

March 15, 1949.

D. M. PACKER
FRONT SURFACE REFLECTOR AND METHOD
OF MAKING SAME
Filed Feb. 5, 1944

2,464,256

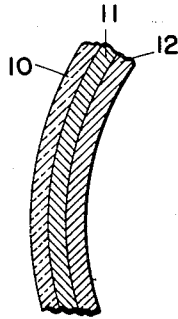


FIG. 1

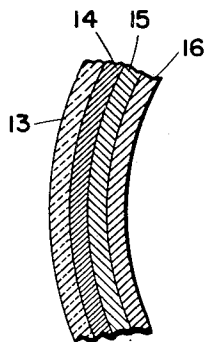


FIG. 2

Inventor
DONALD M. PACKER

334

A. D. O'Brien

Attorney

UNITED STATES PATENT OFFICE

2,464,256

FRONT-SURFACE REFLECTOR AND METHOD
OF MAKING SAME

Donald M. Packer, Arlington, Va.

Application February 5, 1944, Serial No. 521,267

7 Claims. (Cl. 88-105)

(Granted under the act of March 3, 1883, as
amended April 30, 1928; 370 O. G. 757)

1

This invention relates to front surface reflectors and has particular relation to the formation of front surface reflectors for use in precision optical instruments such as are employed in fire control equipment and the like and for use in other equipment where front-surface reflectors are desired.

While the advantages of front-surface mirrors over back-surface mirrors are obvious, the stringent requirements of reflectivity and durability demanded of the reflecting material of the former type have greatly restricted the usefulness of front-surface reflectors in service instruments. The reflectivities of silver and aluminum are sufficiently high, but both metals deteriorate rapidly upon exposure to air and salt spray, and in addition, both metals are relatively soft and easily scratched when cleaned with lens tissue or cloth. Metals or alloys such as chromium, platinum, stainless steel and Stellite have the requisite abrasion and corrosion resistance but have low reflectivities. The only material, at the present time, which affords a reasonable compromise between reflectivity and durability is rhodium. This metal has corrosion and abrasion resistant properties at least equal to those of Stellite, chromium and platinum, and a reflectivity of 70 to 75 per cent, which is 10 to 15 per cent higher than that of the aforementioned metals.

The two principal procedures by which rhodium is deposited directly upon a glass base to form front-surface mirrors are sputtering and vacuum distillation. The time required to form a full-reflecting surface by cathode sputtering is approximately an hour. This process requires, moreover, a sheet of rhodium metal having an area at least as large, and approximately the same shape, as the finished reflector. The latter requirement, in conjunction with the long sputtering period, serves to render the process impractical for production purposes. The deposition of rhodium by evaporation in vacuo lends itself to production because a number of mirrors may be coated simultaneously and the size is restricted only by the dimensions of the evacuation chamber. However, the melting point of rhodium is 1966° C., a temperature difficult to realize in conventional high-vacuum filming equipment. In addition, considerable metal is lost by condensation on surfaces other than the mirrors, an item which must be considered in view of the cost and the limited supply of pure rhodium. The reflectivity of evaporated rhodium, moreover, is usually around 66 per cent, as opposed to the 72-75 per cent reflectivity of sputtered rhodium. This relatively low reflectivity of evaporated rhodium mirrors is generally attributed to contami-

2

nation by tungsten from the filament used to heat the rhodium.

Rhodium can be electroplated very easily from solution, it has great covering power, and the reflecting power of electrodeposited rhodium surfaces is about 72 per cent. However, it is impossible to electroplate rhodium directly onto a dielectric base material such as glass. Methods for obtaining a tenacious film of nickel on glass are known. One such method involves the disassociation of nickel carbonyl upon contact with a hot glass surface, with the nickel depositing on the glass and the remainder of the compound being removed as a gas. Such nickel films adhere sufficiently to the glass to allow a reflecting layer of rhodium to be electrodeposited thereon. However, front-surface reflectors made in the foregoing manner have the disadvantage that the front-surface films formed thereby are relatively soft, easily scratched, streaked and they exhibit accompanying low reflectivity.

An object of the present invention is to provide a front-surface reflector characterized by its relatively high reflectivity and extreme durability.

Another object of the invention is to provide a front-surface reflector having a high reflectivity, great surface hardness, resistance to abrasion and heat, resistance to the corrosive action of sea water, salt spray, salt fog and resistance to the action of corrosive chemicals and vapor.

