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METHOD OF MAKING A TRITIATED SELF-LUMINESCENT BODY

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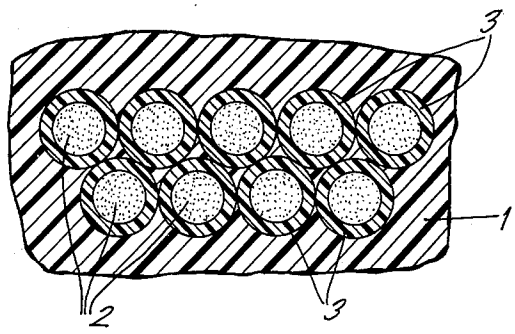

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METHOD OF MAKING A TRITIATED SELF-LUMINESCENT BODY

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The present invention relates to a light emitting body and to a method of making the same.

More particularly, the invention is concerned with the light emission by luminous bodies which are activated by being exposed to radioactive radiation.

It is known to form a mixture of luminous bodies such as zinc sulfide or cadmium sulfide, radioactive isotopes and suitable binder materials. As binder materials, synthetic resins are preferred and as radioactive isotopes, for instance radium or thorium salts are added which in addition to alpha rays also emit beta and gamma rays. While the emitted alpha rays have a destructive effect on the binder material and on the luminous substance the beta and gamma rays will pass through the light emitting body into the surrounding atmosphere and thus expose the surrounding area to potential harmful radiation.

It is therefore desirable to excite the light emission of luminous substances exclusively with beta radiation of low energy which will be incapable of prematurely destroying the binder material or of endangering the surrounding area.

It is therefore an object of the present invention to provide a light emitting body and a method of making the same wherein the light emission of a luminous material is excited by exposing the luminous material substantially exclusively to relatively harmless low-energy beta radiation.

It is another object of the present invention to provide a simple and economical manner of producing luminous bodies and, furthermore, to provide luminous bodies which possess the desired intensity of light emission, are relatively stable and do not emit harmful radiation.

Other objects and advantages of the present invention will become apparent from a further reading of the description and of the appended claims.

With the above and other objects in view, the present invention comprises a luminescent body consisting essentially of a solid mass of an at least translucent, tritium-containing synthetic resin having distributed therethrough particles of a luminous material, whereby radiation emanating from the tritium of the synthetic resin will excite the emission of light by the luminous particles.

According to a preferred embodiment, the luminescent or light emitting body of the present invention comprises, in combination, a solid body consisting essentially of an at least translucent substantially tritium-free synthetic resin, and of a plurality of composite luminescent particles distributed throughout the solid body, each of the composite luminescent particles comprising a luminous particle and a coating of tritium-containing at least translucent resin covering the luminous particle, whereby radiation emanating from the tritium of the coating will excite the emission of light by the luminous particles.

The present invention is also concerned with a method of exciting light emission by a luminous body which comprises the step of contacting the luminous body with a tritium-containing, at least translucent synthetic resin, whereby radiation emanating from the tritium-containing synthetic resin will excite the emission of light by the luminous body.

According to a preferred embodiment, the method of

producing a light emitting body, in accordance with the present invention, comprises the steps of coating the individual particles of a mass of finely sub-divided luminous material selected from the group consisting of activated zinc sulfide, cadmium sulfide, luminous manganates, luminous tungstenates, luminous silicates, fluorescein and eosine with a thin layer of a tritium-containing at least translucent synthetic resin selected from the group consisting of polymethacrylate, polystyrene, polycarbonate and polyethylene, forming a mixture of the coated particles and an at least translucent binder material adapted to form a coherent solid body, and transforming the mixture into a coherent solid body consisting essentially of the binder material having the coated particles distributed therethrough, whereby the tritium of the coating will excite the emission of light rays by the luminous particles and the light rays will pass through the solid body so as to emit light from the same.

Thus, according to the present invention, the light emission of the luminous materials is excited by the radioactive radiation emanated by tritium which is chemically attached or forms part of the binder material surrounding the individual particles of luminous material.

