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(54) **Title:** COATING FOR LAMPS AND LAMP AT LEAST PARTIALLY PROVIDED WITH SUCH A COATING

(57) **Abstract:** The invention relates to a coating for lamps, comprising a network obtainable by conversion of an organically modified silane by means of a sol-gel process, wherein silica particles obtainable from a stabilized colloidal silica dispersion are substantially incorporated in said network. The invention also relates to a lamp comprising a vessel or a bulb, wherein said vessel or said bulb is at least partly provided with such a coating. The invention further relates to an electronic device comprising at least one such lamp.

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Coating for lamps and lamp at least partially provided with such a coating

The invention relates to a coating for lamps, comprising a network obtainable by conversion of an organically modified silane by means of a sol-gel process, wherein silica particles obtainable from a stabilized colloidal silica dispersion are substantially incorporated in said network. The invention also relates to a lamp comprising a vessel or a bulb, wherein said vessel or said bulb is at least partly provided with such a coating. The invention further relates to an electronic device comprising at least one such lamp.

It is commonly known to apply coatings to bulbs or vessels of different kinds of lamps to achieve a desired optical effect, for example to absorb, to reflect, and/or to convert incoming light with (specific) wavelengths. For this purpose, the international application WO2004/0377838 discloses an improved coating for low-pressure mercury vapor discharge lamps capable of converting UV light to other wavelengths, for example to UV-B light and UV-A light for tanning purposes (sun panel lamps) or to visible radiation for general illumination purposes. Such discharge lamps are also referred to as fluorescent lamps. The improved known coating comprises a network obtainable by conversion of an organically modified silane by means of a sol-gel process, resulting in an improved adhesion to a vessel of the low-pressure mercury vapor discharge lamp at higher temperatures compared with the familiar prior art coatings based on organic lacquers. Commonly, the critical layer thickness of the known coating is less than 4 microns. However, if a relatively thick coating layer (with a layer thickness of up to 20 microns) is to be applied, the solution is proposed to add a stabilizing agent to the network obtainable by conversion of an organically modified silane by means of a sol-gel process in order to prevent shrinking and slumping of the coating layer. This would result in an irregular coating thickness, which would have a negative effect on both the optical and the aesthetical properties of the coating. The stabilising agent comprises sodium- or ammonium-stabilized silica nanoparticles in water, in particular an aqueous silica sol, for example marketed under the trade name Ludox® TM50 (obtainable from E.I. Dupont de Nemours and Co., Wilmington, Del. under the trade designation Ludox®).If thicker layers are needed, however, said coatings will still show a loss of adhesion.

It is an object of the invention to provide an improved coating for lamps with a relatively high critical layer thickness.

The object can be achieved by providing a coating according to the preamble, characterized in that in addition high-surface particles having a BET specific surface area of more than 100 m^2/g are incorporated in said network. Surprisingly, it has been found that the critical layer thickness of the coating can be significantly increased by incorporating said high surface particles into the network obtainable by conversion of an organically modified silane by means of a sol-gel process. The addition of the high-surface particles to the coating increases the critical layer thickness by up to about 30 micrometers without the risk of loss of adhesion. The high-surface particles improve the flexibility of the coating layer, resulting in a diminished stress concentration within said layer, in particular during curing of the layer. The coating according to the invention thus provides an improved coating which can be applied to a lamp surface in relatively thick layers in a relatively sustainable way without the coating layer flaking off or being exfoliated during curing of the layer and/or during operation of the at least partly coated lamp. The high-surface particles are preferably amorphous and/or porous to realize the relatively large external surface area of the high-surface particles with respect to the total volume of these particles. It is noted that the lower limit of the BET specific surface area of 100 m^2/g is determined by nitrogen absorption capacity using the commonly known Brunauer-Emmitt-Teller (BET) procedure.

