

Dec. 9, 1947.

H. R. MOULTON
REFLECTION REDUCING COATING HAVING A GRADUALLY
INCREASING INDEX OF REFRACTION
Filed March 12, 1943

2,432,484

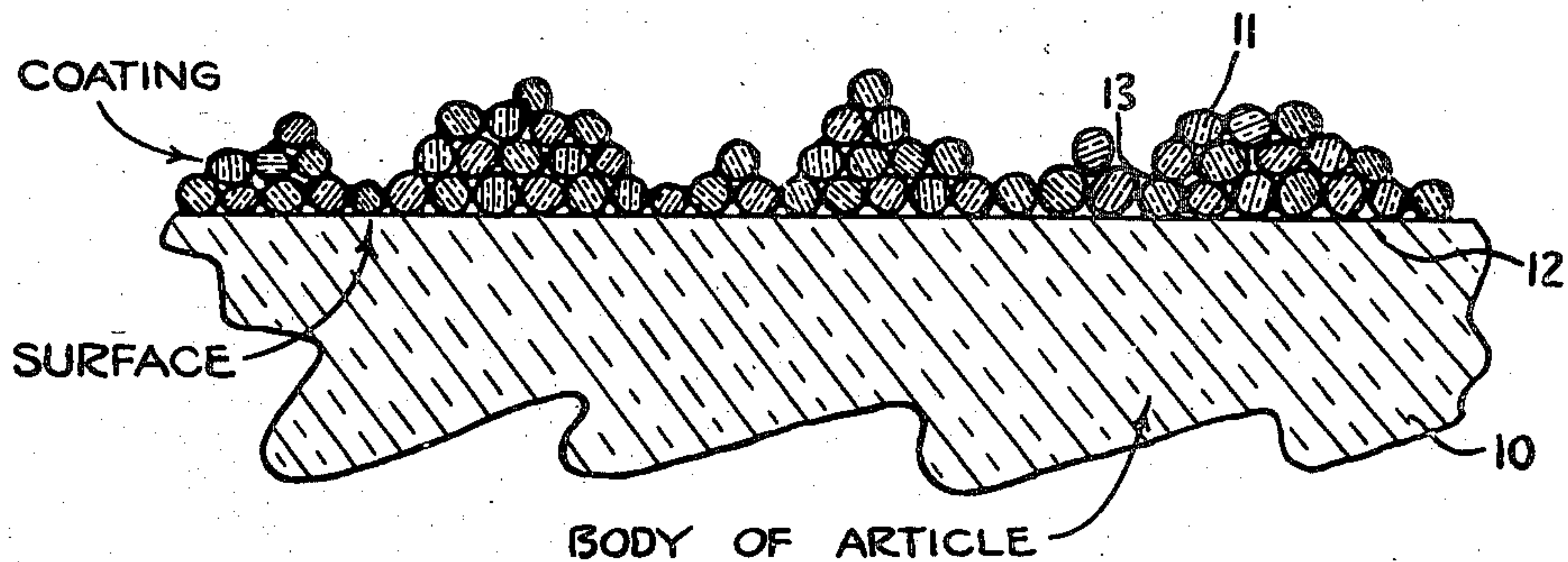


Fig. 1

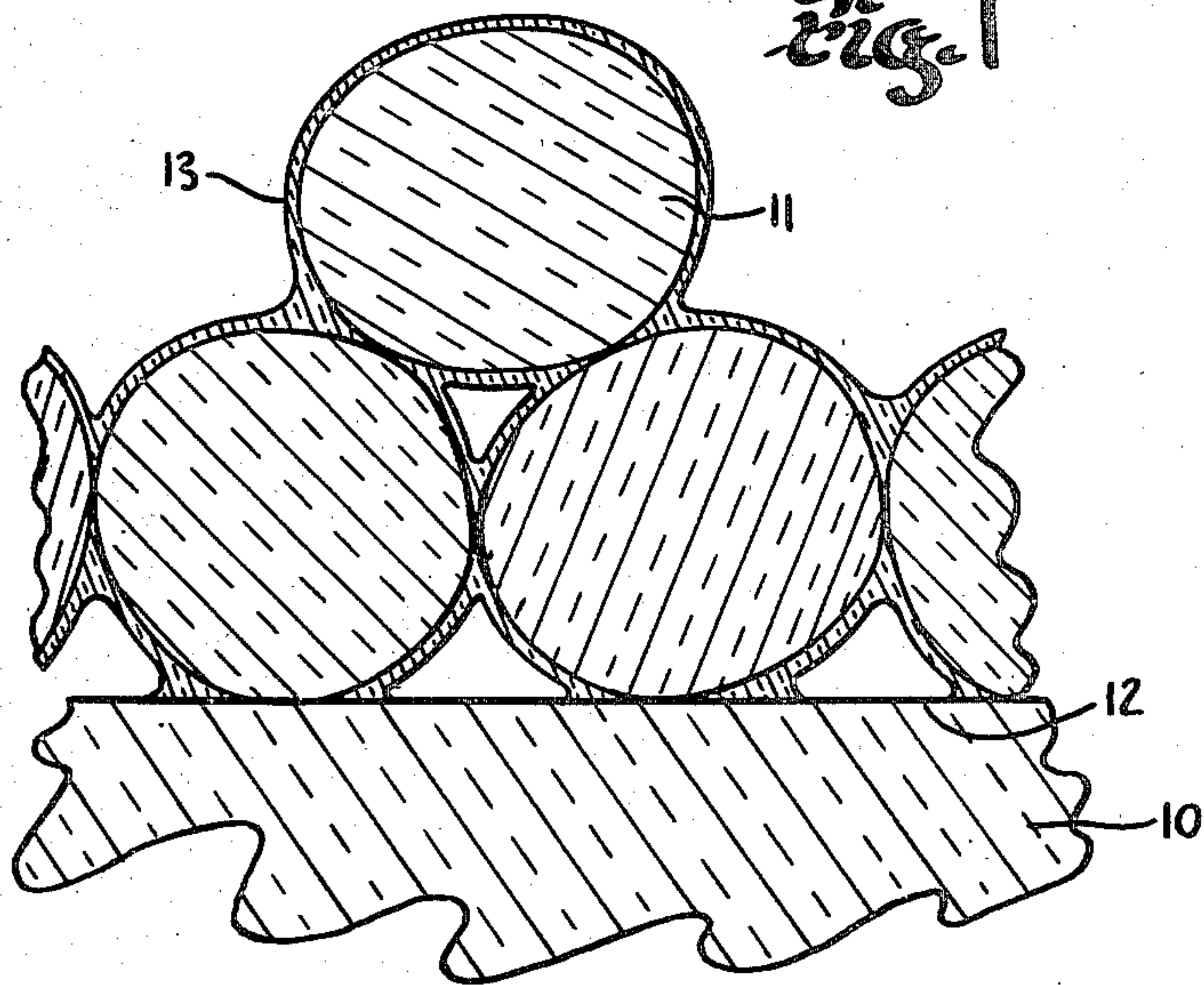


Fig. 2

INVENTOR.
HAROLD R. MOULTON

BY

Louis L. Lagoon

ATTORNEY

UNITED STATES PATENT OFFICE

2,432,484

REFLECTION REDUCING COATING HAVING
A GRADUALLY INCREASING INDEX OF
REFRACTIONHarold R. Moulton, Southbridge, Mass., assignor
to American Optical Company, Southbridge,
Mass., a voluntary association of Massachusetts

Application March 12, 1943, Serial No. 478,980

6 Claims. (Cl. 88—1)

1

This invention relates to new and novel means for reducing surface reflections and of producing articles having such surfaces thereon.

This application is a continuation in part of my copending application, Serial No. 452,356, filed July 25, 1942.

One of the principal objects of the invention is to provide novel and improved means for reducing the reflection of light impinging upon the surface of an article whereby, in the case of a transparent article, a greater percentage of incident light will traverse said article, and in the case of an opaque article the reflectivity of said articles will be reduced.

Another object is to provide surface coatings of the above character which are relatively durable and permanent.

Another object is to provide an article with a reflection reduction coating thereon and to provide said reflection reduction coating with a bonding coating with substantially no altering of the reflection reduction characteristics of the initial coating.

Another object is to provide a unitary coating mixture having embodied therein means for reducing surface reflections and means for rendering said coating more resistant to removal.

Another object is to provide novel means for rendering a coated article more resistant to impact, more resistant to rapid temperature changes and strong temperature gradients without damage to the coating.

Another object is to provide a surface coating composition which may be more uniformly applied to the articles to be coated through the reduction of surface tension of the coating compound.

Another object is to provide novel means for modifying surface coating compositions of the character described for rendering them more adaptable to particular coating conditions.