By chemically incorporating gaseous tritium into a synthetic resin in which luminous particles are distributed, the soft radioactive rays emanated by the tritium will be nearly completely absorbed in the luminous layer formed of the luminous particles and the polymer serving as binder material and the major portion of the radiation emanating from the chemically bound tritium will be available for exciting light emission of the luminous particles. Only a small fraction of such radioactive rays will pass outwardly through the surface of the luminous particles containing synthetic resin body so that the exposure of the surrounding area to radiation is minimized. Furthermore, the useful life span of the luminous body, i.e., of the luminous particles and of the synthetic resin binder is prolonged due to the fact that the soft beta rays have only very little effect on these materials.

For these as well as for other reasons, luminous masses formed in accordance with the present invention as broadly described above possess great advantages for instance as the material for producing luminous dials and the like.

Preferably, according to the present invention, a relatively large proportion of tritium is to be chemically incorporated in the synthetic resin so that per gram or other unit of the luminous body, i.e., of the body comprising the synthetic resin and the luminous substance such as cadmium sulfide distributed therethrough, a relatively large amount of beta radiation is made available for exciting the luminous particles, resulting in increased emission of light by the luminous body.

Thus, the present invention is also concerned with a method of incorporating relatively large proportions of tritium in a synthetic resin which is to be used as the binder material for holding and exciting luminous particles, and also with a luminous body which includes such synthetic resin containing a large proportion of tritium.

While it has been attempted to incorporate tritium in organic compounds by conventional synthetic methods such as hydrogenation, or by catalytic exchange of hydrogen for tritium in the organic compound, these prior art methods are only of very limited practical use due to the fact that the methods are either too complicated and expensive, or will result in the incorporation of only a relatively small proportion of tritium.

Attempts to achieve a chemical binding of tritium to an organic compound by introducing the organic compound into a tritium atmosphere and allowing the organic compound to remain therein for a considerable length of time, were found to accomplish only a very limited introduction

of tritium into the organic compound particularly when the reaction time, i.e., the time of exposure of the organic compound to the tritium atmosphere is to be kept within manageable limits.

These difficulties are overcome according to the present invention which provides a method whereby the organic compound while in contact with the tritium atmosphere is exposed to additional radiation or electric discharge. Surprisingly, it has been found that in this novel manner incorporation of relatively large proportions of tritium in the organic compound can be achieved within a relatively short period of time.

The novel features which are considered as characteristic for the invention are set forth in particular in the appended claims. The invention itself, however, both as to its construction and its method of operation, together with additional objects and advantages thereof, will be best understood from the following description of specific embodiments when read in connection with the accompanying drawing, in which the drawing shows a fragmentary cross sectional view through a luminous layer or body according to a preferred embodiment of the present invention.

Referring now to the drawing, reference numeral **1** denotes a tritium-free synthetic resin serving as binder material and having incorporated therein crystals or particles **2** of luminous material such as cadmium sulfide. The individual particles **2** are covered by a coating **3** consisting of tritium-containing synthetic resin.

The radiation emanating from the tritium in the coating will excite luminous particles **2** which will emanate light rays, the latter passing through coating **3** and binder material **1** and thus becoming visible.

As illustrated and described above, only a relatively small quantity of tritium-containing polymer is required, namely only as much as is needed to form coatings **3**. However, it is of course also possible to use a uniform tritium-containing material in place of binder **1** and coating **3**, in other words to incorporate tritium in the entire binder material and to distribute coating-free luminous particles therethrough.

According to the present invention, the tritium which will serve to excite the luminous material is chemically incorporated into the synthetic resin or polymer which serves as binder material for the final luminous layer, by introducing the binder material into a tritium atmosphere and subjecting the binder material while in contact with tritium to an additional ionizing radiation or to an electric discharge. The term "additional radiation" will serve to denote that the source of such radiation is not the tritium atmosphere but some other radioactive material.

