

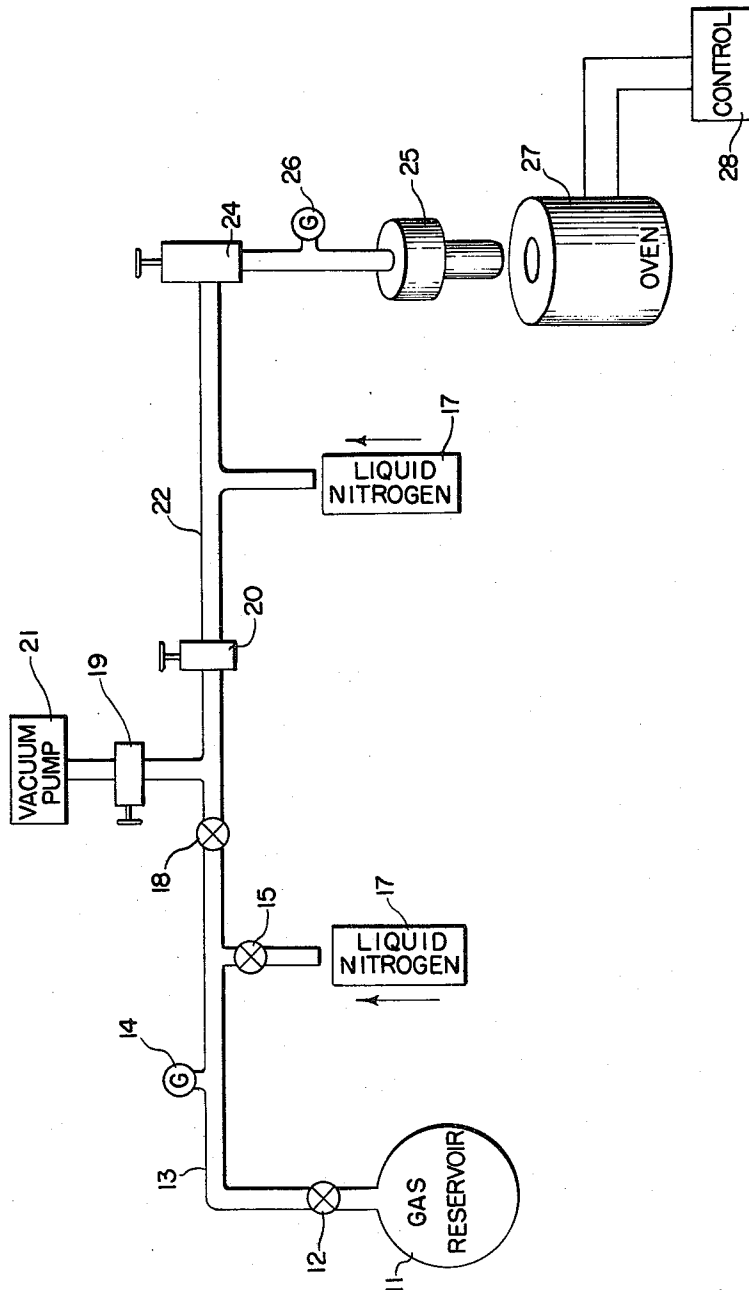
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METHOD OF PRODUCING LUMINOUS SURFACES

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METHOD OF PRODUCING LUMINOUS SURFACES

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10 Claims. (Cl. 117—33.5)

The present invention relates in general to self-luminous articles and more particularly to a process for the production of self-luminous compositions particularly adapted for use as paints.

The use of self-luminous paints in the manufacture of self-illuminated surfaces such as watch dials, compass dials and warning strips and lettering is a well known technique. The essential characteristics of a self-luminous paint are that it provide a sufficiently bright surface to be visible without other illumination in the dark, and that the source of power for generating the light be contained within the paint itself. Self-luminous paints, heretofore available, have generally employed materials having the property of phosphorescence. Phosphorescence is the emission of visible light at low temperature as a result of the absorption of electromagnetic radiation by a material, which emission continues for some period after these radiations have stopped. The luminous paints have generally consisted of a mixture of phosphor material together with a source of electromagnetic radiation and a binder material to render the mixture a homogeneous paintlike consistency. Perhaps the most widely used mixture for self-luminous paints has been a mixture of zinc sulfide (activated) phosphor and radium, the latter being a radioactive substance emitting beta radiation. This paint is commonly referred to as "radium paint."

