Photoluminescent Paints


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Abstract

Energy conservation and disaster management being the need of the hour, many alternative energy sources have become the buzzword in the industry. Photo luminescent paints, a novel, efficient, non-toxic and non-hazardous technology unlike its predecessors fluorescent and radioactive paints, have generated widespread interest in this regard. Of particular importance are Strontium aluminate based paints doped with rare earth metals and auxiliary activators like transition metal and other rare earth metals. The mechanism of electron hole trapping of photons by the lattice defects in the crystal of the pigment, leading to an afterglow of about eight to ten hours even when the energy is cut off, is studied. The synthesis of these pigments by high temperature method and its effect on afterglow properties is determined. These pigments can be dispersed in water compatible organic film formers and can easily be applied by normal paint application techniques. Compared to other alternate energy resources these perform favorably in terms of cost, maintenance and time constraints and are an intelligent solution which will serve the purpose of energy conservation, road safety and disaster management combined with aesthetic appeal.

Keywords: Photo luminescent paints, non-toxic, Rare earth doped Strontium aluminate, road safety, disaster management.

1. Introduction

Luminescence is a general term applied to all forms of light. There are several kinds of luminescence: chemoluminescence (including bioluminescence from living organisms such as sea plankton, fireflies, glowworms, certain fungi etc., produced by chemical reactions (primarily oxidations, at low temperatures), crystalloluminescence, electroluminescence, photoluminescence (i.e., phosophorescence, fluorescence), radioluminescence, sonoluminescence, thermoluminescence and triboluminescence.[1] Photoluminescent paints have evolved a lot since their inception. Fluorescent paints were largely ineffective from the disaster management and energy conservation point of view. Also, for sustained phosphorescence, radioactive luminescent paints were used, but in view of their toxicity, hazardous nature and cost considerations they have been discarded lately.

Their predecessor ZnS:Cu based pigments were in use since the late 1800's and the early 1900's, however due to their lack of brightness and inability to maintain phosphorescence for more than a couple of hours they have made way for better and brighter Strontium aluminate based pigments.[2] Of particular commercial importance are the strontium aluminates that are activated with small amounts of rare earth containing oxides and compounds along with transition metal elements in which a number of stoichiometric compounds are formed and remain stable at room temperature.

2. Mechanism of Action

A material can emit light either through incandescence, where all atoms radiate, or by luminescence, where only a small fraction of atoms, called emission centers or luminescence centers emit light. In inorganic phosphors, these inhomogeneities in the crystal structure are created usually by addition of a trace amount of dopants, impurities called activators. (In rare cases dislocations or other crystal defects can play the role of the impurity.) The wavelength emitted by the emission center is dependent on the atom itself, and on the surrounding crystal structure. [3]

The persistent after-glow is attributed to electron-hole trapping and subsequent recombination process. Phosphorescence of the pigment phosphor is a function of the depth of the trapping level. If it is too deep, the phosphor would no longer show phosphorescence at room temperature. Therefore for persistent afterglow, it is crucial to have trapping levels located at a suitable depth.[4]The rather schematic mechanisms presented involve either a direct or valence band assisted transfer of a hole from Eu^{2+} center after excitation. However these mechanisms involve the creation of Eu^{+} and Rare earth $^{+4}$ ions.

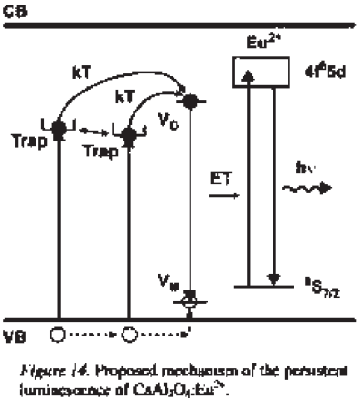

Fig. 2.1.1. Mechanism of Persistent Luminescence
Ref. : Jean-Claude Krupa, Nikolai Aleksandrovich Kulagin, Physics of laser crystals, Volume 126, 47

2.2 Effect of Temperature on The Afterglow

Random thermal fluctuations in the crystal structure of the pigment nudge the electrons out of the energy trough that has them trapped. This is why phosphorescent paints glow weaker but longer when cold and brighter but shorter when hot. [5] The following picture illustrates this:

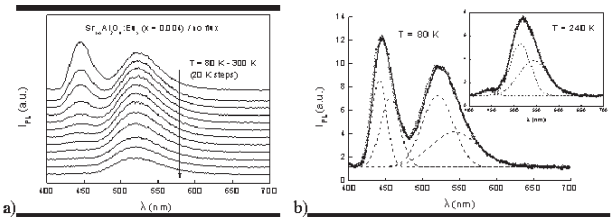

Fig. 1: a) PL spectra of $Sr_{1-x}Al_2O_4:Eu_x$ (x = 0.004) measured in dependence on the temperature (T = 80– 300 K); b) deconvolution of the PL spectrum at T = 80 K / 240 K by four / three Gaussian profiles

Fig 2.2.1 Effect of Temperature on Photoluminescence
Ref.: G. Blasse, B. C. Grabmeier, Luminescent Materials, Springer, Berlin (1994)

3. Manufacturing of The Pigment [6]

A photoluminescent aluminate comprising $SrAl_2O_4$:Eu,Dy,Gd,Sc wherein the following materials and quantities are combined and reacted to form the aluminate:
$SrCO_3$ (1.0 mole), Al_2O_3 (1.0 mole), Eu_2O_3 (0.005 mole), Dy_2O_3 (0.01 mole),
Gd_2O_3 (0.005 mole), Sc_2O_3 (0.005 mole), B_2O_3 (0.2 mole).

