

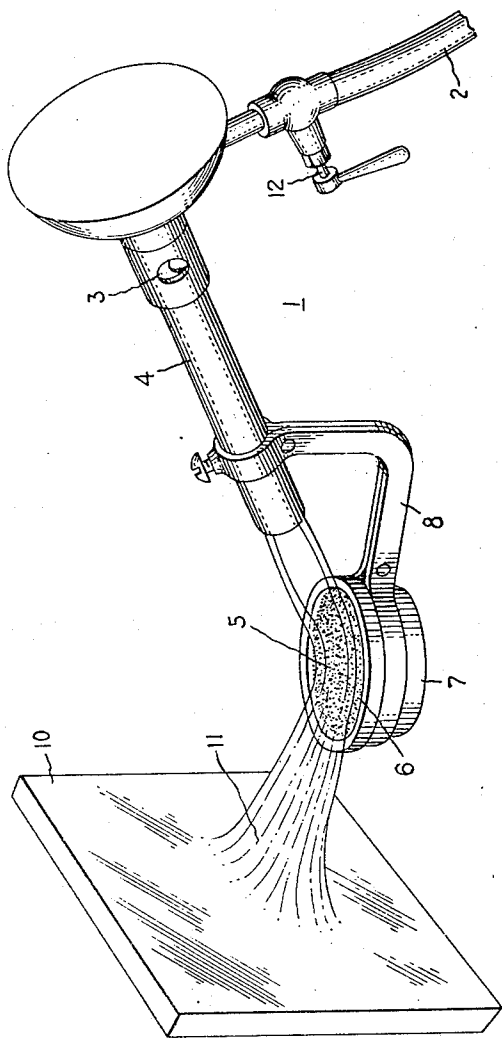
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METHOD OF FORMING GERMANIUM FILMS

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## UNITED STATES PATENT OFFICE

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## METHOD OF FORMING GERMANIUM FILMS

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The present invention relates to a method of forming germanium films. It is concerned more particularly with a method of forming a film or coating of germanium on a solid surface.

One object of the invention is to provide an effective and inexpensive method of applying a film or coating of germanium to a solid surface.

Another object of the invention is to provide a method of coating a surface with a film or layer of germanium using a germanium oxide as the source of the coating material.

Various processes other than electrolytic methods have been proposed and used for forming films or coating of metals on surfaces. Such prior processes have included the vaporization of the coating metal and the condensation of the metal vapor on the surface to be coated. In another process finely divided metallic particles or mixtures of finely divided metal and oxides or other non-metallic substances are projected in a gas stream against the surface to be coated with such high velocity that the force and heat of impact are sufficient to flatten and weld the particles into a smooth, homogeneous coating. In still another procedure a projecting stream of reducing gas is ignited to heat the particles they impinge on the surface to be coated.

The present process of forming germanium films or coatings differs essentially from those known heretofore in that the sole source of the coating material is an oxide of the metal, specifically a germanium oxide and in the fact that a gas stream of relatively low velocity is used both to reduce the oxide and to convey the resultant metal vapor to the relatively cool surface to be coated where the metallic vapor is precipitated as a film or coating.

Briefly, the present process comprises bringing a low velocity high temperature stream or flame of burning reducing gas into contact with a germanium oxide, such as germanium dioxide,  $\text{GeO}_2$ , and then directing the tip of the flame onto or immediately adjacent the surface to be coated. The temperature of the gas stream contacting the germanium dioxide should approach closely its melting point, and at least a portion thereof should further have such reducing character as to convert the oxide to metal before it is swept onward in the vapor state by the burning gas stream to the surface on which it is deposited. The common Bunsen burner affords a burning gas stream or flame very well adapted to use in the present invention. When ordinary illuminating gas is burned in such a

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burner with no primary air introduced into the gas stream between the gas inlet and the flame, the latter is wholly luminous. However, as primary air is introduced, three cones appear; a short inner non-luminous cone just above the jet consisting of unignited gases and air; a second cone which is nearly invisible and comprising hot partial combustion products of the gas and primary air mixture, and an outer cone comprising finally ignited burning gases which cone surrounds the reducing cone. The gases within the reducing cone consists largely of carbon monoxide and hydrogen and have the proper temperature and reducing character required in the process, and the outer cone affords a gas stream to assist in vaporizing the reduced metal and sweep it on to the surface to be treated.

