

[54] DEPOSITION MATERIALS AND METHOD

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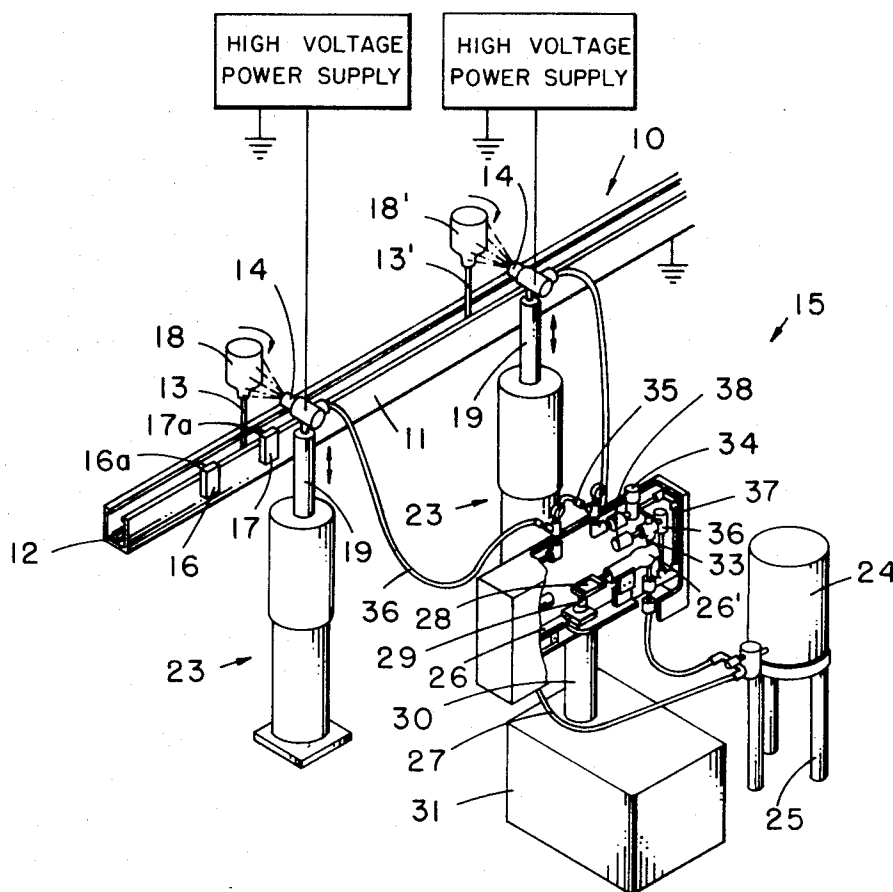
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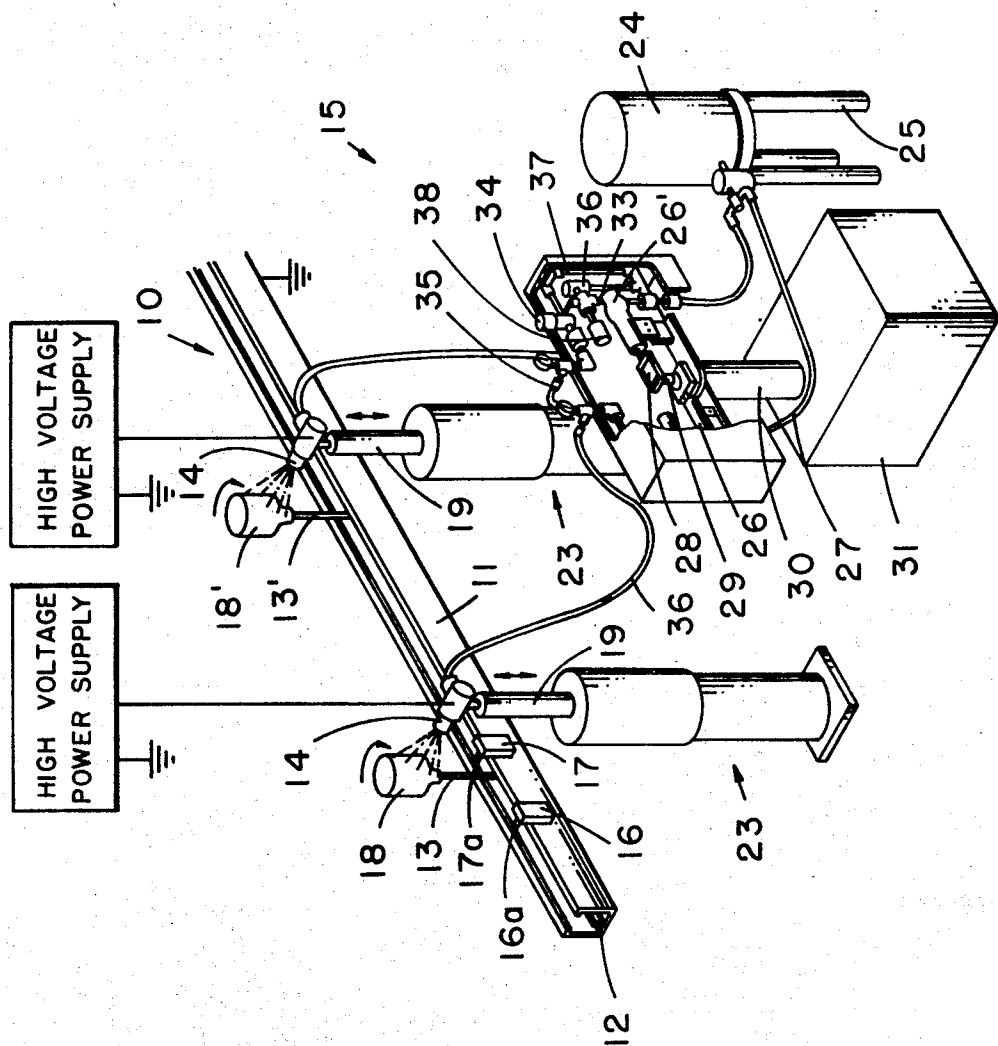
ABSTRACT

