

1

3,033,797

SELF-LUMINOUS PAINTS

Felix R. De Leo, Needham, and Edward Shapiro, Newton, Mass., assignors, by mesne assignments, to Luminous Products Corp., Boston, Mass., a corporation of Massachusetts

No Drawing. Filed Apr. 19, 1957, Ser. No. 653,733

3 Claims. (Cl. 252—301.1)

This invention relates to a self-luminous paint and more particularly to a self-luminous paint comprising the radioactive isotope tritium.

Heretofore self-luminous paints have been made using as the exciting agent a compound of radium. Generally the radium compound is in intimate admixture with the phosphor crystals and is not an integral part of the paint vehicle. Unfortunately radium is a particularly dangerous form of radioactive material since when ingested by the body, it has a tendency to lodge in the bony structure with its radiations causing serious damage to surrounding tissue. In addition, radium and its radioactive descendants emit penetrating gamma radiation which results in continual radiation doses to those who are exposed to it as, for example, workers who apply radium self-luminous paints to watch, clock and instrument dials. A further disadvantage of radium paints lies in the fact that the alpha particles emitted by radium are capable of destroying the phosphorescent quality of the phosphor crystals in the paint, so that a radium paint loses about one-half of its original brightness each year following compounding of the paint. Thus there is a limited useful period for any radium paint. A luminous watch, clock or instrument dial which is several years old will be found to have lost most of its original luminosity.

Because of these and other disadvantages, efforts have been made to produce self-luminous paints superior to radium paints.

Accordingly it is the purpose of this invention to provide a self-luminous paint which avoids the aforementioned difficulties common to radium paints.

In particular it is the object of this invention to provide a self-luminous paint in which the radioactive isotope tritium is used to furnish the energy for excitation of the phosphor to produce luminescence, thereby eliminating radium with all of its concomitant disadvantages.

Another specific object of this invention is to provide a self-luminous paint which can be prepared and used without hazard to personnel and which can be applied by brushing, dipping or silk screening, as desired.

Another object of the present invention is to provide a self-luminous paint comprising a predetermined amount of phosphor particles of predetermined size and tritiated hydrogenous paint vehicle which is substantially non-volatile.

Other objects and many of the attendant advantages of the present invention will become more apparent as reference is had to the following detailed description.

By the present invention it is proposed to provide a self-luminous paint comprising an intimate mixture of a pigment which is a phosphorescent material, a tritiated vehicle, the vehicle comprising either a substantially non-volatile hydrogenous plastic binder alone or a plastic binder combined with an hydrogenous substantially non-volatile paint modifier such as a plasticizer, and a solvent for the vehicle.

In developing this invention it has been determined that the choice of phosphor is determined by two factors: (1) the efficiency of conversion of beta-ray energy to visible light, and (2) the size of the phosphor particles. The first factor is believed to be obvious. The second factor can be demonstrated as follows:

Assume a paint mixture which upon drying contains

2

100 grams of phosphor dispersed uniformly throughout 100 grams of tritiated plastic, the phosphor and plastic having the following physical characteristics:

- (1) Density of plastic----- 1.25 grams/cm.³.
- (2) Density of phosphor----- 4.00 grams/cm.³.
- (3) Volume of plastic----- 100/1.25=80 cm.³.
- (4) Volume of phosphor----- 100/4.0=25 cm.³.
- (5) Volume of paint----- 105 cm.³.

The linear dimension of a cube having a volume of 105 cm.³ is found to be 4.7 cm.

Consider now two cases, A and B.

Case A:

Average diameter of phosphor particles is 1 micron (.0001 cm.).

Volume of a single particle is 5.2×10^{-13} cm.³.

Weight of a single particle is 2.1×10^{-12} grams.

Number of phosphor particles is

$$100/2.1 \times 10^{-12} = 4.8 \times 10^{13}$$

Number of phosphor particles in the length of a cube is $(4.8 \times 10^{13})^{1/3} = 3.6 \times 10^4$.

