March 12, 1940. P. DEREN 2,193,555

PROCESS OF MAKING REFLECTING SURFACES

Filed Sept. 26, 1935 2 Sheets-Sheet 1

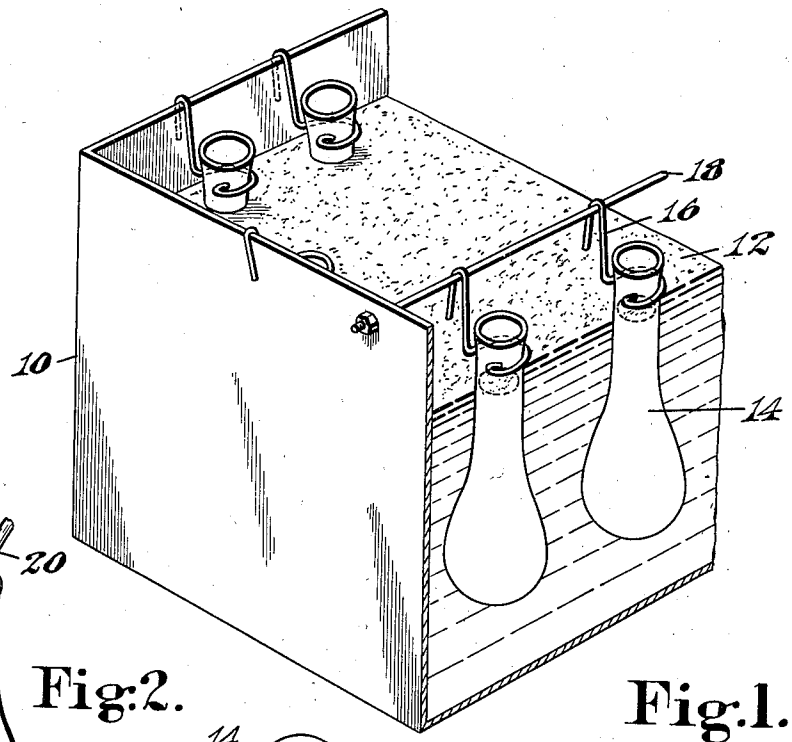


Fig.1.



Fig.2.

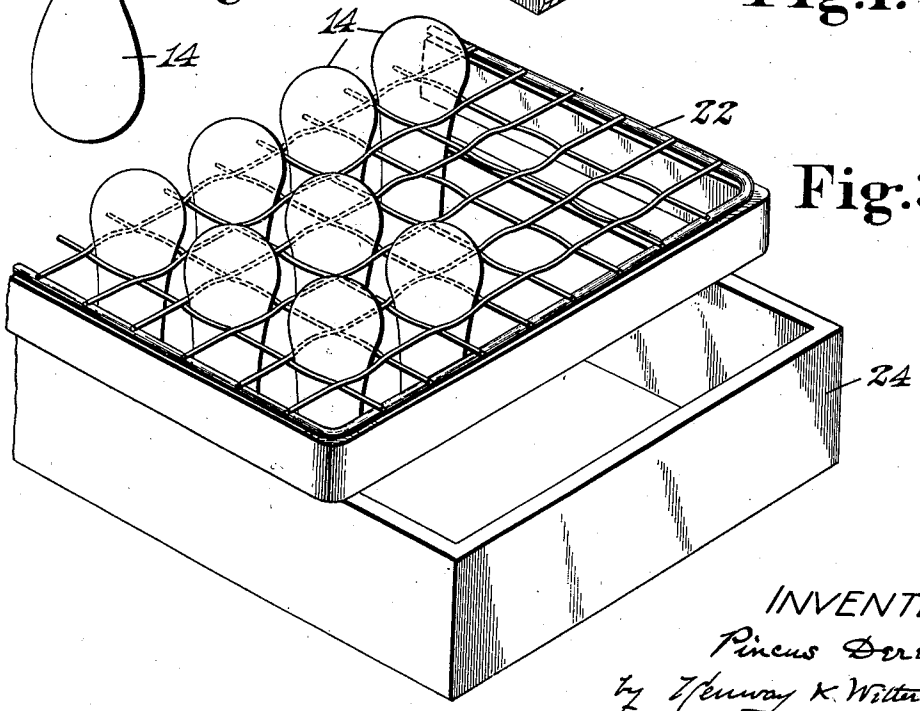


Fig.3.

