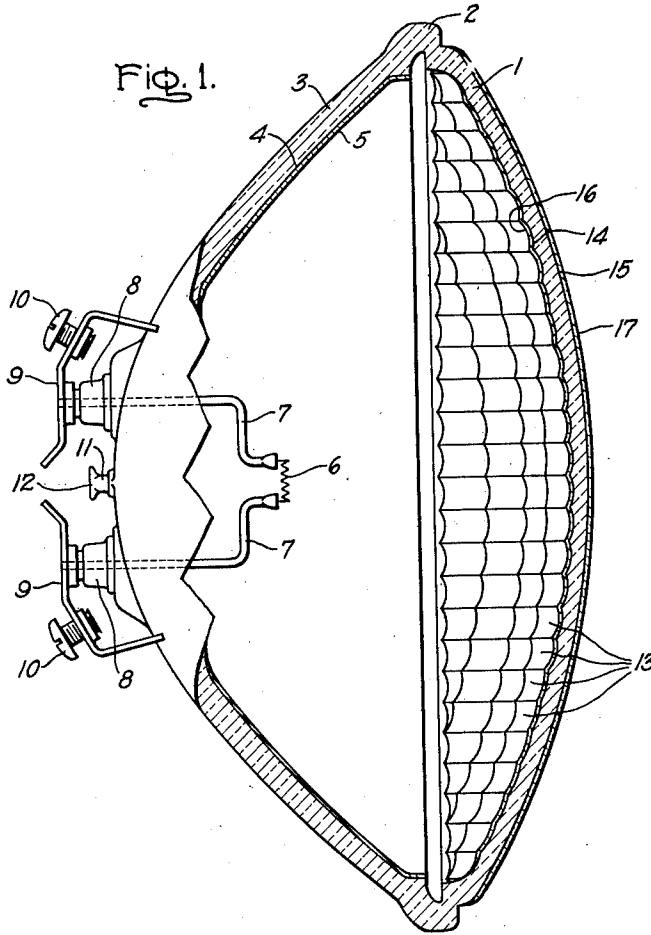
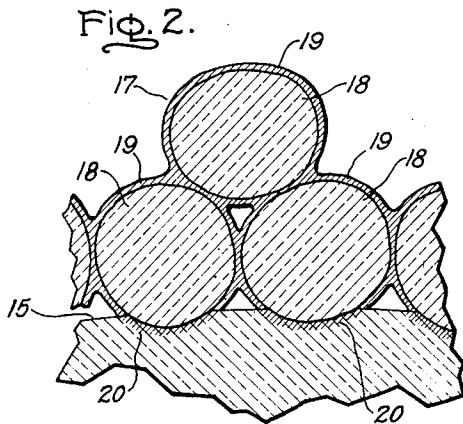


May 26, 1953

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METHOD OF FORMING A TRANSPARENT REFLECTION
REDUCING COATING ON GLASS AND THE
ARTICLE RESULTING THEREFROM
Filed Oct. 29, 1949

2,639,999



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UNITED STATES PATENT OFFICE

2,639,999

METHOD OF FORMING A TRANSPARENT REFLECTION REDUCING COATING ON GLASS AND THE ARTICLE RESULTING THEREFROM

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Application October 29, 1949, Serial No. 124,449

8 Claims. (Cl. 117—71)

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My invention relates to reflection-reducing coatings and articles provided with such coatings, and to a method of producing such coated articles. The present application is a continuation-in-part of my co-pending U. S. application Serial No. 105,535 filed July 19, 1949 and assigned to the assignee of the present application, and now abandoned.

It is well known to apply coatings of various nature to the surface or surfaces of an article for the purpose of reducing the surface reflections from the article with substantially no light absorption. Thus, the presence on the surface of a glass article of a coating of colloidal silica having an optical thickness of the order of, or an odd multiple of, one-fourth the wave length of the light transmitted will substantially eliminate the surface reflections from the glass article and increase the percentage of incident light transmitted through the article.

