

## Metallisation of Plastics

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**M**ETALLISATION may be defined as a process by which a thin, uniform and compact layer of a metal is deposited on the surface of a material usually, though not necessarily, non-metallic. The nonmetallic material may be inorganic such as glass or ceramic, or organic such as wood, paper or plastic. Metallisation of plastics is of considerable interest as it is possible to impart certain characteristics to the surface of the moulded articles, normally not obtainable from the plastics by themselves. Thus metallisation of a plastic results in the material being rendered opaque, while at the same time the reflectance can be adjusted to give either a mirror like effect or a dull satin finish; the surfaces are also rendered impermeable to gases, vapours, and liquids there by rendering them immune to the deleterious effects that could result by such exposure. The durability, abrasion resistance, as also the thermal and electrical conductivity are generally enhanced. Thus metallisation of plastics results in both improved performance on the one hand and enhanced decorative effect on the other.

It should be emphasised right at the outset, that metallisation of plastics is not intended to imitate<sup>1</sup> metals but to produce articles that cannot be conveniently or economically made out of metal. Many intricate shapes can be readily moulded in plastics and can be subsequently metallised by comparatively simple techniques. If these very articles were to be fabricated from metals, their cost would be excessive. An additional advantage of the metallisation of plastics is that the density of the article remains essentially the same as the amount of the metal deposited is very small.

Metallisation as a process must be distinguished from other methods, that are employed to impart metallic characteristics to "a non-metallic surface".<sup>2</sup> Thus painting any surface with a composition based on a metallic pigment is not metallisation as the coating is not exclusively that of metal, there being little or no direct contact between the metallic pigment and the substrate. The well known art of covering wooden or other surfaces by means of thin sheets of metal e.g. gold leaf, using an adhesive such as goldsize or shellac, is also a process distinct from metallisation though in both cases the surface characteristics may be comparable. In metallisation there is a direct bond between the metal and the substrate, such a bond being particularly effective with those surfaces which can act as electron acceptors.

The deposition of metal on a substrate can be carried out by a number of methods of which the following are the most important.

(i) Cathode sputtering, (ii) electroplating, (iii) flame spraying, (iv) condensation of metallic vapours, better known as vacuum deposition and lastly (v) chemical method.

Any one of the methods can be employed for the metallisation of plastics, the choice being mainly governed by the following factors :—

(1) The performance expected from the metallised product. (2) The size and shape of the article and the area on which the deposition of the metal is to be carried out. (3) The actual number of articles to be finished. (4) The chemical composition, the physical structure and the history of the material to be metallised. (5) Cost.

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(i) *Cathode sputtering*.—This is accomplished by placing two electrodes of suitable material in proximity to the articles to be coated, in a chamber which is then exhausted. The negative electrode i.e. the cathode is made of the metal which is to be deposited. A potential difference varying between 200 to 3000 volts (depending on the pressure in the system) is then applied across the terminals of the electrodes and the metal is sputtered and gets deposited on the surface of the plastic. The absolute value of the vacuum to be employed depends on the nature of the metal and is generally of the order of 1 to 0.01 mm. of mercury. As the vacuum required is comparatively low, less expensive pumping equipment is required. Furthermore when the process is to be employed for metallisation of continuous sheets a separate degassing chamber is eliminated. The method is particularly useful for sheet materials or articles which has got a plane surface. The sputtering process is very valuable for depositing metal films on to plastic materials containing high percentages of volatile plasticizer, which are thus difficult to coat by vacuum evaporation described later. The rate of deposition of metal by sputtering limit the film speed to about 20 ft./min. whereas 300 to 500 ft./min. can easily be coated by vacuum evaporation method. Not all metals can be deposited by sputtering. Aluminium for example is not a suitable metal but gold and silver are readily deposited. However even with these metals the rate of deposition is much slower as compared with the high vacuum evaporation methods. Even though the cathode sputtering method, even with restricted application has been more or less superseded by high vacuum techniques, it is still employed particularly for the deposition of decorative finishings of precious metals such as gold, because the slow deposition rate leads to careful control of thickness and hence economy in use.

