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(54) METHOD FOR THE PRODUCTION OF BLUE-COLOURED LAYERS PERMEABLE TO LIGHT

(71) We, BALZERS PATENT- UND BETEILIGUNGS - AKTIENGESellschaft, a Liechtenstein joint-stock company, of FL-9496 Balzers, Principality of Liechtenstein, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to a method for the production of blue-coloured layers permeable to light on bases by the deposition of a mixture of oxides from the vapour phase *in vacuo*. Such layers may find use as filters in the optical technology, as coating for eye-protecting glasses, as coatings for decorative gems or other articles of jewelry, in ceramics or for other purposes.

15 It has been proposed to deposit coloured glasses from the vapour phase *in vacuo* for the production of coloured transparent layers on bases. In practice this proposal can hardly be realised since most oxides, and particularly many of those used in glass technology, are decomposed when deposited from the vapour phase so that, as the condensates, layers of essentially different composition and colour are obtained. Moreover glasses coloured in bulk have such a low concentration of the colouring components that although they show in a massive piece an intense colouring, thin layers of say 1/1000 mm thickness, practically do not allow to discern any colouring. Accordingly, when trying to produce thin coloured layers by the vapour deposition of coloured glass, major layer-thicknesses have to be provided which, as experience shows, tend to scaling or flaking-off or at least to the formation of cracks, since the coefficient of thermal expansions of the substratum and that of the layer material in the rarest cases sufficiently conform with each other.

20 It is moreover known to produce coloured layers by deposition from the vapour phase by applying a metal and a non-metal to an atomically disperse mixture as a thin layer on a substratum. Sometimes the metal atoms

embedded in the layer impart to the same directly a certain colouring. In other cases, however, colouration occurs only after heating the layers thus produced when the embedded material is dispersed in colloidal form. For example colloidal gold produces a ruby colouration.

50 However, one has not succeeded so far in producing by the known methods a stable, hard, firmly adhering blue-coloured transparent layer. The known blue layers of tungsten oxide or molybdenum oxide are sensitive to oxidation and soluble in water, and thus not stable.

60 The present invention has the object of providing a method for the production of blue-coloured transparent layers by deposition from the vapour phase, which are hard and resistant, and are suitable for the various applications mentioned hereinabove.

65 The method according to the present invention for the production of blue-coloured layers permeable to light on substrata by depositing from the vapour phase *in vacuo* a mixture of oxides is characterised in that as the starting material a mixture is used, 30 to 40% by weight of which consist of cobalt hydroxide ($\text{Co}(\text{OH})_2$), 5 to 15% by weight of aluminium oxide (Al_2O_3) and the rest other oxides which in the range of wave lengths of visible light are practically free from absorption, preferably of silicon oxide (SiO_2), and that this mixture in deposited in the usual manner from the vapour phase in an oxidizing atmosphere of sub-atmospheric pressure on to the substratum, and the layers obtained are subsequently tempered.

80 Hereinafter an embodiment of the invention will be described by way of example:

85 Firstly the starting material is brought in the usual manner into a form suitable for evaporation. For this purpose a pulverulent mixture of 10% by weight of Al_2O_3 , 35% by weight of $\text{Co}(\text{OH})_2$ and 55% by weight of SiO_2 is sintered in a furnace *in vacuo* at 1250°C for half an hour so as to form a block of solid material. The powder obtained by comminuting the sintered product, which has

the aforesaid composition, serves as the starting material for the subsequent deposition from the vapour phase *in vacuo*. The latter is carried out preferably in a water-cooled copper crucible by bombardment with an electron beam. Care has to be taken, that all constituents are evaporated uniformly, i.e. that preferred evaporation of one or the other constituent is avoided. Such a suitable evaporation technique has been described e.g. in the Patent Specification No. 1,116,857.

In the present embodiment by the deposition from the vapour phase of the aforesaid starting material e.g. on a glass substratum firstly a greyish-blue layer is obtained. The thickness of this layer depends, for a given amount of the evaporated substance, on the distance between the vapour source and the substratum, and amounted in the present embodiment to about 1/1000 mm. The deposition from the vapour phase was carried out at an O_2 -partial pressure in the vapour deposition plant of the order of magnitude of 10^{-4} Torr; and the rate of deposition amount to about 180 nm/min. (A method of depositing from the vapour phase of substances in an oxidising atmosphere has been described in the Patent Specification No. 775,002 in more detail). The glass plate with the greyish-blue layer obtained firstly by the vapour deposition has to be subsequently tempered. In the present embodiment tempering for half an hour in a furnace at atmospheric pressure at about 300°C sufficed.

It has been proved, surprisingly, that it is indispensable to perform the vapour deposition in an oxidising atmosphere. When in the embodiment the aforesaid starting substance is deposited in a high vacuum without oxidising atmosphere, a greyish-blue layer is obtained, which cannot be transformed by tempering treatment into the desired purely blue-coloured layer.

