

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN AND RELATING TO THE PRODUCTION OF A HIGHLY REFRACTIVE OXIDE LAYER PERMEABLE TO LIGHT

(71) We, BALZERS PATENT- UND BETEILIGUNGS-AKTIE-GESELLSCHAFT, 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 the production of a highly refractive oxide layer permeable to light.

Thin oxide coatings are used in technology to a large extent as protective coatings and as coatings for optical purposes. As protective coatings, they serve for protecting sensitive surfaces of bodies, e.g. of lenses, surface mirrors and the like, from corrosion and mechanical damage. In the optical industry, oxide coatings are used for reflection-reducing coatings, interference filters, beam splitters, heat filters, cold light mirrors, coatings for spectacle lenses and the like. The mechanical and optical characteristics of such oxide coatings depend not only on the manner of application. More particularly, the selection of suitably highly refractive coatings for optical purposes is small, especially if high requirements with regard to homogeneity and absorption freedom exist.

20 The production of oxide coatings is known by direct vaporisation of oxidic starting substances in a vacuum and condensation of the vapor onto the substrate to be coated. This method has the disadvantage for optical purposes, that most oxides result in absorbing coatings on vaporisation and condensation in a vacuum, even if absorption free oxides are used as the starting substances. It is now known that this is based on the fact that most oxides are reduced by the vaporisation in a vacuum, and the non-saturated oxide has an optical absorption. There are only a few exceptions from this rule: SiO_2 can be vaporized in a vacuum by means of an electron beam so

that absorption free coatings are obtained.

In order to avoid these difficulties in the production of absorption free oxide coatings, further methods have been developed. It is known to produce absorption-free metal oxide coatings by vaporising the relevant metals and subsequent oxidisation of them, or by cathodic sputtering of the metals in oxygen. Furthermore, the vaporisation of the starting substances is an oxidising atmosphere is known.

In another known method for producing low absorption oxide layers by vaporising an oxidic or oxidisable starting substance, this is mixed with one or more elements of the rare earth group, or combinations of the said elements.

For many optical uses of vaporised coatings, it is essential that they are homogeneous, i.e. that their optical characteristics are the same in all parts of the coating. Coating systems, e.g. reflection reducing layers consisting of two coatings, are practically always calculated on the assumption of homogeneous coatings (since non homogeneous coatings can hardly be reproduced). For the fabrication of such coating systems it is thus a requirement that the homogeneous coatings on which the calculation is based are available. With interference layer systems, the greatest disturbance is the characteristic of many coatings, that their refractive index is not constant in the direction perpendicularly to the plan of the coating. In the following description, coatings in which the refractive index decreases with increasing coating thickness are called "negatively non-homogeneous" and those in which it increases are called "positively non-homogeneous". Experience has shown that especially the highly refractive coatings which have become known up to the present, insofar as they are suitable as a result of their absorption and their mechanical characteristics for optical technical uses, always incline towards non-homogeneity of the refractive index, the degree of the non-homogeneity being subjected to

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heavy fluctuations depending on the manufacturing conditions. Thus, zirconium oxide coatings, which owing to their high refractive index have their freedom from absorption in the visible spectral region and owing to their mechanical characteristics are proposed for the construction of layer systems, unfortunately exhibit a distinct negative non homogeneity, which, e.g. considerably reduces the efficiency of a reflection reducing layer, made up with such a coating. All attempts to avoid this negative non homogeneity by alteration of the vaporising method have failed up to now.

Many vaporised coatings exhibit a positive non homogeneity. There are applications in optical technology in which this can be accepted, e.g. with the highly refractive first layer of a reflection reducing coating consisting of two layers.

In Specification No. 1,149,204 resistors and method and apparatus for producing same have been disclosed, the method comprising bombarding a source of metal and a source of a dielectric with an ionised plasma to generate a mixture of active particles of metal and dielectric in the plasma and depositing particles from the mixture as a film on the surface of a substrate. The deposition on the substrate is to be carried out in an atmosphere of a gas which is substantially inert under the sputtering conditions, in order to preserve the metallic character of the active particles required for the electric conductivity of the resistor to be produced. Amongst a great number of metals and metal alloys suitable for performing that method tantalum, and amongst a great number of dielectrics zirconium oxide have been mentioned, without stating that by the use of tantalum and zirconium oxide as selected materials an unexpected and progressive effect can be attained.

The layers thus produced, though permeable to light, are absorbent to a marked degree owing to the presence of metallic particles therein.

According to the present invention, in contrast, a coating consisting wholly of oxides is to be produced which does not contain any light-absorbing metallic particles and whose electric conductivity is irrelevant and very low. If the starting material consists of oxides only, the atmosphere need not be oxidising; however if the starting material contains a metallic component the atmosphere has to be oxidising in order to produce a wholly oxidic coating.

