

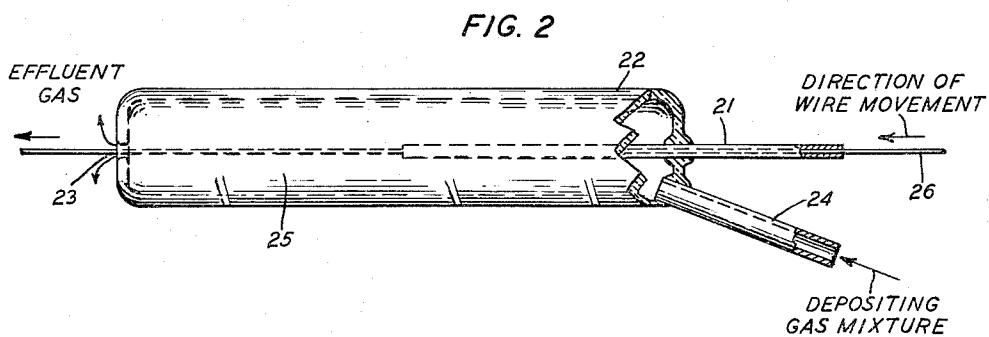
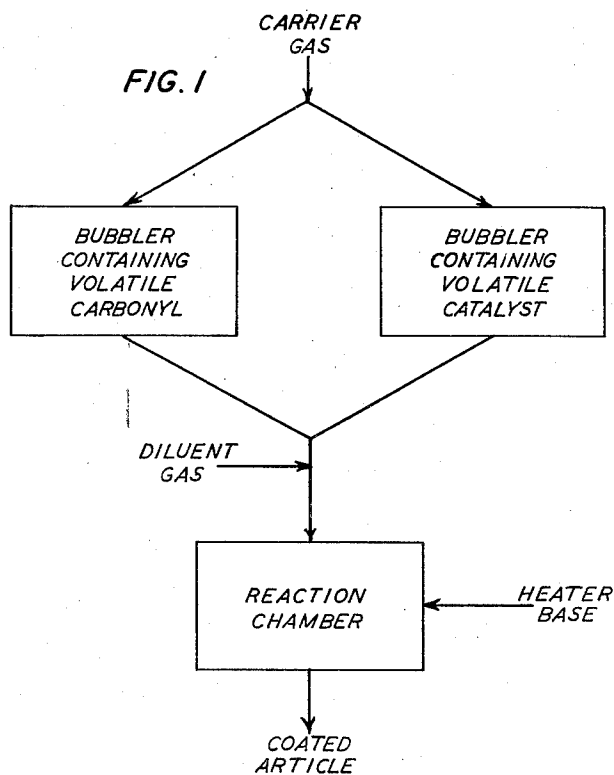
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M. V. SULLIVAN

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DEPOSITION OF METAL FILMS FROM CARBONYLS

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INVENTOR
MILES V. SULLIVAN
BY Edwin B. Cave
ATTORNEY

1

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DEPOSITION OF METAL FILMS FROM
CARBONYLS

Miles V. Sullivan, Summit, N. J., assignor to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

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This invention relates to a method of depositing metallic coatings on the surfaces of bodies, and specifically to the catalytic modification of the rate of surface deposition of metals from their gaseous compounds.

Objects may be coated with metallic films according to four general methods: electrodeposition, evaporation, liquid phase deposition, and gas phase deposition. A choice of coating method is governed by the nature of the substrate to be coated, the metal to be deposited, the thickness of the film desired, and practical considerations of time, effort and expense.

Electrodeposition, for example, is satisfactory as a process for coating many articles with a wide choice of coating metals, and thick films can often be formed efficiently. However, a severe limitation is set by the requirement of a conducting substance as a base for the deposited film. The application of an electrodeposited film on a non-conducting base, such as a plastic article, first requires the coating of the plastic article with a primary conducting film laid down by a second non-electrolytic process.

Evaporation techniques generally require both a high temperature and a high vacuum. The metal to be deposited is heated to a sufficiently high temperature to have an appreciable vapor pressure, and inert, non-depositing gas molecules of other chemical species are removed from the system. High temperatures, however, may be detrimental to the material to be coated, and the necessity of high-vacuum chambers limits the efficiency with which a large number of articles may be coated, as a discontinuous manufacturing process must usually be employed.

