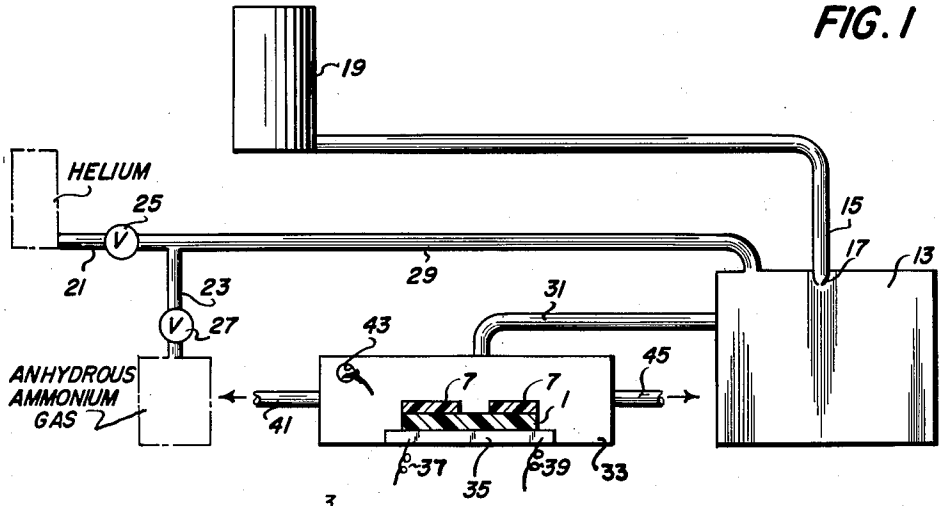
Jan. 31, 1961 W. M. BOLTON 2,970,064

MASKING MATERIAL PARTICULARLY FOR GAS PLATING PROCESSES

Filed May 13, 1957

FIG. 1



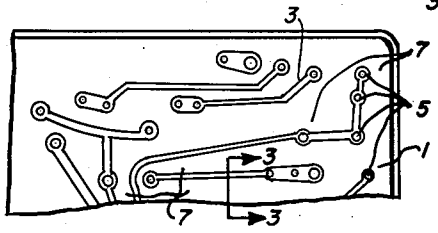


FIG. 2

FIG. 3

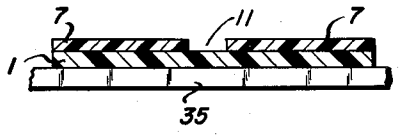
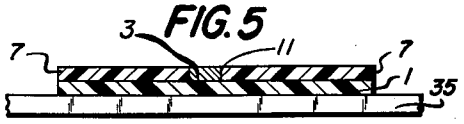


FIG. 5



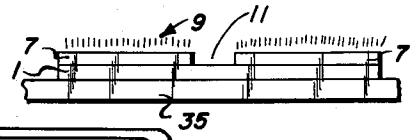


FIG. 4

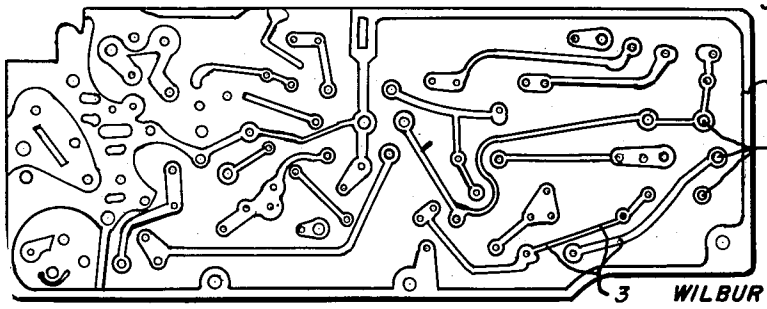


FIG. 6

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MASKING MATERIAL PARTICULARLY FOR GAS PLATING PROCESSES

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4 Claims. (Cl. 117—5.5)

This invention relates to the metallizing of materials by means of deposition of metal from the gaseous state and is particularly concerned with the masking off of selected areas of a substrate to innibit metallic deposition thereon; further, the invention is specifically concerned with masking agents which not only inhibit the metallic deposition but which are readily removed from a substrate after completion of metallizing and which provide a sharp line of demarcation between a metallized and a non-metallized area.

