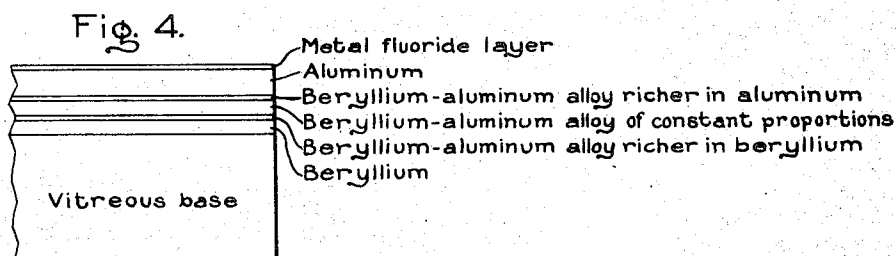
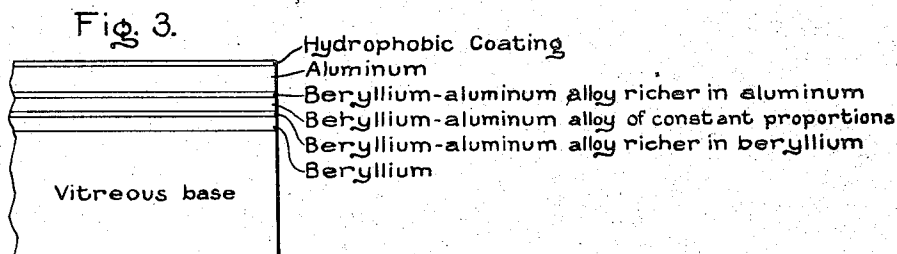
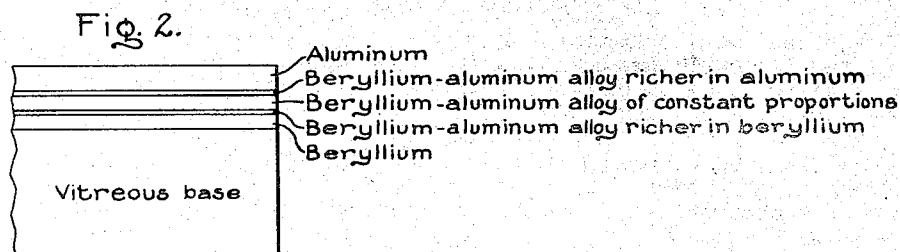
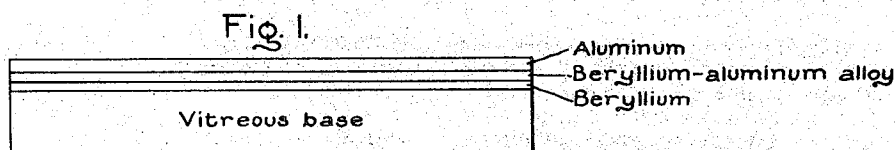


Nov. 5, 1946.

C. W. HEWLETT  
METHOD OF MAKING MECHANICALLY RESISTANT  
AND HIGHLY REFLECTING METALLIC FILMS  
Filed March 6, 1943

2,410,733



Inventor:  
Clarence W. Hewlett,  
by *Harry E. Dunham*  
His Attorney.

## UNITED STATES PATENT OFFICE

2,410,733

## METHOD OF MAKING MECHANICALLY RESISTANT AND HIGHLY REFLECTING METALLIC FILMS

Clarence W. Hewlett, Schenectady, N. Y., assignor to General Electric Company, a corporation of New York

Application March 6, 1943, Serial No. 478,269

1 Claim. (Cl. 117—35)

1

The present invention relates to new articles of manufacture comprising a coating of a metal such as aluminum, silver, or the like on a backing of glass or similar vitreous surface and to a process of preparing the same. It is particularly concerned with mirrors comprising a polished vitreous base provided with novel metallic films which are hard, mechanically resistant to abrasion incident to periodic cleaning, and highly reflecting.

