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PROCESS OF COATING WITH NICKEL BY THE DECOMPOSITION OF NICKEL CARBONYL

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My invention relates to an improved process and composition for plating nickel by thermal decomposition of nickel carbonyl [$Ni(CO)_4$] vapor.

Nickel plating is now extensively employed to provide decorative and protective coatings, particularly on steel.

Nickel is commonly plated by passing nickel carbonyl vapor over the object to be plated at a temperature of at least approximately 356° F. until the desired thickness of nickel is obtained.

While prior methods of plating nickel employing $Ni(CO)_4$ vapor possess many advantages over other plating methods, particularly electroplating, there are still certain disadvantages attending its use. For example, only materials capable of withstanding the relatively high prior art temperatures at which nickel deposits out of nickel carbonyl may be plated. In addition, while the rate of deposition of nickel on surfaces from nickel carbonyl is relatively rapid, even faster deposition might be desirable. Also, at the high temperatures employed, some decomposition of CO reaction product to carbon occurs, thereby contaminating and reducing the quality of the coating.

An object of my invention, therefore, is to provide an improved, more rapid vapor deposition process for nickel plating a surface.

Another object is to provide an improved process for nickel plating a surface employing nickel carbonyl vapor at relatively low temperatures.

Another object is to provide an improved process for nickel plating a surface employing nickel carbonyl vapor in which carbon formation is reduced.

A further object is to provide an improved process for nickel plating a surface from nickel carbonyl vapor employing relatively low vapor flow rates.

Other objects and advantages of my invention will become apparent from the following detailed description and the appended claims.

The above objects, among others, are unexpectedly attained in a striking manner by my invention which comprises, in a process of nickel plating a surface by thermal decomposition of nickel carbonyl vapor, the improvement of providing a small amount of H_2S in said nickel carbonyl vapor.

Employing my invention, a wider variety of materials may be plated with nickel at relatively faster deposition rates and at lower temperatures than has heretofore been possible. The resulting nickel coatings are smooth, lustrous, adherent, and generally superior to prior art coatings as a result of the faster deposition, and contain extremely small percentages of carbon due to the lower temperatures employed.

While my nickel plating process gives tremendously improved results, the reaction mechanism is not known. It is postulated, however, that H_2S functions as a catalyst since its original and final concentration is substantially the same in any particular reaction. The overall reaction appears to be as follows:

$$Ni(CO)_4 \xrightarrow[\Delta]{H_2S} Ni + 4CO$$

Suitable volume percentages of H_2S in the vapor mixture employed in my invention are from approximately 0.1% to approximately 1%, while approximately 0.2% is preferred. The reaction may be catalyzed employing amounts of H_2S in excess of 1%, but sulphur deposition may occur without a corresponding increase in the reaction rate.

The exact percentage of $Ni(CO)_4$ in the vapor mixture is not critical and may vary over a relatively wide range. Generally vapor mixtures containing from approximately 5% to approximately 40% $Ni(CO)_4$ vapor, by volume, are suitable, while I prefer to employ approximately 20% $Ni(CO)_4$, by volume, in the vapor mixture.

Nickel carbonyl, which is a volatile liquid at normal ambient atmospheric pressure and temperature, may be readily vaporized by bubbling an inert carrier gas through the liquid carbonyl at room temperature and at a rate sufficient to saturate it with carbonyl vapor. The volume percent of $Ni(CO)_4$ in the vapor mixture may be varied by adjusting the temperature of the liquid carbonyl through which the gas is bubbled, by vaporizing the carbonyl under varied pressures, or by diluting a $Ni(CO)_4$-H_2S-carrier gas stream with additional carrier gas.

Any gas relatively inert to $Ni(CO)_4$ and H_2S such as H_2, CO_2, N_2 and the noble gases may be employed as the carrier gas and utilization of a particular gas does not appear to be critical to the successful operation of my invention. However, CO_2 is generally preferred.

I find that the inclusion of H_2S in the gaseous mixture permits the plating operation to be conducted at temperatures significantly lower than those utilized by the prior art. Thus, excellent results may be obtained by contacting the gaseous mixture with a target surface in a reaction zone maintained at a temperature as low as approximately 60° C. and it is seldom necessary to exceed a temperature of approximately 200° C. The exact temperature selected will, of course, depend upon the thermal characteristics of the target substance. Generally, however, the rate of deposition increases with temperature, as well as the rate of carbon formation.