Another object is to provide means for producing low surface reflection coatings of high light transmitting power, substantially non-selective as to the color of the reflected or transmitted light.

Another object is to provide new and improved means of fortifying surface reflection reducing coatings which inherently are readily susceptible to injury and novel means for applying said fortifying means either independently of the application of the non-reflection coating or simultaneously with the applications of said non-reflection coating.

Other objects and advantages of the invention

2

will become apparent from the following description and it will be apparent that many changes may be made in the details of composition, construction and arrangement of parts shown and described without departing from the spirit of the invention as expressed in the accompanying claims. I, therefore, do not wish to be limited to the exact details of construction and arrangement of parts shown and described as the preferred forms only have been given by way of illustration.

In the drawing,

Figure 1, illustrates in diagrammatic form a highly magnified fragmentary sectional view of an article having a surface reflection reducing and transmission increasing coating on a surface thereof according to the invention and

Fig. 2 illustrates a more highly magnified fragmentary cross sectional view thereof.

In following the teachings of the invention the article 10 which is to be coated may be of a light transmitting nature such as glass plates, lenses, prisms or other optical elements and similar elements formed of plastics or artificial resins. In this particular instance, the element, as stated above, is to have light transmitting properties and finished optical surfaces thereon.

In the present instance, the articles referred to are particularly of the type which are adapted for use in telescope systems, field glasses, binoculars, projectors, camera lenses, periscopes, windows or for any other uses in which the light is adapted to impinge upon a surface of the article. The surface 12 of said articles 10, in order to reduce surface reflection and to increase light transmission, is coated with a layer of discrete submicroscopic microgranular transparent particles 11 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 10 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.