The number of phosphor particles per centimeter length is

$$3.6 \times 10^4 / 4.7 = 7.7 \times 10^3$$

The average distance between the centers of individual particles is $1/7.7 \times 10^3 = 1.3 \times 10^{-4}$ cm.

Since the average diameter of the phosphor particles is 1.0×10^{-4} cm., the distance between phosphor particle surfaces is 1.3×10^{-4} minus 1.0×10^{-4} , or

$$0.3 \times 10^{-4} \text{ cm.}$$

This thickness of plastic is less than one twenty-fifth the range of tritium beta rays in the plastic, so that an appreciable fraction of beta radiation will strike phosphor particles, exciting them to luminescence.

Case B:

Average diameter of phosphor particles is 10 microns (.001 cm.).

By calculations analogous to the foregoing, it will be found that the average distance between phosphor particles surfaces is 0.3×10^{-3} cm. This corresponds to a plastic thickness nearly one-half the range of tritium beta rays in the plastic. In such a case it has been found that approximately 90% of the beta energy will be expended in the plastic, resulting in poor luminous efficiency.

From extensive research it has been discovered that for a given amount of radioactivity best results are obtained when the phosphor particles have a maximum average size in the range of 1 to 2 microns. At the same concentration of radioactivity, increasing the size of the particles to 3 microns gives satisfactory results, although the efficiency is somewhat lower than with particles of 2 microns. Above 3 microns the efficiency drops rapidly, but the loss in efficiency due to the increase in phosphor particle size can be compensated for by increasing the concentration of radioactivity. As pointed out more fully hereinafter, increasing the concentration of tritium does not increase the rate of loss of brightness. Accordingly, particle sizes up to approximately 10 microns average diameter may be used if the concentration of tritium is also increased. However, in view of the relatively high cost of tritium, it is more economical to use particles having a maximum diameter of 3 microns or less because of the markedly greater efficiency that results. Of course particles smaller than 1 micron will give even better results. Unfortunately smaller particles having good efficiency of conversion of beta-ray energy to visible light are not available commercially.

Fortunately there are various phosphors available in the desired sizes. Zinc orthosilicate: manganese activated phosphor is available in 1 and 2 micron average di-

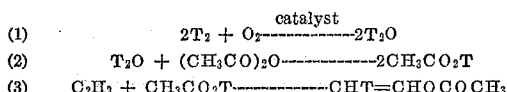
ameter, and has been found to be eminently suitable for use in formulating a tritium self-luminous paint. A silicate phosphor is preferred to a sulfide phosphor inasmuch as it is more resistant to the deleterious action of moisture and high energy radiations. This choice, however, is not to rule out the use of other phosphors such as (1) zinc sulphide: copper; (2) zinc sulphide: silver; (3) zinc cadmium sulfide: copper; or other types such as zinc orthogermanate when these are available as efficient phosphors with small 1 to 3 (and preferably 1 to 2) micron diameters.

The choice of phosphor will determine the color of the paint. A blue paint can be made by using calcium magnesium silicate: titanium activated. A green paint results from using zinc orthosilicate: manganese activated. A yellow paint can be prepared using zinc cadmium sulfide: silver activated. A red paint can be made with zinc phosphate: manganese activated. Similarly, an orange paint can be obtained using zinc cadmium sulfide: silver activated.

Speaking generally a self-luminous paint comprises a phosphor, a vehicle, a solvent and a source of radioactive energy for exciting the phosphor to luminescence. As used herein the term "vehicle" excludes the volatile components of an ordinary paint and includes not only the plastic binder but the plastic binder in combination with any other modifying agent as, for example, a plasticizer, which is compatible with the binder and is non-volatile. In the present invention the tritium is chemically combined in the vehicle, either by tritiation of the plastic binder or by tritiation of the plasticizer or other non-volatile hydrogenous modifying agent included in the vehicle as defined herein.

