3,475,072

GETTER FOR INCANDESCENT LAMPS AND SIMILAR DEVICES

James Arthur Graves, Willowick, Ohio, assignor to General Electric Company, a corporation of New York

No Drawing. Filed May 19, 1967, Ser. No. 639,615
Int. Cl. H01j 7/18, 9/38; H01k 1/56
U.S. Cl. 316—3 14 Claims

ABSTRACT OF THE DISCLOSURE

Improved gettering of electric incandescent lamps is obtained by flashing therein a getter consisting of pure crystalline phosphorous pentanitride (P_3N_5) which is preferably used alone in gas-filled lamps but which may be mixed with an oxidizing agent, and which may be mixed with cryolite in vacuum lamps.

BACKGROUND OF THE INVENTION

Field of the invention

The invention relates generally to the manufacture of electrical devices comprising a sealed envelope containing an electric energy translation element such as a filament or electrodes, and more especially to an improved method of manufacturing incandescent lamps of either the gas-filled or vacuum type wherein is employed an improved type of getter material for use in the cleaning up of the residual deleterious gas content of the lamp.

Description of the prior art

For many years past it has been customary in the art to effect the clean up of residual gases in incandescent elecrtic lamps by means of phosphorous. It has been customary to introduce the phosphorus within the lamp in such a position that upon incandescing of the filament, the phosphorus vaporizes or sublimes and reacts with and cleans up residual gases within the lamp envelope. In the case of gas-filled lamps, it is the practice to use the red phosphorus alone, whereas in the case of vacuum lamps, which are usually those of lower wattages such as 25 watts or less, it is customary to mix the red phosphorus with a material such as cryolite.

In the case of incandescent lamps, it is customary to apply the getter composition directly to the filament, usually a helical coil or coiled-coil of tungsten wire. The getter composition is usually prepared as a slurry or suspension of the red phosphorus in any suitable readily vaporizable vehicle such as amyl acetate, and it is applied by immersing or spraying the filament which is mounted on the usual lead-in support wires extending from the glass flare or stem tube which is fusion sealed to an enclosing glass bulb or envelope in the usual sealing-in operation. The amyl acetate is evaporated by exposing the filament mount to warm air before sealing it into the envelope; if it is not wholly evaporated at that time, it is completely evaporated by the heat of the sealing-in operation. The lamp is then exhausted through a tubulature communicating with the interior of the envelope, filled with gas in the case of a gas-filled lamp, and the tubulature sealed off.

During the sealing-in and evacuation of the lamp it is customary to apply heat which raises the glass envelope to a temperature in the range of about 200 to 600° C. depending upon the composition of the glass of the envelope, for the purpose of eliminating surface adsorbed and absorbed gases. As a result of the heating, the red phosphorus getter on the filament is subject to oxidation and vaporization at a temperature of around 200° C.,

the temperature of the filament being near or above that figure during sealing in. The loss in active getter material can result in variation in life and maintenance of incandescent electric lamps employing this type of getter.

Moreover, variable conditions of atmospheric humidity can have an even more drastic effect upon the lamp quality due to deterioration of the red phosphorus and its inability to clean up the increased water vapor content in the lamp due to the presence of excess water vapor on the lamp parts and on the machine parts. This has been illustrated quite dramaticaly recently due to the advent of an extremely sensitive leak detector or testing device which is incorporated in the production line and which is able to rapidly test each for the presence of excessive oxygen or water vapor in such small amounts that it would not otherwise show up for a period of several months. Such a device is disclosed and claimed in Patent 3,194,110, Eppig et al. During particularly humid weather that device has rejected virtually all lamps, or a very large percentage, such as 90 to 100%, when made with red phosphorus getter in accordance with long estabilshed practice.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a getter material for sealed electrical devices, particularly electric incandescent lamps, which is fast acting and which is stable so as to be resistant to water vapor and to deterioration at the relatively high temperature involved in lamp making. Another object is to provide a stable phosphorus getter composition for use in electric lamp manufacture. Another object is to more efficiently effect the clean up and removal of residual atmospheric gases in incandescent lamps, especially those of the gas-filled type, although it is also highly useful in those of the vacuum type.

