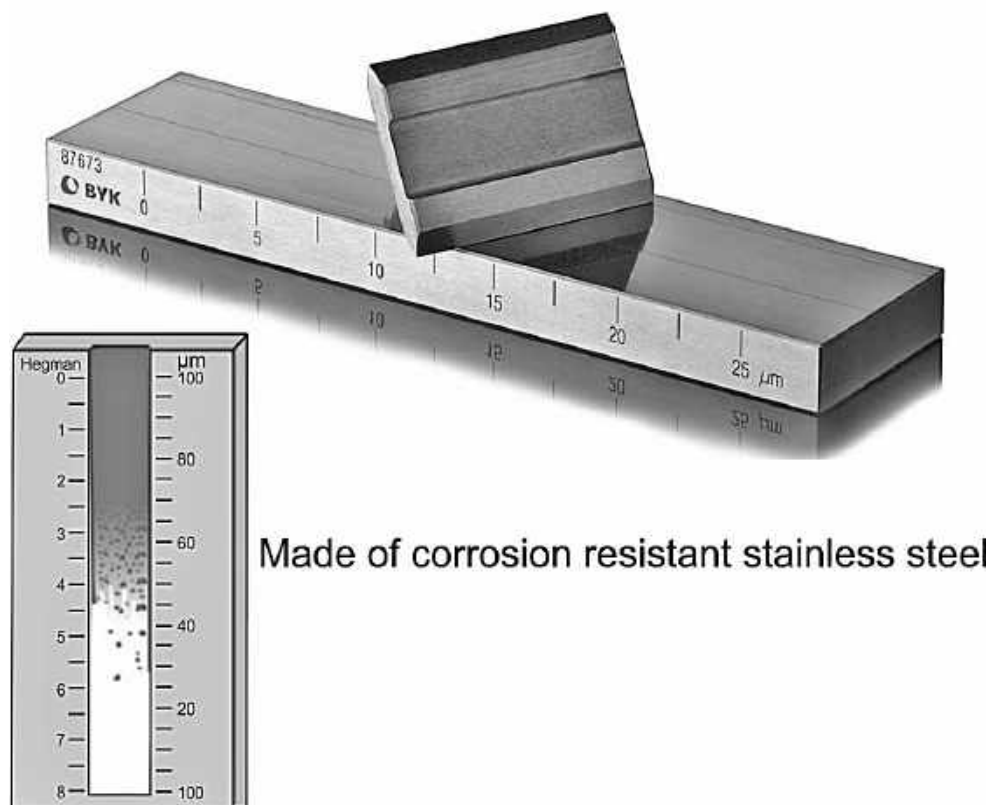
Figure 6.1 – Hegman Gauge for measuring particle fineness

The Meier Gauge (Figure 6.2) is also made of hardened stainless steel and is used to test drying, shrinkage, or cracking of coatings or similar products. The Meier Gauge has a sloping groove of 60 mm wide and 200 mm long, with 1, 2, or 3 mm maximum depth.

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The paint material is applied to the whole area of the groove and visually inspected for the coating defects associated with drying.
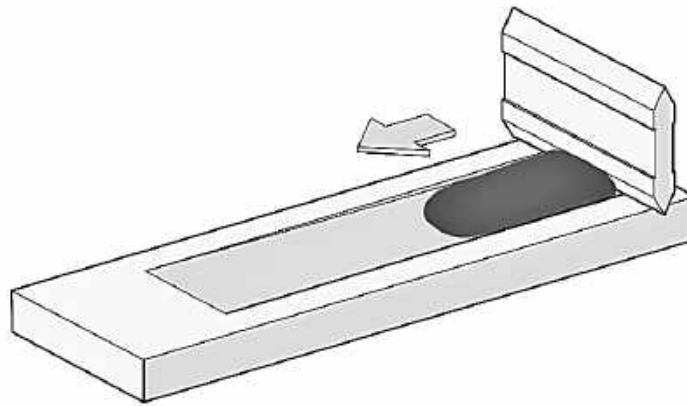
Figure 6.2 – Meier Gauge for testing shrinkage or cracking of coatings

6.2 Humidity Monitoring – Steel

Electronic humidity gauges for the field are now very fast and accurate and generally outperform the more traditional whirling hygrometer (also known as a sling psychrometer) because they acquire the readings in seconds. In contrast, a whirling hygrometer should be operated for at least 20 minutes to obtain stable readings for the wet and dry bulb thermometers.

On site, this time period for the whirling hygrometer is rarely observed, and the tendency is for the relative humidity (RH) to be reported as higher than the true value.

The modern electronic dewpoint meter (Figure 6.3) will display RH, air temperature, surface temperature, and dewpoint temperature, and it will calculate and display the difference between the dewpoint and the surface temperature so that the operator can be sure that the conditions are correct for applying the coating.

Some modern coatings require the RH to exceed a certain minimum for full cure, so knowledge of the climatic conditions is a very important aspect of quality control.

Figure 6.3 – Electronic dewpoint meter with optional liquid probe

6.3 Adhesion and Defects

Other tests can be used to measure coating adhesion and defects like holidays, pinholes, cracks, porosity, and other flaws. These properties can be measured on coated steel.

Adhesion of coatings applied on steel is tested using a 2-inch diameter (50 millimeter) dolly so a special version of the adhesion tester, calibrated for this larger dolly, has been developed.

The testing of coatings on steel for pinholes, cracks, and other flaws can either be carried out using low - volta g e, wet sponge testing or high-voltage spark testing (Figure 6.4), depending on the thickness of the coating. For a coating up to 500 µm, a 90V wet sponge test will detect pinholes through the coating to the steel.

Figure 6.4 – High-voltage pinhole detector

High voltages will detect any electrical weakness in the coating, which is accepted as evidence of a physical weakness likely to cause prem ture failure of the coating at that point.

In certain situations, where the coating is used to protect the structure against attack by the materials contained in the structure, checking for pinholes

will be specified as part of the acceptance testing for the work rather than as part of a quality control regimen, e.g., liquids in pipeline and storage tanks.

The quality control of the coating process and the conditions under which the coating is applied are crucial to the success of the work. It is clear that coatings applied to dirty or contaminated surfaces in humid conditions will not achieve their expected life performance. What is not always clear is that the coating supplied for the job may not be formulated as expected, and this must be considered when planning the quality control test regimen.

Such tests are too often ignored, to the detriment of coating performance. The painter's and inspector's repertoire of field test methods is increasing. As painters and inspectors take advantage of this repertoire, they can optimise coating application and performance through vigilant quality control.

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