In a preferred embodiment, said high-surface particles are formed by microparticles with an average diameter between 0.1 and 0.5 micrometer, more preferably with an average diameter of 0.3 micrometer. High-surface particles with a diameter within this range are found to be suitable for application, i.e. they generate a sufficient relaxation within the coating layer to allow the aforementioned increase of the critical layer thickness of up to about 30 micrometers. Said high-surface particles are preferably formed by an oxide, more preferably by aluminum oxide (Al_2O_3), most preferably aluminum oxide in the gamma phase (γ-Al_2O_3). Gamma-Al_2O_3 is de facto a defective spinel phase of alumina with cation site randomly distributed vacancies. Gamma-Al_2O_3, marketed inter alia under the product code CR125 (obtainable from Baikowski), is formed by particles with an average diameter of 0.3 micrometer having a BET specific surface area of 105 m^2/g. A dispersion of these particles in a liquid dispersant is substantially transparent, the alumina particles having a wavelength-independent, substantially uniform reflection. These properties make gamma-Al_2O_3 particularly suitable to be incorporated into an optical coating. It has been found that the stability and in particular the critical layer thickness of the coating according to the

invention are substantially determined by the content of the high-surface relaxation particles in the network obtainable by conversion of an organically modified silane by means of a sol-gel process. For this reason it is advantageous that the percentage of high-surface particles per unit of volume dry coating should be at least 5% if a relatively thick and yet stable and sustainable coating layer is to be obtained.

Another major drawback of the coating known from the prior art is that sagging of the known coating is very likely to happen when coatings are applied on convex surfaces because of insufficient rheologic behavior. This sagging effect results in an irregular coating pattern which not only has a negative effect on the optical and aesthetical properties of the coating, but commonly also leads to the critical layer thickness being exceeded, which will result in a disadvantageous loss of adhesion. Formation of a relatively inhomogeneous coating layer with an uncontrolled edge definition can be prevented in that a coating according to the invention, and further comprising a thickening agent, is applied. Like the high-surface particles, the thickening agent stabilizes and consolidates the layer formed of the coating according to the invention. However, it should be noted that in an alternative (less preferential) embodiment of the coating, the incorporation of the high-surface particles into the network obtainable by conversion of an organically modified silane by means of a sol-gel process may be omitted, whereas the thickening agent is incorporated into said network just to prevent sagging of the coating. Preferably, said thickening agent comprises at least one cellulose derivative (cellulosics), more preferably hydroxypropylcellulose. However, it is also conceivable to apply a polyacrylate as a thickening agent. Besides the application of conventional cellulosics as a thickening agent it is also possible to apply modified cellulosics, for example a hydrophobic modified hydroxyethylcellulose if thixotropy is needed.

In a preferred embodiment, said coating comprises a pigment for absorbing and/or reflecting part of the visible or UV light. To manufacture coatings having the desired optical properties and having the desired thermal stability during the service life of the lamp, use is preferably made of inorganic pigments. In a favorable embodiment of the coating in accordance with the invention, the pigment is selected from the group formed by iron oxide, iron oxide doped with phosphorus, zinc-iron oxide, cobalt aluminate, neodymium oxide, bismuth vanadate, zirconium-praseodymium silicate, and mixtures thereof. Iron oxide (Fe_2O_3) is an orange pigment and P-doped Fe_2O_3 is an orange-red pigment. Zinc-iron oxide, for example $ZnFe_2O_4$ or $ZnO{\cdot}ZnFe_2O_4$ is a yellow pigment. Mixing (P-doped) Fe_2O_3 with $ZnFe_2O_4$ yields a pigment of a deep orange color. Cobalt aluminate ($CoAl_2O_4$), neodymium oxide (Nd_2O_5) and Hostaperm Blue are blue pigments. Bismuth vanadate ($BiVO_4$), also

