INDUSTRIAL METAL FINISHING FOR CORROSION CONTROL

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ABSTRACT

Industrial Metal Finishing , which includes electrodeposition of metals and alloys, electroless plating, immersion plating, chemical and electropolishing of metals, anodizing etc. form a major component of surface engineering. Corrosion protection is one main reason for the existence of Industrial Metal finishing .Although these processes began for decorative and aesthetic purposes, their contribution to corrosion prevention and engineering applications, especially in electronics, aerospace, automotive and agriculture industries is markedly increasing. The evolution of industrial metal finishing from an art to a science has been a gradual process. The ABC of corrosion protection, principle and mechanism, and the latest developments in terms of 6 Es (Environment-friendly, Economical, Excellent, Energy -saving, Extremely fast, and Expert-system) have been briefly introduced. Relevant references have been cited for ease of access to the original and detailed literature.

INTRODUCTION

"FINISHING" is defined as the "FINAL" operation applied to the surface of a metal to lend it properties not possessed by the article in its unfinished form. It may involve any simple buffing and polishing, chemical or electrochemical polishing or colouring, plating of metals for alloys or electroless plating, anodizing or an organic coating. When done on an industrial scale, it is termed Industrial Metal Finishing. Although these techniques have traditionally been used for the purpose of decorative or aesthetic appeal, their application for corrosion protection represent the most significant in terms of commercial importance as well as deployment of large number of personnel. Industrial metal finishing encompass a wide range of sciences form chemistry or electrochemistry, chemical and mechanical engineering, physics to electrical and electronics and even extend into the realm s of arts. Although the art of industrial metal finishing is very old, even dating back to the bronze age, the techniques applied by finishers in 21st century are going to more science than art and it is going to acquire the status of Surface Engineering Group. Research in this field is going to be contributing significantly towards progress on the theoretical and more on the applied aspects.

The conventional techniques like plating, electroplating as well as electroless, and anodizing are still one of the cheapest methods to provide coatings for various applications, in addition to employing millions of people. These processes have been and are going to be increasingly important in the 21st Century, for all high technology and strategic industries like electronics, telecommunications, photo-optics, computers, aerospace, automobile and other engineering industries. Without these, there would be no ICs, or PCBs, Laser Components, CPUs, Super-conductivity films, thin film products or elctroformed products, or even traditional common items from needles to bicycle, cars or aeroplanes. In the coming years, almost every product will require surface finishing application. The cost of surface finishing is about 5-10% of the total cost of the article, but the properly finished and coated product has much longer life. At present, the share of conventional wet processes in industrial metal finishing is about 80% whereas latest dry processes account for about 18%. (see Figure I).

Industrial Metal Finishing is estimated to be an $ 30 to 40 billion/year industry, employing lakhs of people world wide. Only one company in USA, dealing with electroplating chemicals claims to have a business of more than 2000 crore rupees per year. In India, the total business for industrial finishing is estimated to be around Rs. 1000 crores annually. It is estimated that India shares about 5% of the world Metal Finishing market. However, Howard Smith has predicted migration of large sectors of the finishing industry to less developed nations in response to the increasingly burdensome cost of compliance with safety and environmental regulations. Hence there is a considerable scope for India to expand its activities and increase its share of the world market. India has already gained world wide recognition and acceptance from even technologically advance nations for its equipment, chemicals and metal finishing chemicals as well as services. Export of these chemicals and services to neighbouring and African countries are already a reality and is increasing day by day.

There have been many pulls and pushes in the industrial finishing industry. There was a big boom after the second world war(1945). All traditional surface engineering techniques like electroplating, hot dip coatings, anodizing, organic paints, plastics etc. made significant advances. During the late 70s and 80s, the future of electroplating seemed gloomy, but with the increasing demand in electronics, space, defence and other engineering industries, the commercial applications of deposition processes increased manifold. It is somewhat mindboggling to note the enormous strides in the field of electroplating as applied to elctronic components. It is estimated that plating in electronic and related industries has registered a 16 fold increase just in 5 years. In India also, it has been computed that the consumption of plating chemicals for electronics alone has risen from Rs.0.5 crore in 1989 to Rs. 8 crores in 1994 while it is expected to be more than Rs. 50 crores by 2000 AD

The industrial metal finishing has met the requirements of a wide variety of industries for bright and corrosion resistant finishes for manufacturing articles which are economical and as well as long lasting. These finishing techniques have moved from a hit and trial method to a systematic approach, laying considerable stress on the technical aspects of the process and the product. It is no longer an art, but a complete science and thus the basic knowledge of the principles involved is a must for every engineer and technocrat.