The production of metal-surfaced vitreous bases, such as highly reflecting mirror surfaces, by the evaporation or sputtering of metals such as aluminum, silver, etc. in a good vacuum on to a glass or other vitreous surface is well known. In the usual evaporation process, a tungsten or molybdenum filament charged or coated with the metal (of lower melting point) to be evaporated and the glass or other surface to be coated are mounted in a vacuum chamber with the surface to be coated so oriented that it is substantially uniformly presented to the filament. The vacuum chamber is evacuated by a pump and the filament electrically heated by suitable means until the lower melting metal held thereon has been evaporated. By this process the surface which has been exposed to the filament receives a coating of the evaporated metal.

In the usual sputtering process, a cathode composed of the coating metal, the previously cleaned surface to be coated, and a suitable anode which is preferably made of aluminum or other metal of low atomic number, are suspended in an airtight chamber which is then evacuated and thereafter filled with an inert gas, preferably argon, to a pressure of a few to a few hundred microns. The surface to be coated is placed close and parallel to the cathode and the anode, which may be a metallic bounding wall of the chamber, is situated at some distance from both the cathode and the surface to be coated. The distance between the cathode and the surface to be coated depends on the pressure of the argon in the chamber. When the pressure is about 200 microns, this distance is about one-half inch. The application of a direct current electric potential of from 500 to 10,000 volts (depending on the pressure of the argon gas) to the two electrodes sets up a glow discharge in the argon gas producing positively charged argon ions which "fall" on to the surface of the cathode to be sputtered with sufficient energy to rip off atoms or small atomic aggregates of the latter and project or sputter them in all directions with great speed. Those flying fragments stick to the surface to be coated

2

or any other surface upon which they strike and build up a layer or film of the material composing the cathode.

Films obtained by either of the methods outlined above possess to a greater or less degree the physical and chemical properties of the material composing the cathode. The hardness and tenacity with which these films adhere to the surface upon which they are deposited, and their reflectance for light or other electromagnetic radiation depend on many details of technique employed in the various steps of the procedure. The most important of these are: the precautions taken to thoroughly clean the surface upon which the film is to be deposited, the purity of the argon gas when sputtering, the degree of vacuum obtained during evaporation or before admitting argon gas when sputtering, and the purity of the evaporated or sputtered metal.

But even when the most thoroughgoing care has been bestowed on the above considerations it is found that when such metals as silver and aluminum are used to make films, although the latter may initially have as high a reflectance as could be expected, still they are easily scratched by even gentle rubbing with a soft cloth, adhere poorly to the underlying surface, blister away from the same in a few days, weeks, or months, and, in the case of silver, tarnish rapidly when exposed to the atmosphere. Various remedies have been proposed from time to time to obviate these undesirable characteristics. One of these remedies has been to coat the surface first with a film of chromium and then apply the film of surface material thereon. This procedure has been found to be helpful but not entirely satisfactory. Another, in the case of aluminum films, has been to heat-treat and/or subject the film to transient immersion in water or other chemical liquid solutions. These measures are also helpful but fall short of a satisfactory answer. It is also known that aluminum films harden somewhat with time upon exposure to the atmosphere, but the hardening so obtained is insufficient and the tendency to blister away from the underlying surface still remains.

It is a general object of the present invention to provide means for overcoming the defects described above. A specific object of the invention is to produce metallic films which adhere tightly and permanently to the underlying vitreous surfaces and are sufficiently hard that they may be cleaned from time to time by washing and wiping with a cloth without the production of noticeable scratches. A further object of the inven-

tion is to provide means for treating films so produced that they are permanently unaffected by the ordinary atmosphere.