A further object of the invention is to provide a front-surface reflector, the front surface of which will retain the same contour as the finished surface of the base body to which the coating layers are applied.

A still further object of the invention is to provide a front-surface reflector, the front-surface layer of which need not be polished or buffed in order to provide a suitably finished mirror.

Still another object of the invention is to provide a method whereby front-surface reflectors having the above-mentioned characteristics may be produced.

These and other objects of the invention will be better understood by reference to the accompanying description and drawing, in which Figure 1 shows a reflector body 10, intermediate layer of thermally evaporated nickel 11 and finish electro-deposited coating of rhodium 12. Figure 2 shows reflector body 13, thermally evaporated chromium layer 14, thermally evaporated nickel layer 15 and finish electro-deposited coating of rhodium 16.

I have discovered a method for the production of high quality front-surface reflectors of rhodium electro-deposited upon base films of metals deposited by volatilization in vacuo upon a con-

ductive or dielectric base body surface. The surface of the base body may be flat, or curved in a regular or irregular figure, and may have any desired finish, such as polished, pebbled, glazed, or ground, and the base body may be a dielectric material such as glass or ordinary plastic or it may be a conductive material such as Stellite or other metal, conductive rubber or conductive plastic.

In one embodiment of the invention, a primary layer of nickel is deposited upon a finished surface of a base body by volatilization in vacuo and a front-surface layer of rhodium is electrodeposited thereon. In a preferred embodiment of the invention, a primary layer of chromium or magnesium fluoride is deposited by volatilization in vacuo onto the finished surface of the base body and an intermediate layer of nickel is evaporated onto the primary layer. The front-surface layer of rhodium is then electrodeposited onto the intermediate layer. Other metals such as copper, silver, gold, platinum and the like may be deposited by volatilization in vacuo in place of the nickel, and magnesium fluoride, cryolite, nickel, silver, gold platinum and the like may be deposited in place of the chromium. The operating conditions for the deposition by volatilization in vacuo and electrodeposition are well known and they may be varied in accordance with the characteristics desired of the front-surface reflector.

Examples illustrative of the manner in which the present invention may be practised and of the resultant improved front-surface reflectors formed thereby are as follows:

Example 1

The surface of the article to be coated, in this example a smooth glass plate, is given a finished surface by being smooth polished, cleansed in order to remove grease or other foreign matter and then dried. The clean glass plate is placed in a vacuum chamber and a primary layer of chromium is evaporated by vaporization in vacuo onto the finished surface thereof. An intermediate layer of nickel is then evaporated onto the primary chromium layer. The nickel-on-chromium plate is then transferred to an electroplating bath and electroplated with rhodium as hereinafter described. If it is not possible to affect this transfer without impairing the cleanliness of the evaporated nickel layer, it may be cleansed in any suitable manner to prevent the succeeding front-surface rhodium layer from presenting a streaky appearance. In a preferred operation, cleansing is accomplished by immersing the nickel-on-chromium reflector in a 95% alcohol solution from three to five minutes. While still wet, the reflector is immersed in a hot (140°-150° F.) alkaline cleaning solution from three to five minutes. A suitable cleaning agent is one which will not attack nickel or chromium and will remove fingerprints, other forms of grease and other foreign matter. A suitable cleaner is 4 ounces per gallon of water of alkaline metal cleaner ("Wyandotte No. 140", manufactured by Wyandotte Chemicals Corporation), or "Anodex," prepared by MacDermid, Inc., plus 2 ounces per gallon of water of a wetting agent ("Nacconol NR," manufactured by National Aniline and Chemical Co., Inc.). After removing the reflector from the alkaline cleaning solution, it is rinsed in clean running tap water. At this point the reflector is observed by lifting it momentarily from the rinse. If a "water break," that is, a

failure of certain areas to wet, appears when the water drains from the reflector surface, the cleaning operation is repeated. The reflector is next rinsed in distilled water to prevent tap water impurities from being carried over into the rhodium plating bath and is immediately placed in the plating solution while still wet. It is important that the surface of the reflector be not allowed to dry from the beginning of the cleaning operation to immersion in the rhodium plating bath, inasmuch as drying of the surface tends to result in a streaky rhodium deposit.