The method according to the invention for the production of a highly refractive light transmitting oxide coating on a substrate by heating a starting mixture under vacuum until vaporisation thereof and condensing of the resultant vapour on the substrate to be coated, is characterised in that the starting mixture

contains the elements zirconium and tantalum in metallic or oxide form, at least one of said elements being in oxide form.

Exemplary embodiments of the invention will be further described in the following.

For the production of a coating, a mixture consisting of 30% (of the weight of the total mixture) of tantalum metal and 70% zirconium oxide (ZrO_2) is placed in the heatable vaporisation crucible of a vacuum vaporisation installation, and heated with a heating power of about 2.5 kw. Thus, a temperature of the material in the crucible to be vaporised, of about 1800°C is reached, and on the substrate (glass plate) arranged opposite the vaporisation crucible, a layer is deposited having a thickness of 250 nm with a growth rate of 35 nm per minute. The temperature of the substrate amounted to about 300°C. The vaporisation was performed in known manner in an oxygen atmosphere of 10^{-4} Torr. A coating was obtained which was hard and adhered well to the glass substrate and which was completely absorption free in the visible spectral region, and having a refractive index of $n=2.05$, constant over the entire coating thickness.

The latter can be checked in a simple manner if the highly refractive coating to be investigated is vaporised onto a glass plate of a lower refractive index until with illumination with light of a given wavelength, a minimum in the reflection occurs. If the vaporised coating is homogeneous, then the reflection capability of the surface of the glass plate provided with the coating, for the wavelength in question, can not be distinguished from the reflection capability of the uncovered glass surface; a coating then exists for which the relation $\frac{\lambda}{2} = nd$ applies, where λ is the wave-

length in question, n is the refractive index of the coating material and d the thickness of the coating. Thus, relative to the uncovered glass surface, there is a higher reflection capability if the coating is positively non homogeneous and a lower reflection capability if the coating is negatively non homogeneous.

For the performance of the invention, starting mixtures in which the element tantalum is present as a metal, and the element zirconium is however present in oxide form, are particularly preferred. The proportion of tantalum metal should in this case not be below 20% of the weight of the total mixture; the same is true for the zirconium oxide component.

However, the coating produced by the method according to the invention is surprisingly only slightly dependent on the mixture proportions of the components in the starting mixture, as has been shown by thorough investigations.

In this respect, various mixtures of tantalum metal and zirconium oxide were produced and vaporised onto glass plates from a tungsten crucible. By X-ray fluorescence analysis, the ratio of the number of tantalum atoms to the

number of zirconium atoms in the coating was established. The following Table 1 shows the surprising result for three different coatings.

TABLE 1

Example No.	Weight ratio Ta : ZrO ₂ in the starting mixture	Ratio of the atom numbers Ta/Zr in the Starting mixture	Coating (XF analysis)
1	30 : 70	1 : 3.3	1 : 1.7
2	50 : 50	1 : 1.46	1 : 1.78
3	70 : 30	1 : 0.62	1 : 1.36

From this table it is seen that the ratio Ta/Zr in the vaporised coatings is approximately constant (within 20%) in spite of strong alteration (by the factor 5) in the starting material.

This characteristic of the method according to the invention represents a great progress in manufacturing technology relative to the known vaporising methods. It is not necessary, as hitherto in the vaporisation of mixtures, to pay regard to a particularly precise composition thereof. It has furthermore been shown that also the usual decisive factors of the vaporising method can be altered in relatively wide limits. Hitherto, in the vaporisation of mixtures, the question of the vaporising speed (vaporising rate) was particularly critical. With the same starting material, with different vaporising speeds, quite different condensates were obtained. Contrary to this, the invention has opened a path which can be reliably proceeded upon without great expense, for the production of highly refractive coatings of good reproducibility.

In the following Table 2, several further embodiments for the method according to the invention are given. For all of these examples, the following applies: The vaporisation is performed in a conventional vacuum vaporising installation, the starting mixture being heated in a crucible to a sufficient temperature

(e.g. 1700 to 1800°C) at which it vaporises. The heating of the mixture in the crucible can take place in known manner, whether it be by use of an electrically resistance heated tungsten crucible or whether the heating is performed by means of an electron beam. In the latter case, the electron beam is directed onto the surface of the mixture to be vaporised, which can thus be directly heated to the vaporising temperature. The heating power of the electron beam, as known, is given by the product of the beam current strength and the applied voltage. In all following examples, coatings are obtained which in the sense described in the introduction, are completely homogeneous, although the vaporisation was performed with a growth rate of the coating of about 350 Å per minute and up to coating thicknesses of about 300 nm. In order to obtain hard and resistant coatings as absorption free as possible, it is advisable to heat the substrates onto which vaporisation is to be carried out (in the examples glass plates are used for this) to a temperature of about 300°C before the vaporising. Furthermore, depending on the purpose of use of the coatings to be produced, it is advisable to perform the vaporisation in known manner in an oxidising atmosphere, e.g. with an oxygen pressure of about 2×10^{-4} Torr, see Patent Specification No. 775,002.