Evaporation of the mixture from a carbon-containing crucible or from a tungsten crucible is not recommended since then reactions between the constituents of the mixture and the crucible could take place, which would lead to unsuitable layers.

It is a particular advantage of the method according to the present invention, that in contrast to the ceramic methods, wherein colourations are obtained by the tempering of glazing layers, the tempering temperatures can be kept low. According to the invention 300°C is sufficient while according to the known methods considerably higher temperatures (above 500°C) are required. This means that the known technique—apart from the fact the blue-coloured transparent layers of the quality attained by the present invention could not be produced at all by vapour deposition—was applicable to such substrate only which could stand high temperatures of that order. However, many glass sorts must not be subjected to such a high temperature or else their

quality deteriorates when the so-called transformation point is exceeded. Moreover such high temperatures may have the consequence of deformations which prohibit the use of the known methods in many cases.

For the choice of the second oxide or of further oxides in the starting mixture the point of view has to be taken that it is undesirable in most cases of application that the vapour-deposited layer should cause an increase in the reflection of the substratum deposited upon from the vapour phase. When an increase of reflexion is to be avoided, it is advisable to use such oxides whose refractive index does not depart too much from the refractive index of the substratum. The usual glass substrate of a refractive index of 1.52 have given excellent cooperation with SiO_2 (quartz). For substrata of a refractive index of 1.52 a refractive index of between 1.45 and 1.57 is permissible without the variation in reflectivity caused by the layer being detrimentally noticeable. For mating the refractive index in the visible length of waves range practically absorption-free oxides such as e.g. quartz, titania, zirconia, beryllia and others or mixtures of these oxides are particularly suitable.

A further advantage of the layers according to the present invention consists in that owing to their strong absorption and the intense blue colouration connected therewith they may be very thin. It is preferable to attain the desired intensity of the blue colouration in transparency by suitable selection of the layer thickness than by variation of the content in $Co(OH)_2$.

It is probable that the low tempering temperature, which is made possible by the method according to the present invention is due to the content in alumina of the starting material used for the production. It has been proved by the way that in any case the two oxides mentioned are required, and that the desired layers cannot be produced for example by the exclusive use of alumina or by dispensing with the alumina.

By the vapour deposition in an oxidizing atmosphere and the subsequent tempering the cobalt hydroxide contained in the starting material is converted into an oxydic form and possibly forms a mixed crystal with the other oxides contained in the layer.

Accordingly the layers produced by the method according to the present invention by vapour deposition on substrata have an oxydic basic substance practically not absorbing the visible light, wherein the colouring substances are embedded, and are characterised in that they contain a proportion of 5 to 15% by weight of alumina and of 20 to 40% by weight of cobalt in oxydically bound form.

WHAT WE CLAIM IS:—

1. A method for the production of blue-coloured layers permeable to light on substrata



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WHAT WE CLAIM IS:—

1. A method for the production of blue-coloured layers permeable to light on substrata



- by deposition from the vapour phase *in vacuo* of a mixture of oxides, wherein as a starting material for the evaporation a mixture is used, 30 to 40% by weight of which consist of cobalt hydroxide ($\text{Co}(\text{OH})_2$), 5 to 15% by weight of aluminium oxide (Al_2O_3) and the rest of other oxides which in the range of wave lengths of visible light are practically free from absorption, and wherein this mixture is deposited from the vapour phase in an oxidising atmosphere of sub-atmospheric pressure on to the substratum, and the layer obtained is subsequently tempered.
2. A method according to claim 1, wherein said mixture contains 10% of Al_2O_3 .
3. A method according to claim 1, wherein said mixture contains 35% of $\text{Co}(\text{OH})_2$.
4. A method according to claim 1, wherein a mixture is used of oxides the refractive index of which is substantially equal to the refractive index of the substratum to be deposited upon.
5. A method according to claim 1 or to claim 4, wherein said mixture contains silicon oxide (SiO_2).
6. A method according to claim 1, wherein the vapour deposition is carried out in an atmosphere the partial pressure of oxygen of which is of the order of magnitude of 10^{-4} Torr.
7. A method according to claim 1, wherein the layer is tempered for 30 min. in an atmosphere containing oxygen at substantially 300°C .
8. A blue coloured layer permeable to light produced on a substratum by the method according to claim 1, wherein the colouring substances are embedded in an oxydic basic substance practically free from absorption of visible light, which layer contains a proportion of 5 to 15% by weight of aluminium oxide and of 20 to 40% by weight of cobalt in an oxydically bound form.
9. A method according to claim 1, substantially as herein described.
10. A layer according to claim 8, substantially as herein described.

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