Following immersion of the reflector in the rhodium plating bath, the plating solution is stirred sufficiently to mix the water film on the reflector with the plating solution. The reflector is connected as the cathode and plated immediately for about two minutes at a cathode current density of 0.063 amp./in.² at a solution temperature of about 85° F. The rhodium plating solution employed is of the phosphate type containing 2 grams per liter of rhodium metal (added as rhodium phosphate syrup) and 40 ml. per liter of 85% orthophosphoric acid. A sulphate bath is also usable in this connection. Since the rhodium is plated from solution, platinum anodes, preferably in sheet form, are used. The anode area should be from two to six times as great as the cathode area; that is, the area of the reflector surface. If too small an area is employed, it is difficult to maintain a constant current because of excessive gas evolution, and higher voltages are necessary.

It is obvious that variations in the operating conditions may be employed. In a preferred form of the invention, the rhodium bath is operated at about 85° and the current density is kept low to reduce gassing at the cathode to a minimum. The voltage requirements are small, being about 2.5 volts for an anode to cathode distance of 2.5 inches. However, suitable deposits have been obtained using cathode current densities varying from .0063-.375 amp./in.² at voltages from 1.9-8.0 with the solution at temperatures varying from 80°-100° F.

Example 2

In this embodiment of the invention, a primary layer of nickel is evaporated directly onto the finished surface of a glass plate in the same manner as the primary layer of chromium is applied in the above example. The front-surface layer of rhodium is then electrodeposited onto the evaporated nickel layer in the manner described in the foregoing example.

Example 3

A primary layer of magnesium fluoride is deposited by volatilization in vacuo onto the finished surface of a glass plate in the same manner as the primary layer of evaporated chromium is deposited as described in Example 1. The intermediate evaporated nickel film and the front-surface layer of electrodeposited rhodium are then deposited in the manner described in Example 1.

The glass base bodies utilized in the foregoing examples varied in size from two to six inches square and it was observed that the characteristics of the various sized front-surface reflectors were not affected by the area of the finished surface to be coated. The thickness of the rhodium deposit was found to be limited by the adherence of the evaporated films to the glass base.

5

As the plating proceeded on nickel films deposited directly onto the glass (see Example 2), the increasing thickness of rhodium exerted an increasing tension on the nickel layer until a point was reached where the nickel was stripped from the glass. On the other hand, the adherence of the nickel-chromium films to the glass (see Example 1) was adequate so that no difficulty was experienced from the stripping of these films during the plating process.

The amount of rhodium deposited under the conditions outlined in foregoing procedures (0.063 amp./in.² for two minutes) was estimated to be about 0.00035 gm./in.², equivalent to a film thickness of about 0.0000015 inch. The limiting thickness of rhodium which could be applied to the available nickel-on-chromium films on glass was between 3 and 6 millionths of an inch. The 0.0000015 thickness of coating applied on the test samples is well within the above limits, and on the basis of laboratory tests, is satisfactory for the purpose intended.

In order to determine the corrosion resistance of the finished mirrors, three samples (2 inch squares) of rhodium-on-nickel-on-chromium films were subjected for a period of 1000 hours to the corrosive action of synthetic sea-water fog. At the end of the exposure, two of the samples exhibited no evidence whatever of deterioration or corrosion, while there were two very small brown spots on the third specimen. These spots first became noticeable after 900 hours' exposure and did not expand during the next 100 hours. The only apparent effect of the salt water was to clean the surfaces thoroughly and to increase slightly the reflection values. The hardness of the rhodium surfaces was such that vigorous rubbing with a typewriter eraser ("Comfort" No. 494—Eagle Pencil Co.) for a period of 35 seconds failed to mar them. A piece of optical Stellite was badly scratched by only five seconds' rubbing. This and other comparative tests have shown that the rhodium surfaces will resist abrasion to a degree slightly superior to that exhibited by chromium.

The spectral reflectivity of the front-surface rhodium reflectors of the present invention was measured in a spectrophotometer at wave lengths from 400 to 760 millimicrons with a 45° angle of incidence of light on the reflector surface. The calculated luminous reflection percentage obtained from the spectro-reflectance data proved to be considerably higher than that of known front-surface reflectors which were measured for comparison as shown by the following table.

