finely divided pigments suspended in sodium silicate vehicle ... the silica to soda in the silicate having the ratio of 3.22 to 3.86.

Examiner

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LIGHT-DIFFUSING COATING MATERIAL

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This invention relates to coating material for hollow glass bodies or hollow vitreous articles such as incandescent electric lamp bulbs, or for translucent screens, such material being especially adapted to produce a light-diffusing film.

The method by which the coating material of the present invention is applied, and the product of such method, are described and claimed in an application filed jointly by the present applicant, Alfred F. Bahlke and Stuart F. Marvin, filed concurrently herewith.

In the manufacture of electric incandescent lamps it has been recognized for some years that there are important advantages in providing a translucent or "frosted" bulb. Included among these advantages are the reduction of glare of the incandescent filament and the diffusion of the light emanating therefrom. Various methods have been employed to render the bulb light-diffusing; for instance, a common method of accomplishing this result is to frost the glass either inside or outside by means of an etching fluid, or the bulb may be made either partially or wholly of an opal glass, or a coating of light-diffusing nature may be applied either to the inside or to the outside of the bulb.

The production of good light-diffusing bulbs has become increasingly important with the increased efficiency rating of lamps at present manufactured. For instance, a 60 watt lamp at first had an efficiency of 11.6 lumens per watt, whereas a lamp of this same wattage now has an efficiency of 13.97 lumens per watt, the increased efficiency being in the main due to the use of filaments, notably tungsten, which concentrate the light source to a relatively small space. Because of the increased intensity and concentration of the light source, bulbs hitherto designed or treated to produce translucent light-diffusing surfaces are now inadequate properly to diffuse the light. The result is that such lamps manifest a very considerable amount of the very localized brightness and glare which present methods of frosting or coating, or making of opalescent glass, were originally designed to eliminate.

Opal glass is very expensive and has not been found to be practicable in the quantity production of electric incandescent lamp bulbs. Frosting by etching requires great care in controlling the action of the etching fluid, and invariably results in a bulb considerably weaker than a clear, unfrosted bulb.

The coating of such bulb with a specific coating material has been thought by many to be the most practicable method of obtaining the desired translucent bulb. However, no satisfactory method has hitherto been devised to coat the inside of lamp bulbs of all types and wattages. It has not hitherto been practical to coat gas-filled lamps of the kind known in the industry as "type C" or gas-filled incandescent lamps, and even in the case of vacuum lamps it has been found unsatisfactory to coat lamps larger than 40 watt size. It is true that gas-filled lamps are on the market which have an inside coating on the round of the bulb only, but such lamps must be burned in a position with the base upward in order to avoid rapid blackening and unduly short life.

The reasons for the lack of practicability and the unsatisfactory character of inside-coated bulbs are manifold. I shall endeavor to point out those reasons and to outline the problems involved in the preparation of efficient and lasting coatings, in order that the character of the present invention may be more clearly and fully understood.

It is a well recognized fact that the blackening of electric incandescent lamps, comprising a tungsten filament, is caused by the presence of water vapor in the lamp, and to its subsequent cyclic reaction with the tungsten filament, to form tungsten oxide and hydrogen, which later recombine in the cooler parts of the lamp to form tungsten and water vapor. The liberated tungsten is deposited on the walls of the glass container as a black deposit, and the water vapor reacts with more of the tungsten filament to form more tungsten oxide and hydrogen, which again combine in the cooler parts of the lamp to form more black tungsten metal and water vapor, and so on. It will be seen that the tungsten filament is continually corroded by the water vapor, and the black tungsten powder is continually deposited on the walls of the bulb to form a thicker and thicker coating which prevents the light of the incandescing filament from shining through. Thus, it is seen that the amount of light emitted by such a lamp is considerably cut down, and the useful life of the lamp is shortened by the rapid deterioration of the filament.

In the process of lamp making, it is the practice to take every precaution to eliminate this moisture from the lamps, by pre-heating the various parts, during sealing-in and exhaust, to a predetermined temperature for a specific period of time, to drive off from the walls of the bulbs and stems, any moisture which may be adhered thereto. It is imperative that this tem-

perature of the exhaust ovens be kept as high as possible without burning off the "getter" or oxidizing the filaments.

In the case of gas-filled lamps, the gases which are used, both to wash the bulbs during the exhaust processes, and to fill or partly fill the completed lamp, are carefully cleaned and purified before they are put into the lamps, in order to remove traces of water vapor, and other impurities. Among these other impurities may be carbon dioxide, and hydrogen, and hydrocarbons, or other carbonaceous materials, which may decompose or react with small amount of oxide which occurs on the nickel leads and molybdenum anchors to form water vapor.