A method of depositing a metallic material onto a non-metallic substrate by depositing electrostatically charged particles of an admixture or solution including a thermally decomposable metal salt and a combustion retarding solvent to the non-metallic substrate. The non-metallic substrate is heated to an elevated temperature prior to the transference of the admixture to the substrate. The combustion retarding constituent of the admixture tends to partially decompose and vaporize at the elevated temperature of the non-metallic substrate and the metal salt tends to thermally decompose depositing a metallic material onto the non-metallic substrate. If the substrate is heated to a sufficiently high temperature, the metallic material tends to diffuse into a non-metallic substrate such as glass to thereby alter the color of the substrate.

The solution to be formed into electrostatically charged particles contains a metal salt and a combustion retarding solvent.

17 Claims, 1 Drawing Figure





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DEPOSITION MATERIALS AND METHOD

This application is a continuation of application Ser. No. 797,329, filed Jan. 13, 1969, now abandoned.

The present invention relates generally to a solution adapted to be formed into electrostatically charged particles and to a method of depositing electrostatically charged particles including a metallic material to a non-metallic substrate or body.

The deposition of a metallic material onto a non-metallic substrate such as glass, ceramic, glazed ceramic, silicon oxide and the like may be accomplished using any one of several different techniques. Generally, the method selected to deposit the metallic material onto the non-metallic substrate depends on a number of factors such as the desired uniformity of the metallic coating, the thickness of the metallic coating, the composition of the metallic coating, the availability of the required coating equipment and the composition of the material being coated. The foregoing suggests but a few of the several factors one should consider in selecting a technique to deposit a metallic material onto a non-metallic substrate.

Vacuum evaporation techniques may be used to coat non-metallic substrates or bodies with different metallic materials. Vacuum evaporation may be carried out in an evacuated glass bell jar using a tungsten filament heated to a very high temperature generally by passing an electric current through the filament. Usually, the metallic material to be evaporated and deposited onto the substrate is in contact with the filament thereby heating the metallic material to a temperature sufficient to cause the material to vaporize. The molecules of the evaporated metallic material tend to radiate in all directions from the source. The method works well for many metals and for some compounds. However, elaborate equipment is required to provide the necessary vacuum evaporation environment. In addition, the vacuum evaporation technique does not generally lend itself to automated processing techniques capable of economically mass producing metallic coated substrates. In addition some metals are combustible at elevated temperatures or are refractory or react with tungsten so quickly that electron bombardment is necessary to vaporize them properly for coating of substrates.

Deposition of metallic materials using cathode sputtering may be performed using equipment similar to that used for vacuum evaporation. Generally, a low vacuum is maintained by bleeding a gas, usually argon, into a bell jar while pumping on the bell jar with a high vacuum. A glow discharge may be established by applying a high voltage between the cathode element which serves as a source of metallic material to be deposited on a substrate and an anode element. The body to be coated, that is the substrate, may be positioned on the cathode or placed in the glow region. The argon ions produced by the glow discharge are accelerated toward the cathode and gain sufficient energy to displace atoms from the cathode. The atoms displaced from the cathode by the argon ions usually have sufficient velocity so as to adhere to the substrate when they impinge the substrate. The cathode sputtering technique is generally slower than the vacuum evaporation technique, that is, cathode sputtering requires minutes to hours to deposit a metallic film on a substrate whereas the vacuum evaporation technique requires seconds to minutes to deposit a metallic film of comparable thickness on the substrate. However, many of the same draw-

backs associated with the vacuum evaporation technique are also associated with the cathode sputtering technique, such as the necessity of using expensive equipment which does not lend itself to economical, automated techniques of fabricating metallic coated substrates.

Vapor-phase deposition of a metallic material onto a heated substrate at atmospheric pressure generally includes reducing or decomposing a volatile metal halide so that a coating of metallic material is provided on the heated substrate. The thermally decomposable metal halide is capable of being divided into its component atoms by dissociation or reduction at a temperature below the melting point temperature of the metallic material being deposited and below the melting point temperature of the substrate. In addition, the volatile material should be stable enough to reach the deposition surface before thermal decomposition takes place. Generally, a suitable gas such as hydrogen is passed over a liquid metal halide which is heated to a temperature necessary to provide the required partial pressure of the metal halide vapor. The gas mixture is passed over the heated substrate in a plating chamber where the metal halide is thermally decomposed to the free metal plus a halogen. The metal deposits on the substrate and the halide may be recovered by condensation techniques. The process has good flexibility and is generally more economical than the above-mentioned techniques, however, expensive equipment is required and the process may not provide uniform deposits unless high gas flow rates are utilized.