In accordance with the invention, I have discovered that pure crystalline phosphorus pentanitride (P_3N_5) provides superior gettering action. It is resistant to deleterious reaction with water vapor and other atmospheric gases at temperatures applied to the lamp during the sealing-in and exhaust operations, and it may be subsequently thermally decomposed, presumably into its component elements phosphorus and nitrogen, by heating to more elevated temperatures of approximately 1000° C. When P_3N_5 is thermally decomposed, the phosphorus so produced is nascent and extremely active. This white phosphorus component is extremely effective and fast acting in clean up of oxygen and water vapor, and some of it deposits on the interior lamp parts including the bulb walls so that it also persists in its clean up action during lamp life. In gas-filled lamps it is presently preferred that the pure crystalline P_3N_5 be used alone as the getter composition, but very successful results have also been obtained by admixing it with a quantity of oxidizing agent. In vacuum lamps, the P_3N_5 (with or without oxidizing agent) is preferably mixed with cryolite as is conventional with red phosphorus getter. In this case it may also be desirable to add red phosphorus to maintain a low vacuum; or, stated differently, it may be desirable to replace some of the red phosphorus with P_3N_5 in the conventional getter for vacuum lamps. The amorphous form of phosphorus pentanitride has been found to be unsatisfactory.

Further features and advantages of the invention will appear from the following more detailed description.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Crystalline P_3N_5 is a commercial product. It is preferably prepared by the reaction of P_2S_5 with ammonia, a process which is described by A. Stock and B. Hoffman in the German publication "Berichte der Deutschen Chem. Gesellschaft," volume 36, pages 314 to 319, 1903, and which is also referred to in "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," by J. W. Mellor, volume VIII, page 123, in "Handbook of Preparative Inorganic Chemistry," G. Brauer, Editor, 2nd edition, volume 1, pages 574 and 575, 1963. See also the paper entitled "Crystalline Phosphorus Pentanitride, P_3N_5," by Huffman, Tarbutton, Elmore, Smith and Rountree in Journal American Chemical Society, volume 79, page 1765, (1957).

By way of example, a slurry or suspension may be prepared consisting of pure crystalline P_3N_5 in amyl acetate in proportions of 1 gram P_3N_5 to 100 ml. (milliliters) of amyl acetate. The powdery P_3N_5 is broken up, mixed with the vehicle and then preferably milled to form very fine particles which can be applied uniformly to the filament coil.

The slurry is applied in any convenient manner to the lamp filament coil, for example by dipping or immersing the filament which is mounted on the usual lead-in wires carried by a glass flare or stem tube forming part of the ordinary household variety of incandescent lamp having a coiled or coiled-coil tungsten filament. The mount may then be carried past a heated strip, for example, to cause the amyl acetate vehicle to be evaporated. The mount is then united with the enclosing glass bulb or envelope by fusion sealing the flared stem tube to the envelope in the usual sealing-in operation. The lamp is then exhausted through a tubulature communicating with the interior of the envelope, after which it may be filled with inert gas, and the tubulature then sealed off. The gas filling may consist of an inert gas such as nitrogen, argon, krypton or xenon or mixtures thereof, usually argon containing approximately 2 to 12% by volume of nitrogen at a pressure close to atmospheric. The lamp envelope may then be provided with a conventional base having terminal contacts to which the lead-in wires are connected. The filament is then heated by application of a suitable voltage to the base terminal contacts to heat the filament to a temperature sufficient to vaporize and decompose the P_3N_5 into its elemental components, white phosphorus and nitrogen. The white phosphorus is extremely reactive and quickly cleans up the residual oxygen and water vapors in the lamp envelope.

Tests of lamps made in identical manner except for the use of the pure crystalline P_3N_5 as the getter in one group, and red phosphorus in the other group, and made in highly humid weather, resulted in rejection of from 90 to 100% of the red phosphorus gettered lamps by the leak detector device heretofore referred to, as compared to rejection of less than 1% of the P_3N_5 gettered lamps, some of which may have been normally defective lamps having fine cracks therein which caused them to be rejected because of air leakage.