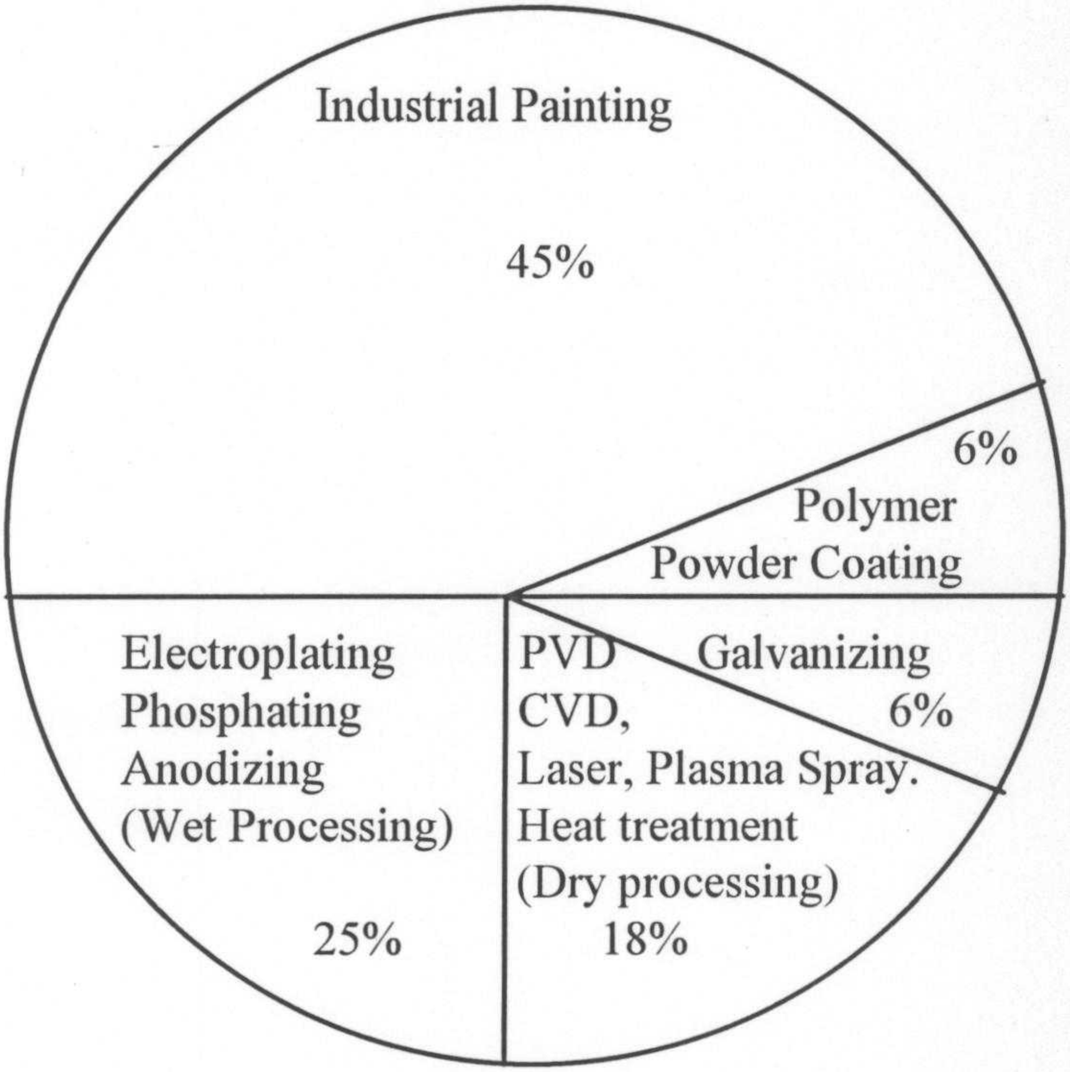

Fig. 1. Share of surface modification techniques in Industry

PRINCIPLES AND MECHANISM

The basic principle behind any corrosion or deposition processes , whether electrolytic or without current, is the same viz. all these are *electrochemical.* All the processes take place in an electrochemical cell or electrolytic cell. Any such cell is composed of three parts- A, B and C where