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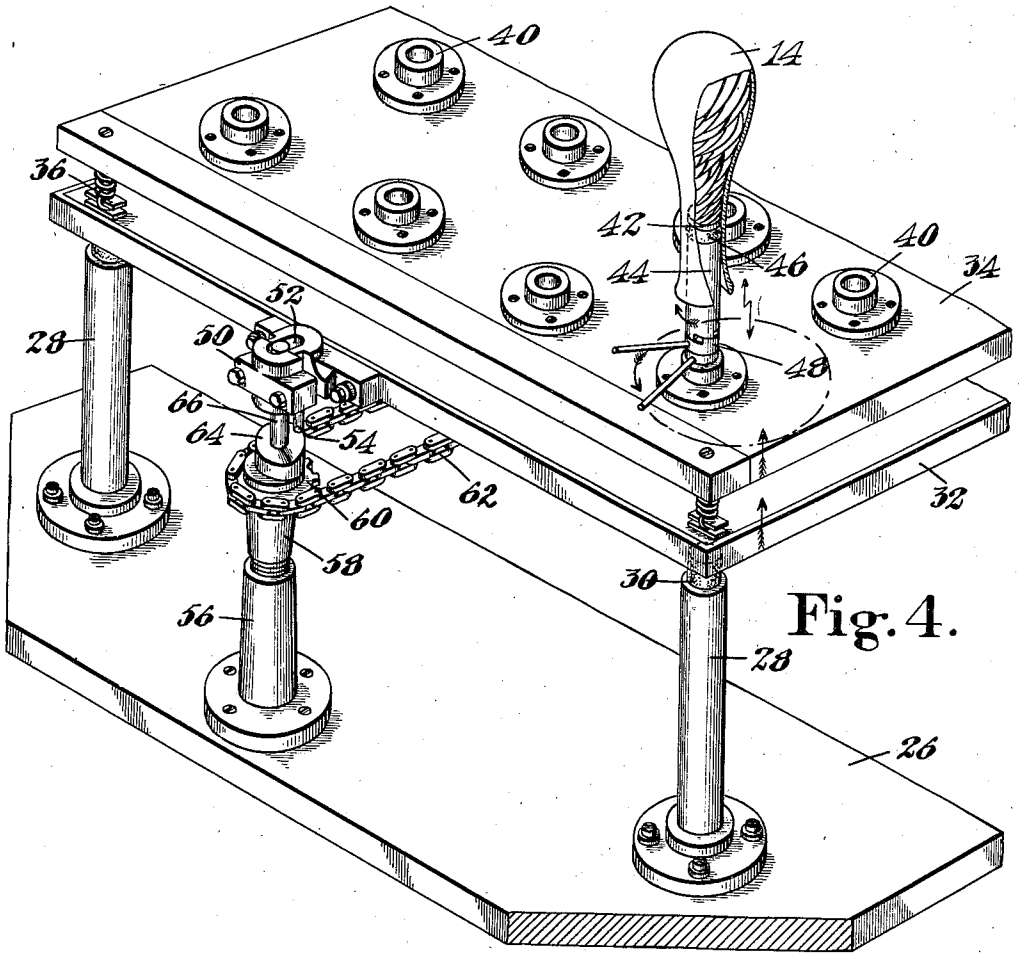
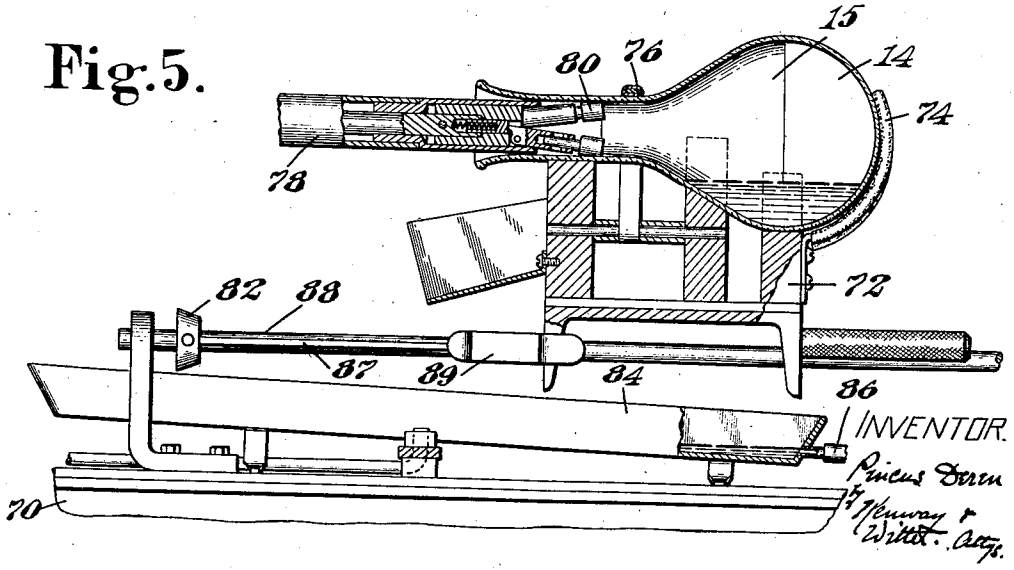