Electroplating is yet another process for coating substrate with a metallic material. Generally, an ionic compound such as a metal salt dissociates into cations and anions when dissolved in water. Upon the insertion of metal electrodes into an aqueous bath and connection of the electrodes to a voltage source, the ions transport an electric current through the electrolyte. Faraday's law applies to the process, that is, the weight of the metal deposited at the cathode or dissolved from the anode is proportional to the quantity of electricity passed through the bath and inversely proportional to the valence of the metal ion. However, the efficiency of the electroplating a substrate may be influenced by several factors such as the temperature and the viscosity of the bath, the current, the size and stability of the deposit on the cathode, agitation of the bath, the concentration of the constituents of the bath, the pH of the bath and the like.

Electroless deposition of a metallic coating onto a substrate is achieved without the use of an electric current by reducing the metal ion in solution to the free metal and depositing the free metal as a metallic coating onto the substrate. The process may be used to deposit metals on a plastic, ceramic and the like. Electroless plating involves the reduction of a metal ion by simultaneous oxidation of a chemical reducing agent. However, electroless plating results in very little, if any, diffusion of the metal into the substrate.

Another process used by industry for depositing a metallic material onto a non-metallic material is the silk screening process. All the areas of the screen except for the pattern to be deposited are blocked out on the screen. It is seen that this method is only applicable to depositing patterns onto the substrate. As with the electroless process, the metallic material exhibits very little, if any, diffusion into the substrate.

Therefore, it is the object of the present invention to provide a method for transferring a metallic material to a substrate which overcomes the problems enumerated hereinbefore.

Another object of the present invention is to provide a method for electrostatically transferring a metallic material to a substrate.

Yet another object of the present invention is to provide a process for electrostatically transferring to and diffusing a metallic material into a non-metallic substrate.

Still another object of the present invention is to provide a method for electrostatically transferring an admixture containing a metallic material to a heated, non-metallic substrate whereby the admixture thermally decomposes and/or volatilizes so as to deposit a metallic material onto the substrate thereby providing a substrate having an exterior surface including a diffused metallic material.

Another object of the present invention is to provide an electrostatic coating solution containing a metal salt and a combustion retarding solvent.

A further object of the present invention is to provide an electrostatic coating solution including about 2 grams of cobalt octoate, about 68 grams of toluene and about 30 grams of trichlorethylene.

Yet another object of the present invention is to provide an electrostatic coating solution including a thermally decomposable metal organo salt, a vaporizable organic solvent and at least a partially thermally decomposable and vaporizable flame retarding material.

Another object of the present invention is to provide a method for tinting and coating a non-metallic substrate of glass, ceramic, refractory oxide, semiconductive materials and the like with a metallic material.

A further object of the present invention is to provide a method for electrostatically transferring a metallic material to a substrate using an electrostatic depositing device.

Another object of the present invention is to provide a non-metallic substrate coated with a metallic material.

A further object of the present invention is to provide a method for electrostatically transferring a thermally decomposable metallic material to glass heated to about its softening temperature, the metallic material decomposing and diffusing into the glass to thereby tint the glass.

Further objects will become apparent upon further review of the specification. Other objects will appear in the following description, appended claims and appended drawings.

In the drawings:

The FIGURE is a perspective view of an electrostatic device which may be used to electrostatically transfer a metallic material to a non-metallic substrate.

Generally speaking, the present invention relates to an electrostatic coating solution including a metal salt and a flame retarding solvent and to the method for electrostatically transferring the solution to a non-metallic substrate heated to an elevated temperature. The metal salt decomposes to provide a metallic deposit which tends to diffuse into the substrate. If the substrate is glass, the diffusion of the metallic deposit into the glass tends to tint or color the glass. Continued deposition of the solution tends to deposit a layer of

metallic material on the surface of the substrate. The combustion retarding solvent tends to volatilize and partially decompose during the deposition process.

The metallic salt is an organo metallic salt which may be any of the Group II, Group III, Group IV, Group V, Group VI, Group VII and Group VIII metals or combinations thereof of the Periodic Table of the Elements. Of the several metals listed in the Periodic Table of Elements Co, Pb, Mn, Ce, Cr, Cu, Ag, Au, B, Al, Mo, Ni, Fe, Sn, Va, Zr, Ca, Zn, Ba, Ta, La, Nd, Nb, Cd or combinations thereof are preferred. Of the several preferred metals Co, Mn, Zn, Fe, Cr or combinations thereof are the most preferred. Of the most preferred metals, Co is preferred over the other metals.

