

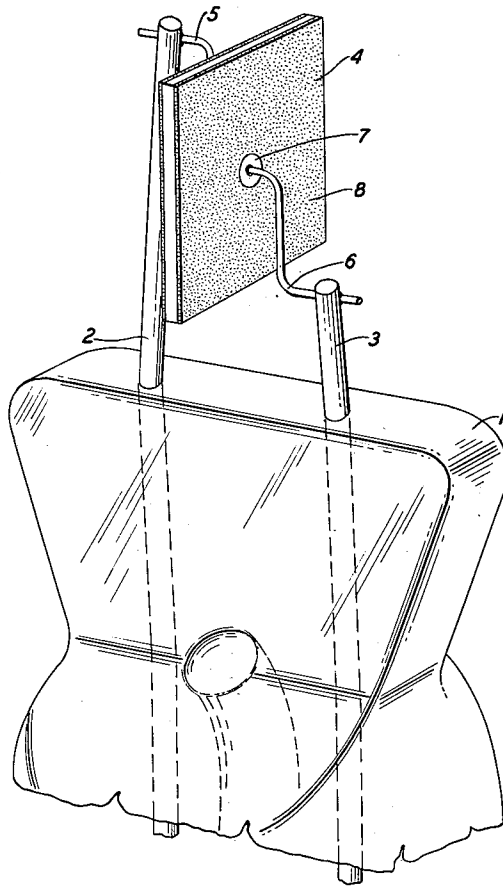
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METALLIZING COMPOSITION

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METALLIZING COMPOSITION

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This invention relates to metallizing compositions and more particularly to metallizing compositions comprising a finely divided metal-containing substance, an inorganic flux, and an organic vehicle, which metallizing compositions are useful for forming on quartz, ceramic material, glass or other materials metallic layers which are highly adherent and which if soldered to provide strong soldered joints.

Metallizing compounds comprising a finely divided easily reducible metal such as silver, a finely divided inorganic flux, and an organic vehicle have been used heretofore for forming on glass, ceramics and other base materials metallic layers, usually for decorative purposes. In general, such prior metallizing compounds are employed by spreading the metallizing composition in a layer on the base material which is to be metallized, and then heating the layer to a suitable temperature usually between about 500° C. and about 800° C. The heating is intended to volatilize the organic vehicle and to melt the flux and cause it to bind the finely divided metal particles together and to the underlying base material to form an adherent metallic layer.

It has been found, however, that the metallizing compositions of this type heretofore available do not produce layers having properties as good as are desired for many purposes. Often the metallic layers are characterized by roughness, cracking or crazing, blistering, non-uniformity of composition or poor adherence to the base material. Even more serious disadvantages often arise when the metallic layers are employed in soldered joints.

Thus, when it is attempted to fix a metal element to a base material such as a quartz piezoelectric crystal, ceramic material or glass by first applying and baking a layer of such metallizing composition to form a metallic layer and then soldering the metal element to such metallic layer, the connection between the metal element and the base material often is weak because the metallic layer does not adhere sufficiently well to the base material, or because the solder does not adhere well to the metallic layer, or for both reasons. Such disadvantages are particularly troublesome in connection with the soldering of metallic elements to quartz crystals, since it is important that a strong joint be provided between the quartz crystal and the metal element which may act as an electrical lead or as a supporting lead or both.

It has been found that poor adherence of the metallic layer to the base material or to solder

or to both may be caused by one or more of several factors.

