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NICKEL PLATING PROCESS

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Our invention relates to an improved method and composition for plating nickel and more particularly to an improvement in a method and composition for plating nickel by the vapor decomposition of nickel carbonyl [$Ni(CO)_4$] in a mixture of nickel carbonyl vapor and H_2S.

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

Reference is made to co-pending application, "Nickel Plating Process," filed July 16, 1953, S.N. 368,502, by Thomas B. Hoover, which discloses an unusually efficacious improvement in a nickel carbonyl vapor process for plating nickel which comprises providing a small amount of H_2S in said nickel carbonyl vapor.

However, the method of the co-pending application, although requiring a considerably lower reaction temperature than earlier prior art methods, still requires a temperature of at least approximately 60° C. In addition, an enclosed, heated reaction chamber is necessary, and materials whose surfaces decompose or are otherwise adversely affected at temperatures of 60° C. and above cannot be plated.

Furthermore in "Metal Plating From Carbonyl Gases," Chemical Engineering, vol. 56, October 1949, p. 119, the following is stated:

"Nickel carbonyl is a strong reducing agent. Mixed with oxygen it may explode violently at temperatures as low as 60 deg. C. This explains the thorough flushing of both carburator and deposition chamber with inert gases before introduction of $Ni(CO)_4$."

An object of our invention, therefore is to provide an improved composition from which nickel may be plated at room temperature by vapor decomposition.

Another object of our invention is to provide an improvement in a vapor decomposition, nickel plating process employing a mixture of nickel carbonyl vapor and H_2S wherein no reaction chamber is required.

Still another object of our invention is to provide an improved vapor decomposition method of plating nickel on thermally sensitive substances.

Another object of our invention is to provide an improved vapor decomposition method of plating nickel which is nonexplosive.

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

In accordance with our invention, all the herein stated objects may be achieved and an unexpected and striking improvement may be obtained in a vapor decomposition process of plating nickel employing a mixture of nickel carbonyl vapor and H_2S, by providing in said mixture a small amount of at least one atmospheric oxidizing agent selected from the group consisting of O_2 and H_2O vapor.

Employing our invention, we find, that for presently unexplainable reasons, nickel unexpectedly may be plated out in an eminently satisfactory manner at room temperature. Consequently, no reaction chamber and associated heating means are required. As a result, an even wider

variety of materials may be plated with nickel than was possible by prior methods. Thus, relatively heat-sensitive materials such as certain kinds of papers, low melting thermoplastics, paraffins, waxes, etc., can be nickel plated. Furthermore, we find that an electrically conducting, but very thin, transparent layer of nickel may be plated upon transparent materials. The latter discovery may be extremely valuable in providing easily defrostable glass or plastic windows, particularly in airplanes.

Another advantage of our process, resides in the nonexplosive nature of the reaction mixture when mixed with oxygen. In the prior art, unusual precautions were practiced to prevent leakage of moisture or oxygen into the reaction zone from the atmosphere. However, explosion hazards are completely eliminated in our process, perhaps due to the relatively low temperature employed.

Suitable quantities of water vapor or oxygen for addition to the nickel carbonyl-H_2S mixture are from about 0.02% to about 1.5% by volume, the amount of inert carrier gas, if employed, or the nickel carbonyl, being correspondly reduced.

However, particularly satisfactory amounts of water vapor are from about 0.02% to about 0.16% by volume while approximately 0.08% is generally preferred. Particularly satisfactory amounts of oxygen are from about 0.5% to about 1.5% while approximately 1% is preferred.

The oxygen or water vapor may be added to our mixture from conventional industrial supply sources, while a portion or all of either agent could also be added from the ambient atmosphere.

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

Nickel carbonyl, which is a relatively volatile liquid at normal ambient atmospheric pressure and temperature, may be vaporized readily by bubbling an inert carrier gas through the liquid carbonyl at room temperature at a rate sufficient to saturate it with carbonyl vapor. The volume percentage of $Ni(CO)_4$ may be varied by either adjusting the temperature of the liquid carbonyl through which the gas is bubbled, by varying the pressure under which the carbonyl is vaporized, or by diluting a $Ni(CO)_4$ vapor-H_2S-carrier gas mixture with additional carrier gas. However, the slight improvement resulting from the latter procedures is insufficient to justify the additional effort.

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 approximately 5% to approximately 40% $Ni(CO)_4$ vapor, by volume, are suitable, while approximately 20% $Ni(CO)_4$ is preferred.

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 our invention. However, CO_2 is generally preferred.

Since in the complete mixture of our invention the nickel carbonyl tends to decompose at room temperature, only the nickel carbonyl and H_2S may be premixed and stored while the atmospheric oxidizing agent should be added just before impingement of the resulting mixture upon the target. The latter may easily be accomplished, for example, by employing two concentric feed nozzles or two opposing feed nozzles, the nickel carbonyl vapor-H_2S mixture being supplied by one nozzle and the atmospheric oxidizing agent being supplied by the second nozzle.