One embodiment of the present invention will be specifically described with reference to the accompanying drawing in which the figure shows a simple and inexpensive, yet efficient apparatus for applying a film or layer of germanium to a solid surface. The apparatus shown in the drawing comprises Bunsen burner 1, to which illuminating gas is supplied from conduit 2 thru a valve operated by valve stem 12, this gas being mixed with primary air entering the gas stream thru adjustable ports 3, the ports and valve being so adjusted that there will result a low velocity gas flame with a substantial reducing cone 5. In the practice of the present process the reducing portion 5 of the gas flame is brought directly into contact with a mass of germanium dioxide 6 which is preferably in finely divided form. For convenience the germanium oxide is shown as being contained in a shallow quartz boat or container 7 which is supported by a cradle 8 adjustably secured to the tube 4 of the Bunsen burner whereby the quartz boat and its contents are held in the proper position adjacent the tip of the burner.

Employing such an assembly of the Bunsen burner and the germanium oxide container, the surface of a solid such as the glass plate 10 shown in the drawing can be conveniently coated with a thin film of germanium by bringing the tip 11 of the flame into contact with or immediately adjacent the solid surface and moving the flame back and forth over the surface with about the same movement as if a metal spray gun were being used.

Coatings of any desired thickness can be obtained in accordance with the present process provided the surface to be coated is maintained at a temperature low enough to effect

thermal precipitation of the germanium thereon.

A typical coating applied to a glass surface in accordance with the present method appears to the eye as a smooth continuous silvery deposit when the coating is thick enough to be opaque to transmitted light. Successively thinner coatings show blue, red, light pink and light silver sheens when viewed as reflectors. Coatings prepared in accordance with the present invention have been analyzed by electron diffraction methods and found to consist essentially of pure germanium with a primary crystal size less than about 2,000 Angstrom units.

It is believed that the mechanism whereby a germanium coating is obtained in accordance with the process described herein comprises the heating of the oxide to a temperature close to its melting point, whereby it is reduced to metallic germanium which is vaporized and carried away by the low velocity gas stream and deposited on the surface of the solid to be coated by thermal precipitation. It has been found that the rate of deposition of the coating metal and hence the thickness of the coating obtained in a given unit of time depends upon the relative thermal conductivity of the surface being coated. For example, when the surface to be coated is mounted in thermal contact with a block of copper or other metal having a high degree of heat conductivity, it is possible to obtain a thicker coating of germanium than when the block is not used.

From the above description it will be apparent that the present invention provides a method for applying a coating or film of germanium on the surface of any solid body which does not readily burn or become otherwise damaged at the temperatures employed. It will also be apparent that the body need not have a melting point above that of the gas stream employed in the process provided the gas stream is so manipulated that the body is at all times maintained below its melting or decomposition temperature. The process has been found to be particularly effective in the application of reflecting films of germanium on vitreous surfaces, specifically glass surfaces. It can however also be employed in coating of metal and the like, the effectiveness of the process depending on the thermal properties of the surface being coated. Surfaces of most organic materials such as wood, resins and the like are more difficult to coat due both to the rela-

tively low thermal conductivities of such material and the fact that the low velocity gas stream can be kept in contact with a given portion of such surfaces for only a relatively short period of time before combustion, decomposition or melting of the surface takes place.

Films of germanium prepared in accordance with the present invention can be employed for various purposes, for example, germanium films on glass or other insulating base can be employed as resistance elements. The resistance per square area for the germanium films varying from about 0.01 megohms for an opaque film to 1,000 megohms for a film having a silvery color by reflected light, and a very light pink color by transmitted light.

While the invention has been specifically described with reference to germanium dioxide,  $\text{GeO}_2$ , the lower oxide of germanium, namely  $\text{GeO}$ , can also be employed, there being no difference in the apparatus or in the method except that a more rapid reduction to germanium metal would be obtained.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of forming a coating of germanium on a solid surface which comprises bringing the reducing portion of a low velocity gas flame into contact with a mass of germanium oxide and bringing the tip of said flame into contact with the surface to be coated.

2. The method of obtaining a germanium coating on a solid surface which comprises passing a low velocity gas flame over a mass of germanium oxide with the reducing portion of said flame in direct contact with said mass and the flame tip in contact with the surface to be coated.

3. The method of claim 1 wherein the surface to be coated is a vitreous surface.

4. The method of claim 1 wherein the surface to be coated is a glass surface.

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