Liquid phase depositions, exemplified by the techniques used in mirror silvering, employ solutions of soluble compounds of the metal to be plated. Reaction of these compounds to produce the free metal is induced in the presence of the body to be coated.

If relatively thin films of metal are required, vapor phase deposition of metals often proves satisfactory. In this process, a volatile compound of the metal to be deposited is decomposed thermally, actinically, catalytically, or by other means, at the surface to be covered. Relatively unstable compounds of the coating metal may be chosen, permitting thermal decomposition at temperatures low enough to permit heat-sensitive materials to be covered. Techniques using a continuous flow of the vapors carrying the unstable metal compounds eliminate the necessity of a vacuum to promote diffusion processes. The efficacy of a vapor phase plating process is dependent, however, on the nature of the surface to be covered. Certain surfaces are hostile to the coating metal, and the deposits thereon tend often to be scanty or non-adherent. Certain other materials, also, may accept a metal film, but the deposition rate is so small as to render a vapor phase process unfeasible. In some cases pre-treatment of such surfaces either chemically, or by a physical process such as abrasion, will render the surfaces more readily coatable using vapor phase deposition methods.

2

The present invention is a method of coating articles by vapor phase deposition in which the rate of deposition of metals from their carbonyl compounds is greatly enhanced by the inclusion, in the vapor phase, of silicon tetrachloride or titanium tetrachloride. These latter materials function as catalytic agents, increasing the rate of deposition of the primary coating metal without the necessity of a pre-deposition treatment of the surface to be coated.

In the accompanying drawings:

Fig. 1 is a flow diagram of a preferred example of the present deposition technique; and

Fig. 2 is a front view, partly in section, of a deposition cell employed in adapting a preferred example of the process described herein to the coating of insulated wires.

In Fig. 1 separate streams of an inert carrier gas are passed through such apparatus as will essentially saturate the carrier streams with vapors of a volatile metal-carbonyl and a volatile catalyst. Mixing and any further dilution with an inert gas as is necessary are accomplished before contacting the deposition mixture with the object to be coated, said object being heated to a temperature sufficient to decompose the carbonyl component of the mixture. Such decomposition at the heated surface leaves a thin film of the metal previously in the carbonyl compound deposited on the surface.

In Fig. 2, a hollow tube 21, conveniently formed of heat resistant glass, such as "Pyrex," and conveniently having an inside diameter of $\frac{1}{16}$ inch, is sealed within a second concentric tube 22, also preferably formed of heat resistant glass, such as "Pyrex," which is conveniently $1\frac{1}{2}$ inches in inside diameter. Wire 26, insulated with a thin coating of organic resinous material, is fed through tube 21 along the axis of larger cylinder 22, emerging from said cylinder at aperture 23, said aperture being so aligned with tube 21 as to lie on the longitudinal axis of said tube 21. For a preferred embodiment of a deposition cell, wherein the inside diameter of tube 21 is $\frac{1}{16}$ inch, wire having an outside diameter of approximately 10 mils or less is suitable to be passed through said tube. Thirty gauge copper wire, nominally of 10 mils diameter, and coated with a polystyrene film approximately 0.1 mil in thickness, has been used successfully in a preferred embodiment of the coating process. The diluted deposition mixture is introduced into deposition chamber 25 under pressure slightly above atmospheric through tube 24. Said tube 24 is conveniently formed of a heat resistant glass, such as "Pyrex," having an approximate diameter of $\frac{1}{4}$ inch. Excess gas escapes through aperture 23, a dynamic atmosphere being continuously maintained in deposition chamber 25. The overall length of cylinder 22 is conveniently kept at 6 inches, the length of tube 21 being such that the longest dimension of reaction zone 25, in which the wire surface is exposed to the depositing vapors, is preferably about 3 inches.

Any metal which forms volatile decomposable carbonyls is suitable for vapor phase deposition, as, particularly, iron, molybdenum, chromium, cobalt, tungsten, ruthenium and nickel. The carbonyls of these metals vary in their volatilities and decomposition temperatures.