The organic radical of the organo metallic salt may be an octoate; naphthenate; resinate; stearate; linoleate; borate; acetate; tallate; monocarboxylic acids having a C₉, C₁₀ and C₁₁ chain length and the like. Of the possible organic radicals of the metal organo salt, the octoate; naphthenate and monocarboxylic acids having a C₉, C₁₀ and C₁₁ chain length are preferred with octoate being the most preferred organic radical. Several examples of the metallic octoate salts would be cobalt octoate including up to about 6 weight percent cobalt metal and manganese octoate including up to about 6 weight percent manganese metal. Several examples of the metal organo naphthenates would be cobalt naphthenate including up to about 6 weight percent cobalt, lead naphthenate including up to about 30 weight percent lead, manganese naphthenate including up to about 6 weight percent manganese, copper naphthenate including up to about 8 weight percent copper, iron naphthenate up to about 6 weight percent iron, calcium naphthenate including up to about 5 weight percent calcium, and zinc naphthenate including up to about 8 weight percent zinc.

The organo metallic salt should be capable of decomposing in an air atmosphere at about atmospheric pressure so as to form a metallic material on the heated, non-metallic substrate. If the metallic salt is not capable of thermally decomposing, one may be able to remove the metallic salt from the substrate merely by subjecting it to friction or the like. The organo metallic salt should be capable of being divided into its component atoms by dissociation at a temperature below the softening temperature of non-metallic materials such as glass and the like and at a temperature below the melting point temperature of non-metallic materials such as refractory oxides and the like. In addition, it is desirable if the metal organo salt is sufficiently stable so as to come in close proximity to or to reach the deposition surface prior to decomposition thereof. The deposition of a metallic material onto the substrate at about atmospheric pressure provides a metallic material which tends to diffuse into a heated, non-metallic substrate such as glass whereby the glass is tinted or colored by the diffused metal. Continued deposition of the metallic material onto the non-metallic substrate tends to result in a coating of metallic material over the exterior surface of the non-metallic surface. It is seen that the metallic coating may be to any desired depth over the exterior surface of the substrate. For example, if metallization of a substrate of semiconductive material is desired so as to provide, for example, ohmic contacts therefor, the metallic material may be deposited on the surface of the semiconductive substrate to the desired angstrom thickness.

Other electronic devices including thin film capacitors, thin film resistors, metallization of integrated circuits fabricated from substrate materials such as silicon and the like may have the metallic films deposited thereon using the teachings of the instant invention. An example of a thin film capacitor which may be fabricated, in part, using the teachings of the instant invention is a silicon dioxide capacitor wherein a silicon substrate acts on one plate, a layer of silicon dioxide grown on the substrate acts as the dielectric and a film of aluminum metallization deposited using the teachings of the instant invention provides the other plate of the capacitor.

In order to provide good atomization characteristics, the organo metallic salt should be dissolved in an organic solvent. The combination of the organo metallic salt and the organic solvent may be atomized electrostatically or atomized using mechanical means such as hydraulic, air, combinations thereof and the like. A suitable organic solvent may be an alcohol, a polyol, an ester, a ketone, a glycol ether, an aromatic hydrocarbon, a terpene hydrocarbon combinations thereof and the like. A suitable alcohol solvent may be amyl alcohol, sec.-amyl alcohol, iso-butyl alcohol, n.-butyl alcohol, sec.-butyl alcohol, iso-decyl alcohol, n-decyl alcohol, cyclohexanol, ethanol, 2-ethyl butyl alcohol, n-hexanol, methyle alcohol, methyl amyl alcohol, 3-methoxy butyl alcohol, iso-octyl alcohol, n-octyl alcohol, iso-propyl alcohol, and n-propyl alcohol. A suitable polyol solvent may be ethylene glycol, diethylene glycol triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, 1-3 butylene glycol, hexylene glycol, and polyethylene glycol. A suitable ester solvent may be amyl acetate, iso-butyl acetate, n-butyl acetate, sec.-butyle acetate, diethylene glycol mono butyl ether acetate, ethylene glycol mono butyl ether acetate, diethylene glycol mono ethyl ether acetate, ethylene glycol mono ethyl ether acetate, ethyl acetate, 2-ethyl hexyl (octyl) acetate, hexylacetate, methyl acetate, methyl amyl acetate, ethylene glycol mono methyl ether acetate, iso-propyl acetate and n-propyl acetate. A suitable ketone solvent may be acetone, acetophenone, cyclohexanone, diacetone alcohol, diethyl ketone, di-isi-butyl ketone, dimethyl formamide, ethyl amyl ketone, ethyl butyl ketone, isophorone, mesityl oxide, methyl acetone, methyl ethyl ketone, methyl iso-amyl ketone, methyl iso-butyl ketone, methyl n-propyl ketone, ethyl ether, and isopropyl ether. A suitable glycol ether solvent may be ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol n-butyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol n-butyl ether, propylene glycol methyl ether, dipropylene glycol methyl ether, and tripropylene glycol methyl ether. A suitable aromatic hydrocarbon solvent may be benzene, toluene, and xylene. A suitable terpene hydrocarbon solvent may be turpentine gum, turpentine steam distilled, alpha pinene, Dipentene No. 122, Alpha Terpeneol, and Herco Pine Oil. Of the several organic solvents, the aromatic hydrocarbon solvents are preferred. Of the aromatic hydrocarbon solvents, toluene is most preferred solvent.