While these colloidal silica coatings are entirely satisfactory insofar as their reflection-reducing properties are concerned, their permanency or durability heretofore has been inadequate for certain applications. Thus, where such colloidal silica reflection-reducing coatings are applied to the outer surface of the lens of a vehicle headlamp which is subject to weathering, wiping, handling, and the like, the coatings do not remain on the article for as long a period as is desired. Usually, such coatings will wash or rub off the first time the headlamp is washed or wiped.

It is an object of my invention, therefore, to provide a substantially transparent reflection-reducing surface coating of the above-described character which is highly durable and permanent, and will withstand a reasonable amount of weathering, washing, wiping and cleaning.

Another object of my invention is to provide an article having a substantially non-reflecting surface of highly durable and permanent character.

Still another object of my invention is to provide an improved method of applying a reflection-reducing coating to the surface of an article whereby the coating is rendered more resistant to removal.

In accordance with the invention, the durability or permanence of reflection-reducing coatings is increased to a considerable degree by the incorporation in the coating medium, prior to the application thereof to the article to be coated, of a suitable amount of a substance which under the action of heat to the proper degree will act in the manner of a flux to stick the particles com-

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prising the reflection-reducing coating to the surface of the article.

Further objects and advantages of my invention will appear from the following detailed description of a species thereof and from the accompanying drawing.

In the drawing, Fig. 1 is an elevation partly in section of an electric incandescent lamp of the reflector type provided with a reflection-reducing coating according to the invention, and Fig. 2 is a greatly enlarged fragmentary sectional view of the lens of the lamp shown in Fig. 1.

While the invention is applicable in general to any article which is of a light-transmitting character, such as glass lenses, plates, prisms, or other optical elements and similar elements formed of plastic or artificial resin, it is herein illustrated as applied to the cover glass or lens of a reflector-type electric incandescent lamp of the well-known "sealed beam" form described and claimed in U. S. Patent 2,148,314, D. K. Wright, issued February 21, 1939, and assigned to the assignee of the present invention.

As shown in Fig. 1, the said lamp comprises a preformed glass lens or cover glass section 1 constructed in accordance with the invention and fusion-sealed at its periphery, as indicated at 2, to the rim of a preformed concave glass reflector section 3 to form therewith the envelope of the lamp. The concave inner surface 4 of the reflector section 3 is of approximately paraboloidal shape and is covered with a coating 5 of a suitable metal, such as aluminum for instance, to form a reflecting surface. A concentrated light source or filament 6, preferably in the form of a horizontally extending linear coil of tungsten wire, is mounted within the lamp envelope at approximately the focal point of the reflecting surface 5. The filament 6 is electrically connected to and is supported in place within the lamp envelope by lead-in wires 7 which extend through openings (not shown) in the wall of the reflector section 3 at the rear thereof and are secured at their outer ends, as by soldering for instance, to metal thimbles or ferrules 8 fusion-sealed at their rims to the exterior of the reflector section 3 around the said openings. Metal contact or terminal lugs 9 are suitably secured, as by soldering, to the closed ends of the metal thimbles 8 and are provided with terminal screws 10 for connecting the lamp to a suitable source of current supply. The lamp envelope is exhausted and, if desired, filled with a suitable inert gas such as argon, nitrogen, or mixtures thereof, through an exhaust tubulation 11 at the apex of the re-

flector section 3, which tubulation is afterwards tipped-off, as indicated at 12, to hermetically seal the lamp envelope. As shown, the cover glass section 1 may be provided with suitable light-refracting media 13 in the form of flutes, prisms, or both, to constitute a lens for redirecting the light rays passing therethrough from the reflector 3 into a beam of the desired form or pattern.