In accordance with the present invention a hard, tightly adhering, scratch-resistant film of a metal such as aluminum, silver, gold, nickel or the like on a glass or similar vitreous surface is obtained by vacuum-depositing a foundation coating or layer of beryllium on to the clean vitreous surface and thereafter vacuum-depositing a coating or layer of a second metal such as aluminum, etc. over this beryllium base. Preferably the two metals are so applied that a layer of an alloy of beryllium and the metal of the top coating is formed intermediate the two coatings.

Composite metal films produced in accordance with the present invention have been found to adhere with great tenacity to the polished base and do not loosen up or blister away from the base even after long periods of exposure to the atmosphere.

A further improvement in the scratch-resistance of the metal film is obtained by treating the film with a polar compound such as a soap capable of reacting with the film metal. It is also within the scope of the invention to coat the film with a vapor-deposited layer of a metal fluoride to improve its resistance to corrosive gases and vapors present in the ordinary atmosphere. If desired, the metal fluoride and soap treatments may be combined to obtain the composite results of both treatments.

The present invention will be specifically described in connection with the manufacture of mirrors provided with a reflecting coating of aluminum such as are shown in Figs. 1, 2, 3, and 4 of the accompanying drawing wherein the various layers or coatings are indicated by suitable legends.

For maximum strength and mechanical resistance the composite film is preferably formed in one continuous process or operation in which a thin vacuum-deposited layer of beryllium is first applied to the glass base followed by the simultaneous application of beryllium and the reflecting metal to form an intermediate layer of an alloy of these two metals, which layer is caused to become progressively richer in the reflecting metal as the distance from the base increases until finally a layer of pure reflecting metal is deposited over the alloy layer. These operations are preferably carried out in the following manner:

Two heating filaments of tungsten, mounted in a vacuum chamber, side by side, but shielded from one another by a partition, are employed. These filaments are preferably made helical in form and mounted with their axes horizontal and parallel. Fragments of beryllium are placed inside one helical filament, and fragments of aluminum, or other metal employed to form the top layer of the film, in the other. A shutter adapted to be opened and closed from outside the vacuum system, for example by means of a magnetically controlled mechanism, is mounted between the filaments and the glass plate which is to be exposed to these sources of metal vapors and upon which the film is to be deposited. The vacuum jar or chamber is provided with a reentrant flask into which liquid air or other refrigerant may be introduced. The surface of this cooled reentrant flask exposed in the space being evacuated serves as a pump of great speed for condensable vapors released in the vacuum chamber dur-

ing the process of evaporation. It is best to delay the introduction of the refrigerant into the reentrant flask until a good vacuum has been obtained and the evaporation is to be initiated. When the chamber has been evacuated to a pressure of 0.1 micron or less, refrigerant is introduced into the reentrant flask. The shutter is closed and the filament bearing the aluminum or other metal to form the top layer of the film is heated until this metal is melted down and starts to evaporate, and the surface impurities on the liquid metal bead have disappeared. The heating current to this filament is then shut off and the heat applied to the filament carrying the beryllium. When the beryllium beads have become clean and are evaporating copiously the shutter is opened and the beryllium vapor is allowed to condense on the glass surface to be coated. When the beryllium film on the glass surface has grown to such a thickness as to transmit only 10 to 20 per cent of the light from the filament (this thickness is not critical; it could be such as to transmit from 10 to 90 per cent of the light without materially altering the final result) the filament bearing the aluminum or other metal is again heated and evaporation of this metal reinitiated. Both the beryllium and the aluminum are then preferably allowed to evaporate simultaneously for a while, thus forming an intermediate alloy film by deposition of the mixed vapors on top of the beryllium coating. When this film has built up to a substantial thickness so as to be practically opaque to light, the temperature of the filament bearing the beryllium is gradually lowered to decrease the rate of evaporation of this metal and finally the heating current to this filament is shut off entirely. The heating current to the filament bearing the aluminum is still maintained until a sufficient quantity of pure aluminum has been deposited on top of the intermediate coating of beryllium-aluminum alloy to form a top coat having the optical properties of pure aluminum. Finally, the heating current to the filament bearing the aluminum is shut off and the film is completed. The quantitative control of the amounts of the various metals evaporated in the several stages of the process is best achieved by preliminary evaporations in which the rate of evaporation and hence the relative proportions of each metal in the metal vapors coming in contact with the glass surface is measured as a function of the amount of metal introduced into the helices and the temperature of the helices.