The character of the metallic layer which is formed is greatly influenced by the nature of the organic vehicle employed. The vehicle should keep the particles of metal and flux suspended in uniform distribution; it should be of sufficient viscosity to make a metallizing composition of such consistency as to facilitate the formation of a layer by spreading, brushing or spraying; the vehicle moreover should be removed in the heating operation and after removal should leave an adherent metallic layer which for some uses should adhere well to solder. However, many metallizing compounds heretofore available include a vehicle which does not keep the metal and flux particles dispersed but permits the particles to agglomerate so that the resulting metallic layer is not homogeneous or smooth. This impairs adhesion to the underlying base material or to solder. It also appears that in the formation of a metallic layer from such a prior metallizing composition the organic vehicle decomposes during the heating operation and leaves behind in the metallic layer a residue of carbon which impairs adhesion to the underlying base material or to solder, or which, if it is burned out in the heating operation, leaves the metallic layer in a porous non-compact state. Moreover, in many cases when metallic layers are formed from the prior metallizing compounds, removal of the organic vehicle during the firing operation results, because of the nature of the vehicle, in blistering of the metallic layer and impairment of adhesion to the base material. In other cases the resulting metallic layer is cracked or crazed during the heating operation because the portion of the organic vehicle temporarily remaining after its more volatile portions have evaporated, has such a strong cohesive action that the metallic layer shrinks excessively relative to the base and cracks.

The inorganic flux should have a relatively low melting point so that when the layer of metallic composition is heated, the flux melts and binds the metal powder particles together and to the surface of the base material. The flux should be of such a character that it wets the metal particles and base material, and preferably fuses to the base material. The metallizing compositions heretofore available often do not embody fluxes having these properties, so that the adherence of the metallic layer to the base material and the strength of the layer are not as good as could be desired.

It appears that if the metallizing composition

is to form a metal layer which adheres well to the underlying material, which solders well, and which has good electrical conductivity the metallizing composition should comprise metal particles which are all of extremely small size; often the prior metallizing compositions do not have metallic particles of sufficiently small size.

The present invention provides a metallizing composition which overcomes these disadvantages and which forms smooth homogeneous metallic films which adhere well to quartz, ceramic material, glass and other materials, and which adhere well to solder. The metallizing composition of the present invention may be employed for various purposes including the formation on quartz, ceramic material, glass or other materials of adherent metallic layers which when soldered to provide strong soldered joints, or which are useful for decorative purposes. Metallizing compositions embodying the invention may be employed to particular advantage in the formation of soldered joints between quartz piezoelectric crystals and metal elements, and for the purpose of illustration will be primarily discussed hereinafter in that connection.

The drawing illustrates a quartz piezoelectric crystal having connected thereto metallic members which serve as electrical connections and supporting members, which are soldered to metallic layers adhering to the quartz and resulting from heating of a metallizing composition embodying the invention.

The present invention provides a metallizing composition comprising a finely divided noble metal-containing substance, a finely divided low melting glass, and an organic vehicle comprising a high molecular weight heat-depolymerizable organic polymer which preferably is a normally solid polymer, and an organic solvent for said polymer. Upon baking of a layer of the metallizing composition the solvent evaporates and the organic polymer depolymerizes sufficiently so that it evaporates without decomposing, and the low melting glass melts and wets and cements the metal particles together and to the base material which may be quartz.

The finely divided noble metal-containing substance employed in the metallizing composition may consist of particles of one or more noble metals as such or alloys thereof, or of one or more noble metal compounds which are easily reducible to the noble metal upon heating in air at temperatures of about 550° C. or less and which are insoluble in organic solvents, or of mixtures of particles of noble metals and particles of such compounds of noble metals. Examples of noble metals which may be employed as such or in the form of such compounds are silver, gold and platinum; of these silver is the most commonly used because of its greater availability and lower cost; the term "noble metal" as used herein and in the claims is intended to include alloys of noble metals. The oxides and carbonates are examples of compounds of noble metals which are easily reducible by heating in air at the indicated temperatures and which are insoluble in organic solvents; silver oxide and silver carbonate may be employed to particular advantage. Such a noble metal compound will be reduced to the metal during baking of the metallizing composition. Particular advantages in making possible the formation of strong metallic layers which adhere well to quartz and to solder are provided if the particles of noble metal or compound thereof employed

in the metallizing composition are of a particle size of 300 mesh or smaller.

