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(54) **Yttrium oxide based gas mantle**

Yttriumoxid enthaltender Gasglühkörper

Manchon pour lampe à gaz contenant de l'oxyde d'yttrium

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Description

[0001] The present invention relates to incandescent low-pressure gas mantles useful for fixed fuel-burning lanterns, such as stationary lamp posts, patio lights or wall-bracket mounted lights. Typically, such mantles are used with gas pressures of about 2.7 KPa (280mm H_2O gauge). More particularly, the present invention relates to pre-formed (hard) gas mantles.

[0002] The successful commercial development of an incandescent gas mantle depends on a number of factors. Of primary importance is the illumination provided by the mantle (illuminating power and colour), both in absolute terms and in respect of the amount of fuel consumed. Also important is the durability of the mantle both in terms of its physical strength and period of useful light output.

[0003] Traditionally, incandescent gas mantles have been made from thorium oxide with small quantities of cerium oxide and magnesium oxide and are known as Welsbach mantles (see, for example, US 563524). Thorium is radioactive and decays to give, inter alia, thoron-220 (radon-220) and lead. Although the quantity of thorium used in each mantle is small and may be considered to present an insignificant health risk in the finished article, the industrial production of gas mantles uses large quantities of thorium which require careful and expensive handling procedures. Thus, there is a potential health and environmental hazard at manufacturing sites. In addition these compositions are brittle and so may require an additional hardening procedure during manufacture. This involves coating the head of the mantle with a solution of (usually) aluminium nitrate. It cannot be applied to the body of the mantle because the hardening metals are not luminescent. As a result, these mantles often break on the body of the mantle just below the attachment head.

[0004] EP 0082062 discloses non-radioactive mantles based on zirconia which contain calcium oxide (10 to 25 mol%), aluminium oxide and magnesium oxide (0 to 5 mol% total), and oxides selected from iron, manganese, praseodymium and cerium (0 to 1 mol% total). Calcium oxide is used to promote a cubic zirconia crystal structure which is desirable for resistance to mechanical and thermal shocks.

[0005] EP(UK) 0159212 discloses mantles based on those described in EP 0082062 in which the calcium oxide is replaced partially or completely by yttrium oxide as the cubic zirconia stabiliser. Yttrium oxide is present in the range of 5 to 20 mol%, with magnesium oxide/aluminium oxide (2 to 15 mol%) and one or more of the oxides of iron, chromium, manganese, praseodymium and cerium (0.01 to 1.0 mol% total).

[0006] EP 0101086 discloses gas mantles comprising a host metal oxide (eg. yttrium, thorium, zirconium or rare earth metal oxide), a rare earth metal oxide (different to the host metal oxide) as a radiation modifying dopant, and a strengthening dopant (eg. an oxide of aluminium, magnesium, beryllium or calcium).

[0007] GB 2145811 discloses an yttrium oxide based gas mantle mainly for use in portable lanterns which are supplied with high pressure gas from a bottle or cylinder. The mantle contains cerium oxide to improve the illuminating power and a small amount of a crystal growth inhibitor such as magnesium oxide and/or aluminium oxide. To obtain satisfactory illuminating power, a critical amount of cerium oxide of 1.8 to 3.8 parts per 100 parts of yttrium oxide by weight is essential. This corresponds to a maximum range of 2.3 to 4.8 mol% of the total composition. The disclosed quantity of magnesium oxide and aluminium oxide, 0.1 to 2.0 parts per 100 parts of yttrium oxide by weight, corresponds to 0.54 to 9.9 mol% magnesium oxide and 0.21 to 4.2 mol% aluminium oxide of the total composition. However, the only composition specifically disclosed is unsatisfactory for low pressure gas mantles because it has inadequate light output characteristics and tensile strength (see Table 1).

[0008] The expression "pre-formed" is used herein to describe a mantle which has been burnt off by the manufacturer of the mantle before sale, the mantle usually being tied onto a ring prior to the burning off.