The powdered materials are then agitated for several minutes in a blending vessel in order to achieve a uniform powder mixture. Subsequent to mixing, the powder is loaded into a pelletizing press and isostatically compacted under a pressure of 25,000 psi. The powder pellets are then loaded into a circulating air furnace at a temperature below 250°C. until a uniform temperature is achieved. The pellets are then heated to a temperature above 800°C. in a circulating air furnace for a period of 4 to 8 hours in order to permit calcination of the strontium carbonate followed by formation of the strontium aluminate according to the intended stoichiometric reaction.

Subsequent to this reaction sintering step, the sintered material is optionally crushed or milled to an intermediate powder form of 120 mesh and then re-pelletized. However, in cases where the initial pellets possess a high surface to volume ratio, the re-crushing step may not be necessary. The powder or pellets are then heated to a temperature between 1100°C. and 1350°C. for a period of 2 to 6 hours in a flowing gaseous atmosphere of 5% N_2 to get the pigment crystal. The first batch glows the brightest with subsequent dimming of the next batch and so on.

4. Paint Formulation and Application

Environmentally friendly and energy saving water-based photo luminescent paints can be produced which have the desired characteristics of ease of application, short track time, suitable long duration and higher intensity of afterglow luminescence as well as the most desired characteristic of extended service wear time under traffic conditions even when subjected to the detrimental factors of ultraviolet radiation and/or moisture. Light-emitting paints achieve the above objects, among others, by providing a composition suitable for use in marking roadways or for use in water-based highway or roadway paints comprising photo luminescent pigments and a epoxy resin or a polyurethane resin which is water compatible. When either the epoxy resin or the polyurethane resin is admixed with the water sensitive luminescent substance, the resulting mixture protects the luminescent substance from being attacked by the moisture in the air and the water in a water-based paint composition. Thus, the luminescent substance is protected immediately after being mixed with the epoxy or polyurethane resins in the compositions. [7] While the luminescent substance and the polyurethane resin may be added directly to a paint composition, in a preferred embodiment a premixture is formed by mechanically mixing small incremental amounts of the luminescent substance with the water compatible/miscible polyurethane resin to thoroughly coat the luminescent substance with the polyurethane resin. The formation of the premixture permits even distribution of the luminescent particles within the polyurethane resin and assures that all or most of the pigment particles are coated. This premixture may be stored or immediately added to and mixed with water-based paint compositions with adequate mechanical mixing to ensure high integration and distribution of the premixture throughout the paint composition. The paint composition so produced may be sealed and stored until ready to be used. At the time it is to be used the highway paint composition should be mixed mechanically again with conventional means. When epoxy resin is used, hardener and polymer components thereof are mixed together and then the luminescent particles are mixed therein. This composition may be applied directly to the surface to be marked, or, if desired, the composition may have a quantity of water-based paint mixed thereinto. In either case, the final mixture must be applied to the surface to be marked before the epoxy cures.

After applying a composition containing this novel composition to a surface, upon drying, the composition imparts weatherability to the surface such as resistance to surface wear by tyres of motor vehicles using the roadway and thus provides an extended surface life. The novel luminescent composition protects and shields the phosphorescent phosphor from the oxidizing action and humidity of the atmosphere.

With Polyurethane Resins

When used with a polyurethane resin, most preferred range for the concentration of phosphorescent substance is from about 15% to 60% by volume of the novel luminescent composition in the industry. These compositions contain a water miscible or compatible polyurethane resin. The polyurethane resin (e.g. an acrylic urethane resin in either a semi-gloss or gloss) used in the composition is a thermoplastic polymer derived or produced by the reaction of a polyisocyanate such as a diisocyanate (toluene diisocyanate) and a hydroxyl-containing material, for example, a polyol derived from propylene oxide or trichlorobutylene oxide, containing a water soluble group such as hydroxy, carboxylic acid or amine group. The amount of water miscible polyurethane resin (semi-gloss or gloss) used ranges from about 10% to about 65% by volume of the composition.