Radium paint, while providing initially a satisfactory luminescent surface, is subject to several drawbacks. One extremely important drawback is that radium is a highly toxic material and presents a severe biological hazard to people handling it in a manufacturing process. In the conventional use of radium paint the radioactive material is contained within the paint at the time when the delicate and time consuming manual operations, such as painting the numbers on the dials of watch faces, take place. The severe biological hazard presented by these materials to personnel performing this operation has necessarily resulted in unwieldy and inefficient procedures for applying these paints in order to minimize the danger to the operating personnel. A second factor limiting the desirability of radium paint is that a residuary amount of radioactive paint must necessarily remain on the painting implements and in the cleaning materials for these implements. Another drawback stems from the fact that radium decays into a radioactive gas, radon, which diffuses from the luminous coating, providing another hazard.

Radium emits several types of radioactive particles, one being high energy alpha radiation, which causes damage in the phosphor material and thereby considerably shortens the duration of the coating at any given surface brightness.

It is therefore a primary object of the present invention to provide an economical, easily handled luminous paint which has an absolute minimum of biological hazard.

It is another object of the present invention to provide a process for the production of luminous paint which allows the application of the paint to the object to be coated prior to the introduction of radioactivity into the paint.

It is still another object of this invention to provide a safe, economical and simplified process for the manufacture of articles with luminous coated surfaces.

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The present invention utilizes the novel approach of rendering an already applied coating luminescent, rather than applying a luminescent coating. Since the process of this invention does not disturb the physical placement of the coating, intricate time-consuming patterns may be coated on a surface with inactive material, which is subsequently processed to become luminescent.

Broadly speaking, the present invention teaches a process for preparing a surface with a phosphorescent material admixed with a crystal, capable of subsequently forming a clathrate compound with a radioactive gas. The initial phosphor-containing coating is biologically non-hazardous, and the radioactive gas may be introduced in a remotely controlled process. The process is particularly advantageous when it employs an inert radioactive gas, since these radioactive gases themselves do not provide a serious biological hazard.

Radioactive clathrate compounds are compounds in which the molecules of one component (the radioactive inert gas in this case) are trapped within an enclosing structure formed by the crystal lattice of a second component. This second component has up to the present been limited to the crystals formed by quinol and compounds of similar structure.

Broadly speaking, the process by which these radioactive clathrate compounds are produced involves the melting of crystals of quinol under a high pressure of the radioactive inert gas and controlled slow cooling back to normal room temperature, followed by evacuation of the non-clathrated radioactive gas from the vessel in which the crystals were contained. A mixture containing the phosphor and quinol crystals together with a thermal plastic or thermal setting binder may be prepared, adding a solvent to provide the right paint consistency. This mixture is then coated, as would be any other paint in a predetermined configuration, such as, on the surface of the watch dial, compass, etc. Since there is no radiation present, the paint at this point is entirely harmless from the biological point of view and may be manipulated at great length and close range by personnel. Upon completion of the coating of the object with this compound, the entire object may be inserted within a pressure vessel and heated to the melting point of quinol which is approximately 175° C. under a pressure of several hundred pounds per square inch of radioactive gas, for example krypton-85. The vessel and its contents are then slowly cooled over a period which typically may vary between four and seventy hours back to room temperature. The excess radioactive gas is pumped out of the vessel and the object may then be removed from the vessel. The coating is now completely luminescent and will attain a brightness equal to or greater than that of radium paint. Since this entire latter part of the operation involving the clathrating process itself may readily be done by remote control and since the only radioactive element is an inert rare gas, the entire operation may be done without any problem of contamination of equipment and subsequent contamination of cleanup materials. Other objects and advantages will become apparent from the following detailed description when taken in conjunction with the accompanying drawing in which the single FIGURE is a schematic illustration of a process system suitable for producing the clathrated compounds.

