

ALIEN PROPERTY CUSTODIAN

METHOD FOR PRODUCING LAYERS ON SOLID OBJECTS

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The reflection occasioned on the outer surface of a transparent object when light rays from the air pass into that object, same as the reflection occasioned when light rays from a transparent object pass into the air, can be diminished in a known manner by applying to the object a thin layer of a substance whose refractive index is lower than that of the object in question. Suitable choice of this refractive index of this substance and of the thickness of the layer provided, it is even possible to wholly eliminate said reflection. It is furthermore known that the said reflection can be diminished by the application of several thin layers, though it is not expedient in that case that all of them have a lower refractive index than the object. However, the previously known methods for producing such layers are unsatisfactory, because, for instance, of the layers obtained thereby offering little resistance to chemical or mechanical attacks.

According to the invention highly effective layers offering strong resistance at the same time to chemical and mechanical attacks can be obtained if for their production a low-hydrated gel-like hydroxide (either alone or with other additions) of an element capable of forming colloidal hydroxides difficultly soluble in water is precipitated on the object when the latter is heated to a temperature which lies at least 50° below its fusing temperature. In place of a single one of such hydroxides also a mixture of several hydroxides can be used. Precipitation can be effected thereby in the most various ways; for instance, by precipitating the hydroxide from vapors, or applying it mechanically by the atomising of solutions of the hydroxides; furthermore by dipping the object to be coated into the solution and thereby producing upon it a film of that solution.

The production of hydroxides can be effected in known manner by the chemical decomposition of salts containing the respective elements in the form of acidifiers, furthermore by substances separating H-ions, as through the precipitation for instance of sodium silicate solutions with the aid of muriatic acid or by the action of water or of other substances separating hydroxide groups either on halides or on other similarly decomposable compounds (as ester, f. i.,) of the elements in question.

On the hydroxides thus obtained being colloiddally dissolved in water or in organic liquids the objects to be treated can be dipping, pouring or spraying etc. be coated with a more or less thick layer, or with several such layers, hardening colloiddally as the solvent evaporates. By

careful heating the gelatines loose more or less of the solvent and the hydrate water still held by them and thereby shrink in a manner numerically determinable by preliminary tests until they form very thin layers of good durability both in a mechanical and chemical respect. At the same time their refractive index changes so that their finally effective refractive index must be determined before the more exact production of reflection-diminishing layers can be proceeded with.

The final stage of the hardening of the gelatines is generally reached when heated to a temperature of not exceeding 250° C., at which stage low-hydrated layers of hydroxide of the respective elements have been arrived at. This hardening can also be effected while the layers are being produced in that the hydroxides or a mixture of them is precipitated upon the more or less heated objects by the atomisation, for instance, of their colloidal solutions.

What very likely is the simplest method of producing uniform layers is to expose the object to a fog formed of the substance to be precipitated. Fogs of this kind and of particularly fine dispersal are obtained if a vapor-flux of a compound decomposable by water is allowed to mix with steam, say, by spraying the halide with the aid of a nozzle upon the object located in room-air.

A rather low refractive index being already obtainable, for instance, with water-containing layers of silico-oxide, the application of one single layer is in many instances sufficient for producing an adequate diminution of the surface reflection. Its performance can be still further enhanced in that, during or after precipitation, evaporatable, or decomposable substances as well as substances, separatable by chemical means, such as f. i. paraffines, organic acids or their salts etc., are made effective and embedded by heating. By greater heating as well as by chemical decomposition or other reactions these substances or parts of them can then be removed again thus resulting in a porous structure of the hardened layer of hydroxide and bringing about a lower refractive index without decreasing the mechanical resisting capacity.

Layers of a particularly pronounced resisting capacity and of a refractive index, which can be as low as about 1.4 and still go beyond 2.0, are obtainable when proceeding from the hydroxides of tungsten, molybdenum, or from elements of the third group of the periodic system, furthermore, from the fourth group excepting carbon, or from the fifth group with the exception of nitrogen, provisions being made that each of the

finally produced layers consist to a least one half of a hydroxide of one of these elements or of a mixture of same. To produce highly refractive layers it is advisable to proceed from the hydroxides of titanium, circonium, tin or lead, while for lowly refractive layers the hydroxides of aluminium or silicon should be proceeded from. Lanthanium, tantalium and thorium are likewise well-suited for producing highly refractive layers, but are less resorted to on account of their high prices. By way of example, it may be mentioned that the refractive index of a low-hydrated layer of silicon hydroxide is about 1.45 and that of a low-hydrated layer of titanium hydroxide about 2.10.