During electrostatic transference of an admixture of organo metallic salt and an organic solvent such as an admixture of cobalt octoate and toluene to a substrate, the particles of admixture tends to burst into flame. The addition of a flame retarding substance to the ad-

mixture of cobalt octoate and toluene appears to prevent combustion of the admixture when deposited onto the heated substrate using electrostatic techniques.

A suitable flame retarding substance may be halogenated solvents such as the chlorinated solvents. Suitable chlorinated solvents appear to be trichlorethylene; carbon tetrachloride; 1, 1, 1 trichlorethane; 1, 1, 2 trichlorethane; perchlorethylene; dichloroisopropyl ether; trichlorobenzene methylene chloride and the like. A prerequisite characteristic of the halogenated solvent is that it have no flash point. In addition, it appears that the halogenated solvent volatilizes and partially decomposes when exposed to an elevated temperature. The partial decomposition of the halogenated solvent appears to prevent air from combining with volatilized aromatic hydrocarbon thereby preventing the volatilized aromatic hydrocarbon from bursting into flame when using electrostatic techniques. The addition of up to about 30 grams of a halogenated solvent such as trichlorethylene to about 70 grams of a mixture of a metallic salt and an organic solvent appears to prevent the mixture from bursting into flames in an air atmosphere at about atmospheric pressure when electrostatically charged by about 70,000 volts and deposited onto a glass substrate heated to about 1,100°F.

The electrical resistivity of the coating solution appears to have an effect on the atomization characteristics of the solution. For example, electrostatic-hydrostatic devices generally include a means for electrically grounding the solution at the handle of the dispensing device. As the resistance of the solution decreases, the solution present between the handle of the dispensing device and the exit orifice of the device conducts more current. As a result, the charging voltage at the dispensing device electrode is reduced. The dispensing device electrode may be liquid, solid or combinations thereof. The resultant voltage reduction may become sufficiently large to affect the efficiency of the electrostatic device. Therefore, better performance may be obtained with electrostatic equipment using solutions having high electrical resistivity, that is, about 0.05 to about 1 megohm centimeters or higher.

The pH of the solution to be atomized, electrostatically charged and transferred to the heated substrate should be acidic, that is have a pH of less than about 7 on the pH scale. The acidity of the solution should be sufficient to maintain the constituents dissolved in the solution. It appears that if the solution becomes alkaline, that is the pH of the solution exceeds about 7 on the pH scale, the metallic constituent of the solution may precipitate. Precipitation of some or all of the constituents of the solution tends to render it unusable in the instant application.

The percent by weight of constituents of the coating solution may vary over a wide range dependent on factors such as the desired resistivity of the solution, the desired pH of the solution, the desired viscosity of the solution, the desired flowability of the solution, the desired amount of deposition of the solution per unit of time and the like. The resistivity and the pH of the solution are discussed above. Solutions of lower viscosity appear to require less atomizing force. Lower velocity appears to result in high transfer efficiency of the solution to the substrate to be coated and a corresponding decrease of solution sprayed beyond the substrate. The range of viscosity of the solution varies considerably for different solution constituents. Increased flowability of

the solution may be accomplished by replacing a solvent with one having a slower evaporation rate. In general, the degree of flowability which can be tolerated by the system is governed by the physical requirements of the application. The amount of deposition of solution per unit time varies according to the composition of the solution. For example, if one desires to tint glass, a solution of 2 grams of cobalt octoate, 68 grams of toluene and 30 grams of trichlorethylene is satisfactory. If one desires to render the glass non-transparent by the use of cobalt rather than to tint the glass with cobalt, the amount of cobalt octoate in the solution may be increased.

The non-metallic substrate on which the electrostatic coating solution is deposited may be a glass substrate, a ceramic substrate, a refractory oxide substrate, a semiconductive substrate and the like. Suitable glass substrates are soda-lime or lime glasses including about 20 weight percent sodium oxide, about 5 weight percent calcium oxide, about 70 to about 75 weight percent silica and small amounts of other compounds. Other suitable glass substrates are silicate glass, soda-lime-silica glass, borosilicate glass which contain up to about 5 weight percent boric oxide, aluminosilicate glass, soda-zinc glass, potash-lead glass, and 96 weight percent silica glass. Where the glass is to be used for decorative purposes, glass having a softening temperature occurring at lower temperatures such as the soda-lime, soda-lime-silica and potash-lead glasses are preferred. The metal deposited onto the glass tends to diffuse into the glass when the glass is heated at or near its softening temperature thereby tinting or coloring the glass. The diffusion of the metal into the glass appears to occur to a depth of several angstroms. The diffusion of cobalt metal into a soda-lime glass tends to tint or color the glass blue. The diffusion of other metals into glass tend to color or tint the glass various other colors. For example, zirconium tends to tint the glass blue, iron tends to tint the glass brown, zinc-whitish, chromium-green, copper-green and cerium-red. The borosilicate glasses appear to be more satisfactory for high temperature environments than the low softening temperature glasses.

Examples of suitable ceramic substrates onto which the metallic material may be deposited are steatite, zircon, and alumina. Of the several ceramic substrates suitable for deposition of the coating solution thereon, alumina is preferred.

