PHOSPHORESCENT PIGMENTS : OPPORTUNITIES AND CHALLENGES

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Phosphorescent pigments are some of the special effect pigments. These have become of great interest as new functional pigments of high potential in diverse areas. The aim of this article is to take a closer look at phosphorescent pigments. Some new approaches in the development of novel pigments and their applications have been discussed based on the current research and existing products.

INTRODUCTION

Phosphorescent pigments are speciality pigments and often known as after-glow pigments. Phosphorescence comes under the broad term 'luminescence' meaning the emission of radiation as a result of process other than thermal emission or incandescence. Luminescence includes fluorescence, phosphorescence, triboluminescence and chemiluminescence (Table 1). 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. We are generally interested only in those pigments that emit in the visible portion of spectrum. Several criteria were used in the past for differentiating between fluorescence and phosphorescence. Fluorescence, for our purpose, refers to the emission that ceases as soon as the excitation ceases, while phosphorescence is the emission that continues even after the excitation ceases. These two phenomena are quite distinct, although closely related. A substance may be fluorescent but not phosphorescent or vice versa, whilst some substances like zinc sulfide are both phosphorescent and fluorescent. Phosphorescent materials found applications in optical and thermal uses, scintillation films, paints, inks and plastics, security applications, probe compounds and emergency source of illuminations, thermoplastic polymers and in temperature detection. Electronic price tags, flexible computer screens and disposable cell phones are among the other potential applications. Phosphorescent paints can be used under blackout conditions and as fire safety signs[1-2].

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Table 1 : Different Forms of Luminescence Pased on the Source of Excitation

Luminescence type	Excitation source	Application
Cathodoluminescence	Electron	TV sets, monitors
Photoluminescence	(UV) Photons	Fluorescent lamps, plasma displays
X-ray luminescence	X-rays	X-ray amplifiers
Electroluminescence	Electric field	LEDs, EL displays
Sonoluminescence	Ultrasound	
Solvatoluminescence	Photons	Detectors, analytical devices
Chemoluminescence	Chemical reaction energy	Analytical chemistry
Bioluminescence	Biochemical reaction energy	Analytical chemistry
Triboluminescence	Mechanical energy	

TYPES OF PHOSPHORESCENT PIGMENTS

Quite a large number of inorganic compounds have been found 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. Many organic dyes, both natural and synthetic, exhibit the property of luminescence but only in certain concentrations and are used after absorption on suitable carrier matrix. Phosphorescent pigments include the following :

(i) **Inorganic materials** : (a) Aluminates of rare earths e.g. La, Ce, Tb etc. and alkaline earths e.g. Sr, Ca etc[7-12]. (b) Sulphides of alkaline earth and transition metals e.g. Ag doped ZnS, CdS etc[10]. (c) Mixed halides, carbonates and borates e.g. barium europium flouro bromide etc[10]. (ii) Organometallic complexes like ruthenium dipyridine phenenthroline complex etc. (iii) Organic polymers like aromatic polyimides, polyalkylthiophenes, etc. (iv) Radioactive materials like radium, mesothorium, etc.

THEORY OF LIGHT EMISSION

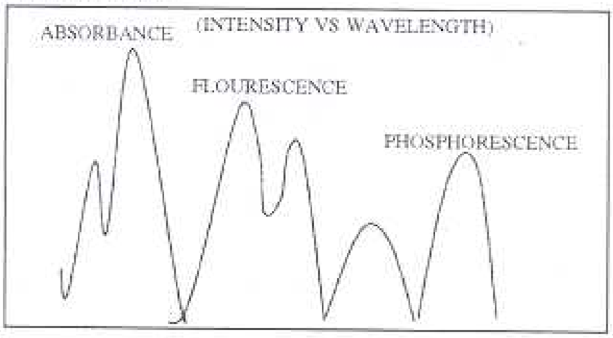
When a pigment absorbs energy, a portion of that energy may be released in the form of light. This light is radiated when molecules and atoms have their electrons excited to such a state that they begin to loose energy in the light particles called photons. It can be divided into two categories depending upon the type of source : (i) Incandescence : When heat or thermal energy causes electrons to release photons. (ii) Luminescence : When chemical, electrical or light energy excites electrons.

