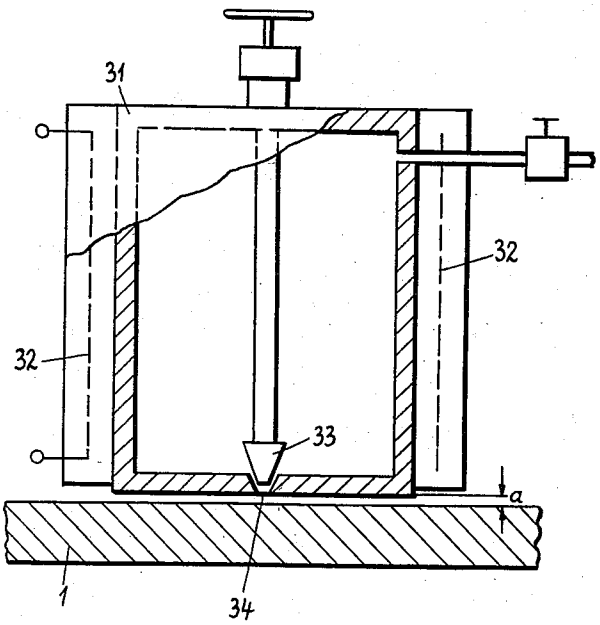
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METAL DEPOSITION PROCESS

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METAL DEPOSITION PROCESS

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9 Claims. (Cl. 117—107)

This invention relates to a process for the production of metal deposits, and has for its object to produce by thermal decomposition of metal compounds completely uniform fine-grained metal deposits of great adhering strength on substances of all kinds, that is to say, both on inorganic and on organic substances, regardless of the configuration of the surface of those substances. In contrast to known processes, this metal deposition is effected with great economy. A particular object is to produce metal deposits on heat-sensitive organic substances of very fine structure, for example, textile fibres or fabrics. The method is also useful to metallize the inner surface of porous bodies, such as wood or ceramic.

The present application is a continuation-in-part of my copending application Serial No. 190,306, filed October 16, 1950, now Patent No. 2,698,812, in which the claims were restricted to that phase of the invention relating to alternately heating the surface to be coated and directing jets of decomposable metal compound thereagainst in rapid succession.

The claims of this invention are directed to other methods of effecting this type of coating as originally disclosed, such as effecting decomposition of the metal compound at a distance from the surface to be coated but under substantial pressure, the pressure being explosively released to direct jets of extremely high velocity against the surface whereby the mean free path by such great velocity becomes extended. Alternately the metal compound may be coated upon the surface and decomposed immediately upon the surface.

In the process according to the invention, such metal deposition is effected by separating the metal from the metal compound at such a short distance from the surface of the material to be metallized that the agglomeration (coarsening of the grain) of the metal particles before they are deposited is prevented, by maintaining the temperature of the surface to be metallized at an equal level during the separation process, and by limiting the maximum heating of the material to be metallized preferably to the surface layer.

In order that this process may achieve the desired result, the conditions of dissociation of the metal compound must be maintained as uniform as possible on or above the deposition surface during the separation of the metal. The maintenance of constant dissociation conditions in the thermal decomposition of metal compounds is a necessary pre-condition for ensuring a uniform, fine-grained and firmly adhering deposit.

If it is desired to obtain a fine-grained deposit having excellent adhering strength on any desired materials, including more sensitive organic substances and on smooth, rough or porous surfaces, or surfaces of any other form, care must be taken to compensate for the heat losses occurring during the metalizing operation, by heating the surface of the substance to be metallized to the decomposition temperature from the outside and constantly supplying heat from the outside during the separating

process. The temperature of the surface of the material must not in any circumstances be higher than the temperature of the decomposition of the metal compound. Experience has shown that this is of particularly great importance in the metallization of organic substances, since otherwise the organic substance is damaged and the adhering strength of the deposited layer is greatly reduced. In order to maintain constant decomposing conditions, it is proposed in accordance with the invention, in all the decompositions hereinafter described, to maintain a minimum path of movement of the metal atoms or fine metal particles from the point at which they are separated from the metal compound to the point at which they are deposited, that is to say, to ensure that the metal atoms or particles pass along the shortest path to the surface of deposition without having too great an opportunity of aggregating during their movement, since the finer the deposited patricles remain the better are the molecular binding forces, by which they are bound to the surface of the article and by which they are incorporated in the growing metal film, able to take effect. It must be borne in mind that the length of the path of free movement is so small under normal pressure conditions that in the separation of metal from the compound the danger exists, even in the neighborhood of the surface, of the metal particles agglomerating to form coarser particles before they reach the surface. It is therefore desirable either to cause the decomposition actually to take place only immediately on the surface of the articles to be metallized or to ensure, when the separation takes place at a distance from the surface, that the metal atoms or fine particles pass as rapidly as possible to this surface, by superimposing on their free movement a preferred direction towards the surface. This is done by directing a stream of the metal compound at great velocity towards the surface of the article, it being possible for the decomposition to take place at a more or less great distance from the surface.