Suitable refractory oxide substrates onto which the metallic material may be deposited are beryllia, calcia, magnesia, thoria, zirconia and the like. Of the several refractory oxide substrates suitable for use, alumina and beryllia are preferred with alumina being the most preferred substrate material.

Suitable semiconductor substrates onto which the metallic material may be deposited are germanium oxide, gallium oxide, and silicon oxide. Of the several semiconductive substrate materials suitable for use, silicon oxide is preferred.

An electrostatic field provides the mechanism by which the electrostatic coating solution may be charged and deposited onto the substrate and in some instances and explained hereinafter, the field may have an effect on atomization. The use of an elevated velocity air device which does not have associated therewith an electrostatic field to atomize the coating solution and to provide the means for transporting the atomized

solution to the heated substrate appears to result in poor deposition efficiency of the solution onto the heated substrate. Among other things, the heat radiated by the heated substrate appears to deflect the atomized particles of the solution. In addition, the high velocity air stream used to transport the atomized coating solution appears to cool the heated glass substrate so that diffusion of the metallic material into glass substrate appears to be reduced.

However, when an electrostatic device is used to charge and deposit the coating solution, the transfer efficiency of the solution to the glass substrate appears to increase. In addition, the heated glass substrate does not appear to be cooled to the point that the diffusion of the metallic material into the glass substrate is materially effected. It is seen that one advantage realized using an electrostatic depositing technique is that the electrostatic field developed thereby assists in improving the transfer efficiency of the solution to the substrate. Furthermore, the use of electrostatic deposition techniques permits the advantageous use of production line techniques to deposit metallic materials onto a heated substrate. For example, the use of a charging and depositing electrostatic field results in preventing substantial loss of the coating solution which may result as underspray, that is, deposition of atomized particles before the particles reach the substrate and which may result as overspray, that is, the passage of the atomized particles of the solution beyond the heated substrate into the background. As pointed out before, the heat radiated into the surrounding environment by the heated substrate appears to cause uncharged atomized particles of the coating solution to be deflected away from the substrate thereby resulting in poor transfer efficiency. Suitable charging of the spray particles by an electrostatic device and proper utilization of the electrostatic field between the electrostatic device and the substrate results in the deposition of the charged atomized particles of the coating solution which may otherwise be dissipated as either underspray or overspray or which may be deflected away from the substrate because of the heat radiation associated with the heated substrate. It is seen that the transfer efficiency of the coating solution to the heated substrate is improved by the use of electrostatic techniques.

Several factors including the characteristic or characteristics of the electrostatic field appear to have an effect on the transfer efficiency of the coating solution to the heated substrate. For example, the charge on an individual atomized particle of coating solution appears to be a function of surface area of the droplet. The smaller the diameter of the atomized particle the greater the charge-to-mass ratio on the particle. It appears, the smaller the atomized particle, the more control the electrostatic field between the electrostatic device and the substrate has over the path traversed by the particle between the electrostatic device and the heated substrate. An electrostatic field having an average potential gradient of 5,000 volts per inch or higher appears to provide a satisfactory result.

The atmosphere in which the solution is atomized may be an air atmosphere or an inert gas atmosphere such as helium, neon, argon and the like. The inert gas atmosphere appears to retard oxidization of the metallic material deposited onto the heated substrate. The metallic material may oxidize to a degree if the atmosphere surrounding the heated substrate contains oxy-

gen such as the air atmosphere. However, in the fabrication of electronic components such as thin film resistors it may be desirable to oxidize the film of metal such as tin in order to provide a resistive film of tin oxide. Therefore, deposition of metallic material such as tin in an air atmosphere may be advantageous where one is preparing a tin oxide thin film resistor.

An apparatus for electrostatically applying coating materials is illustrated in U.S. Pat. No. 2,893,894.

An electrostatic device of the type illustrated in U.S. Pat. No. 3,169,882 may be used in lieu of the electrostatic device illustrated in U.S. Pat. No. 2,893,894. The use of a high pressure air stream to assist in atomization of the solution appears to have a cooling effect on a substrate such as glass thereby effecting the diffusion of the metallic material into the glass. However, where the depth of diffusion of the metallic material into the glass is not a consideration, the electrostatic device illustrated in U.S. Pat. No. 3,169,882 may be satisfactory.

An electrostatic device of the type disclosed in U.S. Pat. No. 3,169,883 is another device which may be used for dispensing the charged, atomized particles of the solution to the heated substrate. The pressure used to deliver the coating solution to an exit orifice of the device may be about 300 psi or higher with about 800 psi or higher being preferred. A proposed embodiment of the electrostatic equipment used to transfer the solution to the substrate is illustrated in the FIGURE of the drawing appended to this specification.

Referring now to the drawing, a conveyor means 10 includes a substantially U-shaped track 11 within which an element 12, such as a conveyor chain and the like, may be displaced. The chain 12 may be displaced longitudinally by a suitable conveyor drive means (not shown). At appropriately spaced intervals, the chain may be provided with a plurality of substrate supports 13 and 13', which support and displace substrates 18 and 18' to be coated with metallic material. It is suggested that the substrates be electrically grounded during the deposition process. The conveyor illustrated is adapted to move the substrate at any desired speed such as at a speed of approximately 10 feet per minute through the coating zone provided by one or more spray heads 14 of electrostatic equipment 15. If desired, microswitches 16 and 17 may be adjustably mounted on and supported by the conveyor track 11 and are provided with movable switch actuating fingers 16a and 17a which are engaged by the substrate supports during passage of the substrates along the conveyor path. Contact of the substrate support 12 with an actuating finger 17a, for example, initiates atomization of the solution, and contact by substrate support 13 with the actuating finger 16a terminates atomization so that the solution is not atomized and sprayed into the background thereby wasting the solution.