From the above description it will be seen that a film produced in the manner described is composite and that it may be broadly described as comprising an inner coating of beryllium, an intermediate or transition coating of beryllium-aluminum alloy and an outer or surface coating of aluminum. In the preferred films prepared as described hereinbefore, the intermediate or transition coating actually consists of three distinct zones or layers as shown in Fig. 2. The first of these three intermediate layers in a transition layer composed of an alloy of beryllium and aluminum which becomes progressively richer in aluminum and poorer in beryllium as the distance from the glass surface increases, until the second intermediate layer of a beryllium-aluminum alloy of substantially constant proportions is reached. Thereafter, the second intermediate layer extends for some distance to the third intermediate layer in which the proportion of beryllium continually decreases until no more

beryllium at all appears. The outermost part of the composite film is pure aluminum.

Although films comprising five recognizable layers or coatings are preferred, films comprising a fewer number of metal layers are also within the scope of the present invention. For example, the intermediate alloy layer or layers may be omitted and a layer of the second metal applied directly over the beryllium layer. However, better adhesion of the two layers is obtained through an intermediate alloy layer or layers. For example, an intermediate alloy layer in which the beryllium content thereof decreases gradually and continuously as the distance from the underlying beryllium layer increases may be used. Such a layer can be formed by gradually lowering the temperature of the filament bearing the beryllium at the same time that the filament bearing the aluminum is gradually heated to maximum evaporating temperatures. The composition of the intermediate layer or layers may also be controlled by employing separate and independently operable shutters for the beryllium and aluminum filaments. In either case, the relative proportions of the metal vapors may be readily controlled and varied.

Composite metallic film of beryllium-aluminum, beryllium-silver, beryllium-gold, etc. prepared in accordance with the present invention have been found to adhere permanently and with great tenacity to glass surfaces and to be so hard that they could be removed with only the greatest difficulty unless abrasives or chemicals were used. Moreover, these films have the reflectance for light of the metal forming the top layer. Ordinary cleaning processes are quite ineffective in removing the films and they do not loosen up or blister away from the underlying glass surface with time or exposure to the atmosphere. While such films with top surfaces of aluminum, silver, gold, nickel, etc., when rubbed vigorously with a handkerchief or towel, will show fine scratches, such as are formed when these same polished bulk metals are subjected to the same treatment, it is very difficult to rub through the top layer. The films are not torn, wiped away, or otherwise disintegrated, by ordinary cleaning processes used to free such a surface from dust, finger prints, etc. I shall presently describe further measures or treatments which will reduce materially the fine scratches which may be produced on the otherwise untreated metal top layer by vigorous rubbing with a handkerchief or towel. The most durable films are those composed of five recognizable layers: namely, two pure layers, one of beryllium and one of aluminum, silver, gold, nickel, etc.; two transition layers composed of beryllium and the metal of the top layer of continuously varying proportions; and separating the transition layers, an intervening layer composed of an alloy of beryllium and the metal of the top layer of constant and controllable proportion, which layer has a composition intermediate the average composition of the two transition layers.

It is well known that alloys of beryllium and other metals are usually very hard, and that certain alloys are harder than others. By the method described above it is possible to select the particular alloy composition of the two metals concerned that has the greatest mechanical strength, and to evaporate the two metals at such rates during the formation of the middle layer of the five layer film that this layer will be composed of the two metals in the desired proportions. If necessary, a subsequent heat treatment of the

composite film would be adequate to develop the required alloy structure. I do not wish to imply that the various layers in the composite films containing an intermediate alloy layer or layers are separated by definite boundaries. Rather, they are continuously graded one into the next adjacent one and so on. There is nothing therefore in their structure in the nature of discontinuities which might favor a separation or disintegration of the composite film into component parts.