In one of the typical plants "the sputtering glow discharge is operated" from a high tension rectified supply of 3,000 V at 500mA connected to 18.5-in diameter cathode; metal is sputtered from both sides of the cathode at a working pressure of 0.01 mm. mercury. The cathode is watercooled to prevent overloading of the plastics product. The operating pressure can be obtained by a diffusion pump specially designed to have high pumping speeds at 0.01 mm. mercury (i.e. the sputtering pressure) and which is backed by a single-stage rotary pump. A typical application of the plant is the deposition of gold on to cellulose nitrate gramophone record masters which have an abnormally high plasticizer content. Other applications are the closely controlled deposition of precious metals on plastic articles, where economy is of overriding importance. The distribution of the sputtered film follows different laws from that of vacuum evaporation described later".

(ii) *Electroplating*.—This is a process wherein metallic ions from an electrolytic solution are deposited on the object to be plated under the influence of a direct current. The metallic ions are provided either by the continuous dissolution of the metallic anode or by having a salt of the metal as the electrolyte. The object to be plated is the cathode and as such, it is essential that the object is electrically conductive. As plastics are poor conductors of electricity it becomes necessary to give a pre-treatment to the plastics so that the surface becomes electrically conductive. Rubbing with graphite is the simplest method of rendering the surface conducting but is not preferred. The usual method consists in treating the surface with a solution of stannouschloride. It is essential that the plastic be unaffected by the solution in which it is dipped. The method however has not acquired any importance as it is difficult to get smooth and coherent finishes.

However electroplating<sup>2</sup> is resorted to wherever a heavy deposit of metal is desired for greater strength or better electrical properties. Since the initial conductive coat is very thin the current density must necessarily be low to begin with, which restricts the rate of deposition of metal. It may be added that the method is applicable to all metals though wide variations in the conditions of deposition may be necessary for different metals.

(iii) *Flame spraying*.—In this process the powdered metal is made to flow<sup>3</sup> through a oxy-hydrogen or oxy-acetylene flame and the softened metal is deposited on the surface to be coated. Instead of the powdered metal, thin rods or wires of the metal may be held in the path of the flame and globules of the molten metal are then carried away by the hot gases of the flame. One type of pistol requires that the metal to be sprayed be melted separately in a furnace but this method is rarely employed. A high degree of skill is necessary in order to produce uniform coating by this technique. Even under the best conditions the finish obtained is far from smooth. Besides the plastics must have sufficient thermal resistance in order to withstand the heating effects. As far as is known this method is not used to any extent for the metallisation of plastics.

(iv) *Vacuum deposition*.—The principle of the process consists in vapourising a metal, either from the metal itself or from one of its salts and allowing the vapours to condense on the surface of the plastic to be metallised. As the vapour pressure of metals is generally very low, it becomes essential to work under high vacuum to the extent of 0.5 micron. Both the metal to be deposited and the article to be coated are enclosed in a chamber which is evacuated to the required vacuum. In addition the metal or the metal salt is to be heated in order to enhance its rate

of evaporation. The article to be coated may have to be cooled though it is generally not necessary. The method is very rapid and despite the high vacuum that is required, has found a ready application for the finishing of plastics. Aluminium is the most commonly used metal as it is easily vapourised and as it gives mirror-like<sup>2</sup> finishes. The finish is in many ways comparable to that imparted by platinum or rhodium. The low price of aluminium is the distinct advantage. The finish retains its optical properties even on normal outdoor exposure but a finishing coat of a clear lacquer may be given in order to enhance its abrasion resistance. The surface can also be dyed to simulate metallic colour.

Aluminium metal is used in the form of small staples<sup>5</sup>,<sup>2</sup> which are hung from the coils of stranded tungsten filaments. These filaments are connected through electrodes to the source of electric current so that the necessary heating can be readily achieved. All other metals are evaporated from "boats" made of tungsten or molybdenum sheets. The boats are V-shaped<sup>2</sup> the edges being crimped. The boat is fastened at each end to the electric leads and becomes incandescent when the current is flowing. In all the cases the idea is to have as large a surface as possible for the evaporation of the metal.