Hence, it is seen that water vapor is a bugaboo in tungsten filament lamp-making and many precautions are taken to eliminate it from the bulbs. I have found, however, that the many sources of water vapor, particularly those which frustrate the successful production of inside-coated bulbs, have not been adequately investigated and identified, nor have sufficient precautions been taken to eliminate them.

It is an object of my invention to provide such a coating for the inside of electric incandescent lamps comprising tungsten filaments,—a coating which contains light-diffusing solid materials completely free from water, and which will not give off water vapor during the normal burning life of the lamp. By "completely" free of water I mean complete in the practical sense of the word, so complete that no appreciable water is formed or given off under practical conditions of operation.

A further object of the present invention is to provide a coating material adapted to produce an efficient and lasting inside coating of light-diffusing character on an electric incandescent lamp bulb, or on similar articles. Lamps coated with the composition of the invention may range from the smallest sizes to the largest of 300 watts or larger, and these lamps may be either the vacuum type or gas-filled, and may be burned in any position required by ordinary fixtures, without undue blackening within the normal commercial life of the lamp.

Briefly described, the invention comprises a novel coating material, the ingredients of which, though simple, are of a precise composition and specific nature. The coating consists essentially of a pigment and a binder each having particular properties.

With the above objects in view I use such materials as are free from water, either water of hydration, water of crystallization, water of hydroxides, or occluded or adsorbed water.

By water of hydration I mean the water which has been taken up by a mineral or other chemical compound, by its slow physical or chemical combination with water by long contact with water. As an example I refer to the reaction between anhydrite, $CaSO_4$, and water to form gypsum, $CaSO_4.2H_2O$. This water may be liberated by heating, without destroying the original nature of the compound.

By water of crystallization I mean the water which is combined in a chemical compound when said compound crystallizes from an aqueous solution of the substance, and as an example I may cite the compound $CuSO_4.5H_2O$, which is copper sulphate with 5 molecules of water. This water may also be liberated by heat without destroying the original nature of the compound.

By hydroxide water I mean the water which may be liberated by the heating or calcining of an hydroxide which is decomposable by heat. As an example I give the reaction which takes place when calcium hydroxide, $Ca(OH)_2$, commonly known as slaked lime, is heated.

$$Ca(OH)_2+heat=CaO+H_2O$$

In this case the original nature of the compound is destroyed and a new chemical compound is formed. Ferrous hydroxide, ferric hydroxide, magnesium hydroxide, barium hydroxide, and other similar hydroxides also fall in this class.

By occluded and adsorbed water I mean water which may be mechanically held within, or on the surfaces of grains of solid materials, without being chemically combined with said materials.

Heretofore it has been the custom to use kaolinite, also called kaolin and china clay, as the basis of the white, light-diffusing material when making a coating medium to be applied to the inside of electric incandescent lamp bulbs. Kaolinite, or kaolin, is a hydrated aluminium silicate, with a chemical formula commonly expressed as $Al_2O_3.2SiO_2.2H_2O$ or by the formula $Al_2Si_2O_7.2H_2O$, the said silicate containing 13.96% by weight of water. It is known that this water of hydration can be gradually driven off by the heating and calcining of the kaolin, as when ceramic articles made from it are baked and roasted in kilns and ovens.

I have found that a similar dehydration of the kaolin takes place within an electric incandescent lamp comprising a tungsten filament, and having the inner walls of the bulbs coated with a light-diffusing medium comprising all or in part kaolin. I have found that this is especially true of the high wattage lamps of the gas-filled type, in which the filaments are incandescing at high temperatures, and emitting a great deal of heat, which is radiated and conducted and convected to the light-diffusing coating which covers the inner walls of the bulbs. This intense heat acts to partially dehydrate the kaolin with the consequent liberation of water vapor. This liberated water vapor then unites with the tungsten filament to cause blackening of the bulbs, and poor life and early burn-outs as previously explained.

Another material which has sometimes been used as a light-diffusing material is talc, also called steatite, soapstone and French chalk. This material, too, is a hydrated silicate, being the hydrated silicate of magnesium, and the formula is commonly expressed as $3MgO.4SiO_2H_2O$, or by $Mg_3Si_4O_{11}.H_2O$. This material, though it contains only 4.75% by weight of water, is similarly unsatisfactory as a light-diffusing material to be used as a coating on the inner walls of an electric incandescent light bulb.

