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# METHOD OF APPLYING AN ALKALI-EARTH METAL GETTER

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Our invention relates to a method of coating the inner wall of a vessel, for example the bulb of an incandescent lamp with a getter layer consisting of a metal or a mixture of metals of the group formed by magnesium, calcium, strontium and barium.

A getter is usually employed for binding unwanted residual gases in a vessel in order to improve the vacuum or to maintain the same or to avoid the presence of gases which are harmful to filament wires and the like provided in the vessel.

To this end use is sometimes made of phosphorus in incandescent lamps. Phosphorus is applied for this purpose to the filament wire or to another place in the lamp, where a temperature is reached sufficient for the phosphorus to be evaporated. After exhausting at a raised temperature and after filling with inert gases, if desired, the lamp is sealed. By burning the lamp the phosphorus is evaporated and any residual gases in the lamp, for example residual oxygen and water vapor are bound.

The use of phosphorus as a getter involves a few disadvantages. The temperature of the lamp during the sealing process and the exhausting must, for example, not exceed the evaporation temperature of phosphorus or the temperature at which phosphorus burns spontaneously in air. This means in practice that the evacuation is carried out at a temperature, which lies 100° C. to 200° C. below the softening temperature of the glass of the bulbs of incandescent lamps for general use.

However, it is desirable to carry out degasification at an optimum temperature, since it has been found that during the lifetime of the lamp gases may be released, for example water vapor, which may adversely affect the lifetime of the filament wire.

A further disadvantage resides in that the quantity of phosphorus must be applied in an accurately defined measure, since otherwise yellow-brown deposits may be formed of the wall of the bulb, so that the light output of the lamp is reduced.

This excess quantity of phosphorus is inactive; gettering takes place only in the vapor state.

It has been proposed to use a getter barium and other alkali-earth metals, inter alia in radio tubes. To this end an alkali-earth metal oxide or such a carbonate may be heated in the vessel in contact with a reducing agent. The reducing agent may be formed by the metal of the filament wire of an incandescent lamp.

However, various alkali-earth metal oxides are hygroscopic, while the carbonates introduce free carbon dioxide gas into the lamp, which gas is capable of reacting with the alkali-earth getter, which is thus wholly or partly poisoned.

The invention has for its object to overcome these difficulties and to provide a more efficaceous method and a better defined product.

It has been found that getter layers can be obtained using, as a getter, a substance formed by a compound of the gross formula: $(MeO)_nXO_m$, wherein Me is Mg, Ca, Sr, Ba or a mixture of the same, X is a metal for example W, Mo, Ti and $m$ is equal to the valency of the metal X divided by 2, the said difficulties being thus avoided.

In the compounds suitable for use in the method according to the invention the metal X may be formed by



one or more metals of the fifth, sixth and seventh group of the Periodical System. As a rule the oxides of metals of these groups are capable of forming compounds with alkali-earth metal oxides, in which case in the said gross formula $n$ is higher than 1. It is advisable to choose such compounds in incandescent lamps that the metal X cannot form alloys with the metal of the filament wire during burning likely to shorten the lifetime of the filament wire. In general, the compounds are at most slightly hygroscopic and are not at all reactive or only slightly reactive with carbon dioxide, so that they can be better handled than the oxides and carbonates of the alkali-earth metal oxides, particularly the barium oxide and barium carbonate. It has been found that the compounds are dissociated, in general, at temperatures in excess of 1300° C. in contact with metals such as tungsten, molybdenum, tantalum, zirconium, alkali-earth metal being set free, which is evaporated at this temperature.

The group of compounds particularly suitable within the scope of the invention includes inter alia $Ba_3WO_6$, $Ba_2CaMoO_6$, $Ba_2TiO_4$; other suitable compounds are, for example, $Ba_3TaO_5$, $BaSr_2MoO_6$, $Ba_2LaTaO_6$.