In order to reduce the surface reflection from the lens 1 and to increase the light transmission therethrough, the inner and outer surfaces 14 and 15 of the lens are provided with substantially transparent reflection-reducing coatings 16 and 17, respectively, similar to that described and claimed in U. S. Patent 2,432,494, Moulton. These coatings 16 and 17 comprise a layer of discrete, sub-microscopic, microgranular, transparent solid particles 18 (Fig. 2) of colloidal nature whereby a layer is produced in which the index of refraction behaves as if it varied from substantially unity at the outer or layer-air surface thereof to an index of refraction approaching that of the article itself at the inner or layer-article surface thereof. This is accomplished by applying on the article 1 to be treated a suspension comprising a liquid having dispersed therein colloidal particles which, upon the evaporation of the liquid, deposits such a layer upon the article, which article may be of glass, plastic or other material which is the substrate.

The coating suspension employed may comprise any of those described in the above-mentioned Moulton patent, but because of its chemical inertness and stability in the form of a sol, a colloidal silica sol in water, alcohol or other suitable solvents such as ethylene glycol monoethyl ether, or a mixture of solvents, is most useful for this purpose, the silica being present in the form of sub-microscopic, discrete, microgranular, transparent solid particles.

While the thickness of the reflection-reducing coatings 16 and 17 may be varied over a relatively wide range within limits of the order of, or an odd multiple of, one-quarter wavelength of the light transmitted, the color of the reflected light and consequently the color of the transmitted light is affected by the thickness of the colloidal layer. However, it has been found that in general the most efficient layer and one having the least effect upon the color of the transmitted light results from the application of a layer of such thickness that the reflected light is of a reddish-purple color. For use on a vehicle headlamp, it is preferable to employ such a coating which presents a distinct colored appearance by reflected light since such a colored reflection provides a readily visible indication of the presence of the coating and therefore serves to distinguish lamps or lenses provided with the reflection-reducing coatings from those which are not.

In accordance with the invention, the durability and resistance of these coatings 16, 17 against removal by weathering, washing, wiping, etc., is greatly increased to the point where it becomes practical to use such coatings on the lens surfaces of vehicle headlamps by incorporating in the coating suspension a relatively small amount of a suitable metallic compound which is soluble in the alcohol or other solvent employed for the suspension and which, upon heating or baking of the coated lens or other glass article 1 at a suitable elevated temperature below the softening point of the glass article and for a suitable length of time, will react with the glass

of the article and act in the manner of a flux to either cause the silica or other particles of the coating material to stick to the glass article or, if not to stick, to leave impressions in the glass surface which serve to produce the same reflection-reducing effect of the silica particles themselves. For ordinary type hard glasses having a softening point of around 700-800° C., the heating or baking temperature of the coated glass article may be from around 500-700° C. or so, i. e., at a temperature slightly below the temperature at which the glass article would normally soften and cause the silica particles of the coating material to soak into the glass article and disappear thereinto. The time of heating or baking may vary according to the nature of the coating material as well as of the glass article, and according to the temperature at which the heating or baking operation is carried out. Ordinarily, however, a heating or baking time up to around one-half to one hour or so will prove sufficient in most cases. In the case of certain types of additive materials according to the invention, the heating or baking of the coated article, instead of being performed as a separate operation, may be combined with the usual glass fusion operations which normally accompany the manufacture of electric incandescent lamps.

For the purposes of the invention, the additive metallic material employed should be a metallic compound which is soluble in the alcohol or other solvent employed for the coating suspension and which will dissolve or be absorbed into, or will decompose into compounds or elements which will dissolve or be absorbed into the glass of the lens 1 or other substrate forming the glass article to be coated at the elevated temperature which is employed to heat or bake the coated glass articles in carrying out the process according to the invention. As examples of suitable additive materials for the purposes of the invention, suitable compounds of one or more of the metals zinc, silver, copper, nickel, iron, titanium, tin, lead, manganese and chromium may be employed, for instance, salts such as zinc acetate, silver nitrate, silver chloride, silver sulphide, cupric or cuprous chloride or sulphide, iron chloride, tin chloride, manganese chloride, titanium tetrachloride, lead nitrate, or other compounds such as chromic oxide for instance. Of these materials, however, it is preferred to employ those which, in the small amounts required to accomplish the objects of the invention, do not impart a separate color of their own to the glass article or materially affect the substantially transparent character of the coating, which discoloring may be objectionable for some reason or other. For example, where one of the compounds of zinc, silver, titanium, tin or lead specifically enumerated above is employed, the small amount of the metal present in accordance with the invention does not affect in any way the normal reddish-purple reflection color of the reflection-reducing coating per se, which colored reflection serves as an indication of the presence of such coating on the article. However, if an excess amount of one of such compounds is employed, the metal component may then impart a distinctive color, e. g., a red color in the case of silver, to the glass article and reduce the transparency of the coated article. The amount of the added ingredient necessary to provide the desired effect in accordance with the invention may be determined by trial, but in any event it should not be more than the amount that will dissolve in the solvent of the