Preparation of Tritiated Plastic Binder

The vehicle of the paint may comprise a tritiated plastic. Thus, for example, tritiated polyvinyl acetate can be used as the plastic binder component of the vehicle of a self-luminous paint. This plastic is prepared first as a monomer, vinyl acetate, by the following reactions, and the monomer subsequently polymerized to polyvinyl acetate:



Ten (10) millimoles of tritium gas (10 millimoles=60 milligrams=600 curies) is allowed to react slowly with oxygen in the presence of a palladium catalyst by allowing tritium gas to diffuse through a heated palladium thimble into a flask containing oxygen. Tritium oxide produced by reaction (1) is continuously removed by freezing into a small tube attached to the flask. After completion of reaction (1) the palladium thimble is cooled and unreacted tritium gas is collected on powdered uranium.

Tritiated water contained in said tube is transferred by freezing into a flask containing ten millimoles of acetic anhydride. When the transfer is complete the contents of the flask are warmed to room temperature, and reaction (2) proceeds rapidly to completion, forming tritiated glacial acetic acid. Tritiated glacial acetic acid reacts with acetylene according to reaction (3) in the presence of a mercuric salt catalyst. The product, tritiated vinyl acetate, is purified by distillation, allowed to polymerize into polyvinyl acetate, then dissolved in amyl acetate. The specific activity of the material prepared by this series of reactions is 60 curies per millimole of vinyl acetate, which can be reduced to any desired specific activity by addition of inactive polyvinyl acetate solution in amyl acetate.

Preparation of a Tritiated Paint Modifier

Ten millimoles of diisooctyl maleate weighing 3.40 grams is dissolved in 20 ml. of ethyl acetate contained in

a pressure flask. 300 milligrams of pre-reduced 30% palladium on charcoal catalyst is added to the solution. 20 millimoles of tritium gas (1200 curies) is added to the flask and the contents of the flask including the tritium are shaken until no further takeup of tritium is observed as measured on a mercury manometer. The unreacted tritium (about 600 curies) is collected in a reservoir for future use. The catalyst is removed from solution by filtration, and ethyl acetate is evaporated from the filtrate by a stream of nitrogen. The residue, tritiated diisooctyl succinate, is dissolved in a suitable high-boiling solvent such as xylene, and stored in solution. This material functions as a plasticizer to modify the characteristic of a paint.

Self-luminous paints may be formulated using a tritiated plastic binder or a non-tritiated plastic binder in conjunction with a tritiated paint modifier, an example of which is tritiated plasticizer. Following are two examples illustrating how such a paint may be prepared.

20 Preparation of a Self-Luminous Paint Using a Tritiated Plastic Binder

A self-luminous paint comprising a tritiated binder can be prepared according to the following procedure. A mixture of 45 grams of zinc orthosilicate; manganese activated phosphor, having an average particle diameter of 1 to 2 microns, is mixed together with 5 grams of aluminum stearate in a solution of 50 grams of polyvinyl acetate (not radioactive) in 100 grams of amyl acetate. The amyl acetate functions as a solvent or thinner. This mixture is milled gently for 10 minutes until the mixture is homogeneous. 60 curies of tritiated polyvinyl acetate (1 millimole of material prepared as previously described) is added to the paint mixture and dispersed homogeneously by stirring. 15 grams of a non-radioactive plasticizer, such as dioctyl phthalate, is added if a high initial paint film flexibility is required. The resultant mixture constitutes a self-luminous paint which can be made more viscous by evaporation of amyl acetate or less viscous by addition of more amyl acetate, depending upon the method by which the paint is to be applied.

The brightness of a given thickness of coating will depend upon the amount of radioactive polyvinyl acetate added per gram of paint. It will also depend upon the coating thickness for thicknesses up to about 20 milligrams/cm.².