Similar results have been obtained with lamps in which an oxidizing agent was added to the crystalline P_3N_5. While various materials may be used as oxidizing agents, provided only that their decomposition does not yield substances deleterious to operation and performance of the lamp, the preferred materials are oxygenous compounds of metals of Group V of the periodic table and which break down upon heating to yield oxygen. Particularly suitable materials are, for example, Sb_2O_4 and $BiPO_4$.

By way of example, one such composition which gave good results under conditions of high humidity when comparable lamps containing red phosphorus were being rejected, was a mixture in proportions of 4 grams pure crystalline P_3N_5, 2 grams Sb_2O_4 and sufficient amyl acetate to make 400 milliliters of getter slurry. Lamps containing such a getter composition were processed in the conventional manner stated above. It is hypothesized that

the P_3N_5 decomposed into elemental white phosphorus and nitrogen at the same time as a small amount of oxygen was liberated from the decomposition of the antimony tetraoxide, probably to the lower antimony trioxide. The oxygen and phosphorus would form some P_2O_5 which is known to be an excellent water getter. Nevertheless, as stated above, excellent results are also obtained with the presently preferred use of pure crystalline P_3N_5 alone as the getter composition.

As pointed out above, amorphous phosphorus nitride was found to be unsatisfactory. Without wishing to be held to any theory, it may be that the amorphous material breaks down to gaseous PN without ever forming any, or any appreciable amount of, elemental phosphorus and nitrogen. The pure crystalline P_3N_5 (as determined by X-ray diffraction) on the other hand, is a very stable compound which probably retains its identity until the entire crystal becomes hot enough to decompose directly to elemental white phosphorus and nitrogen.

The amount of phosphorus nitride used in each lamp is not particularly critical and varies with the size or wattage of the lamp. It may be governed by the amount of solids per unit volume of the vehicle. As the slurry thickens, more solids will be picked up by the filament. When the conventional red phosphorus is used, its concentration is limited, as a practical matter, by the occasional appearance of a brown color on the bulb of finished lamps. On the other hand, the white or phosphorus nitride getter may be limited when a white haze begins to show on some lamp bulbs; if more is used in the slurry an occasional brownish lamp will be observed. However, even in such cases the amount of getter is not as harmful since the haze and brownish color occasioned by use of the larger amounts of P_3N_5 tend to disappear as the lamps are burned, whereas the browning effect of the conventional red phosphorus tends to increase with subsequent lamp burning, causing some absorption of light and what may be considered to be an appearance defect. In general, a greater amount by weight of phosphorus can be added by the use of the crystalline P_3N_5 than by using the conventional red phosphorus.

Flashing, i.e., operation of the filament at increasing voltages for short periods for the purpose of vaporizing the getter and for setting and recrystallizing the tungsten wire structure, has been found to be less critical with respect to burn outs when using P_3N_5 as compared to red phosphorus gettered lamps. Poorly or inadequately flashed lamps which contain red phosphorus getter can lead to arcs and burn outs. It has been found impossible to duplicate that problem when lamps have been gettered with P_3N_5.

A mass spectrometer analysis was conducted on lamps gettered with P_3N_5, with red phosphorus, and some containing no getter. The following is a table of the results:

MASS SPECTROMETER ANALYSIS
[Micron-liters]

	No getter	Red Phosphorus	P_3N_5
CO_2	.09	.03	
H_2O	Trace		
CH_4	.12	.20	
CO	6.2	7.0	
H_2	.42	1.3	.02

The blank spaces denote that none of the indicated material was detected.

Photomicrographs of 60 watt lamp coils produced from the same bobbin of tungsten wire showed no grain difference between ungettered coils and P_3N_5 gettered coils after flashing, whereas red phosphorus gettered coils had a different grain structure in the coil ends or legs. After 100 hours of burning there was no difference detectable between the three sets of samples. These early tests thus indicate a superior microstructure of recrystallized tungsten filaments when P_3N_5 is used than when red phosphorus is used.

