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PLATING WITH METAL CARBONYL

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2 Claims. (Cl. 117—47)

1 This invention relates to methods for plating or coating various surfaces with metals, and more particularly relates to coating metal surfaces. One of the important objects of the invention is to provide a non-porous, continuous coating of metal capable of sealing the capillary channels along the boundaries of the metal grains which make up the surface of the metal body being plated. This object has been attained with carbonyl solutions.

The ultimate object accomplished by such coating of metals is the complete avoidance of corrosion of the coated metals. The thorough sealing of the pores of a rapidly corrodbale metal by a continuous coating of a suitable metal such as nickel, chromium, and the like, apparently prevents aspiration, or breathing of the base metal, thereby preventing corrosion. Also, the formation of fungus growths on metal surfaces, has also been prevented in accomplishing the objects of the present invention.

A further object of the invention is to provide a process for applying continuous metal coatings of such tenacity that they may be used for plating precision instruments and the like without affecting the dimensional tolerances permitted, such coatings at the same time being uniform and providing complete protection against corrosion.

A further object is to provide a process for the coating of metals and other objects with thin metal layers which will not check or crack in subsequent use and which at the same time will be so tenaciously bonded to the surface of the articles that such coatings cannot be caused to separate.

According to the principal embodiment of this invention, metal surfaces, such as iron, brass and the like, are provided with very thin protective nickel coatings by employing appropriate solutions of nickel carbonyl.

Suitable solvents are hydrocarbons which are normally volatile, and therefore not capable of interfering with the plating operation. For example, benzol, toluol, hexane, octane, sulphur-free gasoline and kerosene, and kindred aromatic and aliphatic hydrocarbons may be employed. However, hydrocarbons of ally nature which are relatively non-volatile will so coat the surfaces of the articles being plated as to prevent deposition of metal upon such surfaces and may not be used. In other words solvents may not be employed having boiling points above about 450° F. Also hydrocarbons contaminated with oxygen, sulphur, chlorine and other halogens, and the like, are not acceptable because they usually result in the formation of black deposits instead of the desired pure metal deposits. In other words, so far as is now known, only substantially pure hydrocarbons within the indicated ranges of volatility are acceptable.

The carbonyl to be employed according to this invention is preferably nickel carbonyl Ni(CO)4. Nickel carbonyl, which is rather volatile at normal temperatures, having a boiling point of 199.4° F., is readily dissolved in appropriate hydrocarbon solvents such as benzol (B. P. 175° F.) by passing gaseous nickel carbonyl through the hydrocarbon until an appropriate concentration is obtained. In general, a benzol solution containing about one percent of dissolved nickel carbonyl is initially employed, and very much less, even down to an insignificant proportion such as about 0.001 percent, may be very satisfactorily used. In preparing such solutions, all water content must be avoided because the carbonyl is extremely unstable in the presence of water.

The coating or plating operation is accomplished by employing an indicated solution of nickel carbonyl, as distinguished from nickel carbonyl in gaseous or vapor form, the temperature of the liquid being held at or below about 80° F. for best results. For example, the solution temperature may be about 100° F. or as low as —20° F. The article to be coated is heated preferably to a temperature of around 500° F., or between about 500° F. and 575° F., and is then quickly dipped into the carbonyl solution, the time of contact being so short that the temperature of the object being coated will not fall below about 450° F. or in any event not below 400° F. Otherwise, instead of obtaining a bright nickel metal surface, black stains or streaks are formed, thereby resulting in an improper coating not providing a continuous uniform metal seal.

This, the article must be heated at least to 450° F. The practical upper temperature limit to which the article may be raised is about 575° F. The apparent absolute upper limit is 625° F., beyond which decomposition appears to be of such nature that proper coating cannot be obtained. The time interval for dipping will vary accordingly to the temperature to which the object is heated and to its size. For example, the time may be from a half second for an object weighing 15 grams to 5 seconds for an object weighing 1000 grams, and correspondingly greater times for heavier articles.

The coating phenomenon involves decomposition of the carbonyl, that is the carbonyl radical.
separates from the nickel so that the nickel deposits upon the article being coated. The coating action is not a straight line action like that of electrophating, but the nickel moves in all directions and deposits uniformly on all faces. As a consequence, this method of coating is highly satisfactory for platting threaded and other irregular surfaces where a coating of absolutely uniform thickness is required.

It is to be noted that temperature within the limits stated is a critical factor, and that time is also an important factor in so far as it concerns maintenance of temperatures within the indicated limits. However, as the stated limits indicate, there is a considerable choice of temperatures to which articles to be coated may be heated. Heating of the articles to be coated may be accomplished in any manner appropriate for the particular operation. Such may be oven heating, induction heating by electric coils, or otherwise as desired.