$\text{Mo}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ are volatile solids whose vapors decompose at about 150°C . Similarly $\text{Ru}(\text{CO})_5$ is a very volatile solid, while $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ are liquid at ordinary temperatures. Other carbonyl compounds which can be adapted to deposition are $\text{Fe}_2(\text{CO})_9$, $[\text{Fe}(\text{CO})_4]_3$, $[\text{Co}(\text{CO})_3]_4$ and $[\text{Co}(\text{CO})_4]_2$, which have minimum decomposition temperatures between about 50°C . and about 140°C . Those carbonyls volatilizing and thermally decomposing at temperatures which will leave the material of a particular substrate unaffected by those temperatures are suitable for use in

deposition of their metallic constituent. $\text{Ni}(\text{CO})_4$ has proved particularly effective as a gaseous material from which to deposit thin nickel films on a variety of surfaces. Mixtures of two or more carbonyls can be used to deposit their respective metallic constituents simultaneously, providing that the decomposition temperatures of the carbonyls lie roughly within the same temperature range.

For those surfaces on which deposition tends to be difficult or sluggish, the addition of silicon tetrachloride or titanium tetrachloride to the carbonyl vapor may increase the deposition rate by an order of magnitude or more, facilitating the use of such normally slow depositions in commercial processes.

Thus, the catalyst-promoted depositions have been used, in one adaptation of the process, to facilitate the coating of wires insulated with a variety of resinous organic materials and other materials forming continuous insulating coatings. For example, thin films of nickel have been laid down on wires of different diameters, said wires having been previously covered with similarly thin films of materials such as polystyrene, slightly oxidized polystyrene, polyisobutylene-styrene copolymer, and hydrated silica. The substances mentioned, all of which are normally relatively inactive to nickel deposition, can be coated with nickel deposited from nickel carbonyl at low temperatures at a feasible rate when silicon tetrachloride or titanium tetrachloride is used as a catalyst.

Although deposition may proceed at a practical rate in the absence of a catalyst, the presence of a catalyst will also accelerate deposition on other insulating materials such as "Formex" (polyvinyl formal), 2,5-dichlorostyrene, and the polymer formed by thermal initiation of polymerization of p-xylene, which have relatively more active surfaces.

Metal deposits may be formed on surfaces in systems either static or dynamic with respect to the surface being covered. In a static system, the surface to be coated is heated to a chosen temperature, dependent on the nature of the surface and the rate of deposition desired, and the heated sample is kept in a chamber in contact with a flowing stream of the carbonyl and catalyst gas mixture for a specified time. A dynamic system was found particularly convenient for forming thin metallic films on the outer surface of wires insulated with organic resins. In such a dynamic system, the wire, previously coated with a thin film of insulating resin, was continuously drawn through a reaction chamber where the metal film was deposited. The principles of deposition, with minor exceptions, are similar in both the static and dynamic systems, some differences in operational details being required, of course, by the additional variable of wire movement in the latter case.

Throughout the following specification it will often be found convenient to exemplify the principles of the coating process by reference to the aforementioned method of coating wires insulated with a thin film of organic resin. It should be understood, however, that the process is of much wider applicability, adaptable to depositing thin metallic films on articles of innumerable shapes and uses, and having a variety of surfaces, resinous and nonresinous in nature.

An important factor affecting most aspects of the deposition is the geometry of the cell in which the deposition reaction is carried out. A cell of the type shown in Fig. 2 was used to coat samples of resin-insulated wire with nickel deposited from nickel carbonyl. Excessive turbulence has been found undesirable, as it may result in nickel deposition on the glass cell walls, or in excessive cooling of the heated wire at which deposition is to occur. A cell of the type shown has been devised to make gas flow approximately laminar in the direction of wire movement, aiding in the suppression of the undesirable effects of turbulence encountered when gas flow is directed at right angles to the line of wire movement. The cell dimensions, which fix the length of the reaction zone, may

affect or determine optimum total flow rates, reaction times, rates of wire movement, and, to some extent, the optimum composition of the depositing gas mixture with respect to content of active ingredients. In addition to the effects of the cell geometry on fluid flow, the considerations mentioned above emphasize the dependence of some of the critical variables affecting the deposition on the particular cell used in the technique. Further discussion herein will have reference to the deposition process as pertinent to a cell of the preferred type shown in Fig. 2.