The inorganic flux employed in the metallizing composition of this invention is a low melting flux in the sense that it melts at a temperature below about 500° C. While any one of various finely divided low melting glasses may be employed as a flux in a metallizing composition embodying the present invention, exceptional advantages are provided if the finely divided glass employed in the metallizing composition of the invention comprises by weight about 50 to 90 per cent PbO, from about 5 to 25 per cent of B₂O₃, and a minor proportion of at least one of the glass-forming constituents or modifications SiO₂, Bi₂O₃, PbF₂ and TiO₂. Advantageous proportions of these constituents are from about 1 to about 20 per cent of SiO₂, from about 5 to about 25 per cent Bi₂O₃, from about 1 to about 10 per cent of PbF₂, and from about 1 to about 5 per cent of TiO₂. The glass may be made by mixing together and firing the finely divided constituents in known manners and then grinding to a suitable particle size.

The smaller the average particle size of the glass, the more effective will be the bond between the metal particles themselves and between the metal particles and the base material which is coated with the metallic layer. The particles of glass, like the particles of noble metal or compound thereof, should be as small as possible for best results. When a layer of metallizing composition embodying the invention and comprising such a glass is baked at a suitable temperature, the glass melts at a relatively low temperature and readily wets the glass and the base material and firmly cements the metal particles together and to the base material. As a result there is formed a strong metallic layer having excellent adherence for the base material and for solder applied thereto. Such a glass has a melting point well below 573° C., the temperature at which a change in structure of quartz occurs, and therefore a metallizing compound embodying it may be advantageously used to form a metal layer on quartz crystals.

Examples of particularly useful glasses of the above type are the following, in which the proportions are by weight:

Glass A

PbO	82.5
B ₂ O ₃	11.4
SiO ₂	1.1
PbF ₂	5.0

Glass B

PbO	72.6
B ₂ O ₃	6.1
SiO ₂	16.3
PbF ₂	5.0

Glass C

PbO	87.5
B ₂ O ₃	11.4
SiO ₂	1.1

Glass D

PbO	55.0
B ₂ O ₃	17.0
PbF ₂	5.0
Bi ₂ O ₃	23.0

The relative proportions of the glass flux and the metal in metallizing composition is important. If too little glass is used the resulting metallic

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layer is soft and does not adhere well to the quartz. If too much glass is present the electrical conductivity of the resulting metallic layer is decreased and the solderability is diminished. The amount of flux which it is necessary to employ is somewhat dependent upon the noble metal employed and the size and shape of the particles thereof, and upon the size and shape of the particles of the flux. In general, most advantageous results are provided when the glass flux is finely ground and constitutes between about 3 and about 10 per cent of the weight of the noble metal present in the metallizing composition as such or in a noble metal compound.

The organic vehicle may comprise one or more heat depolymerizable binders and one or more solvents therefor; various heat depolymerizable organic polymers and various solvents therefor are suitable. The heat-depolymerizable organic polymers which may be employed in the metallizing compounds of the present invention are normally solid at room temperatures and are capable of being depolymerized upon moderate heating, i. e., at temperatures below about 500° C., into monomeric or low molecular weight compounds which at such temperatures are vapors. Examples of highly satisfactory heat depolymerizable organic polymers which may be employed are such vinyl or substituted vinyl polymers as polymethylmethacrylate, polybutylmethacrylate, polyisobutylmethacrylate, polyethylmethacrylate, which are polymers of alkyl esters of methacrylic acid, polyisobutylene, and other polymers such as the recently developed itaconic acid polymers may also be employed. Examples of suitable organic solvents for such a polymer which may be employed in a metallizing composition of the invention are "Cellosolve acetate" (ethylene glycol monoethyl ether acetate), "Carbitol acetate" (diethylene glycol monoethyl ether acetate), benzene and certain higher alcohols. Other solvents for such polymers which may be employed will be apparent to those skilled in the art.