[0009] The object of the present invention is to provide a low pressure pre-formed gas mantle having good light output, tensile strength and durability.

[0010] According to a first aspect of the present invention, there is provided a pre-formed low pressure gas mantle having a body comprising:

(A) 77.1 to 85.3 mol% yttrium oxide as the predominant metal oxide, (B) 1.4 to 3.1 mol% of at least one lanthanide oxide, (C) 2.2 to 5.0 mol% of at least one of magnesium oxide and aluminium oxide, and (D) 11.1 to 14.8 mol% of calcium oxide, based on the total molar content of (A), (B), (C) and (D).

[0011] The above ratio of components (A), (B), (C) and (D) is critical in obtaining a low-pressure gas mantle which is of high illuminating power and produces a light of satisfactory colour. More particularly, the durability (i.e. length of time over which the mantle can be burnt without significant deterioration of the light output) of mantles according to the present invention is good. In addition, mantle bodies having this composition are of a sufficient strength that a hardening procedure to avoid rupture of the mantle is not required.

[0012] Preferably said body consists only of components (A), (B), (C) and (D).

[0013] Preferably component (B) consists of at least one of cerium oxide, praseodymium oxide and erbium oxide and more preferably is cerium oxide.

[0014] Component (C) is preferably magnesium oxide.

[0015] A preferred molar composition range is:

yttrium oxide 78.7 to 83.2 %;
cerium oxide 1.7 to 2.9 %;
magnesium oxide 3.3 to 4.8 %;
calcium oxide 12.6 to 14.2 %.

[0016] A highly preferred molar composition is:

yttrium oxide 80.4 %;
cerium oxide 2.55 %;
magnesium oxide 4.00 %;
calcium oxide 13.05 %.

[0017] According to a second aspect of the present invention, there is provided a process for the preparation of a pre-formed low pressure gas mantle, including the steps of:-

(i) impregnating a combustible reticulated material with an aqueous solution of metal salts;
(ii) converting said salts to the corresponding metal hydroxides; and
(iii) converting the metal hydroxides to the corresponding oxides so as to form a body comprising: (A) 77.1 to 85.3 mol% yttrium oxide as the predominant metal oxide, (B) 1.4 to 3.1 mol% of at least one lanthanide oxide, (C) 2.2 to 5.0 mol% of at least one of magnesium oxide and aluminium oxide, and (D) 11.1 to 14.8 mol% of calcium oxide, based on the total molar content of (A), (B), (C) and (D).

[0018] Step (ii) may be achieved using ammonia vapour, aqueous ammonia solution, an amine and/or a caustic alkali solution. The use of an amine, such as triethanolamine, results in a soft, flexible impregnated material which is easy to shape, although it has been found that after step (iii) mantles so prepared contain less magnesium oxide and cerium oxide than expected. It is thought that this may be due to selective dissolution of magnesium and cerium in the triethanolamine, thereby leaching these components from the knitted mesh. Preferably, step (ii) is effected using an aqueous KOH solution (25% by weight) at room temperature, when such loss does not occur.

[0019] The combustible reticulated material may be any woven combustible filamentary material. Such filamentary material preferably has a fineness of about 220 to 350 Dtex, with a Dtex of about 330 being particularly preferred. Preferably said material is rayon.

[0020] Preferably, the concentration of the metal salts in step (i) is 25 to 50 % by weight. The metal salts are preferably nitrates. It has been found that, at lower concentrations, there is a risk that insufficient metal salt may be absorbed into the reticulated material, resulting in weak mantles. At higher concentrations, the conversion step (ii) tends to be less efficient, which can lead to uneven conversion. In addition, the impregnated material tends to be stiff and it becomes progressively more difficult to achieve the required mantle shape without breakage.