With Epoxy Resins

When used with only an epoxy resin, the preferred range of

concentration for the luminescent substance is from about 15% to about 25% by volume. When used with an epoxy resin and a highway paint, the optimum range of concentration of the components, based on ratios of volumes of luminescent substance: epoxy resin in the paint : total paint composition (without the additives and solvents), are from about 8.3:41.6:50 to about 12.5:62.5:25. With either type of resin, the selection of the amount of luminescent substance, epoxy resin (when used), polyurethane resin, and colored paint dispersion from within the ranges discussed above, is effected, by the color of the paint dispersion. Yellow paints require increased amounts of luminescent material in comparison to white paints. The compositions, when used in highway paints, prevents or minimizes the flaking of the exposed surface by the tyres of motor vehicles using the roadway, this eliminates the need for an overcoat. Optionally, a particulate may be used to impart abrasiveness to the compositions and is either a natural abrasive material such as fine sand, silica, ground marble (white marble preferred). The more important synthetic types are silicon carbide, boron carbide, cerium oxide and fused alumina; or even some reflective substances (for example crushed reflective glass). This abrasiveness reduces the likelihood of skidding by motor vehicles both in clear weather as well as on the wet surface. The operable range is an additive amount from about 1% to about 15% parts by volume.

5. Applications [8]

These paints find a huge potential in various fields like construction, advertisement, hoarding, glow signs, path marking, auditorium, stadium, hotels, instrumentation, marine engineering, emergency routes, etc. Enhancing the aesthetic value of car, luxury coaches, buses, etc. Stickers made with PLP withstand rains, sunlight, extreme cold, snowfall, etc. As they are visible in dark, the vehicle itself becomes a moving advertising illuminated sign. It is useful in brand development and advertisement. Light emitting paint plays an important role in transport equipments like airplane, automobiles, lorries, container vehicles, ships, etc. as these night glow paint can effectively be used. The rear ends of the vehicles are used with yellow & black strips of light emitting paints & radium film. They glow very much in dark avoiding accidents. In absence of the rear tail lamp these strips add safety to the vehicle in dark. Specially containers fleet,which are huge vehicles,the side wall painted with light emitting paints offers good visibility in the dark. Trucks, tempos, lorries face much difficulties while parked in night time on road. They are dangerous for passing by vehicles. This danger can be eliminated using light emitting vinyls. Containers marked with light emitting vinyls glow in dark adding the brand name to the logistics companies. PLP for interior decoration is one of the famous interior decoration concept galaxy at home, which is widely used in children room and master bed room. Path markings reduce lot of expense on lighting installations as well as maintenance in petroleum complex & chemical plants where a flame proof wiring is statutory. It also finds application in clubs, restaurants, hotels etc. The switches coated with night glow ink are easily detectable in dark. Staircase is an integral part of any construction place residential building, hospitals, hotels, commercial complex, shopping mall, multiplex, auditorium, high rise tower or office premises. All the lobbies, passages, emergency routes, escape routes & fire exit lead to staircase.

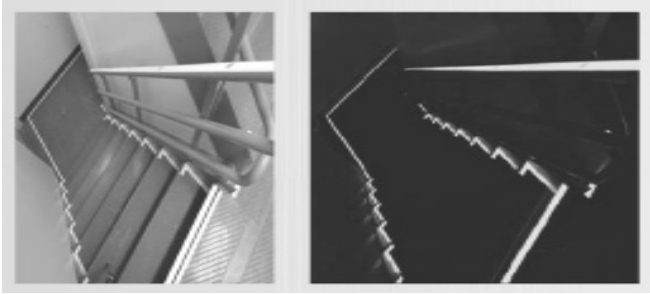

Fig 5.1 Emergency Exit Route painted with Photo Luminescent Paints
Ref.: http://www.starysky.com/tape_sign.html

Light emitting paints play an important role at the staircase. It ensures illumination at the event of mishap like fire, earthquake, building collapse. Infamous 9/11 World Trade Center buildings were painted with light emitting paints. With the illumination provided by light emitting paint the fire brigade evacuated as many as 18000 people. Since light emitting paints offer a fail safe lighting source the rescue operation becomes easy. Most of the modern buildings are provided with lift, elevators & escalators. In power failure condition all of these devices fail as well as go into dark. The ceiling of lift & steps for the escalator painted with light emitting paint provides a quick relief. It provides a much economic substitute to inverters, generators & emergency lamp.

6. Comparison Between Fluorescent and Photoluminescent Paints and Alternative Energy Sources

Fig 5.2 Light Emitting Wallpaper
http://artslibrary.files.wordpress.com/2008/07/wallpaper-5.jpg

The present hot melt plastics & fluorescent paints used for lane marking and road marking are visible only when light fall on it in a particular angle. Whereas light emitting paints offer great visibility in the dark Also the fluorescent paint loses its luster within a short period. [9] Alternative energy sources like solar panels, windmills etc. require a huge installation cost as well as greater space for effective output. The output of these is also dependant on the local climatic

conditions, geographical locations and the time of the day etc. Storage batteries further add to their cost. On the contrary light emitting paints offers illumination for long period, require almost zero maintenance, can be painted in the space available and incur only installation cost.

7. Conclusion

Photo luminescent materials, after being excited, remain luminous with a soft, slowly decaying emission or radiation. Such materials can generate a useful level of luminous flux(on an average 23 mcd / m^2, which is 10 times more than the normal industry safety regulations) after being activated when exposed to sunlight or artificial light (such as from headlights of automobiles in the dark of night. Inspite of them being in the nascent stages of commercialization,in the near future,with developed technology, they will offer energy conservation, road safety and disaster management combined with aesthetic appeal to the user.

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