Fig. 4.

Fig. 5.



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2,193,555

PROCESS OF MAKING REFLECTING SURFACES

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Application September 26, 1935, Serial No. 42,227

5 Claims. (Cl. 91—69.1)

The present invention consists in an improved process of applying a metallic reflecting surface to glass articles such as lamp bulbs. An important field of use is in the application of a coating of metallic silver to the inside surfaces of lamp bulbs and for purposes of illustration the invention will be described in that connection.

Many attempts have been made heretofore to provide an inside silvered surface for lamp bulbs, but serious difficulties have been encountered and prior to the present invention no commercially successful process has been available. Consequently resort has been had to the application to lamp bulbs of an outside coating of silver. An outside silver coating is noticeably less efficient as a reflector than an inside coating because of the fact that the light must pass twice through the glass in reaching and leaving the reflecting surface. This loss, of course, is eliminated in the case of an inside reflecting surface. Further, the outside reflecting surface is likely to become damaged or scratched in used. In fact, this danger is so pronounced that it is the practice to protect outside reflecting surfaces, as heretofore used, by a shell of copper or the like and this expedient introduces another problem because in time the copper tends to diffuse into the silver and impair its reflecting efficiency.

On the other hand, it is difficult to secure a smooth continuous and tightly adherent silver coating upon the inside of the bulb on account of the severe treatment imparted to the bulb in lamp manufacture and use. In the first place, it is necessary to remove every particle of occluded air or gas from the walls of the bulb before depositing the silver coating thereon, because if any gas is left beneath the silver coating, it will expand and rupture the coating when the bulb is exhausted prior to the sealing step, thus damaging the reflecting surface.

Further, I have found that secure and continuous adhesion of a silver coating is prevented by a hydrated alkali film which tends to form upon the surface of glass exposed for any length of time to the atmosphere, and of course any grease or other foreign substances upon the walls of the bulb results in a defective coating.

Where a silver-depositing solution is employed it also becomes important to prevent contact of precipitate which may be formed in the solution as a result of secondary reactions or otherwise with the walls to be plated. If such precipitate is allowed to settle against the walls the silver will not subsequently unite with the glass in the contacted spots and pin holes or imperfections in coating will result. Further problems arise on account of intense heat developed within the bulb under conditions of use, caused by the concentrated heat rays reaching the reflecting surface of the bulb.

The difficulties above discussed are successfully solved by the present invention. I have discovered that the objectionable hydrated film may be removed from the walls of the bulb by proper chemical cleaning and I have found that hot chromic acid is effective for this purpose. This treatment is also effective in removing occluded gases from the walls of the bulb and from the infinitesimally small pits sometimes occurring therein, especially in old bulbs.

The problem of preventing contact or settling of precipitate in the silver-depositing solution upon the walls of the bulb I have solved by only partially filling the bulb with the solution and then imparting a special movement of predetermined character to the bulb, such that the solution is caused to flow or slosh continuously across the surfaces to be treated, and a liquid film is thus interposed at all times between the glass and the precipitate and consequently no detrimental contact occurs.

These, and other novel characteristics of my invention will be best understood and appreciated from the following description of one preferred manner of putting it into practice in connection with one form of suitable apparatus.

In the drawings,

Fig. 1 is a view in perspective, partly in section of apparatus for chemically cleaning the bulbs,

Fig. 2 is a view in perspective of a bulb in process of rinsing,

Fig. 3 is a view in perspective of a draining rack for the cleansed bulbs, showing some bulbs in position,

Fig. 4 is a view in perspective of a portion of the apparatus for agitating the bulbs during the silver-depositing operation, showing one bulb in position and partly broken away, and

Fig. 5 is a view in elevation, partly in longitudinal section of apparatus for removing surplus silver from selected areas in a bulb, the bulb being shown in section.