As examples, such suspensions of colloidal particles may be given with aqua sols or organo sols of lithium fluoride, magnesium fluoride, strontium fluoride, calcium fluoride, barium fluoride, cryolite and in general transparent solids in the

form of sols. If desired, sols of titanium dioxide, silicon dioxide or the like may be used.

Because of its chemical inertness and stability in the form of a sol a colloidal silica sol in water or other suitable solvents such as ethylene glycol monoethyl ether or a mixture of solvents is most useful for this purpose.

Such a suspension may be prepared as described in "Inorganic Colloid Chemistry," by Weiser, volume II, published by John Wiley & Sons, Inc., New York, 1935, or a chemical composition which falls within the following formula may be used:

| | | |
|---|------------|----------|
| SiO ₂ ----- | per cent-- | 10 to 12 |
| Na ₂ O, less than ----- | do----- | 0.1 |
| Na ₂ SO ₄ , less than----- | do----- | 0.05 |
| Fe ₂ O ₃ +Al ₂ O ₃ , about----- | do----- | 0.1 |
| pH about----- | | 9.5 |

in which the silica is in the form of sub-microscopic, discrete, micro-granular, transparent solid particles.

A water suspension containing approximately 3 parts colloidal silica as described above, and 100 parts of water when applied to the surface of the transparent material, it has been found by experiment, produces a coating of the nature described which is highly efficient. This coating may be applied in several ways. The lens or other articles may be immersed in the liquid, removed and immediately spun to remove excess liquid or the article to be coated may be spun and while still spinning a suitable quantity of the suspension poured upon it or otherwise applied. The speed of spinning controls to a certain extent the amount remaining on the surface and therefore the resultant thickness of the coating. Upon the evaporation of the solvent in either case the colloidal particles 11 remain attached to the surface 12 of the article 10 and it is believed that the surface then consists of minute irregularities whose spacings are considerably smaller than the wave length of the light, which irregularities become less and less as the surface of the article is approached whereby there is a gradual increase of effective index from approximate unity at the layer-air interface to a value approaching that of the substrate at the layer-substrate interface.

While coatings of the nature described are less sensitive to thickness variations and the disadvantageous effect of said variations upon the efficiency as to reflection reduction than reflection reducing coatings depending upon the building up of a layer from some odd multiple of 1/4 wave length optical thickness as in the prior art, at the same time it is desirable to control the thickness of the deposit of solid sub-microscopic, micro granular colloidal particles.

The thickness may be varied over a relatively wide range as compared to prior art coatings with good efficiency but the color of the reflected light and consequently the color of the transmitted light is affected by the thickness of the colloidal layer. 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. The concentration of solution which will produce such a deposit depends upon its method of application. For example, if the coating is applied by spinning or is applied by dipping and spinning or by pouring the liquid containing the colloidal particles on the article

the higher the speed of rotation the more concentrated the solution can be and the lower the speed of rotation the lower the concentration of the solution.

In the case of articles which are coated by being dipped into the solution and withdrawn continuously the more rapid the withdrawal the lower the concentration of the colloidal particles of the solution should be and conversely the lower the rate of withdrawal the more concentrated the solution should be. The use of other methods such as withdrawal of the liquid from the stationary article by pumping, syphoning, draining, etc., has the same effect and requirements.

If the coating is to be applied by spraying, the pressure at the spray gun of the impelling gas, the concentration of the solution, the distance of the spray gun from the article to be sprayed, the viscosity of the solution and the concentration of the solution are all variations which may be independently varied but which must be controlled.

If the dipping or draining method is used, as stated above, the rate of removal of the article from the solution and the concentration of the sol, the volatility of the solvent used and to a certain extent the temperature must be taken into account.

The criterion in all cases is the appearance of the coat after the solvent has evaporated. As stated above, the most advantageous coat is one in general which appears reddish purple by reflected light. If the coating is too thick the trend is toward the blue but if the thickness of the coating is increased above that which will produce a blue cast, red, yellow, green or blue coats may result indicating that there is some influence of thickness upon the color of the reflected light. If the coating is extremely thin the efficiency will be relatively low as to the reduction of surface reflections and as the thickness is increased to a point still under that which will produce the red purple reflection the color of the reflected light passes through a brown stage indicating that the surface reflection reduction is not at its maximum and that the thickness of the coating resulting from the evaporating of the solvent carrying the dispersed colloidal material is too thin. A little experience in one or two preliminary tests will serve to correct and overcome any difficulties which may arise because of the wrong thickness being applied. Once a method of application has been selected the easiest control consists in varying the concentration of the colloidal suspension by the addition of suitable solvents such as set forth herein. Even too thick a coating unless it greatly exceeds the thickness which will produce the red purple is still rather efficient but as a few trials will indicate the proper dilution for the given method of application it is clear that the red purple should be aimed at. For example, it may be desirable in order to compensate for the color absorption in the transparent substrate to reflect selectively certain portions of the spectrum whereby the sum total of the effects of absorption and reflection will be neutral or uncolored or it may be desirable in certain of the components of an optical system to introduce an intentional slight distortion of the color of the transmitted light in order to compensate for an opposite distortion in other optical elements thereby functioning as compensating means. It should again be stressed that the method of reflection reduction described is a general one wherein the actual transparent submicro-

scopic colloidal microgranular particles actually used would be selected with a due regard to chemical and physical stability and that at the present time the composition of choice is colloidal silica but for special uses materials more sensitive chemically and physically might be used such as the fluorides mentioned above.