This factor is of primary importance in the continuous metallising of sheet stock. Special arrangements for rotation<sup>6</sup> have to be made if all the sides of an article are to be uniformly coated by the metal.

The difficulties<sup>7</sup> of using vacuum evaporation for the metal finishing of plastic mouldings are directly related to their vacuum properties, particularly, the degassing properties and the weaknesses in the early vacuum systems. It is found that the deterioration of the pumping performance of a plant arises from

contamination of the system by volatiles liberated from plastics. Constant sources of trouble are the use of (1) highly volatile plasticisers i.e. with vapour pressures greater than 0.5 micron Hg. and (2) base lacquer films incompletely cured prior to coating. Hence a knowledge<sup>s</sup> of the volatile content of a plastic is essential in determining its suitability for coating by vacuum evaporation. It may contain ingredients, such as moisture, solvents and plasticizers, which are desorbed at low pressures. Excessive liberation of one or a combination of such components may make it impossible to obtain a vacuum sufficiently low for coating i.e. lower than 1 micron Hg. The liberation of volatiles from plastics undergoing batch or continuous processing will in time lead to a fall in the pumping efficiency of even the best-designed exhaust equipment, and periodic cleaning of the coating chamber becomes essential to remove volatile contaminants adsorbed on the walls.

“Plasticizers<sup>7</sup> with low volatility are general in plastics, otherwise the plasticizer concentration would slowly decrease because of evaporation losses during service. But a plasticizer which evaporates slowly at atmospheric pressure and thus is suitable for normal service may evaporate sufficiently in vacuum to raise the chamber pressure considerably. The evaporation rate of a plasticizer from a material depends, among other things, upon the vapour pressure of the plasticizer in the combined state, which is obviously not directly related to the vapour pressure of the pure substance and is usually less, depending upon the chemical or physical forces between the molecules of the two components. The evaporation rate in vacuum is further conditioned by the rate at which plasticizer molecules are able to diffuse from the interior of the plastic to the emitting surface. It is found that plasticizers with boiling points above 300°C (roughly) are not unduly volatile i.e. have vapour pressures in the pure state less than one micron Hg”.

The following plastics are arranged in the increasing values of their degassing<sup>s</sup> properties.

Polytetrafluoroethylene, polystyrene, cellulose acetate butyrate, polyethylene, ethyl cellulose, cellulose acetate, methyl methacrylate, nylon, cellulosenitrate, plasticized polyvinyl chloride. Among these polytetrafluoroethylene and polystyrene hardly influence the exhaustion time due to their very low moisture content and unplasticized state.

The above arrangement of plastics according to their degassing properties can be misleading in suggesting that polymethylmethacrylate and nylon have bad vacuum properties compared with cellulose acetate. Now cellulose acetate often contains volatile plasticizers which raise the ultimate pressure of the vacuum system considerably, whereas even if plasticized, acrylics have much less effect on the ultimate vacuum. This difference in degassing properties can be explained by the different rates of evaporation of the water content.

It is noteworthy that in determining the degassing properties it is found that the plastics sample showing least degassing on the initial and subsequent heating cycles was a “polystyrene coating”.

From this one can see that any thermoplastic material (which cannot be successfully employed for vacuum metallising) should be capable of being vacuum metallised with a proper coating of polystyrene. The thermosetting plastics have poor adhesion to polystyrene coating.

It is important that the surface be made receptive for the deposition of the metal. The surface of the plastics should therefore be free from all extraneous matter particularly grease and oil. A better method is to give a coat of suitable lacquer preferably of polystyrene either by dipping or spraying. Lacquer serves the dual purpose of minimised

outgassing and levelling small surface defects. Superior performance is obtained when the lacquer coat is backed at low temperatures as it results in enhanced adhesion and hardness. The success of getting a satisfactory finish is dependent mainly on the care taken for preparing the surface.