referred to as pucherite, is a yellow-green pigment. Zirconium-praseodymium silicate is a yellow pigment. Experiments have shown that a network including said inorganic pigments does not appreciably degrade during lamp life and at the relatively high temperature load on the coating. In an alternative preferred embodiment of the coating according to the invention, coatings are obtained wherein organic pigments are used. Particularly suitable pigments are the so-called Red 177 (anthraquinone) and chromium phthalic yellow or chromium phthalic red from "Ciba". Further suitable pigments are Red 149 (perylene), Red 122 (quinacridone), Red 257 (Ni-isoindoline), Violet 19 (quinacridone), Blue 15:1 (Cu-phthalocyanine), Green 7 (hal.Cu-phthalocyanine) and Yellow 83 (dyaryl) from "Clariant". Amber-colored chromophtal yellow, chemical formula $C_{22}H_6C_{18}N_4O_2$ and C.I. (constitution number) 56280, is an organic dye and is also referred to as "C.I.-110 yellow pigment", "C.I. pigment yellow 137" or Bis[4,5,6,7-tetrachloro-3-oxoisoindoline-1-ylidene)-1,4-phenylenediamine. Amber-colored anthraquinone, chemical formula $C_{37}H_{21}N_5O_4$ and C.I. 60645, is an organic dye and is also referred to as "Filester yellow 2648A" or "Filester yellow RN", chemical formula 1,1'-[(6-phenyl-1,3,5-triazine-2,4diyl)diimino]bis-. Red-colored "chromophtal red A2B" with C.I. 65300 is an organic dye and is alternatively referred to as "pigment red 177", dianthraquinonyl red, or as [1,1'-Bianthracene]-9,9',10,10'-tetrone, 4,4'- diamino-(TSCA, DSL). Mixtures of inorganic and organic pigments are also suitable, for example a mixture of chromium phthalic yellow and (zinc)iron oxide. An alternative embodiment of the coating in accordance with the invention is characterized in that the pigment causes a change in the color temperature of the lamp. The application of a coating of the blue pigments cobalt aluminate ($CoAl_2O_4$) or neodymium oxide (Nd_2O_5), for example, raises the color temperature of the lamp. A preferred embodiment of the coating according to the invention is characterized in that the reflecting particles are selected from the group formed by aluminum, silver, aluminum oxide, titanium (di)oxide, calcium halophosphate, zinc oxide, barium sulphate, and calcium carbonate. In a preferred embodiment of the coating according to the invention, aluminum oxide marketed under the product code CR6 (obtainable from Baikowski) is applied as a (reflective) white pigment, CR6 consisting substantially of alumina particles with an average diameter of 0.6 micrometer and a BET specific surface area of 6 m^2/g. Aluminum oxide marketed under the product code CR125 may be applied as a reinforcing agent to improve the strength of the coating. However, no considerable reflectance can be realized based upon solely CR125 owing to the relatively small particle size of CR125. In a particularly preferred embodiment, both CR6 and CR125 are incorporated into the network obtainable by conversion of an organically modified silane by

means of a sol-gel process, wherein the volume ratio of CR6:CR125 is substantially equal to 6:1 (to be able) to achieve both the desired optical properties and the desired strength and toughening of the coating caused by the particular alumina matrix formed within said coating. Preferably, an average diameter d_p of the pigment particles complies with $d_p \leq 100$ nm. Optically transparent coatings are obtained which exhibit relatively little light scattering with the use of pigments of such relatively small dimensions. Since the coating according to the invention is often applied in specially designed reflectors, wherein the light source is embodied so as to be punctiform, light scattering by the coatings is an undesirable property. The effect of light scattering is at least substantially precluded if the average diameter of the pigment particles $d_p \leq 50$ nm. Particularly suitable coatings are obtained when a pigment composed of a mixture of iron oxide and bismuth vanadate, or of a mixture of iron oxide doped with phosphorus and bismuth vanadate, is used in the coating.

Said organically modified silane is preferably selected from a group formed by compounds of the following structural formula: $R^{I}Si(OR^{II})_3$, wherein R^{I} comprises an organic group, preferably an alkyl group or an aryl group, and wherein R^{II} comprises an alkyl group. Replacing the conventional organic lacquer in the coating by a network comprising an organically modified silane as the starting material leads to an optically transparent, non-scattering, coating which can resist high temperatures (up to 400 °C). The use of an organically modified silane in the manufacture of the network causes a portion of the R^{I} groups, i.e. the alkyl or aryl groups, to remain present as an end group in the network. As a result, the network in accordance with the invention has fewer than four network bonds per Si atom. A network partly composed of said alkyl or aryl groups has a greater elasticity and flexibility than the customarily used silica network. This enables relatively thick coatings to be manufactured.