The solution is illustrated in the drawing as being applied at one station. It should be seen that more than one station may be used to apply the solution to the substrate. The station includes the electrostatic equipment 15. The electrostatic equipment includes the spray head 14 carried by a vertically displaceable means 19 fabricated from a suitable, electrically insulative material such as polyethylene and the like. The means 19 is vertically displaced by reciprocator means 23 which may be hydraulically operated. The reciprocator means may reciprocate the spray head vertically

the desired number of times during the passage of the substrate thereby.

A reservoir means 24 such as a tank may contain the solution to be deposited on the substrate. The tank 24 may be carried by support legs 25, fabricated from any suitable, electrically insulative material such as polyethylene and the like.

The solution may be withdrawn from the supply tank by pump means 26 and 26' through conduit means 27 and 27' respectively. The pump means may be of the variable volume, positive displacement piston type. The piston of the pump means may be driven by a scotch-yoke drive means 28 through shaft 29 of suitable electrically insulative material. The shaft 29 may project downwardly through support sleeve 30 to drive means (not shown) housed in base 31. Preferably, the drive means is variable such as a variable speed drive mechanism driven by electric motor.

The high pressure outlet (not shown) of the pump means may be connected through conduit means 33 to a solenoid operated three-way valve 34 to an outlet fitting means 35. Connection may be made through a suitable, high pressure conduit means 36 to the spray head 14.

A pulse damper 38 may be connected to conduit means 33. The pulse damper may have a housing carrying a diaphragm exposed to the high pressure in the conduit means associated therewith. One of the functions of the pulse damper and in particular the diaphragm thereof is to smooth out the pulses of the positive displacement pump by displacing the diaphragm thereby insuring a substantially uniform, high pressure delivery of the solution to the spray head 14. A pressure relief valve 36 may be connected to the conduit means 33. The relief valve may include a return connection to the inlet side of the pump means which may be adjusted to open at some pressure slightly above the pressure being used in the system thereby preventing damage to the system in the event of a stoppage in the outlet.

The solenoid operated three-way valve 34 may communicate with the inlet side of pump 26'. The communication may be effected by conduit means 37. When the solenoid operated valve is in one position, the conduit means 33 communicates with conduit means 36 causing the coating solution to be transported to spray head 14. Actuation of the solenoid to another position by the microswitch 17 may cause communication between the conduit means 33 and the conduit means 37 with resultant recirculation of the solution through the pump which is actuated causing substantially instantaneous cessation of delivery of the solution from the spray head 14.

The electrostatic device contemplated for spraying of the solution may be of the type illustrated in U.S. Pat. No. 3,169,883. The particulars of several types of spray means which may be used to dispense the solution are illustrated in FIGS. 7, 8 and 9 of U.S. Pat. No. 3,169,883.

It should be apparent that the temperature of the substrate need be only high enough to cause decomposition of the metallic organo salt and vaporization of the solvent. If it is desired to assist diffusion of the metallic material into a substrate such as glass, it is suggested that the glass be heated to its softening temperature. Alternatively, after coating the glass with the desired metallic material, the glass may be heated to its softening

ing temperature to thereby cause diffusion of some or all of the metallic coat material thereinto. Generally, the softening temperature of the glass is several hundreds of degrees above the decomposition temperature of the organo metallic salt and the vaporization temperature of the solvent. Accordingly, the solution may be deposited onto a substrate heated at the decomposition temperature of the organo metallic salt so as to coat the substrate with a metallic material. Thereafter, the substrate may be heated to a temperature higher than the decomposition temperature of the organo metallic salt thereby causing some or all of the metallic material to diffuse into the substrate.

The following example is illustrative of the preparation of a soda-lime glass substrate tinted by the diffusion of a metallic material thereinto.

EXAMPLE

A substantially colorless soda-lime glass substrate (a bottle) is heated to a temperature in the range of about 1,100°F to about 1,300°F. The heated glass substrate is passed in close proximity to a spray head of an electrostatic device in an air atmosphere at atmospheric pressure. An electrostatic field is provided between the electrostatic device and the glass substrate. The heated glass substrate is at about ground potential and the electrostatic device is connected to a power source delivering about 70,000 volts DC (direct current) to the electrostatic device. The admixture includes about 2 grams of cobalt octoate containing about 6 weight percent cobalt metal, about 68 grams of toluene and about 30 grams of trichlorethylene. The admixture is atomized and the electrostatic field charges the individual admixture particles. The electrostatic field between the electrostatic device and the glass substrate insures that substantially all of the atomized admixture particles penetrate the heat radiated by the heated substrate to impinge the substrate. The admixture decomposes and/or vaporizes as discussed hereinbefore thereby depositing metallic cobalt onto the substrate. The substrate is heated to a temperature sufficient to cause diffusion of the metallic cobalt into the glass. The glass substrate appears to be tinted bluish by the interaction of the cobalt with the soda-lime glass.