The invention has been found to be of considerable utility in the production of printed circuits wherein an electrically conductive film of metal of relatively narrow width and frequently serpentine configuration is provided on a substrate of insulating material, such as a board of a phenolic resin, for example.

In accordance with this invention a masking agent which exhibits particular utility in gas plating applications, including the plating of printed circuits, comprises a film former and a vehicle of low volatility. With such combination it appears that in the course of gas plating the vehicle is slowly released from the film and creates over the film a vapor pressure of the vehicle which inhibits deposition of the metal from the gaseous constituent on the film. With such deposition inhibitor present deposition may be substantially completely prevented or if it does occur, the deposition is of such a discontinuous nature or is so slight that penetration of the film by a subsequently applied washing liquid is not prevented.

The film itself is preferably of such a nature that it may be removed, with any residual vehicle therein, from the substrate without damage to the substrate by common washing liquids, such as water, soap solutions, water and alcohol solutions, and similar materials.

I have found that film formers which are not reactive with the vehicle to produce materials insoluble in common washing liquids are particularly effective; such film formers also are suitably water-soluble or water dispersible and are not rendered insoluble by moderate temperatures up to 400–500° F. Particularly effective for the practice of the invention are film formers such as plant, vegetable and bacteriological gums; for example, dextrans, celluloses such as carboxy methyl cellulose, and alginates are useful.

The vehicle for combination with the film former is suitably a polyhydroxy aliphatic, such as glycerin, ethylene glycol, propylene glycol and high analogues, and also including the glycol ethers and mixed ethers, for example, butycarbitol is a useful ether.

For ease of practice of the invention I have found that a vehicle which is readily miscible with water, that is glycerine, is to be preferred. Glycerine is readily retained by film formers such as dextran at normal temperatures and is released from the film at plating temperatures at such a rate as to admirably perform the necessary deposition-inhibiting function. In combination with

dextran and water glycerine forms a convenient dispersion for film forming.

The invention will be more fully understood by reference to the following detailed description and accompanying drawings in which:

Figure 1 is a schematic view illustrating apparatus useful in the practice of the invention;

Figure 2 is a plan view of a board of insulating material masked off for the formation of a printed circuit utilizing the apparatus of Figure 1;

Figure 3 is an enlarged and sectional view of the board of Figure 2 taken substantially on line 3—3 of Figure 2;

Figure 4 represents the structure of Figures 2 and 3 in the course of the metallizing operation indicating schematically the vaporization of vehicle from the masking film;

Figure 5 is a view similar to that of Figure 3 after metallizing and before removal of the masking agent; and

Figure 6 is a plan view of the product of the operation in full scale and after removal of the masking agent.

Referring to the drawings and initially particularly to Figure 2 the numeral 1 designates a thin rectangular board of electrical insulating material such as a phenolic resin base board. Coated on the board 1 and outlining a configuration 3 for a printed circuit which is to include terminals as at 5 is a masking agent 7 produced in accordance with the principles of this invention.

An excellent masking agent comprises as the film former, dextran a high molecular weight gum; glycerin as the vehicle of low volatility, and water as the dispersing agent. While the water content may vary with the molecular weight of the gum and may be varied to aid ready dispersibility a convenient formula well suited to the purpose has been found to be approximately equal weights of glycerin and dextran together with water to the extent of about 10 times the dextran weight. Thus a formula employing 10 grams of dextran (M.W. approx. 1,000,000), 10 grams of glycerin and 100 cc. of water has been employed.

The board 1 prior to coating should be cleaned of oil or grease chemically and suitably the board is also roughened by sand-blasting or with a 320 grit emery.

The dispersion is spread on the cleaned board 1 in any convenient manner to form the film and to outline the configuration of the printed circuit on the board (Figure 2). For example, a stencil may be used. The dispersion should be relatively viscous, like a heavy syrup, to prevent flow and the board should be maintained in a horizontal position.