In the coating of the present invention I use one or more insoluble inert high melting substances which do not contain water of any kind, and which do not unite or combine with water, even when said materials are suspended in an aqueous vehicle. For example, I may use lithopone which is an artificial combination of barium sulphate and zinc sulphide, and which is commonly designated as $BaSO_4.ZnS$; or I may use titanium oxide, or suitable mixtures of lithopone and titanium oxide. I may also use barium sulphate alone, or in combination with titanium oxide.

The solubility of some of the substances mentioned is very low, that of barium sulphate being given as .00023 part by weight in 100 parts of water, and that of zinc sulphide as .00069 part by

weight in 100 parts of water. Titanium oxide is practically insoluble. None of these three compounds form hydroxides or hydrates, nor do they take up water of crystallization.

Commercial grades of these materials, however, i. e., those grades commonly known as technical and commercial, sometimes contain impurities which are undesirable because said impurities are detrimental to the life of a lamp coated with a light-diffusing coating made from such technical grades of said materials. I have found it, therefore, advisable to use only such materials as are of the chemically pure, or reagent pure, type, to insure the absence of soluble salts, and such other impurities as would give off water vapor or other undesirable volatile compounds during the normal incandescing life of the lamp. As an example of the purity of the materials which I may use, I give the following typical analysis of reagent pure, barium sulphate:

Loss on ignition	per cent	1.5
Free acid	do	.02
Free alkali		None
Organic matter		No reaction
Chlorides	per cent	.003
Phosphates	do	.001
Arsenic	do	.0001
Soluble barium salts		None
Heavy metals	per cent	.001
Iron	do	.003

In order to insure further freedom from volatile impurities I may fire or calcine the materials previous to their use, to drive off any impurities which I may deem undesirable, said firing or roasting to be done either at atmospheric pressure or under reduced pressure, so that I may maintain conditions similar to those within a lamp.

In the making of the coating medium, which comprises an aqueous vehicle which must be and is completely eliminated during the manufacture of the coated bulb into a lamp, together with the aforementioned anhydrous material of a specified purity, it is necessary to use a binding agent to hold the particles of the light-diffusing material to the inner walls of the bulb. A satisfactory agent is sodium silicate of the particular nature hereinafter alluded to, combined with the vehicle in such proportion as to form a dilute solution of a specific gravity of 1.014.

The nature of this agent is of distinct importance. Heretofore, the importance of the ratio of the silica content to the soda content of sodium silicate has not been discerned, and in making up a coating medium containing sodium silicate as the binding agent, a solution of specific gravity 1.025 has been specified as the vehicle without reference to the effect of the composition of the silicate on the binding qualities or drying qualities thereof. Those solutions of sodium silicate which have a high ratio of silica to soda are more "short" than the tacky solutions of high soda content. These "short" solutions set more quickly than the tacky ones, and hence dry out more quickly. This rapid drying of the high silica content solutions of sodium silicate, I have found to be highly advantageous in the drying and the removal of water from a light-diffusing coating, which has been applied to the inner walls of a glass bulb.

I have also found that when sodium silicates of high silica content are used, much less sodium silicate is necessary to effect a binding action, and hence a solution of a lower specific gravity than the formerly specified 1.025 can be used. I have found that solutions having a specific gravity of 1.014 are very satisfactory, in fact, I may even state that if I go higher than 1.014,—that is to say, 1.02,—I run into a condition of brittleness in the coated bulb which is undesirable from a lamp-making standpoint.

In the preparation of the aforementioned solution of sodium silicate of 1.014 gravity, I use a sodium silicate of a ratio of 3.22 silica to 1 of soda; that is, for each part of sodium oxide (Na_2O) there will be 3.22 parts by weight of silicon oxide (SiO_2). I do not, however, confine myself to the use of sodium silicate which has a silica soda ratio of 3.22 to 1, but I may use a sodium silicate with higher ratios,—that is, a 3.86 to 1 silica to soda ratio,—or mixtures of these two aforementioned sodium silicates.

There is another important factor to be noted in connection with the preparation of the sodium silicate binder, and this is the purity of the water in which it is dissolved. Ordinary tap water contains, besides mud and other colored sediment, mineral salts, among which are chlorides, sulphates, etc., and iron compounds which become hydrolyzed to the hydroxides of iron. These will form precipitates with sodium silicate and throw out of solution part of the silica, as metallic silicates, which sometimes contain free silicic acid. This precipitation not only causes coagulation of the coating materials, making it lumpy and hard to apply, but it also reduces the silica to soda ratio, thus affecting the binding and the drying qualities of the sodium silicate left in solution. Acids and ammonia and such substances as glycerine, alcohol, salt brine, etc., will cause a precipitation of the sodium silicate. Hence, it is seen that the light-diffusing materials which are used for making up the coating should be free from acids, and salts of heavy metals, and such other salts and substances as will effect a precipitation of the sodium silicate.