Table

Front Surface Reflector	Percent Luminous Reflection
Electrodeposited Rhodium (on Evaporated Nickel-on-Evaporated Chromium).....	72.5
Electrodeposited Rhodium (on Evaporated Nickel).....	72.5
Electrodeposited Rhodium (on Evaporated Nickel-on-Evaporated Magnesium Fluoride).....	72.5
Evaporated Rhodium.....	60.0
Evaporated Chromium.....	57.3
Stainless Steel.....	57.0
Stellite.....	56.2
Evaporated Nickel.....	54.0

From inspection of the above results, it is evident that the reflectivity of the electrodeposited rhodium front-surface reflectors of the present invention is, on the average, at least 12 percentage points higher than that of other front-surface type reflectors heretofore available.

6

The invention herein described may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

I claim:

1. A front-surface reflector comprising a dielectric base body portion having a finished surface, an intermediate layered deposit comprising a primary layer of thermal evaporated chromium deposited onto said finished surface, a layer of thermal evaporated nickel deposited on said chromium layer, and a front surface layer of electrodeposited rhodium deposited onto said nickel layer, said electrodeposited front-surface layer having a contour substantially identical to that of said finished surface.

2. A method of forming a front-surface reflector comprising successively depositing on a finished surface of a body by thermal evaporation in vacuo an intermediate layered deposit including at least a primary layer of chromium and an outer layer of a metal of the group consisting of copper, nickel, silver, gold and platinum, and electrodepositing a layer of rhodium on said outer layer.

3. A method of forming a front-surface reflector comprising depositing a chromium layer on a polished surface of a glass body by thermal evaporation in vacuo, depositing a nickel layer onto said chromium layer by thermal evaporation in vacuo, and electroplating a rhodium layer onto said nickel layer; whereby a hard, brilliant, unbroken, corrosion, and abrasion resistant, reflective coating is strongly bonded to the glass body.

4. A method of forming a front-surface reflector comprising depositing a chromium layer on a polished surface of a dielectric body by thermal evaporation in vacuo, depositing a nickel layer onto said chromium layer by thermal evaporation in vacuo, and electroplating a rhodium layer onto said nickel layer, whereby a hard, brilliant, unbroken, corrosion, and abrasion resistant, reflective coating is strongly bonded to the dielectric body.

5. A method of forming a front surface reflector comprising successively depositing on a finished surface of a body by thermal evaporation in vacuo an intermediate layered deposit including at least a primary layer of chromium and an outer layer of copper, and electrodepositing a layer of rhodium on said outer layer.

6. A method of forming a front surface reflector comprising successively depositing on a finished surface of a body by thermal evaporation in vacuo an intermediate layered deposit including at least a primary layer of chromium and an outer layer of silver, and electrodepositing a layer of rhodium on said outer layer.

7. A front-surface reflector comprising a dielectric body having a finished surface, an intermediate layered deposit including first and second layers of different thermally evaporated materials, said first layer deposited on said body and formed of chromium, said second layer deposited on said first layer and formed of a metal from the group consisting of copper, nickel, silver, gold and platinum, and a front surface layer of electrodeposited rhodium on said second layer having substantial identity of contour with said finished surface.

DONALD M. PACKER.

(References on following page)

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,947,180	Bart	Feb. 13, 1934
2,047,351	Alexander	July 14, 1936
2,078,784	Williams	May 11, 1937
2,108,604	Mason	Feb. 15, 1938
2,113,977	Barnes	Apr. 2, 1938
2,207,656	Cartwright et al.	July 9, 1940
2,281,475	Cartwright et al.	Apr. 28, 1942
2,304,182	Lang	Dec. 8, 1942
2,333,534	Lang	Nov. 2, 1943
2,397,583	Wise et al.	Apr. 2, 1946
2,410,733	Hewlett	Nov. 5, 1946

FOREIGN PATENTS

Number	Country	Date
395,611	Great Britain	July 20, 1933

OTHER REFERENCES

Hackh's Chemical Dictionary, page 212, Blakiston Co. (1944).

Protective Coatings for Metals, by R. M. Burns & A. E. Schuh, published by Reinhold Pub. Co., New York (1939), pages 53 to 56, 231.

"Rhodium Plating and Its Application," by K. Schumpelt, in Metal Cleaning and Finishing of March 1938, page 200 of the article relied on.

Methods of Depositing Metallic Films, by Samuel Wein in Electronics of September 1943, pages 110-113.