The actual sols need not be of an inorganic nature. Organic sols, that is, sols in which the solid component is of an organic nature provided it fulfills the other requirements of transparency micro-granularity and sub-microscopic size will also be effective in producing surface reflection reduction but in general the most stable material chemically would be selected. A fortifying solution or composition may be applied as a separate coating or may be mixed with the above described reflection reduction coating with substantially no adverse effect as to the efficiency of said reflection reducing coating.

Another surface reflection reducing solution consists of the suspension of colloidal silica in a substantially anhydrous solvent such as the compound commercially known as ethylene glycol monoethyl ether. Of course, other liquids or mixtures of liquids may be used and the above are given only by way of illustration as they have been found workable and to have desirable characteristics. In the case of the water solution it may be desirable to incorporate in the solution a small quantity of a surface-tension-reducing ingredient such as a compound similar in its action to the sulphonated higher alcohols. The production of the ethylene glycol monoethyl ether suspension of colloidal silica is accomplished by incorporating the desired quantity of ethylene glycol monoethyl ether with the calculated quantity of aqueous suspension of colloidal silica such as the aquasol as referred to above. When the ethylene glycol monoethyl ether is used as the suspending means, it is desirable that at least most of the water be removed. An acidified mixture of ethylene glycol monoethyl ether and aquasol at a pH of less than 5.0 is accordingly heated to a temperature sufficient to evaporate the water which volatilizes more rapidly than the ethylene glycol monoethyl ether which has a higher boiling point. A convenient way to lower the pH to the desired extent is by the addition of hydrochloric acid to the ethylene glycol monoethyl ether before adding the aquasol of silica. Other acids may be used, such as sulphuric acid, hydrobromic acid, acetic acid, etc. If a sufficient reduction in volume has taken place (about 10%) and it has been found that sufficient water has been removed the solution is then made up to the original volume by the addition of ethylene glycol monoethyl ether and is then ready for use. A generally useful solution has a 3% content of colloidal, submicroscopic microgranular silica. Such a solution may be termed solution A. Of course, for certain types of coatings, such as for large areas, the ultimate dilution may be greater than the original strength of the solutions.

After the application of the above described coating the said coating may be readily removed from the article by wiping if the coating, for some reason, is uneven or otherwise unsatisfactory. The coating is very resistant to the attack of many solvents, as silica itself is extremely insoluble and inert chemically. The coating as produced is however not firmly adherent to the substrate in all instances, an advantage in the reclaiming of defectively coated articles.

To render said coating more resistant to wip-

ing and handling, there is applied to the first layer of finely divided micro granular colloidal transparent material, a transparent binder layer 13 which serves to anchor in position the discrete particles 11 forming the surface reflection reducing layer itself without completely filling in the spaces between them. This binder layer sets and binds in place the discrete particles forming the surface reflection reducing layer itself. The binder layer does this at relatively low temperatures such as 100° C. or even at room temperature and can therefore be used for cemented optical components, plastics and the like.

This treatment is applied by means of a dilute solution of tetraethylorthosilicate in an organic solvent such as ethyl acetate-denatured alcohol mixture containing a small amount of hydrochloric acid. This solution, when applied in a manner as described above and evaporated and allowed to react and set becomes a binder for holding the minute sub-microscopic micro-granular colloidal particles in position and in firm contact with the substrate. Other organic solvents or mixtures of such solvents may be used, in which the ethyl silicate and the acid are soluble, such as ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, ethyl alcohol, methyl alcohol, etc., butyl alcohol, and/or mixtures in such proportions and so selected as to give desirable evaporation characteristics.

A binder coating solution is prepared as follows:

A stock solution of from 1 to 10 per cent by volume of tetraethylorthosilicate, 0 to 60 per cent by volume ethyl acetate, 1 to 10 per cent by volume concentrated hydrochloric acid and the balance ethyl alcohol. Denatured alcohol may be substituted for the ethyl alcohol. A preferred stock solution is five parts of tetraethylorthosilicate, 50 parts of ethyl acetate, 50 parts of denatured alcohol and 5 parts of concentrated hydrochloric acid, mixed in the order given. This gives a clear, colorless, stable stock solution termed solution C. An essential feature of this solution is aging for several days before use. The exact reason for this is not known but it is believed to be a partial decomposition of the tetraethylorthosilicate by the hydrochloric acid resulting in an organo-sol of either hydrated or unhydrated silica. With the composition set forth above, an aging of from two to six days is desirable. The organic solvents used are given by way of illustration only. Other solvents which are miscible, such as methyl acetate, methyl alcohol, isopropyl alcohol, etc. may be used.

This binder coating, it is believed, does not fill in the pores between the colloidal sub-microscopic micro granular particles but simply coats and anchors each particle in the related position which they have assumed in the forming of the first coating when applied at proper dilution. The dilution used depends upon the method of application.