Even though the application of the invention being of particular significance for diminishing the reflecting capacity of transparent objects it can also be of importance in applying such layers for other than the specified purposes. It is thus available for instance, for producing very dense and chemically resistant layers completely protecting the object underneath them from corrosion. This may be of importance not only for objects made of chemically sensitive glasses, but also for such objects consisting of metallic or organic substances, capable of swelling, etc. Thus, for instance, the blackening of silvered mirrors can be prevented and the reflexion of aluminium mirrors not only maintained at its initial value, but even increased beyond that value. The invention is furthermore applicable for retouchings on optical surfaces. If for this purpose the refractive index of the layer is chosen equal to that of the glass the retouchings will be entirely invisible, so that they may be applied in the form of secret characters, for instance, discernable but under special conditions, say, by the interferometric observation of differences in thickness. Furthermore, it will be possible to make use of such properties of the said layers as, for instance, their susceptibility to liquids, their altered surface (catalytic) effect or their electrical properties, etc.

It is known that, for decorative purposes, layers causing interference colors (so-called iridescent lustre-colors) can be produced on objects of glass by exposing the latter to metallic-salt vapors or spraying them with solutions of metallic salts after having previously heated said objects to fusing temperature. The method suggested according to the present invention differs from these known methods in that it is carried through at a temperature lying at least 50° below the fusing temperature, as otherwise the surfaces to be treated would become unsuitable for optical purposes; actually, the method applied for can even be carried through, in general, without resorting to temperatures higher than 250° C.

When carrying through the new method certain difficulties may be encountered, inasmuch as layers of a more or less pronounced diffusing power, i. e., surfaces of a smoky to milky appearance, may easily result. This defect may accentuatedly appear when spraying a fog of colloidal solutions (particularly in the case of titanium and silicic acid) as well as during the decomposition in damp air of such halides reacting strongly when in contact with aqueous vapor, as titanium tetrachloride (TiCl_4) of aluminium trichloride (AlCl_3), for instance. Although this defect being presumably avoidable by a careful control of the humidity of the air and by a substantial rarification of the gas-flux, much more simple and reliable methods are, however, to be preferred. A

favorable effect is, for instance, obtained by adding to TiCl_4 -vapor a reactive halide-carrier, as silicon tetrachloride (SiCl_4), for instance. Gaseous muriatic acid has a similar effect. The use of SiCl_4 offers the advantage that it can be mixed in liquid state with TiCl_4 in any desirable proportion. What furthermore proved to be very expedient is that the excessive volatility of the halides or their mixture can be reduced by dissolving them in an indifferent solvent, organic neutral halides, particularly carbon tetrachloride (CCl_4), for instance, being quite useful. A suitable mixture, for instance, consists of 3 volume parts of TiCl_4 , of 1 volume part SiCl_4 and of 10 volume parts CCl_4 . Spraying this mixture through a nozzle, in room-air, onto a plate heated to over 100°, an entirely clear gel-layer is formed of so high a refractive index which practically precludes the presence of any Si, thus representing a pure gel-layer of TiO_2 . With AlCl_3 conditions are similar to those ruling in the case of TiCl_4 .