[0021] The present invention will now be described in further detail in the following examples:-

Example 1

[0022] Knitted tubes of rayon mesh (330 Dtex) are soaked in an impregnating solution of metal nitrates having the following composition:

30 Kg $Y(NO_3)_3.6H_2O$
0.5 Kg $Mg(NO_3)_2.6H_2O$
0.54 Kg $Ce(NO_3)_3.6H_2O$
1.5 Kg $Ca(NO_3)_2.4H_2O$
72.46 Kg H_2O

On saturation, the mesh tubes are removed from the solution, drained and dried. The metal nitrates which are now absorbed onto the mesh are converted to the corresponding hydroxides by immersion in an aqueous solution of aqueous KOH (25% by weight) at ambient temperature. The hose is then washed and dried.

[0023] When dry, the mesh tubes are cut and the mantles shaped in a manner known per se. Since no hardening procedure is necessary, the mantles are now tied to ceramic rings by means of a non-combustible yarn, eg. an aramid or asbestos, for health reasons an aramid is preferred.

[0024] The rayon is then burnt off, to leave a hard lattice of metal oxides. This is done in a manner known per se,

with a powerful flame having a high flow of an air and gas mixture.

[0025] The mantles thus prepared have a molar composition of:-

80.4 % yttrium oxide
4.0 % magnesium oxide
2.55 % cerium oxide
13.05 % calcium oxide.

Example 2

[0026] The same method is employed as for Example 1, using the following impregnating solution:

30 Kg $Y(NO_3)_3.6H_2O$
0.6 Kg $Mg(NO_3)_2.6H_2O$
0.5 Kg $Ce(NO_3)_3.6H_2O$
1.3 Kg $Ca(NO_3)_2.4H_2O$
72.6 Kg H_2O

[0027] The mantles thus prepared have a molar composition of:-

81.32 % yttrium oxide
4.86 % magnesium oxide
2.39 % cerium oxide
11.43 % calcium oxide.

Example 3

[0028] The same method is employed as for Example 1, using the following impregnating solution:

30 Kg $Y(NO_3)_3.6H_2O$
0.35 Kg $Mg(NO_3)_2.6H_2O$
0.51 Kg $Ce(NO_3)_3.6H_2O$
1.4 Kg $Ca(NO_3)_2.4H_2O$
72.74 Kg H_2O

[0029] The mantles thus prepared have a molar composition of:-

82.23 % yttrium oxide
2.86 % magnesium oxide
2.46 % cerium oxide
12.45 % calcium oxide.

Comparative Example 1 (C1):

[0030] The same method is employed as for Example 1 above, using the following impregnating solution:

29.5 Kg $Y(NO_3)_3.6H_2O$
1.0 Kg $Mg(NO_3)_2.6H_2O$
0.54 Kg $Ce(NO_3)_3.6H_2O$
1.5 Kg $Ca(NO_3)_2.4H_2O$
72.46 Kg H_2O

[0031] The mantles thus prepared have a molar composition of:-

77.02 % yttrium oxide
7.80 % magnesium oxide
2.48 % cerium oxide
12.70 % calcium oxide.

Comparative Example 2 (C2):

[0032] The same method is employed as for Example 1 above, using the following impregnating solution:

30 Kg $Y(NO_3)_3.6H_2O$
1.5 Kg $Mg(NO_3)_2.6H_2O$
0.2 Kg $Ce(NO_3)_3.6H_2O$
1.5 Kg $Ca(NO_3)_2.4H_2O$
71.80 Kg H_2O

[0033] The mantles thus prepared have a molar composition of:-

75.57 % yttrium oxide
11.29 % magnesium oxide
0.89 % cerium oxide
12.25 % calcium oxide.

Comparative Example 3 (C3):

[0034] The same method is employed as for Example 1 above, using the following impregnating solution, which has the same molar composition as that disclosed in GB-B-2145811:

286.9 g $Y(NO_3)_3.6H_2O$
5.85 g $Mg(NO_3)_2.6H_2O$
7.3 g $Ce(NO_3)_3.6H_2O$
166.7 g H_2O

[0035] Denitration was effected with ammonium vapour rather than caustic alkali solution. The mantles thus prepared have a molar composition of:-

90.43 % yttrium oxide
5.41 % magnesium oxide
4.06 % cerium oxide.