Preparation of a Self-Luminous Paint Using a Tritiated Paint Modifier

A self-luminous paint comprising a phosphor, and a vehicle therefor comprising a non-tritiated plastic binder and a tritiated plasticizer for the binder can be prepared as follows. A mixture of 45 grams of zinc orthosilicate: manganese activated phosphor having an average particle diameter between 1 and 2 microns is stirred together with 5 grams of aluminum stearate into a solution comprising 33 grams of Acryloid F-10 (manufactured by Rohm & Haas Co., Philadelphia, Pa.) and 25 grams of mineral spirits. Acryloid F-10 is a solution of acrylic resin dissolved in mineral spirits. The additional 25 grams of mineral spirits acts to thin the resin. This mixture is milled gently for 10 minutes until homogeneous. A solution of tritiated plasticizer, diisooctyl succinate-H3, containing 60 curies of tritium and prepared as previously described is added to the paint to make it self-luminous. The radioactive compound must be homogeneously dispersed throughout the paint and this is accomplished by stirring. The viscosity is increased by evaporating the solvent and is decreased by adding solvent.

The brightness of the self-luminous coatings with this paint can be increased by increasing the number of curies of tritiated plasticizer which is added. Similarly the brightness can be decreased by decreasing the number of curies added. The brightness is also dependent upon the coating thickness up to thicknesses of about 20 milligrams per square centimeter.

5

One of the advantages of the present invention resides in the fact that it can be applied to paints comprising various plastic binders and paint modifiers. Following is a list of plastic binders which can be tritiated to produce a self-luminous paint: acrylic resins, alkyd resins, cellulose acetate, ethyl cellulose, hydroxyethyl cellulose, phenol formaldehyde resins, polyester resins, polystyrene resins, urea formaldehyde resins, vinyl resins, polyvinyl resins, polyvinyl alcohol.

The foregoing plastics may comprise all or part of the vehicle of the paint, excluding the volatile constituents thereof. Following is a list of plasticizers which can be tritiated for the purposes of the present invention: dioctyl adipate, diisooctyl azelate, polyethyleneglycol dibenzoate, tri-n-butyl citrate, glycerol tributyrat, glycerol mono-

laurate, amyl oleate, di-n-octyl phthalate, dibutyl sebacate, amyl stearate, dibutyl succinate, dibutyl tartrate.

The foregoing list of plastics and plasticizers is not to be construed as limiting the invention but are presented by way of example only. The primary requisite of this invention is that the paint comprise a non-volatile hydrogenous material which may function either as a binder or as a paint modifier and which is tritiated.

Tritiating the paint modifier is just as effective as tritiating the plastic binder. A self-luminous tritium paint is efficient only if the tritiated compound is homogeneously dispersed throughout the paint. Because a plasticizer or other paint modifier must be compatible with the plastic binder, it readily disperses uniformly throughout the binder. Accordingly, if the paint modifier is tritiated the radioactivity will be uniformly distributed in the paint.

Tritium and tritium paints have many advantages over radium and radium paints. One of the advantages of using tritium is that it is especially suitable as a radiation source for exciting phosphors. It has very low penetrating power, the beta radiation emitted therefrom having a penetration power of about 0.8 milligram per square centimeter. In most plastics this corresponds to a linear range of approximately 8 (10^{-4}) cm. In addition it is readily available at a relatively low cost. Tritium is about 100,000 times less hazardous than radium if absorbed by the human body and no expensive shielding is required in preparing, handling and using the paint. Moreover, the beta radiations from tritium do not result in phosphor destruction so that the rate of loss of brightness of tritiated paints is essentially the same as the rate of radioactive decay of tritium, about 6% per year.

Another advantage of tritium paints is that they can be made in various colors more effectively than radium paints. If it is desired to make a self-luminous paint in a color other than the conventional green but with the same brightness, it would be necessary, due to the human eye's lower response to colors other than green, to increase the concentration of radioactivity in the paint. However, when this is done with radium, it is found that the rate of destruction of the phosphor by the radium is increased tremendously, resulting in an unstable paint having a short useful life.