By exposing the organic compound which is to serve as binder material or which may be polymerized or copolymerized so as to form a synthetic resin which may serve as binder material, either to such electric discharge, preferably a silent electric discharge, or to such additional radiation, it is achieved that hydrogen atoms of the organic compound are exchanged for tritium. This reaction takes place between the tritium gas and the radicals formed of the organic molecules primarily under the influence of the additional ionizing radiation or under the influence of the electrical discharge and the thereby arising ultraviolet rays, and only to a minor degree under the influence of the radiation emanating from the tritium gas.

The replacement of regular hydrogen atoms with tritium may be carried out in accordance with the present invention by placing the synthetic resin or the like in finely sub-divided pulverulent form into a glass flask which is then filled with tritium gas under a pressure which is adjusted with respect to the specific synthetic resin and preferably will be within the range of 100 and 700 mm. Hg. The thus filled vessel, i.e., the vessel containing the synthetic resin powder in a tritium atmosphere is then introduced into a field of radiation of either gamma, X-ray, beta, electron, ultraviolet or ionic radiation. The

source of such radiation may be radioactive preparations, for instance cobalt–60 as a source of gamma rays, X-ray devices or accelerators.

When it is desired to introduce tritium into the organic compound by means of silent electric discharge or Tesla, i.e., corona discharge, then the organic compound and the tritium may be introduced in discharge tubes of conventional structure such as are used for instance in ozonizing apparatus, or Geisler tubes may be used in which the organic material and the tritium gas are confined.

The exchange of hydrogen for tritium under the influence of electric discharge will generally result in a higher yield than the use of ionizing radiation. However, electric discharge can be employed only in connection with such synthetic resins, for instance polystyrene, which will not be destroyed or modified in their structure when subjected to such electric discharge—unless one is willing to accept the partial destruction of the structure of the synthetic resin by such electric discharge in view of the benefit obtained thereby, namely the higher rate of exchange of hydrogen atoms for tritium in the organic compound.

The method of the present invention can also be used for introducing tritium into a monomer or into an intermediate product or pre-polymer with subsequent or simultaneous completion of the polymerization.

For instance in the case of polystyrene, it is possible to introduce tritium into the solid, preferably pulverulent polystyrene, or into a mixture of such pulverulent polystyrene and luminous particles. However, it is also possible to introduce tritium into the liquid monomer (styrene). Here again, the luminous substance may already be admixed to the monomer prior to the exchange of some of the hydrogen atoms thereof for tritium. After introduction of tritium into the monomer the latter is then polymerized in convention manner. Luminous layers may also be produced by dissolving the tritium containing polymer for instance polystyrene, in a suitable solvent such as chloroform and then to incorporate the particulate luminous material in the solution, or to form a pulverulent mixture of tritium-containing polystyrene and pulverulent luminous material and to apply the solvent to the thus formed mixture.

After evaporation of the solvent, a solid layer remains consisting of the tritium-containing synthetic resin having the particles of luminous material distributed therethrough. Depending on the specific physical characteristics of the synthetic resin, other methods of incorporating the luminous particles and of forming the luminescent layer may be used. For instance, tritium-containing polyethylene may be heated to above its melting point and the luminous particles may be introduced into the molten polyethylene. A solid body is then formed by cooling the polyethylene to below its melting or softening point.

It is also within the scope of the present invention to produce the luminescent layer by introducing tritium into the molecule of an intermediate or pre-polymer compound which when combined with other organic compounds will form the synthetic resin. For instance it is possible to introduce tritium into the terephthalic acid molecule and then to introduce glycole in order to form the polyester.

The present invention also contemplates to form a mixture of a monomer and luminous particles and to subject such mixture to an exchange of hydrogen atoms of the monomer for tritium while simultaneously the monor is polymerized to form the synthetic resin which will serve as binder material for forming the luminescent body.

Thus, for instance a mixture of luminous particles and of the liquid methyl ester of methacrylic acid may be subjected to the exchange of hydrogen atoms for tritium under simultaneous stirring of the mixture, whereby it will be accomplished that the ester polymerizes simultaneously with the hydrogen exchange.