Preferably a first coating is applied, dried at 105° C., and then a second coat is applied and dried at the same temperature. Such is a most suitable procedure for the specific formulation noted above. The drying in each instance should take place until the exposed surface of the film is just tacky.

The board with the film formed thereon is then placed in the apparatus of Figure 1, for example, where it is exposed to an atmosphere of a plating gas; such may suitably be nickel carbonyl and the temperature of the board within the chamber is then brought up to 285° to 290° F. as will be noted hereinafter in connection with the specific description of the apparatus.

As the board 1 and film 7 are heated glycerin slowly evolves as indicated at 9 in Figure 4 and a vapor pressure of glycerin exists over the masked areas. This vapor pressure tends to prevent deposition of the metal of the nickel carbonyl on the masked areas but does not prepent the build-up of nickel in the unmasked areas as at 11 (Figures 3, 4 and 5).

With the masking agent specifically referred to above an exposure time of ten minutes to the plating gas has

been found to be satisfactory for securing adequate metal deposition without injurious effect to the masking agent.

Upon completion of the metallizing films of the above described composition may still contain some glycerin which is desirable in aiding the final washing. The washing may be effected with plain water and such is generally preferable; however, as already noted, was liquids which do not affect the insulating board **1** or the deposit of metal may be employed.

The masking agent is completely removable and it leaves a finely delineated circuit configuration (Figure 6).

Referring now more particularly to the exemplary apparatus illustrated in Figure 1, the numeral **13** designates a vaporizing chamber, while the numeral **15** indicates a conduit extending into the chamber, terminating in a nozzle **17**, and which is adapted for the flow of nickel carbonyl to the chamber from a suitable source of liquid carbonyl indicated at **19**.

Leftwardly in Figure 1 the numeral **21** designates a conduit which is connected to a source of helium, while the numeral **23** designates a conduit which is connected to a source of anhydrous ammonium gas. Valves **25**, **27** are provided in the respective conduits for the control of gas flow.

The helium and ammonia mix together in the conduit **29** and flow to the chamber **13**, where they mix and serve as a carrier for the nickel carbonyl gas formed by the flash vaporizing of the liquid nickel carbonyl. This plating gas then passes through conduit **31** to the plating chamber **33** which, in its lower portion, is provided with a platen **35** adapted to be heated electrically through leads **37, 39**. As indicated in Figure 1 the insulating board **1** is placed on and heated from the platen **35**.

Gases are exhausted from the plating chamber **33** through conduits as at **41, 43, 45**. These exhaust gases may suitably be flowed to a burner or to a recovery apparatus as desired.

In connection with the plating operation it is desirable that the plating chamber be of sufficient size, such that no build-up of pressure of the vehicle will occur over the areas which are to be metallized. This is not a critical matter and obviously the volume should be such that no material amount of glycerin, for example, exists in the vapor pressure within the plating chamber, the primary vapor pressure of the vehicle existing only at the masked area as it emanates from the masking film.

When dextran is used as the film former, glycerin may be present to the extent of about 10 percent of the weight of the dextran, or glycerin may be present in considerable excess, for example, ten times that of the weight of the dextran.

Similar considerations apply to the use of the other film forming agents with respect to proportions. However, as already noted, it is preferable that the glycerin be present in the masking agent to such an extent that under the conditions in which it is to be employed, some glycerin will remain in the film after the completion of the metallizing operation.

In some instances some slight deposition of metal has occurred on the masking agent, but in every case this deposition has been in such a state that it is readily permeable by water, and no difficulty has been experienced in removing the films with water alone, although the speed of this operation may be increased by employing a slight alkali, such as a soap solution. Also, if desired, an alcohol-water mixture to the extent of about 50 percent alcohol, may be employed.

The success of this method of plating is attributed to the non-coherency of any metal deposit which occurs on the masking film, thus providing for the penetration of water, while the metal deposit itself which forms the conduction portion of the printed circuit is highly coherent.

While large amounts of glycerin are employable, it is preferable to operate on the side of the minimum of vapor pressure, and hence a small amount of glycerin, in order to avoid the formation of slight halos which tend to prevent sharp delineation of the metal deposits.