The total rate of gas flow through the reaction cell may vary between fairly wide limits. The minimum flow rate is set by considerations of the thickness of the metal film desired to be deposited, though the possibility of passing the wire, already coated with an insulating organic film, through successive deposition cells, or repassing it through the same cell, permits the use of flow rates so low as to be insufficient to transport the desired amount of deposit metal to the surface to be coated during any single exposure of the surface to the depositing gas. Practical considerations will generally set a lower limit on the total flow rate for a particular deposition. The upper limit on the total rate of flow of gas into the deposition cell will be set by the appearance of flaky black deposits, rather than a shiny adherent metal film.

For the cell pictured in Fig. 2 total gas flow rates between 100 cubic centimeters per minute and 550 cubic centimeters per minute were used with success, and variation of the rate between these limits had no observable critical effects on the suitability of the deposits obtained.

The gas from which the metal film is deposited has, of course, several components. Both carbonyl and catalyst are introduced into the system as vapors in an inert carrier gas, which vapors may then be further diluted with inert gas to a desired final concentration of active materials. Any inert non-oxidizing gas, such as nitrogen, hydrogen, and the rare gases, is suitable as a carrier or diluent.

It is convenient to maintain the catalyst and carbonyl each at a fixed temperature, thus fixing their respective vapor pressures. Saturation of carrier gas with either active ingredient at the fixed temperature in question will give a mixture of carrier and active substance, the composition of which mixture is calculable from the known partial vapor pressure of the catalyst or carbonyl, and the total pressure of the mixture. Thus, in the nickel deposition using silicon tetrachloride as catalyst, the nickel carbonyl and the silicon compound were kept in bubblers surrounded by water-ice baths. Separate streams of carrier nitrogen were passed through the compounds in their respective bubblers, and from the known vapor pressures of the carbonyl and the tetrachloride at 0° C., the amount of material absorbed into the carrier stream was determined.

The carbonyl content of the final gas mixture, as determined for nickel carbonyl, was found variable between 0.05 volume per cent and 5 volume per cent. Whereas in a static system the most adherent and coherent deposits were obtained reproducibly when the carbonyl content had an optimum value of 0.4 per cent of the total gas volume, in the dynamic technique compositions with more carbonyl present could be used successfully, the carbonyl concentration in such compositions reaching, as noted above, a maximum value of 5 volume per cent. Variations in the design or dimensions of the deposition cell, affecting the total flow rate permissible, may also affect the range of values found most convenient for the carbonyl content of the gas mixture used in the deposition.

By regulation of the flow of carrier gas bubbled through the carbonyl bubbler, the proper amount of carbonyl can be admitted into the system, said proper amount being that which, when diluted to a fixed total volume, will

5

give the desired volume per cent of carbonyl in the final carbonyl deposition mixture.

Similarly, a regulated flow of carrier gas passed through liquid silicon tetrachloride or titanium tetrachloride preferably kept at a fixed temperature, conveniently 0° C., will admit a specified amount of catalyst into the deposition mixture. In the deposition of nickel from nickel carbonyl, the inclusion of from 0.2 volume per cent to 5 volume per cent of silicon tetrachloride or titanium tetrachloride in the deposition mixture gave good catalytic action. The limits do not appear to be highly critical, some catalytic action being noticeable at the most minute concentrations of catalyst in the final gas. No deleterious effects on the deposition have been found for concentrations of silicon tetrachloride as high as one molecule of silicon tetrachloride for each molecule of nickel carbonyl transported to the reaction chamber. Less than 0.03 per cent of silicon was found in the nickel films deposited with such a high catalyst concentration in the vapor phase, so that the upper limit to the amount of catalyst useful in the final gas mixture seems fixed only by practical considerations. Such considerations may, effectively, determine also the lower catalyst limit. Very small amounts of catalyst are effective, but the accurate operation of flow meters, for example, may necessitate the use of substantial volumes of carrier gas, with a resultant higher catalyst concentration in some cases.