It has also been found that metallic films produced in the manner above described may be effectively protected from the formation of fine scratches caused by vigorous rubbing with a cloth by treating the freshly prepared metal film with liquid compositions composed of long chain polar molecules capable of reacting with the metal film to form a hydrophobic layer. Examples of such materials are undiluted liquid soap, long chain fatty acids such as stearic acid, oleic acid, or the alkali metal salts of such acids. The excess compound is removed by washing with water. These compounds are believed to react chemically with the metallic reflecting surface of the film forming a hydrophobic monomolecular layer, as is shown in Fig. 3, on the metal surface with the OH ends of the molecules adhering tightly to the metal surface and the CH<sub>3</sub> ends exposed. Films treated in this way shed water completely and may be rubbed quite vigorously with a cloth without the production of the fine scratches mentioned above. Each washing with a polar compound will restore any damaged part of the film.

It has further been found that the chemical action on film surfaces due to deleterious gases and vapors in the atmosphere can be overcome to a great extent by evaporating in a vacuum a layer of a metallic fluoride, preferably an insoluble fluoride such as magnesium fluoride, on the freshly prepared metallic films. A section of a mirror treated in this manner is shown in Fig. 4. The thickness of this fluoride film can be of the order of 1 to  $5 \times 10^{-5}$  cm. This thin fluoride layer impairs the reflectance of the film to a slight degree but greatly improves its resistance to mechanical abrasion and decreases its susceptibility to tarnish when exposed to the atmosphere. It is also advisable to treat these fluoride coated films with a polar compound such as liquid soap, as the same water shedding and mechanically protective layer of molecules is produced on a fluoride surface by these materials as is produced on a metallic surface.

Although the invention has been described with specific reference to the production of improved mirrors by the vaporization process, it is to be understood that it may be used generally for the production of durable metallic films on any vitreous base and that the metal films may also be produced by sputtering the various metals in proper order and proportions on to the vitreous surfaces. By the term "vacuum-depositing" or "vacuum-deposited" as used herein and in the appended claims, I refer to the well known vaporization and sputtering processes, both of which are carried out in a partial or complete vacuum. Sputtered coatings are usually harder but the sputtering process is inherently slower than the vaporization process.

Metals other than those specifically mentioned hereinbefore may also be used for the outer or top layer of the composite films, particularly when light reflectance of the product is of little or no importance, as, for example, in the manufacture

of films for use as electrical conductors or resistors, etc. Specific examples of such metals are tungsten, chromium, zinc, tin, lead, antimony, copper, etc.

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

In the process of manufacturing mirrors the steps which comprise exposing a polished glass surface to a source of beryllium vapor to form on said surface a coating of beryllium capable of transmitting from 10 to 90 per cent of the light emitted by the source of said vapor, exposing said beryllium coated surface to said source of beryllium vapor and simultaneously to a source of aluminum vapor while gradually increasing the rate of vaporization of the aluminum until the propor-

tions of beryllium and aluminum vapors are such as to deposit on said metal coated surface a beryllium-aluminum alloy of predetermined composition, thereafter gradually decreasing the rate of vaporization of beryllium until only aluminum vapor is condensed on the resulting metal coated surface, heat treating the resultant product to develop the said beryllium-aluminum alloy structure, vapor-depositing a thin layer of magnesium fluoride on the aluminum coated surface and thereafter treating said magnesium fluoride-coated surface with a material selected from the class consisting of long chain fatty acids and the soluble alkali metal salts thereof capable of forming a hydrophobic layer on said composite film.

CLARENCE W. HEWLETT.