AN OVERVIEW OF LUMINESCENT PIGMENTS

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Luminescent pigments are known from ancient times when they were used mainly for decorative purposes. Now they are classified as speciality pigments and this segment of the pigments, due to their numerous applications is growing most rapidly. This overview gives a closer look at the progress made in the development of luminescent pigments.

INTRODUCTION

In general, the term 'luminescence' means the emission of radiation as a result of processes other than bioluminescence, thermal or electrical luminescence and includes fluorescence, phosphorescence, triboluminescence and chemiluminescence. However, luminescent pigments refer to fluorescent and phosphorescent phenomena only. Fluorescence and phosphorescence are the processes of absorbing energy in the form of electromagnetic radiation and emitting at least a portion of that energy as radiation. General interest in coating formulations is for the pigments that emit in the visible portion of spectrum. There are several concepts for differentiating between fluorescent and phosphorescent pigments. Broadly, fluorescence refers to the emission that ceases as soon as the excitation ceases, while in case of phosphorescence the emission continues even after the excitation ceases. These two phenomena are quite distinct, although closely related. A pigment may be fluorescent but not phosphorescent or vice versa, whilst there are some pigments, which are both phosphorescent and fluorescent. Details of such pigments along with their theory of light emission, synthesis and applications are discussed in this article in brief.

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TYPES OF LUMINESCENT PIGMENTS

The earliest reference to luminescence dates back to the time of Balmiki who described luminescent *Sanjivini* medicine in great Hindu epic *Ramayana*. Besides this, radioactive compounds were known to exhibit luminescence e. g. radium, mesothorium, etc. These were mixed with paints to impart luminescence and were used for decorative purposes and display signs. But these were known to have carcinogenic activity and their use had been restricted.

Other references of luminescent pigments can be traced to early seventies. Around that time luminescent paints were introduced in the market. These were basically based on zinc-sulfide and calcium sulfide. Balmains paints, based on calcium sulfide, were commercially available in various shades at that time. These types of luminescent pigments and paints could not become popular because of their short shelf-life and comparatively higher costs and hence were withdrawn from the market.

Subsequenty various other luminous pigments based on zincsulphide mixed with different metals were introduced. Similarly an amazing number of inorganic compounds have been found to be luminescent. These consist of sulfides, oxides, silicates, tungstates, titanates and selenides. Silicates and tungstates are largely used in luminescent lamps while, for paints normally sulfides and oxides are used. These types of pigments had an inherent drawback of having different luminosity each time they were synthesised. Hence, R & D efforts shifted to the chemistry of their synthesis and purification. By this time the mechanism of light emission of luminescent pigments was also known. All these combined to result in better and newer synthesis of luminescent pigments. Doped zinc sulfides and organometallic complexes were synthesised having good luminescent properties and greater durability. Simultaneously, luminescent organic dyes and pigments were also reported. Some of these are still used. Many organic dyes, both natural and synthetic, exhibit the property of luminescence but only in certain concentrations. They are used after absorption on suitable carrier matrix.

Recent trends and developments in luminescent pigments are centred on the organic polymers and phosphorescent pigments. Among them various luminescent rare earth doped sulfides, rare earth complexes, conjugated organic polymers, aluminates, mixed halides and borates are known. Still the field is wide open for development of more luminescent pigments having stronger luminescence, various colour shades, longer glow periods and better durability. The luminescent pigments can be classified as

(A) ***Fluorescent Pigments*** which include :

(i) Organic polynuclear hydrocarbons like anthracene, chrysene etc.,

(ii) Organic dyes like rhodamine, seframine, etc. and

(iii) Inorganic pigments like sulfides of zinc, calcium etc ; carbonates of strontium, aluminium, etc ; oxides of europium, ytterbium, etc.

(B) ***Phosphorescent pigments*** which include :

(i) Inorganic pigments like, (a) aluminates of rare earths e. g. La, Ce, Tb, etc. and alkaline earths e.g. Sr, Ca, etc. (b) sulfides of alkaline earth and transition metals e.g. silver doped zinc sulfide and CdS, etc. (c) mixed halides and borates e. g. barium europium flouro bromide etc.

(ii) Organometallic complexes : These are mainly rare earth metal complexes with different polydendate organic ligands e. g. ruthenium dipyridine phenenthroline complex, etc.,

(iii) Organic polymers e. g. aromatic polyimides, polyalkylthiophenes, etc. and

(iv) Radioactive / miscellaneous pigments e.g. radium mesothorium, etc.

