Platinum and Palladium Metallising Preparations

COMPOSITIONS AND USES IN THE ELECTRICAL AND ELECTRONIC INDUSTRIES

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Liquid preparations containing platinum and palladium are used in the electrical and electronic industries for the deposition of metal films on heat-resisting non-metallic substrates, such as ceramics of various types, mica and glass. They are available in various viscosities and metal concentrations for application by hand-painting, spraying and screen printing. After application the coatings are dried, and fired in an oxidising atmosphere at temperatures in the range of 550 to 1350°C to burn away the organic constituents and deposit an adherent metal film on the substrate. In the case of films containing a large proportion of palladium, precautions may have to be taken to avoid oxidation of the metal while it is cooling from temperatures above 850°C, either by preventing free access to air or by cooling in an atmosphere of nitrogen.

Types of Preparation

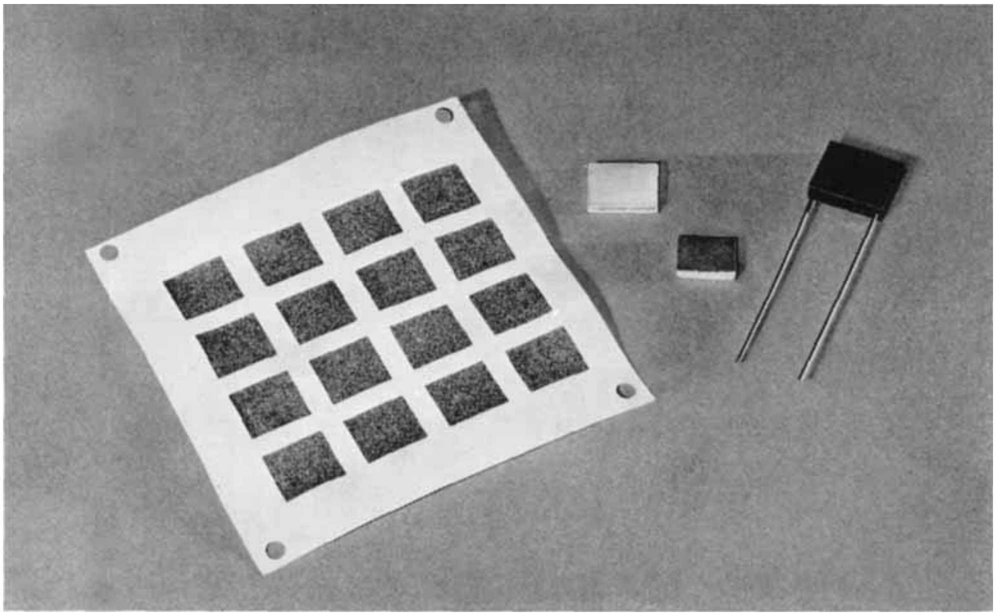
There are two main types of preparation, solutions of organic compounds of the metals, and suspensions of the metal powders or insoluble compounds of the metals. Platinum and palladium can be used alone, or together, or in combination with gold and silver.

The solutions, which usually contain between 5 and 15 per cent of metal, are produced by dissolving the metal sulpho-resinates in a solvent mixture having a controlled rate of evaporation to suit the method by which the preparation is to be applied. Instead of the sulpho-resinates, terpene mercaptides (1) and tertiary mercaptides (2) may be used. Small amounts of organic compounds of rhodium, bismuth and chromium may be included to promote the continuity and adhesion of the fired film. The preparations may also contain natural or synthetic resins to impart a suitable viscosity for application and to give sufficient strength to the coating to allow it to be handled after drying and prior to firing.

The suspensions are produced by dispersing platinum or palladium powders, or in some cases insoluble compounds of these metals, in an organic vehicle consisting of a solution of resins or cellulose compounds in a mixture of solvents. The vehicle must have rheological properties and a rate of evaporation to suit the method by which the preparation is to be applied to the substrate. In addition, the vehicle must be stable so that it is not affected by some of the finer particle size metal powders which can cause a rapid increase in viscosity and gelation of the preparation in storage. As with the solutions, suspension preparations usually contain adhesion promoters, which in this case may be fusible metal oxides or low melting glasses.