A is **ANODE**

B is **BREW or ELECTROLYTE**

C is **CATHODE**

While all the deposition (or reduction) reactions take place at the cathode, the anodic reactions (Oxidation) are basically of three forms:

(I) Metal Dissolution (Corrosion)

$$Zn \longrightarrow Zn^{+2} + 2\,e^-$$

(ii) Oxygen evolution

$$2\,H_2O \longrightarrow 4\,H^+ + O_2 + 2\,e^- \quad (pH < 7)$$

$$4\,OH^- \longrightarrow 2H_2O + O_2 + 2\,e^- \quad (pH > 7)$$

(iii) Oxidative Reactions

$$4\,Al + 3O_2 \longrightarrow 2Al_2O_3 \text{ (as in Anodizing)}$$

$$Fe^{++} \longrightarrow Fe^{+3} + e^-$$

An anode in a plating bath is a conductor (metallic, carbon etc.) which is required to complete the electric circuit from the source of e.m.f. through the electrolyte to the cathode (or workpiece) where the deposition takes place. But in the case of anodizing, the anode is the workpiece while in corrosion, it is always the anodic part which corrodes. The anode serves to remove the electrons introduced at the cathode(negative potential) and is always connected to the positive terminal of the electrolytic cell.

In non-electrolytic deposition, or even in any corrosion process, the electrochemical cell can be represented by ORE viz.

O stands for OXIDATIVE REACTIONS

R stands for REDUCTIVE REACTIONS

E stands for ELECTROLYTE

Corrosion or deposition cannot take place if any of the three components is absent. Without the application of current, there are three techniques for deposition. These are Contact Plating (seldom used now), Immersion Plating (also called cementation or displacement deposition) and Autocatalytic or Electroless Plating. In immersion plating, the deposition of a metallic coating on a baser substrate takes place by chemical displacement from a solution of a salt of the nobler coating metal and the driving force is the difference in potentials between the two metals e.g.

$$\underset{(-0.44V)}{Fe} + \underset{(+o.34\ V)}{Cu^{++}} \longrightarrow Cu + Fe^{++} \quad (i)$$

$$\underset{(+o.34\ V)}{Cu} + \underset{(+1.50V)}{2Au^{+}} \longrightarrow Au + Cu^{++} \quad (ii)$$

$$\underset{(0.34\ V)}{Cu} + \underset{(-0..14V)}{Sn^{++}} \longrightarrow Sn + Cu^{++} \quad (iii)$$

In the last case, the electrode potential of copper is made much more negative by the incorporation of complexing agents like cyanide ions and thiourea in the tinning solution. In autocatalytic or electrodeless or electroless plating, (developed by Brenner and Riddell in 1946), deposition of a metal takes place by a controlled chemical reduction that is catalyzed by the metal or alloy being deposited. Although the overall reaction in Electroless Nickel Plating is

$$2H_2PO^-_2 + 2H_2O + Ni^{+2} \longrightarrow Ni + 4H^+ + 2HPO_3^{-2}$$

The mechanism, as per Lukes is

$$H_2PO_2^- + H_2O \longrightarrow HPO_3^{-2} + 2H^+ + H^- \quad \text{(Anodic or oxidative)}$$

$$2H^- + Ni^{++} \longrightarrow Ni + H_2 \quad \text{(Cathodic or reductive)}$$

$$H^- + H^+ \longrightarrow H_2 \text{ (Cathodic)}$$

The basic equation for electrodeposition is covered by Faraday's laws of electrolysis viz. $w = zct$ where w is the weight of metal deposited in grms when current c in amperes is passed for time t in seconds while z is a constant called electrochemical equivalent of the substance. The Nernst equation provides the theoretical basis:

$$E = E_0 + \frac{RT}{nF} \ln \frac{a}{a_M}$$

where E is the potential, E_o is standard electrode potential, characteristic of the electrode, R is Gas Constant, T is absolute temperature in Kelvins, F is the Faraday (96500), n is valence change and a is activity of the metal ions, whereas a_M is the activity of the metal itself. The relationship between the free energy and the electrochemical potential or decomposition potential is given by:

$$G = -nFE$$

RECENT DEVELOPMENTS- the 6 Es

Major advances, once again need based, in the 21 st Century are going to be in terms of 6 Es :