[0036] The properties of mantles 1 to 3 and C1 to C3 are indicated in Table 1 below.

TABLE 1

Sample	Average Light Output (Lux)	Tensile Strength[1]	Light Quality[2]	Durability (200hrs)[3]	Durability (2000hrs)[3]
1	38	pass	good	pass	pass
2	32	pass	good	pass	pass
3	35	pass	good	pass	pass
C1	36	fail	good	pass	fail
C2	20	fail	poor	pass	fail
C3	15	fail	poor	pass	fail

[1]Ability to withstand at least 800 bumps on a shock treatment machine (pass), such as is available from Messrs. Alexander Wright & Co., Ltd, London.
[2]Qualitative assessment made by experienced workers in the field of mantle production. The light should not be unduly yellow (good).
[3]Light output is substantially unchanged after indicated number of hours continuous burning (pass).

[0037] As can be seen from Table 1, Examples 1 to 3 are superior to Comparative Examples 2 and 3 in terms of average light output, light quality, tensile strength and durability. Examples 1 to 3 are comparable to Comparative Example 1 in terms of average light output and light quality, but superior in terms of tensile strength and durability.

Claims

1. A pre-formed low pressure gas mantle having a body comprising: (A) 77.1 to 85.3 mol% yttrium oxide as the predominant metal oxide, (B) 1.4 to 3.1 mol% of at least one lanthanide oxide, (C) 2.2 to 5.0 mol% of at least one of magnesium oxide and aluminium oxide, and (D) 11.1 to 14.8 mol% of calcium oxide, based on the total molar content of (A), (B), (C) and (D).

2. A mantle as claimed in claim 1, wherein said body consists only of components (A), (B), (C) and (D).

3. A mantle as claimed in claim 1 or 2, wherein component (B) consists of at least one of cerium oxide, praseodymium oxide and erbium oxide.

4. A mantle as claimed in claim 3, wherein component B is cerium oxide.

5. A mantle as claimed in any preceding claim, wherein component (C) is magnesium oxide.

6. A mantle as claimed in any preceding claim wherein the molar composition range is:

   yttrium oxide (A) 78.7 to 83.2 %;
   cerium oxide (B) 1.7 to 2.9 %;
   magnesium oxide (C) 3.3 to 4.8 %;
   calcium oxide (D) 12.6 to 14.2 %.

7. A mantle as claimed in claim 6, wherein the molar composition is:

   yttrium oxide 80.4 %;
   cerium oxide 2.55 %;
   magnesium oxide 4.00 %;
   calcium oxide 13.05 %.

8. A process for the preparation of a pre-formed low pressure gas mantle, including the steps of:-

   (i) impregnating a combustible reticulated material with an aqueous solution of metal salts;
   (ii) converting said salts to the corresponding metal hydroxides; and
   (iii) converting the metal hydroxides to the corresponding oxides so as to form a body comprising: (A) 77.1 to 85.3 mol% yttrium oxide as the predominant metal oxide, (B) 1.4 to 3.1 mol% of at least one lanthanide oxide, (C) 2.2 to 5.0 mol% of at least one of magnesium oxide and aluminium oxide, and (D) 11.1 to 14.8 mol% of calcium oxide, based on the total molar content of (A), (B), (C) and (D).

9. A process as claimed in claim 8, wherein step (ii) is achieved using ammonia vapour, aqueous ammonia solution, an amine and/or a caustic alkali solution.

10. A process as claimed in claim 9, wherein step (ii) is effected using an aqueous KOH solution at room temperature.

11. A process as claimed in any one of claims 8 to 10 in which the combustible reticulated material referred to in step (i) is a woven combustible filamentary material having a fineness in the range of about 220 to 350 Dtex.

12. A process as claimed in claim 11, in which the woven combustible reticulated material has a fineness of 330Dtex.

13. A process as claimed in any one of claims 8 to 12, in which the concentration of the metal salts in step (i) is 25 to 50 % by weight.