The compounds can be obtained by heating a mixture of an oxide or a carbonate of the desired alkali-earth metal with a metal such as tungsten, molybdenum and others, an oxide of such a metal or an alkali-earth metal compound with the metal oxide for example alkali-earth tungstenate, molybdate and others.

With the reduction of the alkali-earth compounds thus obtained the alkali-earth compounds may be mixed with a reducing substance, for example zirconium, tungsten and others. It has been found that already with a quantity of one third of the theoretically required quantity an appreciable effect is obtained, when the mixture is disposed on a heated metal surface. The reduction of the alkali-earth compound is then performed more rapidly and more completely.

In order to provide easy handling of the compounds, they may be applied for example in the form of suspensions, if necessary with a binder or they may be formed by pills, grains or other bodies, by molding.

In certain cases it may be advantageous to use alkali-earth compounds together with phosphorus. Some advantages of the use of the alkali-earth compounds alone are then sacrificed, it is true, but this may be compensated for by other advantages, which may render the use of the combined compounds of alkali-earth metal and phosphorus desirable, which will be explained more fully hereinafter.

It has been found that the method according to the invention is particularly suitable for coating the inner wall of the bulb of an incandescent lamp. An extremely thin, visually imperceptible getter film of barium or one of the other alkali-earth metals or mixtures thereof has a markedly favorable effect on the drop in light output and on the tolerances in lifetime. The method according to the invention will now be described more fully with reference to the use of basic barium tungstenate ($Ba_3WO_6$) in order to obtain a getter film on the bulb of an incandescent lamp.

Prior to or subsequent to the mounting in the base of a lamp the filament wire of tungsten is coated with $Ba_3WO_6$. To this end a suspension of $Ba_3WO_6$ in an organic solvent, if necessary with a binder is applied to the filament wire by dipping, painting, spraying, by cataphoretical agency or by a further method. Then the filament wire is mounted in a bulb; the lamp is exhausted and degasified at a higher temperature.

The value of the degasifying temperature is limited, with the use of $Ba_3WO_6$ and other alkali-earth compounds as the sole source of getter material, only by the properties of the material of the incandescent lamp, particularly by the softening temperature of the glass of the bulb of said lamp. This temperature lies, in general, below the reduction temperature and decomposition temperature of the getter-producing compounds. Degasification may therefore be carried out at a higher temperature than in the case in which phosphorus is used as a getter.

The lamp is then sealed and the cap is applied.

The lamp is then burnt at a voltage which is usually 10 to 15% higher than the voltage to be normally used for the lamp.

During this pre-burning process a gas discharge is produced for a few seconds; this becomes manifest by a bluish light radiation in the proximity of the current supply wires in the bulb. This gas discharge is produced by undesirable residual gases in the bulb. After the getter-producing substance has been decomposed, this gas discharge vanishes and the lamp is then ready for use.

The decomposition and the reduction of the getter-producing compounds according to the invention are usually carried out in excess of 1300° C.

The following reactions may occur on the basis of the reduction of $Ba_3WO_6$:

$$3Ba_3WO_6+2W \rightarrow 6Ba+2WO_3+3Ba_2O_4$$

At the same time the following reaction is likely to take place:

$$Ba_3WO_6+2WO_3 \rightarrow 3BaWO_4$$

The total reaction equation might then be:

$$4Ba_3WO_6+2W \rightarrow 6BaWO_4+6Ba$$

When other reducing agents are used, analogous reactions are likely to take place.

It is found that the barium tungstenate ($BaWO_4$) is also evaporated and deposited on the wall of the bulb. However, the presence of $BaWO_4$ or other compounds released when other getter-producing substances according to the invention are used, is disturbing either on the wall or on the filament wire. On the contrary, said compounds have a favorable effect as blackening getters such as cryolith.