To indicate the improved light output, in lumens, on lamps gettered with pure crystalline P_3N_5 as compared with red phosphorus, as well as no getter, data was gathered on lamps which were operated in so-called slumper cans which simulate hot fixtures in which the lamps operate at abnormally high temperature. The following table lists the lumen output of lamps after burning about 150 hours:

	Test #1		Test #2		Test #3 Inside Frosted Bulbs			Test #4	
	P_3N_5	Red Phosphorus	P_3N_5	Red Phosphorus	No Getter	P_3N_5	Red Phosphorus	P_3N_5	Red Phosphorus
	805	754	839	800	692	805	753	811	796
	823	788	831	805		812	739		761
	806	770	831	779		810	759	808	733
	843	723	836	819		818	754	801	
	834		821	782	708	790	762	760	708
	827	762			686	820	808	803	
Average	823	759	832	797	695	809	763	797	750

The blank spaces indicate lamps which burned out before reaching the 150 hour figure.

By way of further example, a getter composition for vacuum lamps may consist of about 5 grams P_3N_5, 55 grams cryolite, and 2 grams red phosphorus in sufficient methanol to make 100 milliliters of slurry. It will be appreciated that the amount of methanol may be adjusted to deposit the desired weight of getter on the filament coil.

It can be concluded that the pure crystalline P_3N_5 getter is clearly superior to red phosphorus because of the following advantages. It is not affected by the elevated temperatures used in lamp manufacture. It is inert and does not hydrolyze or react with the suspension vehicle. There are no fire hazards in lamp plants occasioned by dried getter. The number of rejections by the sensitive leak detector heretofore referred to, due to getter deficiencies are greatly reduced which obviously results in substantial savings. The P_3N_5 has less effect, if any, on the crystalline structure of the tungsten filaments. It avoids the occasional problem of lamp burn outs as a result of faulty flashing. Since presumably white phosphorus is one of the products of decomposition, it can be concluded that there is more residual gettering action, that is, continued gettering action during the life of the lamp. White phosphorus is effective as a getter at much lower temperatures than is red phosphorus.

It will be appreciated that under the best of manufacturing conditions red phosphorus is, and for many years has been, generally speaking, an effective getter. However, the decided superiority of the pure crystalline P_3N_5 will be especially manifest when the manufacturing conditions with the red phosphorus get out of control, for example when the preheat fires, baking temperatures, atmospheric humidity in particular, and like factors become extremely variable or entirely beyond control, such that for example the red phosphorus becomes badly oxidized or even vaporized from the filament prior to the sealing off of the lamp or is hydrolyzed by high humidity or reacts with the suspending vehicle when allowed to stand for several days such as over a week end. Under such conditions a uniform product is not possible with the red phosphorus. When pure crystalline P_3N_5 is used a uniform highly excellent lamp product may be obtained irrespective of such variables because of its high stability and inertness.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of gettering an electrical device comprising a sealed envelope containing an electric energy translation element which comprises flashing therein pure crystalline phosphorus pentanitride.

2. The method of claim **1** wherein said crystalline phosphorus pentanitride has cryolite admixed therewith.

3. The method of claim **2** wherein said crystalline phosphorus pentanitride and cryolite have an oxidizing agent mixed therewith.

4. The method of claim **1** wherein said crystalline phosphorus pentanitride has an oxidizing agent admixed therewith.

5. The method of claim **4** wherein said oxidizing agent is an oxygenous compound of a Group V metal which breaks down upon heating to yield oxygen.

6. The method of claim **4** wherein the oxidizing agent is Sb_2O_4.

7. The method of claim **4** wherein the oxidizing agent is $BiPO_4$.

8. The method of gettering an electric incandescent lamp comprising a sealed glass envelope containing a tungsten filament which comprises flashing off the filament a getter comprising pure crystalline phosphorus pentanitride.

9. The method of claim **8** wherein cryolite is admixed with said phosphorus pentanitride.

10. The method of claim **9** wherein an oxidizing agent is admixed with said phosphorus pentanitride and cryolite.

11. The method of claim **8** wherein said phosphorus pentanitride has an oxidizing agent admixed therewith.

12. The method of claim **11** wherein said oxidizing agent is an oxygenous compound of a Group V metal which breaks down upon heating to yield oxygen.

13. The method of claim **11** wherein the oxidizing agent is Sb_2O_4.

14. The method of claim **11** wherein the oxidizing agent is $BiPO_4$.

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TOBIAS E. LEVOW, Primary Examiner

ROBERT D. EDMONDS, Assistant Examiner

U.S. Cl. X.R.

252—181.1; 316—25