particular coating suspension employed. Ordinarily, the presence in the coating suspension of around one to a few per cent by weight of the added ingredient will give the desired result. The exact proportions, however, of the materials forming the coating suspension will depend upon the particular mode of application of the coating to the article, it being usually necessary to vary the proportions in order to obtain the desired final coating thickness.

Of the various compounds specifically mentioned above, zinc acetate has been found to be particularly useful because of its distinctive property of absorbing into the glass of the article, in the manner according to the invention, at relatively low temperatures around 500° C. or so. As a result, where the article to be coated constitutes a part of an electric incandescent lamp or similar device, in the manufacture of which glass heating or fusing operations are normally required, the heat of such normal lamp-making processes, e. g., the fusion of a hard glass lens to the reflector section of a "sealed beam" type lamp, can be utilized for the heating or baking of the coated article in accordance with the invention since the glass lens attains a sufficiently high temperature up to around 500° C. for such purpose. A further advantage in the use of zinc acetate as the additive material resides in the fact that where the glass article to which the coating is to be applied is provided with sealing surfaces which are to be fused to another sealing surface, as in the aforementioned case of the fusion of a glass lens to the glass reflector section of a "sealed beam" type lamp, the presence on such sealing surfaces of a coating suspension according to the invention, and having zinc acetate as the additive ingredient, does not prevent the formation of a good fused seal between such sealing surfaces such as occurs in the case where use is made of the colloidal silica solution alone, i. e., without the incorporation therein of zinc acetate or possibly others of the additive ingredients specified hereinabove in accordance with the invention. Therefore, in the application of such a zinc-acetate containing coating to the article, it is unnecessary to remove or wipe the coating suspension off the sealing surface of the article prior to the sealing operation, and, since the labor cost is the major cost item in the application of a reflection-reducing coating to the article, a very appreciable saving in the cost of such coating application is effected by the elimination of such a wiping operation to clean the sealing surfaces. As an example of a suitable zinc-acetate containing coating suspension according to the invention, the following composition, by weight, has been found to be entirely satisfactory:

	Percent
Colloidal silica.....	4.5- 6.5
Zinc acetate.....	0.5- 3.5
Alcohol or other solvent.....	90.0-95.0

While the actual manner in which the additive metallic ingredient functions to produce the results according to the invention is not known for certain, it is thought that the zinc, silver or other metal comprising the addition ingredient coats the colloidal silica or other solid particles of the coating suspension with a thin binder layer 19 (Fig. 2) which dissolves or is absorbed into the glass of the article to be coated, as indicated at 20 in Fig. 2, and either pulls the silica or other solid particles along with it into the glass or else

replaces the soda in the glass and drives the latter out to the surface where the soda then acts as a flux to stick the silica or other solid coating particles to the glass. But regardless of the exact manner in which the addition ingredient functions in the process according to the invention, there is no question but that a much more durable and permanent reflection-reducing coating is produced which will withstand weathering and repeated washings and wiping and cleaning without being rubbed off or removed from the glass article.