The present invention is not intended to be limited to the disclosure herein, and changes and modifications may be made by those skilled in the art without departing from the spirit and the scope of the present invention. Such modifications and variations are considered to be within the purview and the scope of the present invention and the appended claims.

Having thus described my invention, I claim:

1. A method of depositing a metallic material upon a substrate of glass, refractory oxide, ceramic or semiconductor material comprising depositing electrostatically charged particles of an admixture including a vaporizable flame retarding halogenated solvent and a thermally decomposable organo metal salt dissolved in an organic solvent wherein the metal salt includes a metal of the Group II, Group III, Group IV, Group V, Group VI, Group VII or Group VIII metals or combinations thereof of the Periodic Table of Elements and an organo radical of an octoate, napthenate, resinate, stearate, linoleate, borate, acetate, tallate or monocarboxylic acid having a C₉, C₁₀, or C₁₁ chain length, and then using heat to vaporize the solvents and thermally

decompose the metal salt thereby depositing a metallic material upon the substrate.

2. The method of claim 1, wherein the metal of the metal salt is Co, Pb, Mn, Ce, Cr, Ag, Au, B, Mo, Ni, Fe, Sn, Cu, Va, Zr, Ca, Zn, Ba, Ta, La, Nd, Nb or Cd or combinations thereof.

3. The method of claim 2, wherein the substrate is glass, the thermally decomposable metal salt is cobalt octoate or manganese octoate and the halogenated solvent is trichlorethylene, carbon tetrachloride or perchlorethylene.

4. The method of claim 1, further including the step of diffusing at least a portion of the metallic material into the substrate by the application of heat.

5. The method of claim 3, wherein the cobalt octoate and the manganese octoate each contain up to about 6 weight percent of either cobalt or manganese.

6. The method of claim 1, wherein the organic solvent is an alcohol, polyol, ester, ketone, glycol ether, aromatic hydrocarbon or terpene hydrocarbon or combinations thereof.

7. The method of claim 1, wherein the substrate is glass heated to about its softening point temperature for a sufficient period of time whereby the metallic material diffuses into the glass to a depth of several Angstroms or more thereby tinting the glass.

8. The method of claim 7, wherein the substrate is a soda-lime, soda-lime-silica or potash-lead glass.

9. A substrate having metal deposited thereon in accordance with the method of claim 1.

10. A solution adapted to be formed into electrostatically charged particles for deposition upon a substrate of glass, refractory oxide, ceramic or semiconductor material, the solution containing a vaporizable flame retarding halogenated solvent and a thermally decomposable organo metal salt in an organic solvent wherein the metal salt dissolved includes a metal of the Group II, Group III, Group IV, Group V, Group VI, Group VII or Group VIII metals or combinations thereof of the Periodic Table of Elements and an organo radical of an octoate, napthenate, resinate, stearate, linoleate, borate, acetate, tallate, or monocarboxylic acid having a C₉, C₁₀ or C₁₁, chain length.

11. The solution of claim 10, wherein the metal salt includes up to about 30 weight percent metal of the total weight of the metal salt.

12. The solution of claim 11, containing up to about 2 weight percent of the metal salt, up to about 68 weight percent organic solvent, the remainder essentially the halogenated solvent.

13. The solution of claim 12, wherein the metal of the metal salt is Co, Pb, Mn, Ce, Cr, Cu, Ag, Au, B, Mo, Ni, Fe, Sn, Va, Zr, Ca, Zn, Ba, Ta, La, Nd, Nb or Cd or combinations thereof.

14. The coating solution of claim 12, wherein the metal salt includes a metal selected from the group consisting of Co, Mn, Zn, Fe or Cr or combinations thereof, wherein the organic solvent is an aromatic hydrocarbon, and wherein the halogenated solvent is trichlorethylene, carbon tetrachloride or perchlorethylene.

15. In the manufacture of tinted glass, the steps comprising passing glass through a particle deposition zone, the glass heated to at least its softening point temperature, supplying to said particle deposition zone electrostatically charged particles of an admixture including a chlorinated solvent and an organo metallic salt having

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an organo radical selected from the group consisting of an octoate or napthenate or monocarboxylic acid having a C₉, C₁₀ or C₁₁ chain length, the organo metallic salt dissolved in an aromatic hydrocarbon solvent, the admixture particles attracted to and substantially uniformly deposited upon the glass, decomposing the organo metallic salt thereby coating the glass with a metallic material and vaporizing the solvents, and the heat associated with the glass causing the metallic material to at least partially diffuse into the glass.

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16. In the manufacture of tinted glass as claimed in claim 15, wherein the metal of the metal octoate or napthenate or monocarboxylic acid having a C₉, C₁₀ or C₁₁ chain length is selected from the group consisting of Co, Pb, Cu, Ca, Ce, Zr, Zn, Mn, Fe or Cr or combinations thereof.

17. In the manufacture of tinted glass as claimed in claim 16, wherein the glass is a soda-lime, lime, soda-lime-silica or potash-lead glass.

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