Preferably, the R^{I} group comprises CH_3 or C_6H_5. These substances have a relatively good thermal stability. A network comprising methyl or phenyl groups enables thicker coatings to be obtained. Experiments have further shown that coatings in which methyl or phenyl groups are incorporated into a network are stable up to a temperature of at least 350°C. Said groups are end groups in the network and remain part of the network at said higher temperatures. At such a relatively high temperature load on the coating, no appreciable degradation of the network occurs during the service life of the lamp on which the coating is applied. In an alternative embodiment, R_I comprises an organic group in the form of an epoxy-amino group. since the operating temperature and the UV output of

fluorescent lamps are relatively low, such coatings can be applied and are stable during the operational life of the discharge lamp.

Preferably, the R^{II} group comprises CH_3 or C_2H_5. Methyl and ethyl groups are particularly suitable because methanol and ethanol are formed in the hydrolysis process, which substances are compatible with the pigment dispersion and evaporate relatively easily. In general, the methoxy groups ($-OCH_3$) react more rapidly than the ethoxy groups ($-OC_2H_5$) which, in turn, react more rapidly than (iso)propoxy groups ($-OC_3H_7$). For a smooth hydrolysis process, use is advantageously made of R^{II} groups which are not very long. Very suitable starting materials for the manufacture of the network in accordance with the invention are:

methyltrimethoxy silane (MTMS), where $R^I = R^{II} = CH_3$,

methyltriethoxy silane (MTES), where $R^I = CH_3$ and $R^{II} = C_2H_5$,

phenyltrimethoxy silane (PTMS), where $R^I = C_6H_5$ and $R^{II} = CH_3$, and

phenyltriethoxy silane (PTES), where $R^I = C_6H_5$ and $R^{II} = C_2H_5$.

Beside these components, it is also imaginable to apply more complex hybrid sol gels like glycidoxypropyltri(m)ehtoxysilane (GLYMO). Such starting materials are known per se and commercially available. To improve the adhesive capacity of the coating, small quantities of tetraethoxysilane may be used.

The invention also relates to a lamp comprising a vessel or a bulb, wherein said vessel or said bulb is at least partially provided with a coating according to the invention. The lamps provided with a coating according to the invention may be of various kinds. However, the coating is preferably applied to a light-transmitting discharge vessel of a discharge lamp, the discharge lamp further comprising a discharge vessel that encloses, in a gastight manner, a discharge space provided with a filling of an ionizable substance and that comprises means for maintaining a discharge in the discharge space, while at least a portion of the discharge vessel is provided with said coating of a luminescent layer of a luminescent material, and at least a portion of the discharge vessel facing away from the discharge space is provided with the coating according to the invention. The coating may be applied both to low-pressure discharge lamps, for example a low-pressure mercury vapor discharge lamp, and to high-intensity discharge (HID) lamps, for example HID automotive headlights. It is, however, also conceivable to apply the coating according to the invention to conventional incandescent lamps.

The invention further relates to an electronic device comprising at least one lamp according to the invention. Preferably, the device is selected from the group formed by

the following electronic devices: a solarium or other sun panel for tanning, an LCD (in particular LCD backlighting), an automotive device or vehicle, and a signaling device. It should be clear that the use of the lamps according to the invention is by no means limited to the enumeration given above. It will be obvious to those skilled in the art that a lamp provided with a coating according to the invention may be used for purposes other than the purposes explicitly mentioned in this paragraph.

The preparation of the coating according to the invention will be elucidated in the non-limitative illustrative examples described hereinafter.

EXAMPLE 1

A reflecting coating is prepared from 40 g methyltrimethoxysilane, 1 g glycolic acid, 20 g ethanol, and 40 g Ludox® TMA (Aldrich 34 wt.% silica in water, deionized sol). The solution is hydrolyzed for 45 minutes. A pigment paste is prepared from 36 g CR-6, 6 g CR-125, 6 g Disperbyk 190 (0.05 g Disperbyk / g CR-6 and 0.7 g Disperbyk / g CR-125), and 40 g water. The pigment paste is milled with a high-speed dissolver and added to the hydrolysis mixture. The coating liquid is deposited on the outer surface of the discharge vessel by means of spraying. After deposition, the coating is dried at 90°C for 5 minutes and subsequently cured for 30 minutes at 150°C.