If it is desired to remove this fortified reflection reducing coating having the bonding coating applied to it, this can be done by the use of dilute alkaline solutions, such as dilute sodium hydroxide solution, potassium hydroxide solution or other solutions of like nature which have a solvent effect upon such binder coats. After suitable treatment with the alkaline cleaning solution the article is flushed with water to remove the excess alkali and then may be wiped and reprocessed, the article prior to reprocessing being in its pristine condition. The dilute binder coating solu-

tion is prepared from the stock solution C described above. This stock composition is diluted for producing binder coating solution by diluting with suitable solvents, such as ethyl acetate, ethyl alcohol and mixtures of these two or other known desirable solvents such as isopropyl alcohol, ethyl acetate, methyl acetate, etc. until the application of one or more binder coatings does not significantly reduce the amount of surface reflection reduction produced by the first colloidal or base coating. It is, of course, obvious that by suitable dilution this coating can be applied several times if desired with increased mechanical stabilization of the first reflection reducing coating.

The liquids used for dilution should be selected with due regard to their miscibility, evaporation rates, surface tension, etc., in accordance with the known art of lacquer and paint formulation.

The binder coating solution may be applied by the same general methods used in applying the reflection reducing or base coating.

The above is an example of a preferred coating but other binders in suitable dilution and solvents may be used such as gelatin in water, polyvinyl alcohol in water, resins, etc. in organic solvents and the like depending upon the use to which the resultant article is to be put.

It has also been found that other fortifying compositions may be used. For example, a dilute solution in water of sodium silicate may be used, the dilution being such that the reflection-reduction previously produced is not destroyed. If the solution of the sodium silicate is too strong the reflection reduction will be interfered with. A suitable composition consists of H_2O —200 parts and sodium silicate—1 part by weight. This may be applied by dipping, spraying, spinning and the like. Upon drying the sodium silicate serves to bond the colloidal particles to each other and to the glass or article being treated thereby giving increased resistance to wiping. If desired, after the sodium silicate solution has been applied and dried the article may be treated with dilute hydrochloric acid solution in water whereby the sodium silicate is decomposed and silica liberated which serves to bond together the colloidal silica particles which have been previously applied, the sodium chloride formed simultaneously being washed away by the water in the dilute acid solution. Other acids, of course, may be used for this purpose such as nitric, sulphuric, acetic, hydrobromic, etc.

In this case the use of a colloidal silica sol is described. The aqueous sol, while quite effective, is not as easy to apply nor as efficient, in general, as the ethylene glycol monoethyl ether sol. The method described above for producing the ethylene glycol monoethyl ether sol solution A; namely, the addition of freshly distilled ethylene glycol monoethyl ether to the aqueous sol and the subsequent removal of most of the water of the aquasol while heating to approximately $50^\circ C.$, although usable, if obtained by this later method will be greatly improved upon. The heating operation for removing the moisture by following the first described method had to be of long continuation and was very critical, as the mixture had a tendency to jell or coagulate, whereby the colloidal silica had a tendency to separate from the solution and if great care was not exercised the resulting composition was useless and had to be thrown out.

It has now been found that it is a relatively simple matter to produce such compositions by

the addition to the ethylene glycol monoethyl ether of approximately 1% of concentrated hydrochloric acid before the addition of the ethylene glycol monoethyl ether to the aquasol. In fact, it is possible to make a concentrated sol of the silica in ethylene glycol monoethyl ether by the following method:

A certain volume of ethylene glycol monoethyl ether is taken and to it is added 1% of its volume of concentrated hydrochloric acid. A quantity of aquasol equivalent in volume to the ethylene glycol monoethyl ether is then added with stirring. The resulting mixture is placed in a flask and boiled vigorously until the volume has been reduced to that of the original ethylene glycol monoethyl ether or somewhat less. The result is a concentrated ethylene glycol monoethyl ether sol termed Solution B which can then be used as a master composition which is diluted as desired with miscible liquids, such as ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, alcohol, ethyl acetate, etc. Ethylene glycol monomethyl ether, ethylene glycol monobutyl ether, ethylene glycol monoethyl ether acetate and similar compounds may replace the ethylene glycol monoethyl ether with advantages in some cases. Suitable mixtures of low, medium and high boiling point solvents may be used. The solvents described above are given only by way of illustration as other organic solvents compatible with the aquasol and having boiling points above that of water may be used. Even water may be used for diluting the organo sol concentrate but the resulting composition is not preferable to that of the silica aquasol alone. The use of surface active agents, that is, materials which reduce surface tension, makes it possible under some circumstances to use the colloidal silica in the form of an aquasol but for most uses the organosol, such as the ethylene glycol monoethyl ether sol, is preferable. For example, a surface active material such as di octyl sodium sulfo succinate, may be used in the amount of from .01 to .1 of 1% by weight based on the total solution. Palm kernel oil soap in the same proportion is also effective.

Dilution of the concentrated ethylene glycol monoethyl ether sol with 4 to 5 times its volume of pure ethylene glycol monoethyl ether gives a solution corresponding to Solution A described above.