Properties of the Films

The solution preparations give extremely thin films, those produced from one normal coating ranging between 0.05 and 0.3 microns in thickness, depending on the metal content of the solution and the method used for applying the coating. Thicker films can be pro-



United Insulator, the Ceramic Division of the Telegraph Condenser Company, uses a palladium metallising preparation in the manufacture of a certain type of high stability ceramic capacitor. The capacitor is a fired stack of ceramic plates integrally bonded with palladium which also acts as the electrode. A "green" ceramic sheet is screen-printed with a pattern of palladium electrodes; the sheet is then cut up into individual plates that are stacked for firing. The "green" stack is lightly clamped and fired at a temperature in excess of 1300°C giving a bonded capacitor block; lead wires are soldered to the block and the capacitor is then encapsulated in a moulded plastic case. Using a palladium metallising preparation in this way, the ceramic capacitor plates can be fired, metallised and bonded in a single firing operation

duced by multiple coating and firing, but not by one thick application because this would crack and flake when fired. When applied to smooth substrates such as glass and glazed ceramics the films are specular, and those towards the upper thickness limit of the range are electrically conducting. When correctly applied and fired the films are firmly adherent, and taking into account their extreme thinness will withstand a surprising amount of abrasion. They can be soft soldered by immersion techniques, but contact with the solder should be very brief and the bath should not be too hot or the very thin film will be stripped from the substrate by dissolution of the metal in the solder.

The suspension preparations normally give films from ten to twenty times as thick as those from solutions, depending on metal content and method of application, and with some preparations there is virtually no limit to the thickness of film that can be built up with multiple application and firing. The films are mat in appearance, but can be burnished to a metallic lustre by abrasion. The properties of the films are largely governed by the type of platinum or palladium powder used in the preparation. Powders with relatively large irregularly-shaped particles such as sponges produced by chemical or electrolytic reduction of aqueous solutions of the metal salts usually give porous films with an open texture, whereas powders with fine particles of leaf or flake structure similar to those used in aluminium paints, and produced by comminution of the metals, give smoother and denser films.

The films are electrically conducting, and those derived from leaf or flake powders are generally lower in resistivity than those from precipitated powders. All the films are, however, higher in resistivity than platinum or palladium foils of corresponding thickness. The metal oxides or low melting glass included in the preparation to promote adhesion of the film tend to raise its resistivity. When the substrate can withstand a very high firing temperature, for example, in the case of porcelain and some special ceramics, adequate adhesion can often be obtained with little or no oxide or glass addition, and the films have lower resistivities. Suspension preparations give films that can be more easily soft-soldered than the much thinner films derived from solutions. The films can be built up by electroplating.