The beta particles emanated by tritium possess very

little energy and thus are absorbed even by thin layers of the synthetic resin binder. It is therefore preferred according to the present invention to cover each particle or crystal of the luminous material with a thin skin or coating of tritium-containing binder material. In this manner it is accomplished that the beta radiation emanating from the coating will in a large proportion directly contact the luminous particle without being absorbed by interposed portions of binder material. In other words, best utilization of the tritium is achieved with only a relatively small amount of tritium-containing binder material, just sufficient to form coatings on the individual particles of luminous material. However, to use such small proportion of binder material frequently would result in insufficient coherence of the luminescent body. This disadvantage can be avoided by incorporating the composite particles consisting of luminous particles individually coated with a thin layer of tritium-containing binder material, in a larger mass of tritium-free binder material.

It is one of the advantages of the present invention that tritium can be incorporated into the binder material after the same has been mixed with the luminous particles. Furthermore, the difficulties involved in incorporating tritium by hydrogenation into a basic compound and thereafter to synthesize the binder material are avoided, as well as the difficulties which are experienced when tritium is to be incorporated in the organic compound by methods of the type where a lithium salt is admixed and tritium is formed by exposing the mixture to neutron radiation in a nuclear reactor.

Generally it may be said that the method of the present invention permits the introduction of large proportions of tritium in a relatively very short period of time and also allows for introducing the tritium either into the synthetic resin which is to serve as the binder material or into a monomer or pre-polymer constituent thereof.

The luminescent bodies according to the present invention are suitable not only for use as luminescent dials for instance on watches or instrument panels in airplane cockpits but also for road signs or in connection with other signboards or the like and for other purposes.

The tritium-containing binder material according to the present invention may be any commercial transparent or at least translucent synthetic resin. Very good results were obtained with tritium substituted polymethacrylate, polystyrene, polycarbonate and polyethylene.

As luminous bodies or particles which are to be incorporated in the binder material and subjected to tritium radiation, good results were obtained with zinc sulfide activated with silver, copper or the like, cadmium sulfide, luminous manganates, tungstenates, silicates, as well as with fluorescein, eosine and other organic luminous materials.

The size of the individual luminous particles depends to a large extent on the specific luminous compound. For instance, in the case of zinc sulfide, the diameter of the individual luminous particles preferably will be between about 0.02 and 0.06 mm. If the luminescent layer is formed for instance of 400 mg. tritium-containing polymethacrylate and 8 grams zinc sulfide, the thus formed luminescent layer will contain approximately 6×10^7 luminous zinc sulfide particles.

On the other hand, if the individual luminous particles are coated with a thin skin of tritium-containing binder material and the thus coated particles are then embedded in a binder mass which is free of tritium, then the individual luminescent particle will consist of a luminous core and a tritium-containing binder skin. The optimum thickness of the binder skin will depend on the specific type of binder material used. In the case of tritium treated polymethacrylate the optimum thickness of the binder skin or coating will be about 5×10^{-4} cm. Assuming that the diameter of the luminous core equals about 4×10^{-3} cm., the diameter of the composite particle comprising core and skin will be about 5×10^{-3} cm. In this case, the skin of the individual particle will weigh about 3.8×10^{-8} grams while the individual luminous core will weigh about 1.4×10^{-7} grams. Thus, theoretically about 3.8 grams of tritium containing polymethacrylate will be required for forming the coating on 14 grams of luminous zinc sulfide particles.

The following examples are given as illustative only, without, however, limiting the invention to the specific details of the examples.