The working conditions hereinbefore referred to which must be maintained in accordance with the invention in order to produce completely satisfactory metal deposits from metal compounds; namely, constant, reproducible reaction conditions at the point of separation, heating at constant temperature preferably only at the surface of the article to be metallized, and prevention of agglomeration of the metal atoms or very fine particles separated from the metal compounds by adjusting the length of their path of free movement, constitute in combination new working directions.

If the decomposition takes place directly on the surface of the article to be metallized, or at a distance therefrom, it is in all circumstances important that only the surface itself, but not the mass of the entire article, be heated because heating of the mass of the article is completely unimportant to the metallizing process and involves a considerable loss of heat. More especially, if only the surface on which the metal compound is decomposed is heated, the conditions of dissociation can be much more readily maintained uniform and the metallizing process can proceed at great speed over the surface. Thus, only a fraction of the thermal energy otherwise necessary for heating the entire article to the decomposing temperature is required for the metallization. Similarly, the time taken by the metallization is only a fraction of that taken in the known processes.

The heating of the surface to the decomposition temperature does not preclude pre-heating of the article below the decomposition temperature from being expedient in special cases.

Reference is made to my parent application, now Patent 2,698,812, dated January 4, 1955, for further de-

tailed description of the subject matter there claimed. The subject matter claimed in this application will be understood by reference to the single figure of the drawing.

In the metallization of materials or articles by heating and deposition directly on the surface, the metallization may be effected in vacuo in special cases, for example in the metallization of very smooth surfaces, one of the methods already described being applied. Generally, however, the new metallizing process will be most economically carried out at atmospheric pressure.

While the methods claimed in my parent application of which this is a continuation-in-part are described in the foregoing examples which effect fundamentally a heating and deposition by jets on the heated surface of the article to be metallized, the process according to the invention and as herein claimed is carried out, as illustrated by way of example in the single figure comprising the drawing herein by effecting the decomposition of the metal compound, not on the surface, but at a distance *a* therefrom. In order to prevent the agglomeration of the metal atoms or particles in the movement along the path *a* to the surface, these metal particles must be blown on to the surface at great speed, for example at a few 100 m. per second. The order of magnitude of the distance *a* is in this case of a few millimeters.

The metal compound, for example nickel carbonyl, is under high pressure (about 100 atmospheres absolute pressure) in a pressure-proof container 31 which is brought by means of an electric heating element 32 to a temperature (for example, 240° C.) lying above the decomposition temperature of the metal compound at normal pressure. The metal compound is blown at high speed on to the surface of the article 1 through an outlet aperture 34 adapted to be closed by a cone valve 33 or the like. The expansion occurring at the discharge of the metal compound brings the metal compound out of the stable condition into the unstable condition, so that it is decomposed.

In the process according to the invention herein claimed, it will be seen that a metal compound is brought to a high temperature in a pressure vessel and stable in vapor form at the high pressure and is then decomposed by relief of pressure. There is thereby obtained an appreciable simplification of the metallizing process, since the heating of the body to be metallized is wholly obviated, and accordingly there are avoided all those difficulties of temperature control which are associated with the thermal decomposition of metal compounds. In this process the decomposition can take place under unvarying conditions, i. e., with the temperature and pressure kept constant during the relief of pressure, so that therefore bodies of all kinds and having surfaces of any shape can be given a metal coating which is completely uniform, is of very fine grain and adheres extremely well. Since with the present process the body to be metallized does not require to be heated, it is possible to employ this process for metallizing heat-sensitive organic substances, for example paper, textiles and the like.

Metal carbonyls, for example nickel or iron carbonyl, are particularly suitable for use in carrying out the present invention. When using nickel carbonyl it is brought, in a pressure-tight container, to a pressure of for example about 100 atmospheres and a temperature of about 240° C., this temperature being above the decomposition temperature of the metal compound at normal pressure.

The metal compound is allowed to issue from this container through a nozzle. The pressure relief, to a low pressure, which occurs during the emergence brings the metal compound from the stable condition to the unstable condition, so that it is completely decomposed. The metal compound, or the products of decomposition, are blown at high speed on to the surface of the body to be metallized, for example at more than 100 meters per second, by the high pressure existing in the container.

Care must be taken that the relief of pressure, or decomposition, of the metal compound takes place at so short a distance from the surface to be metallized that aggregation of the metal atoms and particles is prevented and at the same time a very firmly adhering, extremely fine grained metal coating is obtained. This distance amounts to a few millimeters, having regard to the high blowing speed.