Applications of Solution Preparations

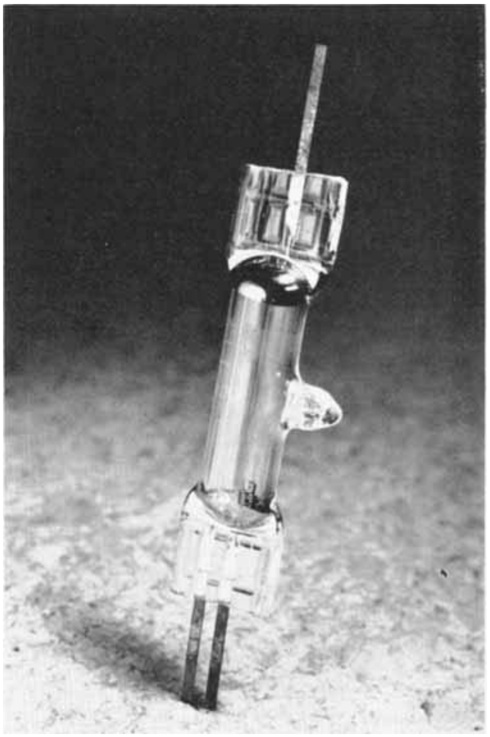
Solution preparations have been used in the production of electrical resistors on a variety of glass, mica and ceramic substrates. Preparations containing mixtures of metals giving alloy films are generally used because these often give higher resistivities and lower temperature coefficients of resistance than single metals. In one type of resistor the film consists of a mixture of palladium and gold derived from a preparation containing the metal sulpho-resinates (3). Metal oxide films have negative temperature coefficients, and in this resistor the oxide formed when the film is fired is utilised to counterbalance the comparatively high positive coefficient of the gold. Resistors with very high values can be produced with films derived from mixtures of bismuth resinate and palladium sulpho-resinate (4), but in these the bismuth and much of the palladium are present as oxides and the resistors have high negative temperature coefficients. Introduction of other noble metals into the bismuth-palladium preparation gives films of lower resistivity that have been used to provide current leakage paths on glass and porcelain insulators. Close control of firing temperature and atmosphere is necessary with thin films containing a large proportion of palladium to ensure a constant ratio of metal to oxide and to prevent a wide variation in resistivity.

Very stable resistors have been produced with a sulpho-resinate preparation giving a film consisting of 80 per cent gold and 20 per cent platinum, which has the highest resistivity and lowest temperature coefficient of any gold and platinum mixture. This film has been fired on flat glass and attenuated by photo-etching to give a variety of resistance values (5). It has also been fired on to glass fibres, which have been wound on to cylindrical formers to give high value resistors (6).

In a recently published paper by E. E. Wright and W. W. Weick of Bell Telephone Laboratories, U.S.A. (7), a method for depositing stable noble metal resistors in microcircuits is described in detail. Specially prepared platinum and palladium-gold sulpho-resinate solutions are applied to glass or ceramic substrates by dipping, the coatings are dried, and fired at 325°C to burn away the organic constituents and reduce the sulpho-resinate to metal, and then at 660°C to bond the metal to the substrate. The resistor configuration is obtained by photo-etching using an aqueous solution of nitric and hydrofluoric acids, and conductors and land areas are subsequently applied by screen printing and firing a paste containing gold and glass frit. Resistivities of 30 to 100 and 10 to 30 ohms per square respectively are obtained from platinum and palladium-gold alloy films. Resistivity values and electrical stability can be controlled to some extent by the firing cycle, the rate of decomposition of the sulpho-resinates determining the initial grain size, and the maturing temperature the recrystallisation of the film. Microcircuits for five-bit computer adders consisting of 57 resistors per substrate were produced by this method with a resistivity of 50 ohms per square (500 and 1200 ohms after attenuation) and a tolerance of $\pm$ 8 per cent from the nominal.

Solutions containing platinum and gold sulpho-resinates have been used in bonding glass and ceramics to each other and to metal. In this application the preparation is fired on the glass or ceramic surface, the metal film is tinned by immersion in a bath of soft solder, and soldering to the other component is done at as low a temperature and as quickly as possible to avoid stripping the metallised surface. This type of preparation has also been used to provide conducting paths in capacitors, and in printed circuits on glass and ceramic substrates where corrosive conditions and high operating temperatures preclude the use of silver. It has also been used in the production of conducting networks of very fine lines on flat glass by two methods, screen printing the design direct on to glass, and photo-etching the design through a resist applied to the pre-fired metal film.