1. **Environment-friendly:** There is no future, even in India, for any process which is not environment-friendly. Cyanide baths have already been replaced commercially by non-cyanide baths e.g. zinc, silver, copper, brass etc. The non-cyanide baths bring about 30-50 % savings because of the heavy expenditure on treatment of the toxic effluent. Chromium plating from Cr^{+3} bath may replace the current Cr^{+6} baths. Cadmium plating may disappear because of toxicity. Even in Gold Plating, acid gold plating is replacing cyanide gold baths. It is worth noting that M/s ICI, UK are investing 32 million pounds (200 crore rupees) for eco-friendly research. In short, Clean Environment and Dry Plating Shops are going to dominate the metal finishing industry in future.

2. **Excellence :** There is going to be race for TOTAL QUALITY and reliability in the coming years. The demand for the ISO 9000 series will grow and without these, there will be no export. Quality of some of the thin electroplated coatings is comparable to or superior to sputtered coatings. The quality and the environmental effect must start from the drawing board stage.

3. **Economical:** The key to continued success of any industrial finishing process is Economy, so that it can face growing competition on a global level. The surface engineering processes themselves are an outcome of the necessity to get properties of gold, nickel and chromium metals on steel at a much cheaper price and getting long corrosion protection. The concepts of value engineering and surface engineering are complimentary and are going to be applied in a much wider proportions than earlier.

4. **Exceedingly Fast :** Conventional methods of plating and painting are very slow e.g. plating rates are of the order of 0.1 to 2 microns/minute. The modern production engineering techniques, like continuous wire and strip plating, where the rates of plating are 10 to 10,00 times more. The application of ultrasonics combined with pulse-plating to improve mass transfer or rate

of deposition is likely to come back with a bang. Use of fluoroborate bath, especially for wire plating, will increase in future, for faster rates of deposition(developed by NML).

5. **Expert System:** Automation or the use of expert system for fully computerized finishing process controls has become a necessity rather than a luxury to achieve uniformly excellent deposits at exceedingly high rates. PLCs and control systems with PC base would dominate the scene in future finishing shops.

6. **Energy-Saving:** Since energy is going to be costly and the electroplating and anodizing are energy intensive, the emphasis will certainly on energy saving processes. Low temperature cleaning, cold sealing for anodized aluminum, cold phosphating, modified electroless nickel plating at room temperature) all developed at NML) etc., are already replacing high temperature processes. Similarly electrogalvanizing, tin plating, and aluminum plating are replacing hot dip galvanizing, tinning and hot dip aluminizing, while immersion and electroless plating of copper, silver, tin, gold are replacing electroplated coatings wherever applicable.

It should be emphasized that corrosion is a natural and electrochemical process. A badly plated or poorly painted job will accelerate corrosion rather than controlling it, as it helps in creating an electrochemical cell. Also in the same sheet or component, one part can become anodic while the other part can become cathodic. For this reason only, pure metals corrode much more slowly than the impure ones. Also good house-keeping, for example dusting cars with a feather, helps in checking corrosion as it offsets what is known as " differential aeration" effect. Industrial finishing basically protects the base metal by changing the surface properties, offering sacrificial protection as in the case of zinc or changing the interface between the base metal and the environment. Any defect or holidays , poor adhesion of the coating or high porosity can lead to more corrosion. Also it should be realized that there are about 120 varieties of corrosion and no one method can be the solution for all problems of corrosion.

CONCLUSIONS

Electroplating, Anodizing, Painting etc. which have about 80 percent share of the total business in the Industrial metal finishing are still one of the cheapest and widely used methods to control corrosion and form a major component of surface engineering. In future, complete restructuring of these processes will become indispensable to deliver what customers need (in terms of the 6Es, shorter lead times, reliability, immediate response) or innovation in terms of new products, processes, finishes and services rather than sticking to traditional way of doing jobs. The gradual degradation of metallic structures on which the modern world depends- from bridges to nuts and bolts, from automobiles and aeroplanes to boiler tubes and nuclear reactors or petrochemical complexes- is a practical problem of vital importance, especially for India . Indian industries and practicing engineers certainly are entitled to better protection from corrosion than they have been getting.

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