As already intimated the step of chemically cleaning the bulbs and of removing the film of hydrated silica from the surface to be silvered is of extreme importance in producing a securely bonded silver coating free of imperfections. As suggested in Fig. 1 the bulbs are filled with the proper cleansing solution and immersed therein as in 12, for a sufficient length of time to accom-

plish the desired results. A receptacle 10 is provided with rods 18 extending between its sides and from these the bulbs 14 may be suspended by spring clips 16 or the spring clips may be hooked over the walls of the receptacle 10. For the cleansing operation I prefer to employ hot chromic acid, in the proportion of 400 grams of chromic acid (CrO_3) to 1 litre of water, and to maintain the bulbs in this solution at the boiling point for not less than twenty-five minutes.

While other solutions may be used for the purpose of cleaning the bulbs, the hot chromic acid treatment is entirely satisfactory and is advantageous in that it does not tend to etch the surface of the glass, and is effective not only in removing the hydrated film, but in cleansing the glass of grease spots or other impurities which may have accumulated on the surface in manufacturing and handling the bulbs. Having completed the cleansing operation by the treatment indicated in Fig. 1, the individual bulbs are then rinsed as suggested in Fig. 2, first with distilled water, and then with a dilute solution of stannous chloride. The spray nozzle 20 may be used for this purpose. The stannous chloride rinse leaves a very thin mono-molecular film of stannous chloride adsorbed upon the surface of the glass, and this has been found beneficial in speeding up the reduction of the silver-depositing solution to metallic silver.

As suggested in Fig. 3, the bulbs 14, having been rinsed with stannous chloride, are next placed in a rack 22 and allowed to drain freely into a tray 24. They are then ready for the silver applying step.

The silver-depositing solution which I prefer to use may be varied to some extent, but one example of a satisfactory solution is as follows:

Silver solution (A)

Silver nitrate per 11 litres of solution_grams__	100
Concentrated ammonium hydroxide 26 Bé. per 11 litres of solution_____cc__	187
10% potassium hydroxide_____cc__	550

In this solution sodium hydroxide of the same normality, or other hydroxide of the sodium group may be substituted for potassium hydroxide in the solution.

Reducing Solution (B)

Concentrated nitric acid (sp. gr.) 1.415 per 1,000 cc. of distilled water_____cc__	2.7
Sucrose ($C_{12}H_{22}O_{11}$) per 1,000 cc. of solution _____grams__	60

In the above solution if desired other organic reducing compounds of carbon, hydrogen, and oxygen such as rock candy, may be substituted for sucrose in the solution.

The two solutions (A) and (B) are now mixed to form a silver-depositing solution in the ratio of 10:1 in the order given above. It will be noted that the solution contains less than 1% of silver nitrate, but when used in the manner herein disclosed, this is entirely adequate to produce a thick uniform coating of metallic silver upon the walls of the bulb.

I will now proceed to describe the apparatus shown in Fig. 4 of the drawings which constitutes one form of apparatus satisfactory for imparting simultaneously to a large number of bulbs the turbulent, non-recurrent agitation to which the silver-depositing solution is subjected during the plating or silver-depositing operation. This apparatus comprises a stationary base plate 26 having a series of vertical standards 28, two only being shown in the drawings, each provided on its upper end with an elastic cushion 30. Upon this cushion rests a carrier plate comprising a lower section 32 and an upper section 34 connected by springs 36 at each corner which permit relative yielding movement of the two sections. The upper section 34 of the carrier plate is provided with a series of sockets 40, each adapted to receive a combined stopper and holder which is inserted into an inverted bulb 14. This holder has at its upper end a stationary disk 42 and includes a rotatable and longitudinal movable sleeve 44. Between the upper end of the sleeve and the head 42 is interposed a rubber washer 46 which, in its uncompressed condition is of proper size to be introduced freely into the neck of the bulb, but which, when compressed by the upward movement of the sleeve 44, is adapted to be expanded into tight sealing engagement with the neck of the bulb. The lower end of the sleeve 44 rests upon a rotatable cam member 48 having a spiral sleeve adapted to elevate the sleeve 44 when the cam is rotated. It will be understood that the combined bulb holder and stopper is adapted to be inserted by hand into the neck of the bulb, then placed loosely in one of the sockets 40, being permitted to sway and to rotate freely in the socket during the silver-depositing operation.