Usually a favorable quantity of the getter-producing alkali-earth compound amounts to not more than about 2% by weight of the weight of the filament wire. The quantity of metal required for the reduction is so small that it can be withdrawn from the filament wire in most cases without any troublesome effects. This quantity is, in most cases, within the weight tolerances of the filament wire. The quantity of metal to be withdrawn from the filament wire may be further reduced by mixing the getter-producing alkali-earth compound with tungsten, zirconium or a different reducing agent in the form of powder; this provides in addition the great advantage of a higher reaction speed and an improved accomplishment of the reaction due to the larger contact surface of the reacting substances.

Since the reduction and the decomposition of the getter-producing alkali-earth compound usually takes place above 1300° C., the gas discharge in the lamp may take too much time in certain cases, particularly when the temperature of the filament wire does not rise rapidly above this value. This may involve the risk of an arc being struck, so that the lamp becomes defective. Such a fatal gas discharge may be avoided by mixing a small quantity of phosphorus with the getter-producing alkali-earth compound. An advantageous ratio between the phosphorus and the alkali-earth compound lies between $\frac{1}{10}$ and 1. The maximum permissible degasification temperature then lies below the evaporation temperature of the phosphorus, it is true, but in this case gasification becomes superfluous at a higher temperature in many cases, since the phosphorus provides the suitable vacuum, while the alkali-earth metal is capable of binding any gases released during the use of the lamp. A suitable suspension of $Ba_3WO_6$ contains for example 6% by weight of $Ba_3WO_6$ and 0.4% by weight of acrylate resin in xylene. To this suspension may be added 0.6 to 6% by weight of phosphorus and, if desired, a powdery reducing agent, for example a metal powder in a quantity lying between $\frac{1}{3}$ of the theoretical quantity and the theoretical quantity required for the reduction of the $Ba_3WO_6$.



With a tubular 40 W lamp the drop in light output was 28.8% after 750 hours, when $Ba_3WO_6$+phosphorus was employed. With phosphorus alone the same lamp had a drop in light output of 40.5% after 750 hours.

In the first case the number of lumens per Watt was about 8 and in the second case about 7, measured on the new lamp. In the first case there was found a smaller difference in lifetime.

With a different type of lamp only $Ba_3WO_6$ was used for producing the getter. The mean lifetime appeared to reach sometimes one and a half times the lifetime with the use of phosphorus; moreover the percentage of the drop in light output may sometimes be 20% smaller. In general, it was found that the number of lamps having an excessively short lifetime was strongly reduced, so that the tolerance in lifetime was smaller.

The method according to the invention may be employed advantageously with vacuum lamps and gas-filled lamps, when said gases are not bound by the metal getter employed.

What is claimed is:

1. A method of coating the internal wall of a closed vessel with a getter layer comprising the step of heating a compound within the vessel having the formula

$$(MeO)_nXO_m$$

in which Me is a metal selected from the group consisting of Mg, Ca, Sr, Ba, and mixtures thereof, X is a metal selected from the group consisting of metals in the fifth, sixth, and seventh group of the periodic table of elements, $n$ has a value greater than 1, and $m$ is equal to the valence of the metal Me divided by 2, in contact with a reducing substance to a temperature at which the said compound is decomposed releasing the metal Me which is deposited on the wall of the vessel.

2. A method as defined in claim 1 in which the compound $(MeO)_nXO_m$ is mixed with a reducing agent.

3. A method as defined in claim 1 in which the compound $(MeO)_nXO_m$ is mixed with phosphorus.

4. A method as defined in claim 1 in which the compound $(MeO)_nXO_m$ is mixed with a powdered metal selected from the group consisting of tungsten and zirconium.

5. A method as defined in claim 4 in which the compound is $Ba_3WO_6$.

6. A method as defined in claim 5 in which the compound is mixed with phosphorus.

7. A method as defined in claim 3 in which the ratio between the phosphorus and the compound $(MeO)_nXO_m$ is between $\frac{1}{10}$ and 1.

8. A method as defined in claim 6 in which the mixture is introduced into the vessel as a suspension together with acrylate resin in xylene.

No references cited.

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