The organic vehicle comprising such an organic polymer and solvent therefor provides numerous advantages in the metallizing composition of the invention. When the metallizing composition after application to the material to be metallized is properly heated, the solvent evaporates and the organic polymer depolymerizes to a monomeric or low molecular state in which it vaporizes readily; therefore, no part of the organic vehicle decomposes and leaves a carbonaceous solid residue in the resulting metallic layer. Moreover, when proper proportions of polymer and solvent are present in the metallizing composition, the composition produces upon baking an uncracked metallic layer. Under such circumstances during the heating operation the organic vehicle on removal leaves, or assists the deposition of, the particles of metal and glass in a compact layer which, on further heating, produces a metallic layer which is well bonded and substantially non-porous.

The proportion of the organic polymer employed in the metallizing composition is also relatively important. If too little of the organic polymer is employed the metallizing composition does not have sufficient consistency to permit good spreading, does not maintain the metal-containing substance and the glass well dispersed in the metallizing composition, and does not permit or assist the metal and glass particles to form a compact metallic layer. If too much of the polymer is employed the resulting metal layer

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may be spongy or cracked. In general, it is advantageous to employ the organic polymer in an amount constituting from about 2 to 25 per cent of the weight of the finely divided glass and the finely divided metal-containing substance in the metallizing composition.

Varying amounts of organic solvent may be employed. Enough solvent should be employed to disperse completely the organic polymer, but apart from this the amount employed will be largely dependent upon the consistency desired in the metallizing composition. The metallizing composition may range in consistency from a stiff paste to a paint-like liquid.

In forming a metallic layer on quartz, ceramic material, glass, or other base material by using a metallizing composition embodying the present invention, the metallizing compound is first formed into a layer on the surface or portion thereof to be metallized, as by spreading, painting or spraying. After drying or while still wet, said layer is then baked at a temperature and for a time sufficient completely to remove any solvent which may be present, depolymerize and completely remove the polymer by evaporation, reduce to metal any metal compound which may be in the metallizing composition, and melt the glass and cause it to wet the metal particles and base material and cement the metal particles together and to the base material. The temperature and time of heating may vary widely. Optimum conditions may be determined by a few experiments. In general, however, a heating temperature of between about 500° C. and about 850° C. may be employed, and a heating time of from about 5 to about 30 minutes at such temperature. The rate of heating should not be so great that the organic polymer decomposes before it can be completely removed by depolymerization or evaporation, or that blistering or porosity of the metallic layer result because of too rapid discharge of gases from the organic vehicle. However, in general the layer of the metallizing composition can be heated quite rapidly without causing these difficulties; indeed in most cases the layer can be placed directly in an oven heated to the maximum temperature with satisfactory results. While the heating may be caused to take place in an inert atmosphere, it appears that particularly advantageous results are provided if the heating occurs in an oxidizing atmosphere such as air. Apparently the presence of oxygen promotes the adhesion of the metallic layer to a base material such as quartz, ceramic material, or glass. In general, a strongly reducing atmosphere should be avoided in the heating since such an atmosphere may reduce compounds in the glass flux, such as lead compounds, and cause poor adherence.

The following are examples of advantageous metallizing compositions embodying the present invention:

Example 1.—The metallizing composition of this example contained the following ingredients:

46.0 grams of polished silver powder, all particles less than 325 mesh
4.0 grams of above Glass A, finely divided
12.5 cc. "Acryloid A-10"
22.0 cc. "Cellosolve acetate"

"Acryloid A-10" was the trade-mark of a solution of polymethyl-methacrylate in Cellosolve acetate in which the polymer was 30 per cent by weight of the solution; therefore the above

metallizing composition contained about 3.85 grams of the polymer. In preparing the composition the above ingredients were thoroughly mixed in a ball mill for between about 30 and about 40 hours. This was done to reduce further the particle size of the glass and noble metal and to mix thoroughly the ingredients and particularly the noble metal and glass particles. Numerous tests of the metallizing composition were made by forming a spot of the composition on a piece of quartz, firing in air at about 520° C. for about 30 minutes, then soldering a headed wire of phosphor bronze to the resulting metallic spot, and then pulling until rupturing occurred. It was found in most cases rupturing occurred when a chip broke out of the quartz rather than by breakage of the soldered joint or by separation of the silver layer and the quartz. This indicated that the resulting silver layer had exceptionally good adherence to the quartz and to the solder.