Another solution found useful has the following composition:

| | Parts by volume |
|---------------------------------|-----------------|
| Butyl alcohol | 75 |
| Ethylene glycol monobutyl ether | 10 |
| Ethylene glycol monoethyl ether | 75 |
| Ethyl alcohol | 150 |
| Solution B | 50 |

Another variant when used for dipping articles having large area, such as windows, window panes, may be made up as follows:

30 parts of aquasol (containing substantially 12% actual colloidal silica) are diluted with 2000 parts of methyl alcohol or acetone. In place of the aquasol an equal quantity of the ethylene glycol monoethyl ether sol concentrate, solution B, described above may be used. A large sheet of material may be dipped in this composition, removed and allowed to drain and dry. After drying, a second coat is applied in like manner and drained in the opposite direction to equalize the coating. For fortifying the coating, that is, rendering it more resistant to abrasion, this may be followed by a single dip consisting of 2000 parts

acetone or alcohol and 200 parts of an aged tetraethylorthosilicate composition consisting of 50 parts denatured alcohol, 50 parts ethyl acetate, 5 parts hydrochloric acid and 5 parts tetraethylorthosilicate, solution C. After having been dipped in this last composition and allowed to dry the article is then heated to a temperature from 50 to 100° C. moist heat for about an hour. If the article is of such a nature that it can be heated to a higher temperature than 100° C. the temperature to which it is heated may be raised to any desired extent within practical limits and the time correspondingly shortened.

It has been found that after the application of a silica organosol to the surface of an article, in this case, glass, followed by the fortifying layer, the article may be advantageously heated nearly to the softening point of the glass. This is particularly desirable in the case of protection lenses which are heat treated to increase their resistance to impact and in the case of large areas, such as searchlight windows, which are heat treated to increase their resistance to rapid temperature changes and strong temperature gradients. When treated in this way the resistance of the coating is greatly increased over coatings which have been heat treated only to the temperature of 100° C. A usual temperature for such heat treatment might be as high as 500 to 800° C. It is usual to heat such articles to this temperature for a period of 1 to 5 minutes depending upon the thickness of the article and its other dimensions. The "hardening" or toughening is accomplished by subjecting the articles to a blast of cool air or other gaseous media.

It has been found that a type of reflection-reducing-coating which is completely new and novel can be produced by a combination of treatments and solutions, for example, if a piece of glass having an index of 1.523 is coated with a composition consisting of 50 parts ethyl acetate, 50 parts denatured alcohol, 5 parts tetraethylorthosilicate, 5 parts of hydrochloric acid, solution C, the composition having been aged for several days and the coated article baked at approximately 100° C. in a moderately moist atmosphere for a period of time which may vary from 5 minutes to 1 hour or more and subsequently coating this article after cooling with a ethylene glycol monoethyl ether sol containing approximately 3% by weight of colloidal silica of the type described above followed by the application in a moist atmosphere of a fortifying coating as described above, that a low reflecting coating is obtained. The original coating produced from solution C is applied in such thickness as to have a pinkish brown appearance by reflected light when both surfaces are coated. This result is achieved by spinning more rapidly than would result in a bluish coating, by dilution of solution C with alcohol, ethyl acetate, ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, or other compatible solvents, by both methods, or by other means such as slow withdrawal from immersion, etc. This coating differs from all coatings previously described or known in that the extremely small amount of light reflected from it is not colored, that is, the glass on which the coating has been produced appears to have a dark gray reflection. This is completely new as far as is known. All other known non-reflection coatings have increased reflection at some portion of the spectrum whereby a blue, purple or brown appearance is imparted to the reflected light, the transmitted light being deficient in the colors which were se-

lectively reflected by the coating. In the case of the truly neutral coating which is produced as described above the light transmitted by the coated article, which may be a lens element, prism, etc., does not have its true spectral properties distorted or changed. This freedom from distortion of color values is particularly desirable in multi-component optical systems in which the number of surfaces is considerable. This is especially true in the case of camera or projection optics which are to be used in combination with color photography inasmuch as the colors will not be degraded. If desired, a small amount of water may be incorporated in the fortifying composition, instead of using the moist atmosphere.

It has also been found that the fortifying layer can be formed simultaneously with the reflection-reducing layer by the addition of a tetraethylorthosilicate containing composition to the ethylene glycol monoethyl ether-silica-sol-containing solutions. The proper quantity to be added depending upon the method of application but in all instances the amount being sufficient to produce the fortifying effects desired without appreciably reducing the reflection-reducing characteristics. For example, a solution for both the production of a reflection reducing coating and for simultaneously fortifying said coating may be formed substantially as follows:

| | Parts by volume |
|-------------------------|-----------------|
| Solution A | 100 |
| Ethyl alcohol | 18 |
| Ethyl acetate | 18 |
| Tetraethylorthosilicate | 2 |
| Hydrochloric acid | 2 |

The proportions of the above may be varied, depending upon the use and method of application as described above.

Another solution may be formed substantially as follows:

| | Parts by volume |
|---------------------------------|-----------------|
| Butyl alcohol | 160 |
| Ethylene glycol monobutyl ether | 95 |
| Ethyl alcohol | 450 |
| Solution B | 100 |
| Solution C | 50 |

The tetraethylorthosilicate may be added directly as part of the mixture instead of being added in the form of Solution C, the acid also being separately added in case the presence of ethyl acetate is objectionable, especially when coating plastics.