The process for preparing a self-luminous surface on an object employs several discrete steps. Initially a mixture of quinol crystals, binder, phosphorescent powder and solvent is prepared. The binder may be any suitable thermal plastic or thermal setting material such as, for example, methyl methacrylate or vinyl acetate. Any of the available phosphor materials which exhibit a high conversion efficiency from absorbed radiation to emitted light are suitable for the phosphor powder. Typical

materials would be activated zinc sulfide or cadmium sulfide. The above ingredients are mixed together using a solvent, generally any one of the ketones, in order to provide a creamlike consistency for easy application to a surface. The exact proportions of these materials to one another are not critical, typical values for them, however, being the ratio of 3 units by weight of phosphor to 2 units by weight of quinol to $\frac{1}{10}$ of a unit by weight of binder. This entire mixture which, by the addition of solvent, has become suitable for painting is then applied to the surface to be made luminescent. As indicated above, the material is not now radioactive and hence presents no significant biological hazard to personnel, even hand painting with the material. The coated object is placed within an evacuated pressure vessel and a radioactive rare gas such as krypton-85 is introduced at a high pressure (in the order of several hundred pounds/inch²) into the pressure vessel. The pressure vessel is heated to a temperature above the melting point of quinol (175° C.) and then slowly cooled under controlled conditions back to room temperature. The coated object then may be removed from the pressure vessel and will provide a stable luminescent surface.

A surface one square centimeter in area which is coated to a thickness of one millimeter with a paint made in the above manner and into which has been incorporated one-tenth of a millicurie of krypton-85 will produce the brightness ordinarily associated with watch dials and the like.

With reference now to the figure there is shown a schematic illustration of a process system for forming clathrate compounds containing krypton-85. The apparatus is seen to comprise generally a gas flow system capable of withstanding gas pressures up to 1000 p.s.i. and preferably fabricated from copper or steel. A flask 11 containing krypton-85 at a pressure of one atmosphere is connected through a low pressure valve 12 to manifold 13. This manifold is generally cylindrical and has a pressure indicator 14 attached. Joined to the manifold 13 through low pressure valve 15 is a small diameter chamber 16 which may be immersed in a flask 17 containing liquid nitrogen. Manifold 13 also connects through low pressure valve 18 to high pressure valves 19 and 20 in such a manner that it may be opened to vacuum pump 21 or manifold 22, or both. This second manifold 22 has a small diameter chamber 23 opening directly from it, which is also capable of being immersed in a liquid nitrogen flask 17. Manifold 22 terminates in high pressure valve 24 connecting to a high pressure vessel 25, sometimes referred to as a bomb, complete with its pressure indicator 26. The high pressure vessel 25 which is detachable at valve 24 has a small volume, which together with the volume of manifolds 13 and 33 and chamber 23 constitutes a total volume about one fiftieth that of flask 11. An oven 27 controlled by thermostatic unit 28 provides a means of controlled heating high pressure vessel 25. Pressure vessel 25 is made a size and shape convenient for containing the object which is to be made luminescent.

Having described the apparatus, the procedure for forming the clathrates will now be discussed. The object, coated with the mixture of quinol and phosphor, is loaded into the pressure vessel 25 and attached to valve 24. Valves 15, 18, 19, 20 and 24 are opened, allowing the entire system except flask 11 to be evacuated. When the atmospheric gases have been removed, valves 15 and 19 are closed. Valve 12 is now opened, allowing the krypton-85 to fill the system to a pressure of almost one atmosphere. The temperature of chamber 23 is reduced below -169° C. by immersion in liquid nitrogen, condensing all the krypton-85 into it; then valve 20 is closed and chamber 23 returned to room temperature, thus expanding the krypton-85 into manifold 22 and pressure vessel 25. Since this volume is very small, the krypton reaches a pressure of about 900 p.s.i. Pressure vessel 25

is now heated by oven 26 to approximately 175° C. to melt the alpha-quinol crystals contained in it. The clathrates are now formed by reducing the temperature back to room temperature over a period which typically may vary from four to seventy hours. More clathrating is achieved using longer time periods. When the process is completed, valve 24 is closed, the pressure vessel 25 is detached, and the object with the coating now including krypton-85 and therefore luminous is removed.