Numerous solid substances may be satisfactorily coated with nickel by my process. Among these are wood, ceramics, cork, cloth, cardboard, glass, metals, plastics, and the like.

I find that my invention may be satisfactorily practiced employing either laminar or turbulent gas flow conditions. The optimum flow rate in a particular plating run is subject to empirical determination and will depend upon a number of variables including the percent of $Ni(CO)_4$ in the vapor mixture, the temperature of the reaction zone and the shape, size and nature of the target substance.

In a preferred form of my invention a solid surface may be plated with nickel by contacting the surface with a mixture consisting of 20% $Ni(CO)_4$ vapor, by volume, 0.2% H_2S, by volume, and the remainder CO_2, in a reaction chamber maintained at a temperature of approximately 60° C. to approximately 100° C., as shown in the following examples, until the desired thickness of nickel on the surface is obtained. The resulting CO and carrier gas are continuously withdrawn from the reaction chamber during the course of the reaction to maintain atmospheric pressure therein.

The following examples will illustrate my invention in greater detail.

Example I

A mixture consisting of 20% $Ni(CO)_4$ vapor, by volume, 0.2% H_2S, by volume, and the remainder CO_2 was passed through the interior of a steel pipe ½ inch in diameter, in a conventional reaction chamber maintained at a temperature of approximately 100° C., at atmospheric pressure and at a nonturbulent flow rate of approximately 0.07 c.f.m. until a nickel coating of a thickness of approximately 0.7 mil was obtained. The resulting CO and carrier gas were continuously withdrawn during the reaction. The nickel was deposited at a rate of 0.02 mil per minute and was smooth, bright, and generally dense, and contained only 0.036% carbon.

A plating rate of approximately 0.01 mil per minute and a product carbon content of 0.083% was obtained in a control run conducted under the same conditions as above, but without the addition of H_2S to the vapor mixture.

Example II

A vapor mixture comprising 15% $Ni(CO)_4$, 0.4% H_2S, and the remainder nitrogen was passed through a ½ inch aluminum pipe at a flow rate of approximately 0.05 c.f.m. (Reynolds number of approximately 315) in a conventional reaction chamber maintained at a temperature of 60° C. for 90 minutes. During the course of the reaction the reaction product gases were continuously withdrawn to maintain atmospheric pressure within the chamber. The resulting nickel coating was smooth, 1 mil in thickness and the plating rate was approximately .01 mil of nickel per minute.

Example III

A gaseous mixture comprising 20% $Ni(CO)_4$ 0.1% H_2S, and the remainder hydrogen was passed through a glass tube six inches in diameter at a rate of 40 c.f.m. in a conventional reaction chamber maintained at a temperature of 60° C. for 90 minutes. During the course of the reaction the product gases were continuously withdrawn to maintain atmospheric pressure in the chamber. The resulting nickel coating was bright and smooth and approximately 2.7 mils in thickness for a plating rate of approximately 0.03 mil per minute. The coating contained approximately 0.036% carbon and 0.12% sulphur.

In general, it may be said that the above examples are merely illustrative and should not be construed as limiting the scope of my invention which should be understood to be limited only as indicated by the appended claims.

Having thus described my invention, I claim:

1. An improved process of nickel plating a surface which comprises effecting contact of said surface with a mixture comprising nickel carbonyl vapor together with approximately 0.1% to approximately 1% H_2S, by volume, while maintaining the surface-gas interface during said contact at a temperature of approximately 60° C. to approximately 100° C.

2. An improved process of nickel plating a surface which comprises effecting contact of said surface with a mixture comprising approximately 5% to approximately 40% nickel carbonyl vapor, by volume, approximately 0.1% to approximately 1% H_2S, by volume, and the remainder an inert carrier gas, while maintaining the surface-gas interface during said contact at a temperature of approximately 60° C. until the desired thickness of nickel on said surface has been obtained.

3. An improved process of nickel plating a surface which comprises effecting contact of said surface with a mixture comprising approximately 20% nickel carbonyl vapor, by volume, approximately 0.2% H_2S, by volume, and the remainder CO_2, while maintaining the surface-gas interface during said contact at a temperature of approximately 60° C. until the desired thickness of nickel on said surface has been obtained.

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