PIGMENT SELECTION

The response of human eyes is limited to the wavelength range between about 3500 Å (violet-ultraviolet) and 7200 Å (red-infrared). Because of the immense variation in the visual sensitivity over this spectral range, the performance of luminescent visible light emitting pigments must be appraised not only by the absolute intensity of the emitted radiation, but also by the relative response (i. e. the luminous efficiency) of the eye at the wavelength of interest. Hence, two important figures of merit have evolved for luminescent pigments. The first is quantum efficiency and second is the brightness. Quantum efficiency is conversion efficiency of the device independent of the eye's response to it. Brightness is a measure of the visual response of the radiation emitted from the luminescent pigments. It is apparent that for high brightness, efficient pigment emitting near the peak of the eye sensitivity is required. Since the upper limit for the emission energy is approximately equal to the energy gap, values of greater than 1.72 eV (7200 Å) and as close to 2.23 eV (5550 Å) are needed.

SYNTHESIS OF LUMINESCENT PIGMENTS

Luminescent pigments can be synthesised broadly under two categories :

1. Solution chemical synthesis techniques (a) Hydroxide preciptation method and (b) Sol gel synthesis
2. Solid-state reaction techniques (a) Conventional high temperature synthesis and (b) Rapid exothermic reaction e.g. Combustion synthesis of oxides and solid-state rapid metathesis reaction of sulfides.

Solid-state reaction techniques have inherent advantages and are preferred over solution chemical synthesis techniques because one can use the as-synthesised pigment directly. Also soild-state reaction techniques take very small time to complete and work up are not required.

Essential requirement and also the principal problem in the synthesis of luminescent especially the phosphorescent pigments is the purity. Phosphorescence is produced by presence of base pigment of selective impurities called activators. Activators must be present in right quantity, because if there is too little or too much activator, the pigment will not be phosphorescent. In addition to the requirements about purity and proper activator addition, the pigment must be properly muffled to develop correct crystal conformation or again it will not be phosphorescent.

These luminescent pigments are prepared by stirring the pigment into a suitable vehicle. Grinding must be avoided and also contact with moisture must be avoided at all costs. Greater care must be taken if organic dyes are used in the selection of solvents, which may attack the carrier or cause the dye to bleed. Principle weaknesses of organic phosphorescent pigments are their tendency to fade on exposure to light.

As compared to the inorganic pigments, organic colour pigments are much more intense and less energy is required to excite luminescence and this is a very practical advantage. If further developments can improve the durability, these organic pigments will have considerable influence on the designing of luminescent systems for the building applications during emergency.

LUMINESCENT COATINGS

These are made by incorporating these luminous pigments with a special type of medium, which must be free from any substance that poisons them, and transparent to the short wave illumination. It must have a low acid value and provides a film substantially impervious to moisture. De-waxed damar is often used on account of its neutral reaction and transparency to UV light but has a disadvantage of limited durability. The selection of luminous pigment depends on the conditions to which the coating is exposed.

It is necessary to apply two coats of luminous pigment to obtain satisfactory results. After drying, the sample is finally protected from access of moisture etc. by applying a single or two coats of clear varnish. This varnish is generally the same as used for the medium of the paint.

Luminous coatings offer a promising field for the future development in interior decoration and emergency way finding systems. Still there is need to do a lot of work to improve both durability of the after-glow and the retention of the luminous property for longer periods of use.

APPLICATIONS OF LUMINESCENT PIGMENTS

There are many applications of luminescence for certain specific needs. A number of these exhibit a low order of luminescence at a variety of colours for use in anaysis i. e. colourimetry and fluorimetry. A more practical use for strong luminescent compounds is as tracers in agriculture and medicine. There is a growing field for the use of these in luminescent paints, lacquers, inks and fabrics. These types of paints can be used under blackout conditions and as fire safety signs. Last decade or so saw revival of the luminescent pigments as better understanding of the mechanism of light emission resulted in the better synthetic methods. Some of these factors affecting the luminescence are now known and investigations are still on as evident from the current literature. Most of the information available on the luminescent pigments in the form of patents and commercial products. These luminescent pigments found uses in the following and many other related areas : ● Colourimetery and Flourimetry, ● B/W and colour televisions & Radar tube screens, ● Dials of watches and compasses, ● Protective equipment like helmets, gloves etc, ● Sensors, ● Light emitting devices, ● Paints, lacquers and fabrics and ● Emergency lights and lamps.

CONCLUSIONS

One can conclude that luminescent pigment can occupy unique position in the new building materials family. These can readily be modified to find applications in diversified field. In the above overview, an attempt has been made to increase the understanding, importance and applications of luminescent pigments. The importance can be gauged from the fact that globally several research groups are actively working in this area and CBRI, Roorkee is also currently engaged in the R & D work of luminescent pigments under CSIR task force project on the development of new construction materials.

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DO YOU KNOW ?

Q5. During the solar eclipse, the moon exactly covers the sun, How ?

Q6. Why water from a shower feels cooler ?