Besides these inorganic materials, ordinary water contains organic substances and microscopic plant life, all of which make tap water undesirable for use as a coating vehicle.

I have found that the use of distilled water prevents coagulation of the paint or coating medium by virtue of its not containing any mineral salts or compounds that would normally bring about a precipitation of the sodium silicate. I have found further that the absence of organic matter, and microscopic plant life also makes for a better quality and longer life of the lamp.

An example of the coating material of the invention, which produces a white light-diffusing coating, is as follows:

Lithopone	grams	575
Solution of sodium silicate in distilled water	cc	1700

(Specific gravity of solution=1.014.)
(Ratio of silica to soda in silicate=3.22 to 1.)

As above indicated, the concentration of the sodium silicate is highly important. Sodium silicate of a gravity of 1.01, for instance, results in a lamp which has undesirable swirling markings in the coating due to the action taking place within the bulb during exhaust. On the other hand, if sodium silicate of a specific gravity of 1.02 is used, the glass bulb is rendered so brittle that it breaks under very slight shocks. At the concentration mentioned in the formula, namely, specific gravity of 1.014, neither of these undesirable results are effected.

Another example is as follows:

Lithopone	grams	525
Titanium oxide	do	50
Solution sodium silicate in distilled water—specific gravity 1.014	cc	1700

I may also use a mixture of—

Lithopone	grams	560
Titanium oxide	do	15
Sodium silicate solution of a specific gravity of 1.014 and having a silica soda ratio of 3.22 to 1, said solution being made with distilled water	cc	1700

Or I may use—

Reagent pure, barium sulphate	grams	800
Sodium silicate solution of a gravity of 1.014, in distilled water, the silica soda ratio being 3.22 to 1	cc	2400

In preparing the mixture I may grind the materials in a porcelain pebble mill until a suspension of the desired thickness and viscosity and grain size is obtained.

The method by which the coating is applied is particularly described in the copending application of Koerner, Bahlke and Marvin hereinbefore referred to. In brief, it comprises preheating the bulbs, spraying on the coating under controlled conditions, drying at room temperatures, baking the sprayed bulbs and sealing mounts therein at regulated temperatures.

In the appended claims I refer to water-free materials as meaning materials free from water of hydration, of crystallization, of hydroxides, and of occluded or adsorbed water, as explained and defined in the foregoing specification.

Having thus described my invention, what I claim is:

1. A coating composition consisting of a pure, refractory, non-volatile, water-free, finely divided pigment incorporated in a vehicle composed of sodium silicate having a silica to soda ratio of 3.22 to 1 dissolved in distilled water, said solution having a specific gravity of 1.014.

2. A coating composition for the interior surface of vitreous articles, consisting of reagent pure barium sulphate and a solution of sodium silicate in distilled water, specific gravity 1.014, the silica to soda ratio being 3.22 to 1.

3. A coating composition consisting of a pure, refractory, non-volatile, water-free, finely divided, light-diffusing and light-transmitting inert material incorporated in a vehicle composed of a distilled water solution of sodium silicate having a silica to soda ratio of 3.86 to 1, and a specific gravity of 1.014.

4. A coating composition consisting of a pure, refractory, non-volatile, water-free, finely divided, inert pigment incorporated in a vehicle composed of sodium silicate having a silica to soda ratio of between 3.22 and 3.86 to 1 dissolved in distilled water and having a specific gravity of 1.014.

5. A coating composition consisting of a pure, inert, refractory, non-volatile, water-free, finely divided, light-refracting substance, incorporated in a vehicle composed of a quickly drying solution of sodium silicate having a silica to soda ratio ranging from and including 3.22 and 3.86 to 1, and a specific gravity of 1.014.

6. A coating composition for the interior surface of vitreous articles, consisting of chemically pure, finely divided lithopone, suspended in a vehicle composed of a distilled water solution of sodium silicate, in which the silica to soda ratio is 3.22 to 1, and the specific gravity is 1.014.

7. A coating composition for the interior surface of vitreous articles, such as incandescent lamp bulbs, consisting of 800 grams of pure barium sulphate incorporated in 2400 cc. of a distilled water solution of sodium silicate in which the silica to soda ratio is 3.22 to 1, and the specific gravity is 1.014.

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