Example I

400 mg. of pulverulent poly-methyl-methacrylate were introduced into a small Erlenmeyer flask having a volume of 2.2 cm.^{3}. The Erlenmeyer flask was then evacuated to a residual pressure of 8×10^{-3} mm. Hg and thereafter 1 curie of tritium (equal to 0.4 cm.^{3} at nearly 100% purity of the tritium) were introduced into the flask. Thereby, the pressure in the flask rose to about 100 mm. Hg. The contents of the flask were then exposed at a temperature between 18 and 20° C. to a dosage of 10^7 roentgen of cobalt–60 gamma radiation, using a radiation source emitting 23,100 roentgens per hour. After completion of irradiation, the gaseous tritium was withdrawn by means of a Toepler pump down to a residual pressure of 10^{-2} mm. Hg and the thus treated powder was allowed to stand in the Erlenmeyer flask under such high partial vacuum for a period of three days.

Subsequent testing showed that the thus irradiated poly-methyl-methacrylate possessed a tritium activity which was 317% higher than the tritium activity obtained under similar conditons however omitting the gamma irradiation.

400 mg. of the tritium-containing polymer obtained as described above were then intimately mixed with 8 grams of pulverulent luminous zinc sulfide and a small quantity of chloroform was added so as to transform the mixture into a thick paste. A layer of the thus formed paste was then air dried and upon thus evaporating the chloroform, a homogeneous luminescent layer was obtained.

Example II

The incorporation of tritium with the help of electric discharge was carried out in an apparatus comprising a Pyrex glass tube closed at one end, having a length of 34.5 mm. and an inner diameter of 10 mm. The wall thickness was 1 mm. The concave part of a ground joint was fused onto the open end of the glass tube and immediately beneath the joint a vacuum cock was fused onto the wall of the glass tube. The vacuum cock served for opening or closing communication between the interior of the glass tube and a vacuum pump or a source of tritium.

A second Pyrex glass tube closed at one end and having an outer diameter of 5 mm. and a length of 32.5 mm. was then inserted into the first described glass tube. The convex part of a ground joint was fused onto the open end of the second glass tube so that upon insertion of the second glass tube into the first glass tube the ground joint portions of the two tubes would contact each other forming a vacuum tight closure. The residual volume between the first and second glass tubes amounted then to 1560 mm.^{3}. Prior to inserting the second glass tube into the first described glass tube, 400 mg. pulverulent poly-methyl-methacrylate having particle sizes of between 0.05 and 0.15 mm. were introduced into the larger glass tube. Thereafter, the inner glass tube was inserted and the reaction area between the inner and outer glasss tubes was then evacuated down to a residual pressure of 8×10^{-3} mm. Hg. Thereafter, 400 mm.^{3} tritium (measured under normal pressure and temperature) corresponding to 1 curie, were introduced into the reaction area through the vacuum cock previously used for evacuating the reaction area. The tritium gas pressure in the reaction area was then equal to about 250 mm. Hg. A

copper wire of 2 mm. diameter was then introduced as electrode through the convex part of the ground joint into the inner glass tube and thereafter, the inner glass tube was filled with tap water. The entire apparatus was then placed into a tap water-filled vessel up to about the level of the ground joints. An alternating current of 50 cycles and 17 kv. was then applied between the copper wire in the inner glass tube and the water bath in which the apparatus was immersed. Thereby silent discharges were created in the tritium and poly-methyl-methacrylate-containing reaction area between the inner and outer glass tubes. This was continued for 8 hours while the glass apparatus was subjected to continuous mechanical shaking in order to achieve even contact between the particles of the poly-methyl-methacrylate powder and the tritium gas. This experiment was carried out at an ambient temperature of 20° C. After thus subjecting the reactants to silent electric discharges for a period of 8 hours, the was was pumped out of the reaction area until the residual pressure therein was reduced to 10^{-2} mm. Hg.

It was then found that the thus tritium treated poly-methyl-methacrylate possessed a tritium activity that was higher by 300% than the activity of the poly-methyl-methacrylate which was treated with additional gamma radiation in accordance with Example I.

The thus treated poly-methyl-methacrylate was then mixed with zinc sulfide particles and chloroform and further processed in the manner described in Example I.