A further difficulty consists in certain halides, as for instance, silicon tetrachloride (SiCl_4) and silicon tetrabromide (SiBr_4), at low temperature (below 400° C), reacting only slowly in the desired manner with gaseous water, but quickly with liquid water. It consequently is not so easy to produce a layer on a plate if the latter is heated to more than 100° C, but not to over 400° C. At room temperature, however, fine fogs of muriatic acid are formed which appear to act as nuclei of condensation for the segregation of liquid water as there is a precipitation on the plates of clear silicon gel-layers if brought into the said fog. The condensation in question, however, being that of minute droplets, the uniform susceptibility to liquids of the base and its perfect cleanliness play an important part, as otherwise stained and irregular coatings will result. By the admixture of phosphorous oxychloride which, perhaps, may have a condensating effect, the uniformity of the precipitation can be considerably improved. Also a mixture of heated SiCl_4 -vapor and super-heated aqueous vapor has proved advantageous. All these substances cannot, however, be fully turned to account, because of the greatest part of the halides escaping in the form of vapor which latter, moreover, are attacking and injurious to health. Neither it is possible thereby to obtain the precipitate on a plate whose temperature exceeds 100° C. That temperature, however, is desirable if the TiO_2 and SiO_2 is intended to be applied in one operation and the mixture of both substances possibly to be arrived at. A far better solution of this problem consists in a flux of combustible gases instead of air being used and in the gas being ignited when leading the nozzle. This considerably accelerates the reaction, resulting in thick white clouds of smoke being given off. As the gas used must not produce any soot, hydrogen, for instance, would be recommendable, though this may lead to the re-appearance of the aforementioned defect, viz., the formation of a cloudy film. However, by the introduction of an indifferent gas, as nitrogen, for instance,—which permits of a reduction of the flame temperature down to 800° C. a clear coating can be obtained. Besides that, the introduction will be expedient of slight quantities of oxygen as in that case, even if lowered by a further 100° C, the flame temperature can be maintained relatively uniform and an extinction prevented. In this manner it is possible to achieve a SiO_2 -precipitate on plates heated to

more than 100° C, i. e., to maintain the same conditions applying in the case of TiO₂. This, furthermore, makes it possible to avoid the halides so inconvenient in handling, and to adopt organic compounds as volatiles since the organic portion of the latter are entirely consumed at the flame temperatures in question. Alkyl esters, as for instance methyl and ethyl ester of silicon, or acetyl acetonates as aluminium and acetyl acetonate, for instance, are well suited for this purpose.

The method described above embodies a special advantage in that it permits the production of layers whose refractive index lies anywhere between the refractive indices of two substances. This can be accomplished by the alternative application of very thin layers consisting of two substances of a different refractive index. Thus, if the object to be treated is placed upon a rotating disc and consecutively subjected to the spray of one nozzle for the TiO₂-layers and to the spray of another nozzle for the SiO₂-layers, a multiple sequence of infinitely thin SiO₂ and TiO₂-containing layers will result. Since after 200 revolutions, for instance, the total thickness of the layers amounts to only about 1 μ, the thickness of a single layer only amounts to about 5 Å, i. e., to the magnitude of a molecule-layer. It is to be presumed now that what has been produced are not actually uniform layers of the said thickness, but that several molecule layers were deposited in some places and none at all in others, so that a structure is very likely to result coming very near to the actual nature of a mixture. Yet, even if the structure were assumed to represent a sharply defined stratification, the effect of such a sequence, optically, would be similar to

that of a mixture. It can be approximately computed by the rule of mixtures as that of a mean refractive index n resulting from the equation

$$n = \frac{p}{100}n_1 + \frac{100-p}{100}n_2$$

where p is the percentage of the content of the totality of layers in the substance having a refractive index of n_1 , and where n_2 is the refractive index of the other substance. In this manner it also is possible to produce layers which have the same refractive index as the object to be coated and therefore represent entirely invisible layers.

The following examples are given to demonstrate the diminution in reflection achievable with the method proposed in the present invention.

By applying to a glass plate of a refractive index 1.89 a layer of SiO₂ it will be possible, by a suitable choice of the thickness of this layer, to obtain a reflection value of 0.3% for a prescribed wavelength, as for 485 mμ (green) for instance, whereas in the case of a non-coated glass plate the reflection value would amount to almost 10%. For the remaining wavelengths the reflection will be somewhat higher amounting to 1%, for instance, for 560 mμ (yellow). With a glass plate having a refractive index of 1.50 the reflection, by the same treatment, can be diminished to 2.9% at the best. However, if on a glass plate of a refractive index of 1.50 a layer of TiO₂ is applied and on top of this a layer of SiO₂ it will be possible to make the reflection for a prescribed wavelength vanish entirely.

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