Accordingly, while the vehicle should be present in sufficient extent to have some glycerin remaining in the film at the end of the operation, it should not be present to such an extent that undue halo formation occurs. When the amount of glycerin exceeds the proportions set out in the ranges given hereinbefore, such halo formation may occur and affects the appearance of the article but does not deleteriously affect the utility.

It will be understood that this invention is susceptible to modification in order to adapt it to different usages and conditions and accordingly, it is desired to comprehend such modifications within this invention as may fall within the scope of the appended claims.

I claim:

1. A process for the production of well delineated metallic deposits covering only a surface portion of an object which comprises applying to the object a masking agent to delineate on the object the contour of the deposit to be formed, said masking agent comprising a film former consisting of a viscous mass composed of dextran and a glycol vehicle releasable from the film former at temperatures below 500° F., said film former being water dispersible and capable of retaining its water dispersibility when subjected to heat, heating the object in an enclosed vessel to a temperature sufficiently high to decompose a metal-bearing heat decomposable gaseous compound and less than 500° F. to induce volatilization of the vehicle and to create a vapor pressure of the vehicle over the masking agent, passing a heat-decomposable gaseous compound which is decomposable at temperatures above 75° F. and below 500° F. to the object to be plated while the object is maintained at decomposition temperature and while said vehicle is being volatilized to thereby deposit on the delineated portion of the object metal while the deposition of metal on the masking agent is inhibited, removing the object from the vessel, and thereafter washing the masking agent from the object.

2. A process for the production of well delineated metallic deposits covering only a surface portion of an object which comprises applying to the object a masking agent to delineate on the object the contour of the deposit to be formed, said masking agent comprising a film former consisting of a viscous mass composed of dextran and glycerine, heating the object in an enclosed vessel to a temperature sufficiently high to decompose a metal-bearing heat-decomposable gaseous compound but to less than 500° F. to induce volatilization of the glycerine and to create a vapor pressure of the vehicle over the masking agent, passing a said heat-decomposable gaseous compound to the object to be plated while the object is maintained at said decomposition temperature and while said vehicle is being volatilized to thereby deposit on the delineated portion of the object metal while the deposition of metal on the masking agent is inhibited, continuing the deposition to produce a desired plating thickness, removing the object from the vessel while some glycerine remains in the masking agent, and thereafter washing the masking agent from the object.

3. A process for the production of well delineated metallic deposits covering only a surface portion of an object which comprises applying to the object a masking agent to delineate on the object the contour of the deposit to be formed, said masking agent comprising a film former consisting of a viscous mass composed of dextran, glycerine and water, preparing the masking agent by heating a film thereof on the object to drive off water until the film is just tacky, heating the object in an enclosed vessel to a temperature sufficiently high to decompose a metal-bearing heat-decomposable gaseous compound to induce volatilization of the vehicle and to create a vapor pressure of the vehicle over the masking agent, passing a said heat-decomposable gaseous compound to the object

to be plated while the object is maintained at said decomposition temperature and while said vehicle is being volatilized to thereby deposit on the delineated portion of the object metal while the deposition of metal on the masking agent is inhibited, continuing the deposition to produce a desired plating thickness, removing the object from the vessel while some glycerine remains in the masking agent, and thereafter washing the masking agent from the object.

4. A process for the production of well delineated metallic deposits covering only a surface portion of an object which comprises applying to the object a masking agent to delineate on the object the contour of the deposit to be formed, said masking agent comprising a film former consisting of a viscous mass made up of dextran and glycerine the same being in approximately equal amounts by weight dextran and glycerine, heating the object in an enclosed vessel to a temperature sufficiently high to decompose a metal-bearing heat-decomposible gaseous compound to induce volatilization of the glycerine and to create a vapor pressure of the vehicle over the masking agent, passing a said heat-decomposable gaseous compound to the object to be plated while the object is maintained at said decomposition temperature and while said vehicle is being volatilized to thereby deposit on the

delineated portion of the object metal while the deposition of metal on the masking agent is inhibited, while glycerine is retained in the masking agent removing the object from the vessel, and thereafter washing the masking agent from the object.

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