The coatings 16 and 17 may be applied to the glass lens or other article 1 in a variety of ways. Thus, the lens or other article 1 may be immersed in the coating suspension containing the addition ingredient according to the invention or the coating suspension poured over the surface of the glass article or the said surface washed with the coating suspension. The article is then immediately spun to remove the excess liquid, or the article to be coated may be spun and, while spinning, a suitable quantity of the coating suspension poured upon it or otherwise applied. The speed of spinning controls to a certain extent the amount of coating material remaining on the surface and therefore the resultant thickness of the coating. Upon the evaporation of the solvent in either case, the colloidal particles 18 remain on the surfaces 14 and 15 of the article 1 and it is believed that the surfaces then consist of minute projecting irregularities whose spacings are considerably smaller than the wavelength of the light, the concentration of the said particles forming the irregularities decreasing from the surface of the article outward whereby there is a gradual increase of effective index of refraction from approximate unity at the layer-air interface to a value approaching that of the substrate at the layer-substrate interface.

After drying of the coating on the glass article 1, the latter is then heated either by the heat developed during the processing of the lamp as previously described, or it may be necessary to bake the article in an oven or lehr at elevated temperatures, from approximately 500-700° C. or so in the case of zinc acetate, or from approximately 600-700° C. or so in the case of the other additive compounds specifically mentioned hereinabove, for periods up to around one-half to one hour or so, as stated above, to effect the sticking or bonding of the colloidal particles 18 of the coatings 16, 17 to the surface of the glass article 1 in accordance with the invention.

While I have shown and described the preferred embodiment of my invention, it will be obvious to those skilled in the art that various modifications may be made without departing from the invention. Thus, instead of providing both the inner and outer surfaces of the lens 1 with reflection-reducing coatings, such coatings may be applied to only one or the other of the said surfaces. Likewise, if desired, only the outer coating 17 may be of the type according to the invention since the inner coating 16 is not exposed and is not subject to removal by weathering, washing, wiping, etc., so that it does not have to be as durable and permanent as the other coating 17.

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

1. The method of forming a transparent reflection-reducing coating on the surface of a hard glass article having a refractive index greater than unity which method comprises, coating the

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said surface of the article with a suspension comprising transparent colloidal particles of silica dispersed in a liquid dispersion medium having in solution therewith from approximately a half to a few per cent by weight of zinc acetate, removing the excess of coating material from the surface of the article and drying the remaining coating material thereon, and then heating the coated article at a temperature of from about 500-700° C. until the colloidal silica is firmly attached to said surface.

2. The method of forming a transparent reflection-reducing coating on the surface of a hard glass article having a refractive index greater than unity which method comprises, coating the said surface of the article with a suspension consisting essentially, by weight, of approximately from 4.5 to 6.5 per cent of colloidal silica, approximately from 0.5 to 3.5 per cent of zinc acetate, and approximately from 90 to 95 per cent of a solvent for the said silica and zinc acetate, removing the excess of coating material from the surface of the article and drying the remaining coating material thereon, and then heating the coated article at a temperature of from about 500-700° C. until the colloidal silica is firmly attached to said surface.

3. The method of forming a transparent reflection-reducing coating on the surface of a glass article having a refractive index greater than unity which method comprises, coating the said surface of the article with a suspension comprising transparent colloidal silica particles dispersed in a liquid dispersion medium having in solution therewith from approximately a half to a few per cent by weight of a metallic salt de-

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composable into free metal at a temperature below the softening temperature of the glass article, the said metal being absorbable into the glass of the article when the latter is in a heated condition at a temperature just below its softening point, and then heating the coated article at a temperature of from about 500° to 700° C., which is above the decomposition temperature of the said metallic salt but below the softening temperature of the glass article for a sufficient time to decompose the said metallic salt into free metal and cause absorption of the latter into the said surface of the glass article at the areas where the silica particles contact the surface of the glass whereby to attach the said colloidal silica particles to said surface.

4. The method as set forth in claim 3 wherein the said metallic salt is a zinc salt.

5. The method as set forth in claim 3 wherein the said metallic salt is a silver salt.

6. The article prepared by the method of claim 3.

7. The article prepared by the method of claim 4.

8. The article prepared by the method of claim 5.

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