In both examples, zinc sulfide which had been activated with either copper or silver was used as the luminous material. The diameter of the individual zinc sulfide particles was between 0.02 and 0.06 mm. In order to form a heavy paste of the tritium-containing poly-methyl-methacrylate, 1.6 grams of chloroform was required for 400 mg. of poly-methyl-methacrylate.

The solid dry luminescent layer formed in the manner described above preferably will have a minimum thickness of 0.1 mm.

The solid luminescent layer or body, i.e., the final product such as a luminescent dial, may be produced immediately after forming the tritium-containing poly-methyl-methacrylate and mixing the same with the luminous particles. However, it is also possible to separately store the tritium treated poly-methyl-methacrylate powder or to store a mixture of this powder and of the luminous materials such as zinc sulfide and at some later time to apply chloroform or another suitable solvent for forming the paste which then is dried into the final product. Or, it is also within the scope of the present invention to form the final luminescent body, to grind the same to a powder and by subsequent repeated application of a solvent to form a paste which will allow to shape the mass in any desired manner, followed by evaporating of the solvent. Furthermore, it is also possible to admix the luminous material such as zinc sulfide to the poly-methyl-methacrylate or the like prior or during reacting the latter with tritium.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. A method of producing a light-emitting body, comprising the steps of coating the individual particles of a mass of finely subdivided luminous material adapted to be excited by radiation emanating from tritium with a thin layer of a tritium-containing at least translucent synthetic resin, said tritium-containing synthetic resin being formed by subjecting a synthetic resin while the same is in contact with tritium to ionizing radiation from a source other than said tritium so as to incorporate said tritium in said synthetic resin; forming a mixture of said coated particles and of an at least translucent synthetic resin; and transforming said mixture into a coherent solid body consisting essentially of said at least translucent synthetic resin having said coated particles distributed therethrough, whereby said tritium of said thin layer will excite the emission of light rays by said luminous particles and said light rays will pass through the at least translucent synthetic resin of said body so as to emit light from the same.

2. A method of producing a light-emitting body, comprising the steps of coating the individual particles of a mass of finely subdivided luminous material selected from the group consisting of activated zinc sulfide, cadmium sulfide, luminous manganates, luminous tungstenates, luminous silicates, fluorescein and eosine, and adapted to be excited by radiation emanating from tritium with a thin layer of a tritium-containing at least translucent synthetic resin selected from the group consisting of poly-methyl-methacrylate, polystyrene, polycarbonate and polyethylene, said tritium-containing synthetic resin being formed by subjecting a synthetic resin while the same is in contact with tritium to ionizing radiation from a source other than said tritium so as to incorporate said tritium in said synthetic resin; forming a mixture of said coated particles and of an at least translucent binder material adapted to form a coherent solid body; and transforming said mixture into a coherent solid body consisting essentially of said binder material having said coated particles distributed therethrough, whereby said tritium of said thin layer will excite the emission of light rays of said luminous particles and said light rays will pass through said solid body so as to emit light from the same.

3. A method according to claim 2, wherein said at least translucent synthetic resin is a poly-methyl-methacrylate being formed by subjecting a liquid ester of methacrylic acid while the same is in contact with tritium to ionizing radiation from a source other than said tritium.

4. In a method of producing a light-emitting body, the steps of contacting a liquid ester of methacrylic acid with tritium; subjecting said liquid ester while the same is in contact with said tritium to ionizing radiation from a source other than said tritium so as to polymerize said liquid ester and to form a tritium-containing synthetic resin; and forming a coherent solid body of said tritium-containing synthetic resin and of a finely subdivided luminous material adapted to be excited by radiation emanating from tritium.

5. In a method of producing a light-emitting body, the steps of contacting a liquid methyl ester of methacrylic acid with tritium; subjecting said liquid ester while the same is in contact with said tritium to ionizing radiation from a source other than said tritium so as to polymerize said liquid ester and simultaneously incorporating tritium therein thus forming tritium-containing synthetic resin; and forming a coherent solid body of said tritium-containing synthetic resin and of a finely subdivided luminous material adapted to be excited by radiation emanating from tritium.

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