The temperature at which decomposition is effected depends on the carbonyl chosen for the plating process, but one must also take into consideration the sensitivity to heat of the surface to be covered, particularly if said surface is composed of an organic material. For nickel carbonyl in the presence of a silicon or titanium tetrachloride catalyst, temperatures between 80° C. and 220° C. can be used, with temperatures between 110° C. and 150° C. being particularly effective. Lengths of wire filmed with an organic insulating resin were preheated in a furnace or oven maintained at a temperature within these ranges, and then reeled at a rate of 20 feet per minute through the immediately adjacent reaction chamber. Greater spatial or temporal separation of the preheating zone and the reaction chamber will require appropriate adjustments in the furnace temperature, so that the temperature of the surface to be coated lies within the effective temperature range when the surface is exposed to the carbonyl vapors. Though higher temperatures may be favorable to more rapid carbonyl decomposition, the organic insulating materials on which metal coatings may be desired often prohibit the use of temperatures so high as to be damaging to their nature.

At a given temperature, the time required for a given surface to take a metal film of the desired thickness is dependent to some extent on the material of the surface, Formex, for example, taking a good film more readily than polystyrene under ordinary circumstances. It is for otherwise relatively inactive materials such as polystyrene that catalyzed deposition is most important. Specifically, for this material, a period of 100 to 1000 seconds was required in the absence of a catalyst to deposit a sufficiently thick nickel film below 100° C. When silicon tetrachloride or titanium tetrachloride was introduced into the carbonyl mixtures, the time required to achieve a similar film on polystyrene was reduced by several orders of magnitude. As mentioned earlier, good nickel deposits were obtained in the presence of a catalyst with a wire speed of 20 feet per minute. As the effective length of the reaction chamber was about 3 inches, the deposits have thus been laid during a period of contact of the surface with the depositing mixture of less than a second.

6

The relative thickness of films on coated samples can be readily determined by measurement of the resistivities of the films, thinner films having a higher resistance per unit length. Absolute values of film thicknesses were found by weighing a length of the metal-coated wire of known diameter, removing the deposited nickel in 16½ per cent sulfuric acid, and washing, drying and reweighing the cleaned wire. By assuming bulk density for the metal in the film, the approximate thickness of the deposit removed by the acid can be calculated.

By remaining within the ranges of temperature, deposition time, and depositing-gas composition suggested in the preceding text, and by employing a deposition cell similar in construction with that shown in Fig. 2, films varying in thickness between approximately ¼₁₀ Angstrom unit and 100,000 Angstrom units may be deposited. A decrease in film thickness below 1000 Angstrom units generally leads to a loss of bulk metallic properties, lending some uncertainty to the aforementioned calculations of thickness at the lower limit.

Although specific embodiments of this invention have been shown and described, it will be understood that they are but illustrative, and that various modifications may be made therein without departing from the scope and spirit of the invention.

What is claimed is:

1. The method of depositing metallic films, which method comprises thermally decomposing at least one metal carbonyl at the surface of a body in the presence of a catalyst for the decomposition, said catalyst being a member of the group consisting of silicon tetrachloride and titanium tetrachloride.

2. The method of depositing metallic films, which method comprises decomposing at least one metal carbonyl by contacting said carbonyl with the heated surface of a body, which surface is composed of an organic resin, in the presence of a catalyst for the decomposition, said catalyst being a member of the group consisting of silicon tetrachloride and titanium tetrachloride.

3. The method of catalyzing the deposition of nickel from nickel carbonyl, which method comprises mixing with said nickel carbonyl a member from the group consisting of silicon tetrachloride and titanium tetrachloride, and then decomposing said carbonyl compound in contact with a surface to be covered.

4. The method of depositing films of metallic nickel, which method comprises contacting a surface to be coated with a gaseous mixture comprising nickel carbonyl and silicon tetrachloride while maintaining said surface at a temperature between 80° C. and 220° C.

5. The method as described in claim 4 wherein said surface to be coated is a polystyrene surface.

6. The method of catalyzing the deposition of nickel from nickel carbonyl, which method comprises mixing with nickel carbonyl a member from the group consisting of silicon tetrachloride and titanium tetrachloride and then contacting said mixture with a surface to be covered, said surface being maintained at a temperature between 80° C. and 220° C.

7. The method as described in claim 6 wherein said surface to be covered is a polystyrene surface.

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