Example 2.—The metallizing composition of this example contained the following ingredients:

46.0 grams polished silver powder, all particles less than 325 mesh
4.0 grams of above Glass B, finely divided
12.5 cc. "Acryloid A-10"
23.0 "Cellosolve acetate"

This metallizing composition was prepared as described in Example 1, and also displaced excellent adherence to quartz and solder when tested as described in Example 1.

Example 3.—The metallizing composition in this example had the following formulation:

46.0 grams polished silver powder, all particles less than 325 mesh
4.0 grams of above Glass C, finely divided
12.5 cc. "Acryloid A-10"
23.0 cc. "Cellosolve acetate"

This silver metallizing composition was prepared in the same manner as that described in Example 1 and displayed excellent adherence to quartz and solubility when tested as described in Example 1.

Example 4.—The metallizing composition of this example had the following formulation:

46.0 grams polished silver powder, all particles less than 325 mesh
4.0 grams of above Glass D, finely divided
12.5 cc "Acryloid A-10"
23.0 cc. "Cellosolve acetate"

The metallizing composition was prepared as described in Example 1 and displayed excellent adherence to quartz and solderability when tested as described in Example 1.

The drawing shows an illustrated piezoelectric crystal structure embodying a metallic coating deposited from a metallizing composition embodying the present invention. The illustrated apparatus comprises a glass press 1 forming part of a container for the piezoelectric crystal, having extending therethrough rigid wires 2 and 3 connected to an electrical circuit not shown. Piezoelectric quartz crystal 4 is supported from and electrically connected to said wires 2 and 3 by means of non-linear wires 5 and 6 each of which is fixed at one end to the rigid wires 2 and 3 and at the other end to a surface of a crystal at its nodal point. Each of wires 5 and 6 is soldered at its crystal-connecting end to a silver spot 7 formed on the surface of a crystal by heating a spot of metallizing composition em-

bodying the invention. While any one of many metallizing compositions embodying the invention may be employed, that described in Example 1 is particularly advantageous. The illustrated crystal 4 also has each of its faces coated with a layer of silver 8 in contact with the silver spot 7 and formed by deposition of silver from silver vapor; layers 8 constitute electrodes.

While the metallizing compositions of the present invention have been described previously in connection with the formation of solderable metal layers on quartz crystals, they may be employed to advantage for forming metal coatings on other materials for soldering or decorative or other purposes. Various modifications may be made in the metallizing compositions described above as embodying the invention without departing from the spirit of the invention. For example, small additions of other substances may be included in the glass flux or in the metallizing composition as a whole.

It is intended that the patent shall cover, by suitable expression in the appended claims, whatever features of patentable novelty reside in the invention.

What is claimed is:

1. A metallizing composition essentially comprising by weight: 46 parts of finely divided silver; 4 parts of a glass flux consisting essentially of constituents which, expressed as PbO, B₂O₃, SiO₂ and PbF₂, are present in the proportions by weight of 82.5 per cent of PbO, 11.4 per cent of B₂O₃, 1.1 per cent of SiO₂, and 5.0 per cent of PbF₂; 3.85 parts of polymethylmethacrylate; and an organic solvent in which said polymethylmethacrylate is dissolved.

2. A metallizing composition essentially comprising by weight: 46 parts of finely divided silver; 4 parts of a glass flux consisting essentially of constituents which, expressed as PbO, B₂O₃, SiO₂ and PbF₂, are present in the proportions by weight of 72.6 per cent of PbO, 6.1 per cent of B₂O₃, 16.3 per cent of SiO₂, and 5.0 parts of PbF₂; 3.85 parts of polymethylmethacrylate; and an organic solvent in which said polymethylmethacrylate is dissolved.