The process system may then be restored in the following manner. Valve 12 is closed and valves 20, 18 and 15 opened; then chamber 16 is immersed in liquid nitrogen, reducing its temperature and condensing all the krypton into it. Valve 18 is then closed, valve 12 opened, and the temperature of chamber 16 slowly returned to room temperature, causing most of the krypton to flow into flask 11. Valve 12 is shut and the small residue of krypton in manifold 13 pumped off.

While the above description has concerned itself specifically with clathrates including krypton-85 as the gas, any of the inert radioactive gases suitable for forming sufficiently luminous compounds may be employed. These gases would include the isotopes krypton-88, argon-39 and xenon-133. While there are radioactive isotopes of the rare gases neon, helium and radon, these are not capable of being clathrated because of the discrepancy between their molecular radius and that of the quinol cage. Therefore a common characteristic of the grouped inert gases included is that they be radioactive inert gases of sufficient molecular size to be clathrated within quinol crystals. In view of the fact that various modifications and departures may now be made by those skilled in this art, the invention disclosed herein is to be construed as limited only by the spirit and scope of the appended claims.

What is claimed is:

1. A paint compound adapted to be used for achieving self-luminous painted articles comprising a mixture of, a phosphorescent powder adapted to emit light in response to absorbed radiation; a substance adapted to form a clathrate with an inert radioactive gas; a light-transmissive thermal plastic binder, and a solvent for said plastic binder.

2. A paint compound in accordance with claim 1 wherein said phosphorescent powder is activated zinc sulfide.

3. A paint compound in accordance with claim 1 wherein said substance adapted to form a clathrate is quinol.

4. A paint compound adapted to be used for achieving self-luminous painted articles comprising a mixture of, a phosphorescent powder adapted to emit light in response to absorbed radiation; quinol crystals; and a light-transmissive, soluble binder.

5. A paint compound adapted to be used for achieving self-luminous painted articles comprising a mixture of, a phosphorescent powder adapted to emit light in response to absorbed radiation; quinol crystals; a light-transmissive, soluble binder; and a solvent for said binder.

6. A process for producing a self-luminous coated surface on an article of manufacture consisting of the steps of: preparing a mixture of phosphorescent powder adapted to emit light in response to absorbed radiation, quinol crystals, a soluble binder and a solvent for said binder; coating said surface with said mixture; inserting said article within a pressure vessel and evacuating said pressure vessel; introducing a radioactive inert gas at relatively high pressure into said vessel; heating said coated article within said vessel to a temperature at least equal to the melting point of said quinol crystals; cooling said article to room temperature; and removing said coated article from said vessel.

7. A process for producing a self-luminous coated surface on an article of manufacture comprising the sequential steps of: coating said surface with a mixture of a phosphorescent powder adapted to emit light in response to ab-

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sorbed radiation, a substance adapted to form a clathrate with an inert radioactive gas and a binder; and clathrating said substance with an inert radioactive gas.

8. A process for producing an article of manufacture having a self-luminous coating of predetermined configuration over at least a portion of the surface thereof comprising the steps of coating said portion with an adhering mixture containing a phosphor adapted to emit light in response to absorbed radiation and a substance adapted to form a clathrate with an inert radioactive gas, and thereafter exposing said coating to an inert radioactive gas to clathrate said substance.

9. A process for producing a self-luminous coating on an article of manufacture comprising the steps of: applying to said article a mixture of a phosphorescent powder adapted to emit light in response to absorbed radiation, a substance adapted to form a clathrate with an inert radioactive gas, and a binder; inserting said article bearing said mixture into a pressure vessel; introducing into said vessel at high pressure a radioactive inert gas adapted to form a clathrate with said substance; heating said article within said vessel to a temperature equal at least to the melting

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point of said substance; cooling said article to room temperature; and removing said article from said vessel.

10. A process for producing a self-luminous coating on an article of manufacture in accordance with claim 9, wherein said phosphorescent powder is activated zinc sulfide.

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