In the case of tritium, however, no such adverse result is produced. When the concentration of tritium is increased, the rate of loss of brightness remains substantially the same. Hence paints in colors other than green in brightnesses perceptible to the human eye are possible under the present invention. Similarly, it is possible to increase the brightness of green tritium paints by adding more radioactivity without affecting the stability thereof. By the present invention it is possible to produce green paints having a brightness 20 to 30 times as great as those paints employing radium compounds, and still not increase the rate of loss of brightness.

Another advantage of tritium paints resides in their adaptability to application by silk screening. Due to the hazards of its radiations, radium paint must be handled in small concentrations. Thus, for example, it is the practice to silk screen only one clock dial at a time.

6

Naturally this increases the cost of manufacturing the dial. With tritium there is no such danger and it is possible to silk screen clock dials in quantity without hazard to personnel. This saving in time reduces the cost of producing clock dials.

Still a further advantage of the present invention is that the radioactive material is a component part of the paint vehicle. Because the plastic binder and the paint modifier, either of which may be modified, are non-volatile, there is no loss of radioactivity to the atmosphere. In this connection it is to be noted that if the plastic binder is tritiated, it must not be in the monomer state since monomers generally are volatile. The plastic binder, if tritiated, must be at least partly polymerized so as to have low volatility. It is recognized that where the paint modifier is tritiated, the plastic binder may be in a volatile state since evaporation of binder will not produce any loss of radioactivity, the tritiated modifier being non-volatile. Nevertheless, the loss of any binder at all is to be avoided for reasons of economy. Accordingly, in practice the embodiments of the present invention will comprise a plastic binder which is at least partially polymerized, that is, in a non-volatile state, regardless of whether the binder or the paint modifier is tritiated, and a solvent or thinner for the binder.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. Therefore, it is to be understood that the invention is not limited in its application to the details specifically described hereinabove and that within the scope of the appended claims it may be practiced otherwise than as specifically described.

We claim:

1. A self-luminous paint consisting essentially of an inorganic phosphorescent material in particle form and a tritiated hydrogenous non-volatile polymerized organic plastic dispersed uniformly in a volatile solvent for said plastic, said plastic selected from the group consisting of acrylic resins, alkyd resins, cellulose acetate, ethyl cellulose, hydroxy-ethyl cellulose, phenol formaldehyde resins, polyester resins, polystyrene resins, urea formaldehyde resins and vinyl resins, the average distance between adjacent phosphorescent particles being less than about 3 microns when said solvent is removed.

2. A composition of matter consisting essentially of an inorganic phosphorescent material in particle form embedded in a tritiated organic polymer plastic, said plastic selected from the group consisting of acrylic resins, alkyd resins, cellulose acetate, ethyl cellulose, hydroxy-ethyl cellulose, phenol formaldehyde resins, polyester resins, polystyrene resins, urea formaldehyde resins and vinyl resins, the average distance between adjacent phosphorescent particles being less than about 3 microns.

3. A self-luminous paint consisting essentially of an inorganic phosphorescent material in particle form dispersed in a tritiated organic plastic selected from the group consisting of acrylic resins, alkyd resins, cellulose acetate, ethyl cellulose, hydroxyethyl cellulose, phenol formaldehyde resins, polyester resins, polystyrene resins, urea formaldehyde resins and vinyl resins, the average distance between adjacent phosphorescent particles being less than about 3 microns.

References Cited in the file of this patent

UNITED STATES PATENTS

2,039,734 Meder ----- May 5, 1936
2,749,251 Shapiro ----- June 5, 1956

FOREIGN PATENTS

646,414 Great Britain ----- Nov. 22, 1950

OTHER REFERENCES

"Luminous and Fluorescent Paints," by Dept. of Comm. Nat. Bureau of Standards, Sept. 9, 1942; Circular Letter LC 703 and 678.