Other suitable solvents may be used, such as heretofore referred to, having a due regard to balancing the evaporation rates etc.

It has been observed that when a layer of colloidal silica of the unfortified type has been applied to a glass surface that writing upon it with a metal point or with a pencil produces a mark. Upon wiping off the unfortified coating the mark is not removed but remains as a permanent mark on the glass surface. Identification or other desirable markings may be made in this manner. This may also lend itself to the production of reticules. The mark may be applied to the fortified coating, both coating and mark being then relatively permanent.

For spraying the sol it is desirable to have a suitable balance of solvents. While the ethylene glycol monoethyl ether sol in proper dilution with ethylene glycol monoethyl ether is usable, the addition of other ingredients, such as higher boiling miscible solvents such as butyl alcohol, ethylene glycol monobutyl ether, ethylene glycol mono-

ethyl ether acetate and the like and the addition of more volatile solvents such as ethyl alcohol etc. as above stated produces better spray-ability whereby a more uniform coating is obtained with the usual spray gun.

Another variant of the coatings may be as follows:

Under certain conditions increased efficiency and reflection reduction can be obtained by applying a coating through the use of the sol, then a coating of the tetraethylorthosilicate stock solution C in full strength (containing 5% tetraethylorthosilicate), heating to stabilize and fortify the coatings following which, after cooling, another layer identical with the first is applied. The final coating may then be fortified by means of a dilute tetraethylorthosilicate-containing composition and coatings thus produced are extremely low in reflection, quite stable and fairly neutral as to color.

It has been found that the application of a layer of the nature described to the surface of a photographic print on paper or other material results in a great improvement in the range of lights and shades delineated on the photographic print. The ordinary photographic print ranges from perhaps 90% reflection of the incident light (in the white portion of the picture) to perhaps 10% reflection in the black portions of the picture. By treatment, as described above, the "black" becomes blacker because the diluting reflected white light from the more or less glossy surface of the paper is substantially eliminated and the print then takes on the appearance of a platinum bromide print.

The application of the base coating of the nature described for surfaces of a photographic print is particularly effective in the case of photographic prints made on matté paper such as is used for the highest grade photographic prints. It is not generally recognized how much diluting white light is reflected from the black portions of a photographic print or matté paper until a coating of the nature described has been applied for comparative purposes. Of course, the coating is also highly effective on glossy prints.

The application of such a surface reflection reducing layer is also extremely effective upon oil paintings whereby again the diluting white light reflection is substantially eliminated and the true values of the colors are visible to an observer without the necessity of elaborate lighting arrangements. In fact, even under the most elaborate lighting arrangements the effect is not as satisfactory as in the case where the above described reflection reducing coating is applied because of the roughness of texture of the surface of the oil painting, which renders it impossible to eliminate all reflection by modification of either direct or indirect light.

The surfaces of maps protected by glossy coatings may also be made less reflecting and more readily visible by means of the coating described above, with the said coating functioning also as a preservative either for the oil paintings or maps or any articles to which it may be applied.

In certain optical instruments it is desired to obtain the effect of front surface mirrors. Ordinarily this requires the reflecting coating to be placed on the front of the article. However, the use of a transparent material with the reflecting surface on the back but having a coating of the nature described above on the front surface becomes in effect a front surface mirror in that the annoying and objectionable reflections from the

transparent front surface are substantially eliminated whereby the double image effect is removed.

It is generally considered that dispersions of solids and liquids, customarily called colloidal solutions, are not true solutions. For convenience, applicant uses the term "solution" for such suspensions of colloidal material in liquids. The mixtures which are called "solutions" are liquids filterable under certain conditions and for all practical purposes may be considered as solutions. A very wide variation in the actual solvent composition may be made in order to adapt the solutions for use with widely varying methods of application by following the teachings set forth herein. Stock solutions of the coating mixture disclosed herein may be provided in which instances solvents may be added according to the particular intended use.

From the foregoing description, it will be apparent that simple, efficient and economical means have been provided for accomplishing all of the objects and advantages of the invention.

Having described my invention, I claim:

1. A coated article comprising a substrate whose refractive index is greater than unity, said article having a transparent surface reflection reducing coating on a surface thereof, said coating comprising a layer of sub-microscopic, discrete, micro-granular, transparent solid particles forming minute projecting irregularities on said surface which are sensibly smaller than a wavelength of the light transmitted, the concentration of the said particles in the irregularities decreasing from the surface of the article outward and the material of the particles being such that the effective index of refraction of said coating varies from substantially unity at the layer-air interface to an index value which progressively increases in a direction inwardly of said coating and approaches the index of refraction of the material of the substrate, and the total thickness of the coating being of the order of $\frac{1}{4}$ wavelength of the light transmitted.