EXAMPLE 2

A reflecting coating is prepared form 40 g methyltrimethoxysilane, 1 g glycolic acid, 20 g ethanol, and 40 g Ludox® TMA (Aldrich 34 wt.% silica in water, deionized sol). The solution is hydrolyzed for 45 minutes. A pigment paste is prepared from 36 g CR-6, 6 g CR-125, 6 g Disperbyk 190 (0.05 g Disperbyk / g CR-6 and 0.7 g Disperbyk / g CR-125), and 40 g of a 1 wt% Klucel M solution in water. The pigment paste is milled with a high-speed dissolver and added to the hydrolysis mixture. The coating liquid is deposited on the outer surface of the discharge vessel by means of spraying. After deposition, the coating is dried at 90°C for 5 minutes and subsequently cured for 30 minutes at 150°C.

It will be clear that, within the scope of the invention, many variations are possible to those skilled in the art. In the sol-gel process, many alternative preparation methods are possible. Furthermore, it is also possible to use pigment combinations to cause the color point to shift towards red. Besides, the color temperature of the light to be emitted by the electric lamp can be raised while, for example, the color co-ordinates remain substantially positioned on the blackbody locus. The scope of protection of the invention is

not limited to the examples given herein. The invention is embodied in each novel characteristic and each combination of characteristics. Reference numerals in the claims do not limit the scope of protection thereof. The use of the term "comprising" does not exclude the presence of elements other than those mentioned in the claims. The use of the word "a" or "an" before an element does not exclude the presence of a plurality of such elements.

CLAIMS:

1. Coating for lamps, comprising a network obtainable by conversion of an organically modified silane by means of a sol-gel process, wherein silica particles obtainable from a stabilized colloidal silica dispersion are substantially incorporated in said network, characterized in that in addition high-surface particles having a BET specific surface area of more than 100 m^2/g are incorporated in said network.

2. Coating according to claim 1, characterized in that said high-surface particles are formed by microparticles with an average diameter between 0.1 and 0.5 micrometer, more preferably with an average diameter of 0.3 micrometer.

3. Coating according to one of claims 1 and 2, characterized in that said high-surface particles are formed by an oxide, more preferably by aluminum oxide.

4. Coating according to one of the foregoing claims, characterized in that the percentage of high-surface particles per unit of volume dry coating is at least 5%.

5. Coating according to one of the foregoing claims, characterized in that the coating further comprises a thickening agent.

6. Coating according to claim 5, characterized in that said thickening agent comprises at least one cellulose derivative.

7. Coating according to claim 6, characterized in that said thickening agent comprises hydroxypropylcellulose.

8. Coating according to one of the foregoing claims, characterized in that said coating comprises a pigment for absorbing and/or reflecting part of the visible or UV light.

9. Coating according to one of the foregoing claims, characterized in that said organically modified silane is selected from a group formed by compounds of the following structural formula: $R^{I}Si(OR^{II})_3$, wherein R^{I} comprises an organic group, preferably an alkyl group or an aryl group, and wherein R^{II} comprises an alkyl group.

10. Coating according to claim 9, characterized in that the R^{I} group comprises CH_3 or C_6H_5.

11. Coating according to claim 9 or 10, characterized in that the R^{II} group comprises CH_3 or C_2H_5.

12. Lamp comprising a vessel or a bulb, wherein said vessel or said bulb is at least partly provided with a coating according to one of the claims 1 to 11.

13. Lamp according to claim 12, characterized in that said lamp is a discharge lamp.

14. Electronic device comprising at least one lamp according to one of the claims 12 and 13.

15. Device according to claim 14, characterized in that the device is selected from the group formed by the following electronic devices: a solarium, an LCD, an automotive device, and a signaling device.