The lower plate section 32 is provided on opposite sides (one only being shown) with a bracket 50, having a transversely elongated slot 52 and a downwardly extending pin 54. The base 26 is provided with standards 56 at each side in each of which is journaled a head 58 for rotation about a vertical axis. Each head is provided with a sprocket wheel 60, and these are driven through a sprocket chain 62 by a motor, not shown. Each of the heads 58 is provided with a cam member 64 and the upper end face of each is formed as a spiral upon which rests the lower end of the pin 54 above referred to. Each head is also provided with an excentric pin 66 which extends upwardly into the slot 52 of the bracket.

When the apparatus is set in motion it will be apparent that a complicated movement is imparted to the carrier plate 32—34, which in the first place is subjected to an up and down movement by reason of the action of the cams 64 upon the supporting pins 54 and this is modified as transmitted to the upper section 34 by the action of the springs 36. In this up and down movement the lower plate 32 is lifted from the elastic cushion 30 and then deposited abruptly thereon in each revolution of the cams 64. In the second place the action of the excentric pins 66 in the slot 52 is to impart a circular or elliptical movement in a horizontal plane to the carrier plate and this again is modified to some extent as transmitted to the upper section 34 by the springs 36. Further, the bodily circular movement imparted to the carrier plate, which may be assumed to be in a counter-clockwise direction, imparts to the individual bulb carriers, a rotation about their longitudinal axes in a clockwise direction.

The resultant motion imparted to each individual bulb is irregular in that its component motions are not fixed in sequence nor uniform in extent when they do occur. The swaying of the bulbs and their rotation in the loosely fitting sockets 40 are both motions that begin and gradually increase after the carrier plate itself has

been set in motion by the cams 64 and the eccentric pins 66. Further, the transverse motion of the carrier plate 34 is modified and made irregular by the swaying action of the springs 36. Finally, the up and down movement is modified by the elongating and compressing of the springs 36 and of the cushion 30. For this reason the silver depositing solution in the bulbs rarely, if ever, follows the same path in passing successively over any given area of bulb surface.

A relatively small amount of the silver-depositing solution is placed in each of the bulbs—perhaps enough to fill the stem of the inverted bulb, and a little more. The result of the complicated movement above described is to cause the solution to slosh or whirl upwardly into the bulb and coat the upper and inner surfaces thereof. The manner of accomplishing this step is of particular importance because a flocculent precipitate of some secondary reaction tends to form in the solution and if this precipitate is permitted to settle against the surface of the bulb the silver of the deposited coating will not adhere firmly thereto, but is likely to peel away and impair the coating. By the expedient above described, however, I maintain the solution while at rest in the neck portion of the bulb which it is usually not desired to coat, so that if there is any contact of precipitate with the glass, it is in an area to be subsequently cleaned. On the other hand, the upper portions of the bulb which it is desired to coat are in contact with the solution only while the latter is in whirling motion and turbulent agitation. Accordingly the precipitate has no opportunity to settle against the glass and is always separated therefrom by a liquid film. This mode of application of the silver-depositing solution not only prevents defect due to precipitate as already explained, but tends to distribute the deposited silver in a uniform manner and so produce a coating of uniform thickness. Thus, as the result of the cleaning step and the application of the silver-depositing solution by the process of mechanical manipulation explained, uniform, heat-resistant and uniformly adherent silver coating is obtained on the inside of the bulb.

In most cases it is desirable to limit the silver coating to the bulb to a predetermined area. For example, in a bulb designed for indirect lighting, the curved end of the bulb may be silvered up to its line of maximum diameter, whereas, for direct lighting, it is preferred to limit the coating to a zone extending from the line of maximum diameter into the neck of the bulb. In Fig. 5 is shown one form of apparatus suitable for removing surplus silver from those portions of the bulb which should be clear. This apparatus comprises a base plate 70 having an adjacent bulb support 72 for holding a bulb firmly at rest in a horizontal position. The support 72 includes a curved cushion 74 for engaging the end of the bulb and a hold-down member 76 for engaging the neck of the bulb. Rotatably mounted upon the base 70 in a frame, not shown, is a rotatable tool 78 provided at its end with a pair of yieldingly mounted scraping or wiping members 80. The tool 78 is arranged to be moved horizontally into and out of the bulb 14 and is rotated at sufficiently high speed to throw the members 80 outwardly into contact with the walls of the bulb whatever may be its diameter. A gage member 82 is provided for controlling the longitudinal position of the scraping tool by connections, not shown. As herein shown the scraping tool has operated inwardly through the neck of the bulb forming a definite line bounding the silver coating 15. It has already operated to clear the curved end of the bulb of silver, thus restricting the coating to a definite zone extending from substantially the line of maximum diameter to the line in the neck.