It is, of course, necessary to provide above the plating solution an atmosphere which is inert under the operating conditions and from which all oxygen and water vapor are excluded, as well as sulphur, chlorine, and other reactants. Appropriate inert atmospheres are those represented by nitrogen, helium and carbon dioxide. Carbon dioxide is preferred because it is heavier than air and easy to supply. Carbon monoxide liberated by the decomposition of the carbonyl passes into the inert gaseous blanket which in practice is confined, the carbon monoxide being recovered therefrom for the preparation of additional nickel carbonyl.

When an article has been dipped and withdrawn from the solution, it should be retained in the inert atmosphere above the bath until the surface temperature has dropped below about 300° F. whereby to avoid oxidation of the freshly deposited metal. For this cooling function, the equivalent of the inert atmosphere may be used, such as pure benzol, kerosene or even water, or a solution containing a deoxidizing agent, such as sodium sulfite, pyrogallic acid, or the like, the article being plunged into such liquid until the required cooling is accomplished. However, an inert atmosphere must be maintained above the cooling liquid such as that maintained above the plating solution. Although water vapor must be excluded from the inert atmosphere above the solutions in order to prevent the nickel from turning black, water may nevertheless be employed as a cooling agent since it does not appear to affect the metal coating due to the very quick cooling of the article when plunged into water. However, in using water, it is preferable that it contain a deoxidizing agent as above indicated.

The individual coatings produced by the method of this invention are continuous and of uniform thickness in the order of a few millionths of an inch, or perhaps between about 0.00001 and .000001 inch. Such a coating may be applied for example by the addition of 0.1 milligram per square inch of coated surface. It is thus apparent that the present process provides coatings so thin that they do not interfere with the tolerances required in the production of precision instruments. It is further apparent that the characteristics by which the metal coating is uniformly applied regardless of surface irregularities, as contrasted with uneven applications on irregular surfaces by electrophating, is of much importance. Where increased thickness is required, dippings may be repeated, each successive layer being applied in uniform thickness so that the ultimate coating is uniformly thick. These coatings, individually comparable in some respects with molecular layers, thus permit the building up of multiple layers to any desired degree in order to insure protection against corrosion without in any way producing undue thickness or overstepping permissible tolerances.

Exemplary of preferred nickel carbonyl according to the process of this invention for the deposition of nickel coatings of extreme thinness is of great importance, especially from the standpoint of corrosion, inasmuch as pure nickel coatings are of very low porosity. In this respect nickel is superior even to chromium and apparently to all other metals, and therefore best for this particular purpose. The value of the metal whose carbonyl is employed lies fundamentally in its own porosity. The less porous and more continuous the metal coating, the greater its value in preventing corrosion. Nickel which has been deposited under the conditions of the carbonyl is considerably more resistant to corrosion than nickel deposited by any other means, this being due probably to higher purity.

For some purposes it may also be possible to obtain solutions of other metal carbonyls in appropriate solvents, such as the indicated hydrocarbon solvents. These carbonyls might be represented by chromium and tungsten carbonyls, and possibly by molybdenum carbonyl, all of these normally being solids and soluble in appropriate organic solvents. As previously indicated, solutions of only very low concentrations need be employed e.g. from about 1% to as low as 0.001% of the metal carbonyl, however, higher concentrations may be used if desired, for example 4%. Inasmuch as the activity of the metal increases as concentration decreases, coating efficiency is maintained even after the concentration has been lowered to relatively insignificant percentages by repeated dippings.

A further advantageous feature which we have discovered is that with a carbonyl such as nickel carbonyl, such as the said carbonyl, coating solutions are desirable especially where thick coatings are desired. Thus, a solution of nickel carbonyl in toluene may be used at 0° F. or as low as -20° F. The result is a much thicker plating than when operating at 80° F., for example around five times as thick, and at the same time greater solution stability is obtained. Such temperatures are quite feasible with nickel carbonyl whose freezing point is -25° F., and coating thicknesses perhaps in the order of 0.00002 inch are obtained. With other carbonyls low temperatures may be employed approaching those at which the carbonyl freezes out of solution.

Since variations in the generic process herein disclosed will become apparent to those skilled in the art to which this improvement relates, it is intended that all such modifications as fall within the scope of the claims.

We claim as our invention:

1. A coating process comprising: heating an object to a temperature between about 450° F. and 600° F.; dipping the heated object into a solution of the carbonyl of the metal of interest in a hydrocarbon to deposit a metal coating; the temperature of the carbonyl solution approaching the freezing-out point of the carbonyl; removing the object before its surface temperature drops below about
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400° F.; reheating the object; re-dipping the object to deposit an additional coating of metal; removing the object as before; and cooling.

2. A process as in claim 1 wherein the carbonyl is nickel carbonyl and the temperature of the solution is in the order of 0° F. to −20° F.

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