14. A process as claimed in any preceding claim, in which the metal salts are nitrates.

Patentansprüche

1. Vorgeformter Niederdruck-Gasglühkörper mit einem Körper, der aufweist: (A) 77,1% bis 85,3 Mol% Yttriumoxid

als das überwiegende Metalloxid, (B) 1,4% bis 3,1 Mol% mindestens ein Lanthanoidoxid, (C) 2,2% bis 5,0 Mol% mindestens ein aus Magnesiumoxid und Aluminiumoxid, sowie (D) 11,1% bis 14,8 Mol% Calciumoxid bezogen auf den molaren Gesamtgehalt an (A), (B), (C) und (D).

2. Glühkörper nach Anspruch 1, wobei der Körper im wesentlichen lediglich aus den Komponenten (A), (B), (C) und (D) besteht.

3. Glühkörper nach Anspruch 1 oder 2, wobei Komponente (B) mindestens aus einem aus Ceroxid, Praseodymoxid und Erbiumoxid besteht.

4. Glühkörper nach Anspruch 3, wobei Komponente (B) Ceroxid ist.

5. Glühkörper nach einem der vorgenannten Ansprüche, wobei die Komponente (C) Magnesiumoxid ist.

6. Glühkörper nach einem der vorgenannten Ansprüche, wobei die molare Zusammensetzung in dem Bereich liegt:

Yttriumoxid (A) 78,7 bis 83,2%;

Ceroxid (B) 1,7 bis 2,9%;

Magnesiumoxid (C) 3,3 bis 4,8%;

Calciumoxid (D) 12,6 bis 14,2%.

7. Glühkörper nach Anspruch 6, wobei die molare Zusammensetzung beträgt:

Yttriumoxid (A) 80,4%;

Ceroxid (B) 2,55%;

Magnesiumoxid (C) 4,00%;

Calciumoxid (D) 13,05%.

8. Verfahren zur Herstellung eines vorgeformten Niederdruck-Gasglühkörpers, einschließend die Schritte:

(i) Tränken eines brennbaren vernetzten Materials mit einer wässrigen Lösung von Metallsalzen;

(ii) Umwandeln der Salze in die entsprechenden Metallhydroxide; und

(iii) Umwandeln der Metallhydroxide in die entsprechenden Oxide, um so einen Körper zu formen, der aufweist: (A) 77,1% bis 85,3 Mol% Yttriumoxid als das überwiegende Metalloxid, (B) 1,4% bis 3,1 Mol% mindestens ein Lanthanoidoxid, (C) 2,2% bis 5,0 Mol% mindestens ein aus Magnesiumoxid und Aluminiumoxid, sowie (D) 11,1% bis 14,8 Mol% Calciumoxid bezogen auf den molaren Gesamtgehalt an (A), (B), (C) und (D).

9. Verfahren nach Anspruch 8, bei welchem Schritt (ii) ausgerührt wird unter Verwendung von Ammoniakdampf, wässrige Ammoniaklösung, einem Amin und/oder einer Ätzalkalilösung.

10. Verfahren nach Anspruch 9, bei welchem Schritt (ii) ausgeführt wird unter Verwendung einer wässrigen KOH-Lösung bei Raumtemperatur.

11. Verfahren nach einem der vorgenannten Ansprüche 8 bis 10, bei welchem das in Schritt (i) bezeichnete brennbare vernetzte Material ein gewebtes, brennbares, filamentäres Material ist, das eine Feinheit im Bereich von etwa 220 bis 350 dtex hat.

12. Verfahren nach Anspruch 11, bei welchem das gewebte, brennbare Netzmaterial eine Feinheit von 330 dtex hat.

13. Verfahren nach einem der vorgenannten Ansprüche 8 bis 12, bei welchem die Konzentration der Metallsalze in

Schritt (i) 25% bis 50 Gewichtsprozent beträgt.