Solutions containing platinum, palladium and gold sulpho-resinates have been used in the production of neutral density glass filters and heat-reflecting mirrors. Thin films of gold are green by transmitted light, but can be converted to neutral grey by the addition of platinum or palladium. These films when applied more thickly are opaque, and give mirrors that are highly reflecting in the infra-red region of the spectrum. These are of particular use in equipment when high operating temperatures prevent the use of silver mirrors. One such application is to reduce infra-red radiation in mercury vapour lamps (8) where gold-platinum mirrors are used to reflect part of the infra-red output of the arc back into the lamp. The quartz arc tube of a 125-watt type MBU mercury vapour lamp by Osram (G.E.C.) Limited containing mirrors is shown in the illustration. Preparations containing platinum and palladium have been used in producing attenuators for high frequency current and fuses for protecting electrical equipment.



The quartz arc tube of a 125 watt type MBU mercury vapour lamp by Osram (G.E.C.) Limited. The reflecting surfaces at each end of the tube are thin films of gold-platinum alloy serving as infra-red reflectors and so eliminating local cold spots in the region of the electrodes

Applications of Suspension Preparations

Suspension type preparations giving relatively thick films are used in the production of high stability ceramic capacitors where a high capacity is required in a small component. Stages in the production of a capacitor of this type produced by United Insulator, the Ceramic Division of the United Condenser Co, using a palladium metallising preparation are shown in the illustration on page 3. Thin leaves of "green" (unfired) ceramic are screen printed with a pattern of palladium electrodes. The leaves are then cut into individual sheets each carrying one electrode which are arranged into stacks for firing. The stacks are lightly clamped and fired at above 1300°C giving bonded capacitor blocks. Lead wires are soldered to the blocks and the capacitor plates bonded in a single firing operation. The silver preparations used for single-plate ceramic capacitors cannot be used in this technique because they will not withstand the high temperature needed to fire the "green" ceramic.

Preparations comprising mixtures of very fine palladium and silver powders with a large proportion of lead or bismuth borosilicate frit in an organic vehicle are used in the production of resistors that are particularly suitable for printed and micro circuits (9). The preparations are applied by screen printing to flat glass and ceramic substrates, and by dipping, or banding machine to rods and other shapes, and fired at 650 to 800°C to produce resistors with values ranging from 1 ohm to 20 megohms, depending on the proportion of palladium, silver and frit in the preparation, and the attenuation of the current path in the resistor design. Good reproducibility of values is claimed by close control of the particle size of the paste constituents and processing conditions. The resistors are claimed to have low temperature coefficients and low current noise; the latter is attributed to sintering of the metal particles when the preparation is fired, resulting from the high alloying tendency of the palladium and silver powders, thus minimising contact resistance between the particles.

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The Release of Hydrogen Atoms from the Surface of a Platinum Catalyst

GASEOUS OR SUPERFICIAL MIGRATION?

The reduction of yellow tungsten oxide, WO_3, to the blue W_4O_{11} is effected at room temperature by hydrogen atoms but not by hydrogen molecules and so this reaction can be used as a means, both qualitative and quantitative (1), for the detection of hydrogen atoms. Khoobiar, of Esso Research and Engineering Company, has recently shown (2) that when molecular hydrogen is passed at 50°C over a mechanical mixture of platinum on γ-alumina reforming catalyst and WO_3, a blue coloration appears immediately. This indicates that hydrogen atoms have been formed on the platinum surface and that they have migrated over the alumina support (possibly as protons) before reaching the WO_3 which is then reduced. A mixture of WO_3 and γ-alumina had to be heated to 200° before any sign of reduction appeared.

Kohn and Boudart, working at the University of California, have reported some further related experiments (3). They observed that on mixing reduced platinum-alumina catalyst with WO_3 in hydrogen no visible reaction occurred at room temperature, but on admission of oxygen the gradual appearance of the blue coloration was noted. They concluded that the migration of hydrogen atoms occurs through the gas phase, hydrogen atoms being released from the platinum surface by the reaction

$$O_{ads} + H_2 \rightarrow OH_{ads} + H.$$

This interesting system deserves further attention, especially since it could provide a ready means of assessing the state of dispersion of platinum on its support. G. C. B.

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