In the scraping or wiping operation the bulb is previously filled with water and the solution removed in this process is received in a tray 84, and drawn off with the water through a pipe 86 to be reclaimed.

Extended experimentation has shown that soon after glass lamp bulbs are manufactured the surface of the glass begins to change or decompose, forming an alkaline silicate layer having properties differing physically, and possibly differing chemically, from those of the glass beneath. This film appears to be of such spongy nature as readily to occlude gases and water vapor which are detrimental to the efficiency and life of incandescent lamps. It has been customary in the art to remove these occluded gases and water vapor by exhausting the bulbs in an oven maintained at a temperature just below that of the melting point of the glass. This is at best an expensive and inconvenient procedure, and in the case of lamps silvered on the inside to produce reflecting surfaces is entirely impracticable, because the gases driven out beneath the silver film blow it off in bubbles of various sizes, or the extreme heat damages the silver itself.

I have overcome the disadvantages by subjecting the bulb to a supplementary treatment with hydro fluoric acid mixed with a buffer reagent, such as ammonium fluoride, in order positively to insure the removal of the alkaline silicate layer and with it all traces of occluded gases from the interior walls of the bulb. The employment of a buffer reagent permits the treatment of the glass of the bulb by the fluoric acid solution for a period of hours without danger of frosting the glass. I prefer to employ 4% hydro fluoric acid mixed with 1% ammonium fluoride, but these proportions may be varied to some extent and will give satisfactory results.

This hydro fluoric acid treatment is particularly useful in the manufacture of inside silvered lamps since it permits a reduction of temperature in the heat treatment of the bulb preparatory to sealing and thus obviates danger of burning the silver of the coating. This supplementary treatment, although a part of my invention, is not claimed herein, but forms the subject matter of my copending application, Ser. No. 86,803 filed June 23, 1936.

I have specifically mentioned silver as a metal suitable for a reflecting coating but contemplate that other metals may be employed within the scope of my invention. For example, nickel may be used or chromium may be deposited upon a thin priming coat of silver.

The silver-depositing solution of the formula above set forth is entirely satisfactory and probably represents the solution containing the least amount of silver which is effective for producing a silver coating of a given thickness. It may, however, be varied within certain limits and as already indicated other organic reducing reagents may be substituted for sucrose.

The method above outlined takes care of the formation of any crytalized precipitate which may form in the solution by causing it to settle in the neck of the bulb without adhering to

the portions of the silver coating to be ultimately retained.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is—

1. The process of silvering lamp bulbs or the like, which consists in partially filling a bulb with a silver-depositing solution, stoppering and inverting the bulb, the solution being confined to the neck end of the bulb, then sloshing the solution upwardly and across the top of the bulb in such a manner that precipitate in the solution is not allowed to settle against the upper part of the bulb while silver is being deposited thereon, and then removing silver deposited below said upper part of the bulb.

2. The process of silvering lamp bulbs on the inside, which includes the steps of introducing a limited amount of a silver-depositing solution into the neck end of a bulb, supporting the bulb neck down, sloshing the solution with a random motion across that portion of the bulb above its point of maximum diameter in such manner as to prevent precipitate in the solution from settling, and then removing silver to form a definite boundary line at substantially the line of maximum bulb diameter.

3. A process of silvering lamp bulbs, which consists in filling the neck portion of an inverted bulb with a silver-depositing solution, imparting irregular vertical and lateral movements to the bulb causing the solution to flow upwardly and across the bowl end of the inverted bulb frequently in different paths, and subsequently removing silver deposited in the neck of the bulb.

4. A process of silvering lamp bulbs, which consists in filling the neck portion of an inverted bulb with a silver-depositing solution, then imparting a cushioned vertical movement to the bulb combined with movements of lateral translation and of revolution about its own axis, causing the solution to flow upwardly frequently in new paths across the bowl end of the bulb.

5. The process of metal-coating lamp bulb or the like, which is characterized by the steps of introducing a relatively small amount of metal depositing solution in the bulb, stoppering and inverting the bulb, and then subjecting it to an up and down movement of a yielding character combined with lateral circular movements such as to throw the solution up and whirl it frequently in different paths upon the upper end of the bulb while metal is being deposited therefrom, and without at any time permitting flocculent precipitate to rest upon the walls of the bulb.

PINCUS DEREN.