The optimum distance of the feed nozzles from a sur-

face being plated may vary with the specific nature of each surface and is best determined by trial and error methods. In any event however, the distance must be relatively short, i.e., a matter of a few inches or less, since the nickel carbonyl begins decomposing as soon as it is incorporated in the complete mixture of our invention.

We find that our 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. Generally, however Reynold's numbers as low as 300 may be utilized, and in any event, employing our invention, considerably lower Reynold's numbers may be utilized than those required in the prior art for satisfactory plating.

Although we find that the inclusion of an atmospheric oxidizing agent, as herein described, permits the plating operation to be conducted at room temperature, higher temperatures may be satisfactorily employed. However, there is no advantage to be gained other than a corresponding increase in the rate of plating while the advantage of being able to plate thermally sensitive materials may be lost.

In addition, our method may also be satisfactorily employed at temperatures as low as the minimum at which a suitable percentage volume of the nickel carbonyl may be maintained in the vapor phase. However, operation at room temperature is preferred.

Thus, in a preferred form of our invention, a solid surface may be nickel plated by subjecting same to contact with a mixture containing approximately 20% nickel carbonyl vapor by volume, approximately 0.2% H_2S by volume and approximately 0.1% water vapor by volume or approximately 1% oxygen by volume, and the remainder CO_2, at room temperature until the desired thickness of nickel is obtained.

The following examples will illustrate our invention in greater detail.

Example I

A mixture consisting of 20% $Ni(CO)_4$ vapor, by volume, 0.2% H_2S by volume, 0.1% H_2O vapor, by volume, and the remainder CO_2 was passed through the interior of a steel pipe ½ inch in diameter, at room temperature and at a non-turbulent flow rate of approximately 0.07 c.f.m. until a coating thickness of 0.7 mil was obtained. The nickel was deposited at a rate of approximately .02 mil per minute and was smooth, bright and generally dense, and contained only about 0.02% carbon.

Example II

The precodure of Example I was employed except that 1% oxygen by volume was substituted for the water vapor. The results were substantially similar to those of Example I.

Example III

The procedure of Example I was employed except that neither water vapor nor oxygen was provided in the nickel carbonyl-H_2S mixture. The deposition of nickel was observed to be impracticably slow.

Example IV

The procedure of Example I was employed except that a sheet of paper was substituted for the steel pipe. The results were substantially identical to those of Example I and the nickel coated paper did not appear to be affected to the slightest degree.

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

What is claimed is:

1. An improved method of nickel plating a surface which comprises effecting contact of said surface with a mixture comprising approximately 5% to approximately 40% of nickel carbonyl vapor by volume, approximately 0.2% H_2S by volume, approximately 1% oxygen by volume and the remainder an inert carrier gas, while maintaining the surface-gas interface during said contact at approximately ambient atmospheric temperature, until the desired thickness of nickel on said surface has been obtained.

2. An improved method of nickel plating a surface which comprises effecting contact of said surface with a mixture comprising approximately 5% to approximately 40% of nickel carbonyl vapor by volume, approximately 0.2% H_2S by volume, approximately 0.08% water vapor by volume and the remainder an inert carrier gas, while maintaining the surface-gas interface during said contact at approximately ambient atmospheric temperature, until the desired thickness of nickel on said surface has been obtained.

3. An improved method of nickel plating a surface, which comprises effecting contact of said surface with a mixture comprising approximately 5% to approximately 40% of nickel carbonyl vapor by volume, approximately 0.1% to approximately 1% H_2S by volume, approximately 0.02% to approximately 1.5% by volume of at least one atmospheric oxidizing agent selected from the group consisting of oxygen and water vapor, and the remainder an inert gas, while maintaining the surface-gas interface during said contact at approximately ambient atmospheric temperature, until the desired thickness of nickel on said surface has been obtained.

4. An improved method of nickel plating a surface, which comprises effecting contact of said surface with a mixture comprising approximately 5% to approximately 40% of nickel carbonyl vapor by volume, approximately 0.1% to approximately 1% H_2S by volume, approximately 0.5% to approximately 1.5% oxygen by volume, and the remainder an inert carrier gas, while maintaining the surface-gas interface during said contact at approximately ambient atmospheric temperature, until the desired thickness of nickel on said surface has been obtained.

5. An improved method of nickel plating a surface, which comprises effecting contact of said surface with a mixture comprising approximately 5% to approximately 40% of nickel carbonyl vapor by volume, approximately 0.02% to approximately 0.16% water vapor by volume, and the remainder an inert carrier gas, while maintaining the surface-gas interface during said contact at approximately ambient atmospheric temperature, until the desired thickness of nickel on said surface has been obtained.

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