In carrying out the process according to the invention, all metal compounds may be employed which are dissociated into metal and residual substance under the action of heat. Such compounds are mainly metal carbonyls, metallic hydrides and metallic halogens. Examples of metal carbonyls are nickel tetracarbonyl, iron pentacarbonyl and the carbonyls of tungsten, molybdenum and cobalt. The hydrides which may be employed include, for example, copper hydride, germanium hydride, antimony hydride and others, while the chlorides include chromium chloride and nickel chloride, and the other types of compounds which may be employed include particularly metallic acetyl acetonates such as copper acetyl acetonate. In addition to these compounds which can be directly separated under heat, metal compounds which liberate the metal on reduction or chemical reaction by thermal means may also be employed for the metallizing process according to the invention. As examples for the reduction method may be mentioned the oxides of the precious metals and of other heavy metals, and for the chemical reaction method the halogen compounds of the heavy metals, for example chromium chloride, are particularly suitable.

The process according to the invention may be employed inter alia to produce metal deposits on compact articles or on and in porous articles or materials. One of the characteristic features of this process resides in the fact that the quantity of metal deposited per unit time is substantially greater than in the metal vaporization process and is even greater than in the galvanic process. Moreover, metallic deposits can be applied by means of the process to bright, oxidized or otherwise coated metals, and especially to non-metals such as plastics, wood, fabrics, papers of all kinds, felts, fibres of organic and inorganic nature, glass, quartz, ceramics, salts and other compounds; that is to say, to all solid or plastic materials whose surface does not undergo any detrimental physical or chemical modification during the metallizing operation.

Extremely fine projections or pores can be filled by the metal deposit. Sensitive organic substances are also not damaged if the metallization process is correctly conducted. For example, papers, textiles and the like may be coated on their outer and inner surfaces with a metal film which embraces each individual fiber and which, if of suitable thickness, cannot be mechanically detached without partial destruction of the fibers.

The metallization is so clean and true to the surface and adheres so strongly that it can be used as a support for a further galvanic deposition of any desired metals. For this purpose, only an extremely thin layer deposited by the process described is required in the case of metallized non-conductors.

Naturally, the conductive layers deposited from the gas phase have, as compared with the layers hitherto produced by the deposition of silver or by the application of layers of graphite or silver sulphide coatings by the wet method, an immeasurably greater adhering strength which can only be compared to the ideal attachment of fine-grained deposits by the cathode atomization or vaporization process. Since the economy of the processes for the separation of metals from compounds according to the invention is nevertheless considerably greater and it must be taken into account that the adhesive strength of a conductive layer on a non-conductor is essential to the

adherence of the metal film subsequently galvanically deposited, the process is also of particular importance in the electroplating field.

I claim:

1. Process of depositing a uniform firmly adherent coating of metallic particles of finely divided sub-crystalline size on the surface of a base material, comprising heating a heat decomposable metal compound to a substantially constant temperature exceeding the decomposition temperature of said compound at normal pressures in a confining vessel whereby to develop high pressure substantially exceeding atmospheric pressure and confining the heated compound under sufficient pressure to prevent its decomposition at the elevated temperature, and then explosively releasing the confined vapors in a jet directed against the surface to be coated, the expansive release bringing the metal compound out of the stable condition into the unstable condition, whereby it is decomposed at the discharge of said vessel.

2. Process as defined in claim 1, wherein the heat decomposable metal compound is heated to a temperature exceeding the decomposition temperature at normal pressures sufficient to develop a pressure of the order of 100 atmospheres prior to release of pressure in a jet against the surface to be coated.

3. Process as defined in claim 1, wherein the heat decomposable metal compound is a metal carbonyl.

4. Process as defined in claim 1, wherein the surface with which the metal is coated is composed of inorganic material.

5. Process as defined in claim 1, wherein the surface with which the metal is coated is composed of organic material.

6. Process as defined in claim 1, wherein the surface with which the metal is coated is composed of a thin heat decomposable sheet of organic material.

7. Process for depositing a uniform firmly adherent coating of metallic particles of finely divided subcrystalline size on the surface of a base material, comprising heating a thermally decomposable metal compound confined in a container to a temperature exceeding its decomposition point and to develop a pressure exceeding about 100 atmospheres, said pressure serving to maintain the compound stable, and then decomposing the compound by relieving the pressure in said container, whereby said metal compound decomposes and is emitted from said container as a high velocity jet, and applying said jet against successive small increments of surface area of the surface to be coated, while regulating the distance of travel of said jet from the point of release of said container to the surface being coated to less than the mean free path of the fine metal particles separated in the decomposition of the metal compound.

8. A coated product having a firmly adherent coating of finely divided particles of metal of subcrystalline size deposited thereon by impinging the jet thereagainst resulting from explosive release of a heat decomposable metal compound heated to a temperature exceeding its decomposition point at atmospheric pressure to a substantially high pressure and held at a distance from the surface to be coated wherein no metal dust is released.

9. A coated product having a firmly adherent coating of finely divided particles of metal of sub-crystalline size deposited thereon by decomposing a heat decomposable metallic compound to finely divided metal and applying said finely divided metal to the surface to be coated immediately before the metallic particles have had opportunity to coalesce into larger particles.

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