14. Verfahren nach einem der vorgenannten Ansprüche, bei welchem die Metallsalze Nitrate sind.

Revendications

1. Manchon préfaçonné pour gaz sous faible pression possédant un corps comprenant : (A) de 77,1 à 85,3% en mole d'oxyde d'yttrium en tant qu'oxyde métallique prédominant, (B) de 1,4 à 3,1% en mole d'au moins un oxyde de lanthane, (C) de 2,2 à 5,0% en mole d'au moins un parmi l'oxyde de magnésium et l'oxyde d'aluminium, et (D) de 11,1 à 14,8% en mole d'oxyde de calcium, basé sur la teneur molaire totale de (A), (B), (C) et (D).

2. Manchon tel que revendiqué par la revendication 1, dans lequel le corps est constitué uniquement par les composants (A), (B), (C) et (D).

3. Manchon tel que revendiqué par la revendication 1 ou 2, dans lequel le composant (B) est constitué par au moins un oxyde parmi l'oxyde de cérium, l'oxyde de praséodyme et l'oxyde d'erbium.

4. Manchon tel que revendiqué par la revendication 3, dans lequel le composant (B) est constitué par de l'oxyde de cérium.

5. Manchon tel que revendiqué par l'une quelconque des revendications qui précèdent, dans lequel le composant (C) est constitué par de l'oxyde de magnésium.

6. Manchon tel que revendiqué par l'une quelconque des revendications qui précèdent, dans lequel l'étendue de la composition molaire est :

pour l'oxyde d'yttrium (A) de 78,7 à 83,2%
pour l'oxyde de cérium (B) de 1,7 à 2,9%
pour l'oxyde de magnésium (C) de 3,3 à 4,8%
pour l'oxyde de calcium (D) de 12,6 à 14,2%.

7. Manchon tel que revendiqué par la revendication 6, dans lequel la composition molaire est :

pour l'oxyde d'yttrium de 80,4%
pour l'oxyde de cérium de 2,55%
pour l'oxyde de magnésium de 4,0%
pour l'oxyde de calcium de 13,05%.

8. Procédé pour la préparation d'un manchon préfaçonné pour gaz sous faible pression comprenant les étapes de :

(i) imprégnation d'un matériau réticulé combustible avec une solution aqueuse de sels de métaux ;
(ii) conversion des sels dans les hydroxydes correspondants de métaux ; et
(iii) conversion des hydroxydes de métaux dans les oxydes correspondants, de manière à former un corps comprenant : (A) de 77,1 à 85,3% en mole d'oxyde d'yttrium en tant qu'oxyde métallique prédominant, (B) de 1,4 à 3,1% en mole d'au moins un oxyde de lanthane, (C) de 2,2 à 5,0% en mole d'au moins un parmi l'oxyde de magnésium et l'oxyde d'aluminium, et (D) de 11,1 à 14,8% en mole d'oxyde de calcium, basé sur la teneur molaire totale de (A), (B), (C) et (D).

9. Procédé suivant la revendication 8, dans lequel l'étape (ii) est exécutée en utilisant de la vapeur d'ammoniac, une solution aqueuse d'ammoniaque, une solution d'amine et/ou d'alcali caustique.

10. Procédé suivant la revendication 9, dans lequel l'étape (ii) est exécutée en utilisant une solution aqueuse de KOH à la température ambiante.

11. Procédé suivant l'une quelconque des revendications 8 à 10, dans lequel le matériau réticulé combustible auquel on se réfère pour l'étape (i) est un matériau en filaments tissé combustible possédant une finesse dans l'ordre de grandeur d'environ 220 à 350 Dtex.

12. Procédé suivant la revendication 11, dans lequel le matériau réticulé tissé combustible possède une finesse de 330 Dtex.

13. Procédé suivant l'une quelconque des revendications 8 à 12, dans lequel la concentration des sels de métaux dans l'étape (i) est de 25 à 50% en poids.

14. Procédé suivant l'une quelconque des revendications précédentes, dans lequel les sels de métaux sont des nitrates.