(v) *Chemical method* :—The principle of this method consists in precipitating a metal from an ionic solution by the action of a suitable chemical. The precipitation is carried out under such conditions that the metal gets precipitated on the surface of the article, which is immersed in the solution. As no electrical stresses are applied the method is restricted to those metals which are readily precipitated. Silver is perhaps the best known metal that could be deposited by this technique. As the process is one where a metal ion is made to accept an electron and convert it into the metal atom the process is one of chemical reduction and as such the precipitant must necessarily be a reducing agent.

Thus, for silver, formaldehyde is the precipitant. Copper, gold and some of the noble metals are also capable of being deposited by this technique.

Uniform coatings however are obtained only if a number of precautions are taken. A typical process involves the following steps.<sup>2</sup>

(i) Degreasing, (ii) rinsing in fresh water and drying (iii) sizing with a thin coat of lacquer and baking dry (iv) sensitizing, then flushing with fresh and drying, (v) silvering, by reduction, then flushing again with fresh water and drying (vi) coating with lacquer and baking dry and (vii) dyeing to the required colour and drying.

Obviously the processing is very involved and as such the method in spite of its simplicity has not acquired much importance. The method however is

used as an intermediate stage for articles which could be subsequently finished by electroplating. It needs no stressing that the plastic should be unaffected by immersion in the solution of a metallic salt.

Generally no finishing operations are necessary after metallisation (by any method) though a coat of clear lacquer can be applied with advantage.

The preparatory treatments of the surface to be metallised are the governing factors which make for the success or failure of metallisation. The chemical composition physical structure and the history of the material to be metallised determine the method of application. Thus a thermoplastic material should not be subjected to excessive heat as softening and distortion will occur. The thermosetting materials contain fillers which render permeable, an otherwise moisture proof article and the porosity must be obviated in order to obtain satisfactory metal coating.

Porous articles are given an undercoat of a lacquer or varnish to prevent absorption of the plating and cleaning solutions, to smooth out any imperfections on the plastic, thus making possible a brighter finish. The ideal undercoat has adhesion to the plastic surface, does not etch the plastic surface, and is a material to which the deposited metal has good adhesion. The undercoat must be completely free from solvent and other volatiles to get compact coatings and as such are properly baked.

As mentioned elsewhere any type of plastic can be metallised, the choice of the method being determined by the performance expected by the finished product. While the major application of metallisation of plastic appears to be one of increasing the "Sales appeal" still many plastics can be metallised in order to enhance their functional uses. It is therefore of interest to know what particular method is to be employed for

the metallisation of some of the more common plastics. In dealing with individual plastics the order followed in the "Survey" of research problems in plastics with special reference to the development of plastics industry in India" has been maintained as it appears to be most convenient.

*Bitumen :*

Bitumen plastics find their use only for those purposes where extreme inertness to various chemicals and superior electrical properties are of primary importance. Metallisation therefore is of no interest, but if required it is best carried out by chemical reduction followed by electroplating.

*Shellac :*

Shellac finds comparatively very few uses in the plastics field mainly because of its high price. However it has been shown that if seed lac<sup>10</sup> is available at As. 8 per pound moulding powders which could be processed by techniques employed with phenol formaldehyde powders can be readily manufactured. Utility articles based on shellac moulding powders may be metallised in order to enhance their usefulness. This has also the advantage that some of the minor deficiencies namely crazing, high water absorption, dark colour are readily masked by metallisation. In view of the fact that shellac contains some volatile matter even when it is "completely cured", vacuum deposition techniques are not suitable, although cathode sputtering is useful. Better method appears to be chemical reduction followed by electroplating if necessary.

*Cellulose :*

Regenerated cellulose as also paper in the form of film or foil or sheets can be metallised and such materials should find a ready use in the packaging and wrapping industry. Metallisation will

result in rendering the cellulosic sheet completely impermeable with the minimum amount of the metal.