2. A coated article comprising a substrate whose refractive index is greater than unity, said article having a transparent surface reflection reducing coating on a surface thereof, said coating comprising a layer of sub-microscopic, discrete, micro-granular, transparent solid particles forming minute projecting irregularities on said surface which are sensibly smaller than a wavelength of the light transmitted, the concentration of the said particles in the irregularities decreasing from the surface of the article outward and the material of the particles being such that the effective index of refraction of said coating varies from substantially unity at the layer-air interface to an index value which progressively increases in a direction inwardly of said coating and approaches the index of refraction of the material of the substrate, the total thickness of the coating being of the order of $\frac{1}{4}$ wavelength of the light transmitted and a transparent thin reinforcing coating on the exterior of said particles bonding them to each other and to the surface of the substrate while maintaining connecting interstices between said particles.

3. A coated article comprising a substrate whose refractive index is greater than unity, said article having a transparent surface reflection reducing coating on a surface thereof, said coating comprising a layer of sub-microscopic, discrete, micro-granular, transparent solid particles of silica forming minute projecting irregularities

13

on said surface which are sensibly smaller than a wavelength of the light transmitted, the concentration of said particles in said irregularities decreasing from the surface of the article outward so that the index of refraction of said coating varies from substantially unity at the layer-air interface to an index value which progressively increases and approaches the index of refraction of silica at the substrate and the total thickness of the coating being of the order of $\frac{1}{4}$ wavelength of the light transmitted.

4. A coated article comprising a substrate whose refractive index is greater than unity, said article having a transparent surface reflection reducing coating on a surface thereof, said coating comprising a layer of sub-microscopic, discrete, micro-granular, transparent solid particles of silica forming minute projecting irregularities on said surface which are sensibly smaller than a wavelength of the light transmitted, the concentration of said particles in said irregularities decreasing from the surface of the article outward so that the index of refraction of said coating varies from substantially unity at the layer-air interface to an index value which progressively increases and approaches the index of refraction of silica at the substrate, the total thickness of the coating being of the order of $\frac{1}{4}$ wavelength of the light transmitted and a transparent thin reinforcing coating on the exterior of said particles bonding them to each other and to the surface of the substrate while maintaining connecting interstices between said particles.

5. A coated article comprising a substrate whose refractive index is greater than unity, said article having a transparent surface reflection reducing coating on a surface thereof, said coating comprising a layer of sub-microscopic, discrete, micro-granular, transparent solid particles forming minute projecting irregularities on said surface which are sensibly smaller than a wavelength of the light transmitted, the concentration of the said particles in the irregularities decreasing from the surface of the article outward and the material of the particles being such that the effective index of refraction of said coating varies from substantially unity at the layer-air interface to an index value which progressively increases in a direction inwardly of said coating and approaches the index of refraction of the material of the substrate, the total thickness of the coating being of the order of $\frac{1}{4}$ wavelength of the light transmitted, and a transparent thin reinforcing coating of silica on the exterior of said particles bonding them to each other and to the surface of the substrate while maintaining connecting interstices between said particles.

14

6. A coated article comprising a substrate whose refractive index is greater than unity, said article having a transparent surface reflection reducing coating on a surface thereof, said coating comprising a layer of sub-microscopic, discrete, micro-granular, transparent solid particles of silica forming minute projecting irregularities on said surface which are sensibly smaller than a wavelength of the light transmitted, the concentration of said particles in said irregularities decreasing from the surface of the article outward so that the index of refraction of said coating varies from substantially unity at the layer-air interface to an index value which progressively increases and approaches the index of refraction of silica at the substrate and the total thickness of the coating being of the order of $\frac{1}{4}$ wavelength of the light transmitted, and a transparent thin reinforcing coating of silica on the exterior of said particles bonding them to each other and to the surface of the substrate while maintaining connecting interstices between said particles.

HAROLD R. MOULTON.

REFERENCES CITED

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

UNITED STATES PATENTS

| Number | Name | Date |
|-----------|----------------|----------------|
| 1,477,938 | Britton | Dec. 18, 1923 |
| 2,230,369 | Wise | Feb. 4, 1941 |
| 1,549,814 | Swett | Aug. 18, 1925 |
| 2,356,553 | Weissenberg | Aug. 22, 1944 |
| 2,207,656 | Cartwright | July 9, 1940 |
| 2,027,931 | Ray | Jan. 14, 1936 |
| 2,269,059 | McLachlan | Jan. 6, 1942 |
| 2,329,632 | Marsden | Sept. 14, 1943 |
| 2,220,862 | Blodgett | Nov. 5, 1940 |
| 2,331,716 | Nadeau et al. | Oct. 12, 1943 |
| 2,348,704 | Adams | May 16, 1944 |
| 2,366,516 | Geffcken | Jan. 2, 1945 |
| 1,809,755 | King | June 9, 1931 |
| 2,347,733 | Christensen | May 2, 1944 |
| 1,809,755 | King et al. | June 9, 1931 |
| 2,369,741 | Jones et al. | Feb. 20, 1945 |
| 1,698,302 | Goss | Jan. 8, 1929 |
| 2,110,363 | Howells et al. | Mar. 8, 1938 |

FOREIGN PATENTS

| Number | Country | Date |
|---------|---------------|--------------|
| 134,160 | Great Britain | Aug. 6, 1919 |

OTHER REFERENCES

Strong, article in J. O. S. A., vol. 26, January 1936, pages 73, 74.