TABLE 2

Example No.	Mixture	Weight Ratio	Vaporisation by
4	Ta ₂ O ₅ : ZrO ₂	30 : 70	resistance heated tungsten crucible
5	Tantalum : Zirconium suboxide ZrO ₂	1 : 1	electron beam 2.5 kw
6	Ta ₂ O ₅ : Zr	60 : 40	resistance heated tungsten crucible
7	Ta ₂ O ₅ : Zirconium suboxide	1 : 1	resistance heated tungsten crucible
8	Ta : ZrO ₂	30 : 70	electron beam 2.5 kw

The tantalum suboxide referred to can be obtained by melting together a stoichiometric mixture of tantalum metal and tantalum pentoxide, the zirconium suboxide referred to can be obtained by melting together a stoichiometric mixture of zirconium metal and zirconium dioxide. The melting together can take place in a preliminary manufacturing procedure for the relevant suboxide, or in the vaporisation crucible itself, mixtures of three components then being started from. In this case, also for example 5, a mixture of Ta, Ta₂O₅ and ZrO₂ is used, and for example 7 a mixture of Ta₂O₅, Zr and ZrO₂.

The coatings produced by the method of the invention can be used for numerous applications. E.g., as already mentioned, they are very well suitable for the construction of multi-layer systems. Compared with single layer reflection reducing coatings, the multi-layer systems have the advantage that they allow an essentially stronger reduction of reflection of a treated surface.

Furthermore, the coatings produced according to the invention can be used for interference systems with good UV transmission, since they can be produced practically absorption free down to 340 nm.

As already mentioned, Examples 1 to 3 indicate that by the method according to the invention a coating of a given composition is obtained and it has been assumed that the coating which is composed of oxygen, tantalum and zirconium in the ideal case has a ratio of the atom numbers of tantalum to zirconium 1:1.5. For practical requirements deviation from this theoretical value is of course possible and moreover it has to be taken into account that the measurement of this ratio is liable to errors. It can however be determined that this ratio for a coating according to the inven-

tion always lies within the limits of 1:1 to 1:2. By X-ray diagrams it has been found that the coatings obtained, contain only a very low proportion of crystalline zirconium oxide, if any at all, and this can be considered to explain the excellent homogeneity.

By the method according to the present invention a light-transmitting coating is produced, which does not have the undesirable characteristic of negative non-homogeneity; which has a high refractive index; is mechanically and chemically resistant and can be readily produced by deposition from the vapour phase.

WHAT WE CLAIM IS:—

1. A method for the production of a highly refractive light transmitting oxide coating on a substrate by heating a starting mixture under a vacuum until vaporisation thereof, and condensing the resultant vapour on the substrate to be coated, said starting mixture containing the elements zirconium and tantalum in metallic or oxide form, at least one of said elements being in oxide form.

2. A method as claimed in claim 1, wherein the starting mixture contains a suboxide.

3. A method as claimed in claim 1 or 2, wherein the starting mixture contains tantalum metal.

4. A method as claimed in claim 3, wherein the starting mixture contains at least 20% by weight of tantalum metal.

5. A method as claimed in any one of claims 1 to 4, wherein the starting mixture contains at least 20% by weight ZrO₂.

6. A method as claimed in claim 1, wherein the starting mixture contains 50% tantalum metal and 50% zirconium oxide.

7. A method as claimed in any one of claims 1 to 6, wherein the condensation of the vapor produced by vaporisation of the starting

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tion always lies within the limits of 1:1 to 1:2. By X-ray diagrams it has been found that the coatings obtained, contain only a very low proportion of crystalline zirconium oxide, if any at all, and this can be considered to explain the excellent homogeneity.

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5. A method as claimed in any one of claims 1 to 4, wherein the starting mixture contains at least 20% by weight ZrO₂.

6. A method as claimed in claim 1, wherein the starting mixture contains 50% tantalum metal and 50% zirconium oxide.

7. A method as claimed in any one of claims 1 to 6, wherein the condensation of the vapor produced by vaporisation of the starting



mixture, on to the substrate to be coated, is performed in the presence of an oxidising atmosphere.

5 8. A coated substrate produced by the method of claim 1, wherein the coating consists of oxygen, tantalum and zirconium and the ratio of the numbers of atoms of tantalum

to zirconium lies in the range 1:1 to 1:2.

9. A method for the production of a highly refractive light transmitting oxide coating on a substrate, substantially as hereinbefore described. 10

S. MITTLER,
Agent for Applicants.

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