3. A metallizing composition essentially comprising by weight: 46 parts of finely divided silver; 4 parts of a glass flux the constitution of which, in terms of oxides, is by weight 87.5 per cent of PbO, 11.4 per cent of B₂O₃, and 1.1 per cent of SiO₂; 3.85 parts of polymethylmethacrylate; and an organic solvent in which said polymethylmethacrylate is dissolved.

4. In combination, a quartz piezoelectric crystal; a metallic silver layer firmly adhering thereto and comprising finely divided silver and a fused glass flux essentially comprising by weight 82.5 per cent of PbO, 11.4 per cent of B₂O₃, 1.1 per cent of SiO₂, and 5.0 per cent of PbF₂; and a metal element fixed by solder to said metallic silver layer.

5. In combination, a quartz piezoelectric crystal; a metallic silver layer firmly adhering thereto and comprising finely divided silver and a fused glass flux essentially comprising by weight 72.6 per cent of PbO, 6.1 per cent of B₂O₃, 16.3 per cent of SiO₂, and 5.0 per cent of PbF₂; and a metal element fixed by solder to said metallic silver layer.

6. In combination, a quartz piezoelectric crystal, a metallic silver layer firmly adhering thereto and comprising finely divided silver and a fused glass flux essentially comprising by weight 87.5 per cent of PbO, 11.4 per cent of B₂O₃, and 1.1

per cent of SiO_2 ; and a metal element fixed by solder to said metallic silver layer.

7. The method of fastening electric leads to a quartz crystal comprising forming on the surface of said crystal a layer containing a finely divided metal and a finely divided glass flux and heating said layer to a temperature above the melting point of said glass flux for a time sufficient to fuse said flux and cause it to bind the metal particles together and to the surface of said body and soldering said electric leads to the resulting metallized surface, said glass flux comprising by weight about 50 to 90 per cent of PbO , about 5 to about 25 per cent of B_2O_3 , and the indicated proportion of a substance chosen from the group consisting of about 1 to about 20 per cent of SiO_2 , from about 5 to about 25 per cent of Bi_2O_3 , from about 1 to about 10 per cent of PbF_2 , and from about 1 to about 5 per cent of TiO_2 .

8. The method of fastening electric leads to a quartz crystal comprising forming on the surface of said crystal an adherent metal-containing layer by applying to said surface a layer of a metallizing composition comprising an organic solvent solution of an organic polymer which is heat-depolymerizable without decomposition mixed with a finely divided metal and a finely divided glass flux, and heating said applied layer of metallizing composition to a temperature and for a time sufficient to depolymerize and volatilize said organic polymer and to melt said glass flux and cause it to bind the particles of said finely divided metal together and to said surface, and soldering said electric leads to the resulting metallized surface, said glass flux comprising by weight about 50 per cent to about 90 per cent PbO , about 5 per cent to about 25 per cent of B_2O_3 , and the indicated proportion of a substance chosen from the group consisting of about 1 to about 20 per

cent of SiO_2 , from about 5 to about 25 per cent of Bi_2O_3 , from about 1 to about 10 per cent of PbF_2 , and from about 1 to about 5 per cent of TiO_2 .

9. A metallizing composition comprising a finely divided noble metal-containing substance, a finely divided glass which melts below about 500°C . present in an amount constituting about 3 to about 10 per cent of the weight of the metal in said metal-containing substance, an organic polymer which is heat-depolymerizable without decomposition present in an amount constituting about 2 to about 25 per cent of the weight of said noble metal-containing substance and said glass, said organic polymer being an alkyl ester of methacrylic acid, and an organic solvent for said polymer in which said polymer is dissolved.

10. A metallizing composition as described in claim 9 wherein the organic polymer is polymethylmethacrylate.

11. A metallizing composition as described in claim 9 wherein the finely divided noble metal-containing substance is finely divided silver, and wherein the organic polymer is polymethylmethacrylate.

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