Vacuum deposition is by far the most convenient method for the purpose. However when regenerated cellulose is employed as opposed to paper it is necessary to see that it does not contain any volatile matter. Alternately if pliability of the film is of importance then a sealing coat should be given.

All the more common cellulose derivatives namely nitrate, acetate, acetate butyrate and ethyl cellulose are used with considerable amount of plasticizers and as such are difficult to metallise by vacuum deposition technique. Cellulose plastics containing non-volatile plasticizers are available but are comparatively costlier. For the usual plastics, metallisation is best carried out by chemical reduction followed by electroplating if necessary, though considering their uses it may not be economical to give such treatments.

*Protein :*

Casein and other protein plastics have only limited uses but such plastic articles which find the largest use in dress auxiliaries etc. can be readily metallised in order to enhance their sales appeal. Chemical reduction appears to be the most suitable process and can conveniently replace the "polishing treatment" given to formalised casein plastics, without in any way increasing either the number of operations or the cost.

Rubber hydrochloride in the form of continuous sheets and films can be metallised by vacuum deposition. It can also be readily coated by flame spraying. Cyclised rubber can also be treated in a similar manner. It is extremely doubtful whether vulcanised rubber which contains considerable amount of combined sulphur should be metallised, but if necessary, can be processed by any one of the methods.

Amido-and amino-resins, as also epoxy and phenolic materials belong to the class of thermosetting compositions which can be metallised very readily, not only to enhance the appearance but also to impart specific properties. Many of the metallised products are finding increasing uses in the field of electrical engineering and electronics. Metallised plastics are also used in aircraft construction thereby replacing aluminium and aluminium alloys. Paper based phenolic laminates are metallised so as to use them in electronics as printed circuits. In all these cases chemical reduction followed by electroplating is by far the preferred process though in certain cases vacuum deposition can be applied with advantage.

Polyamides, polyesters, polyurethanes and their copolymers are best metallised by chemical reduction followed by electroplating if necessary though at the present time because of their high cost they have comparatively little uses.

Polymers and copolymers of vinyls and acrylics are perhaps the important class of thermoplastics which could be metallised with advantage. Because of their inherent nonvolatility they can be readily metallised by vacuum deposition techniques, a method particularly suitable for mass produced articles. Only in the case of non-rigid polyvinyl chloride which contain plasticizers, specific surface treatment may be necessary. Some typical applications of metallised polyvinyls are polystyrene based products as light-weight reflectors, electric insulators requiring screening

against magnetic fields or high frequency emanations, construction of electrical components such as resistors, condensers and printed electronic circuits.

It is not an exaggeration to say that metallisation of plastics particularly from the point of view of industrial applications is still in their infancy. It is generally agreed however that in a few years industrial applications will probably be the largest volume market specially in the refrigeration and automotive industries. Another outlet which we visualise is in the garment field. The metallised sheet can be cut into strips, spun, and converted into a strong yarn that can be dry cleaned<sup>11</sup>.

#### REFERENCES

1. Narcus, H., *Trans.Electrochem.Soc.*, 1945, **88**, 371.
2. Seiter, G. J., *Mod.Plast.Encyclopedia*, 1954, Sept. 234.
3. Holland, L., *Brit.Plast.*, 1951, **24**, 101.
4. Hitchen, J., *Brit.Plast.*, 1947, **19**, 509.
5. Ganesan, A., *Bulletin, Central Leather Research Inst., Madras, India*, 1955, Feb. 12.
6. Hartmen, A. H., *Mod.Plast.*, 1952, **30**, (2), 116.
7. Holland, L., *The Plast.Inst.Trans. and Jour.*, 1956, **24**, (56), 153.
8. Holland, L., *ibid.*, 1953, **21**, (45), 66.
9. "Survey of Research Problems in Plastics with special reference to the development of Plastics industry in India," C.S.I.R., New Delhi, 1954.
10. Kamath, N. R. and Nagarsenkar, V. N., *Paintindia*, 1955, **5**, No. 4, 22.
11. *Mod.Plas.*, 1954, **32**, (1), 228<sup>t</sup>.