There are two basic laws for the excitation of phosphors. First, the material must absorb radiation and exciting radiation must fall within an absorption band of the material. Secondly, the emission must obey Stoke's law, which states that emitted radiation can't have a shorter wavelength than exciting radiation. Generally, luminescent materials emit at longer wavelengths than the exciting light. The process of absorption of energy is helped by addition of activators like silver etc. Phosphorescent material can trap the energy emitted and thus result in delay in light emission. Killer materials like iron, copper, etc. interfere in this absorption-emission process and hence for this very reason, the purity and cleanliness have been overemphasized during the synthesis.

With the help of Jablonski's diagram, it can be explained what happens within the molecules during luminescence (Figure 1). The various photo physical processes can be summarized as :

$S_0 + hv$	→	S_1^v	EXCITATION
S_1^v	→	S_1 + heat	VIBRATIONAL RELAXATION
S_1	→	$S_0 + hv$	FLUORESCENCE
S_1	→	S_0 + heat	INTERNAL CONVERSION
S_1	→	T_1^v	INTERSYSTEM CROSSING
T_1^v	→	T_1 + heat	VIBRATIONAL RELAXATION
T_1	→	$S_0 + hv$	PHOSPHORE-SCENCE
T_1	→	S_0 + heat	INTERSYSTEM CROSSING
$S_1 + A_{(S0)}$	→	$S_0 + A_{(S1)}$	SINGLET-SINGLET TRANSFER (PHOTOSENSI-TIZATION)
$T_1 + A_{(S0)}$	→	$S_0 + A_{(T1)}$	TRIPLET-TRIPLET TRANSFER (PHOTOSENSI-TIZATION)

Among the above photo physical processes, fluorescence and phosphorescence are radiative processes, while internal conversion and intersystem crossing are non-radiative processes involving loss of heat. Intensity of phosphorescence is low in comparison to fluorescence but occurs at longer wavelengths. Here, we are excluding the discussion on photochemical processes i.e. excited molecules undergoing bond cleavage, chain scission, cross linking, cyclization, cycloaddition and oxidation. Emission characteristics for typical pigments are shown below :



SYNTHESIS OF PHOSPHORESCENT PIGMENTS

Synthesis depends on the type of pigment, whether inorganic, organometallic, organic or miscellaneous. Essential requirement and also the principal problem in the synthesis of luminescent pigments, especially the phosphorescent, is the purity of compounds. Phosphorescence is produced by presence of base material 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 material must be properly muffled to develop correct crystal conformation or again it will not be phosphorescent.

The phosphorescent materials 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. Principal weaknesses of organic phosphorescent materials are their tendency to fade on exposure to light.

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

There are basically two routes to the synthesis of phosphorescent pigments. First, solution chemical synthesis techniques like hydroxide precipitation, sol gel synthesis, etc. Secondly, solid-state reaction techniques like conventional high temperature synthesis and rapid exothermic reactions. The last type includes combustion synthesis of oxides and solid-state rapid metathesis reactions of sulfides.

APPLICATIONS OF PHOSPHORESCENT PIGMENTS

Phosphorescent coatings offer a promising field for the future development of finding systems and interior decoration in case of emergency. Recent great advances comprise the development of these pigments and coatings from the point of improving both the durability of the after-glow and the retention of the luminous property for long periods of use. These phosphorescent pigments are used in the following and many other related areas : ● Paints, lacquers & fabrics, ● Emergency lights & lamps, ● Colour television screens, ● Dials of watches & compasses, ● Protective equipments like helmets, gloves etc., ● Light emitting devices & Sensors.

CONCLUSIONS

The phosphorescent pigments have unique position in the materials family. Phosphorescent pigments can easily be modified for the applications in diversified fields including the building applications and CBRI Roorkee is engaged in the R & D work of phosphorescent pigments[11&12]. In this review, an attempt was made towards increasing the understanding, importance and applications of phosphorescent pigments. Still, more efforts are needed from both the researchers and the industrialists to popularise the phosphorescent pigments.

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DO YOU KNOW ?

Q3. Air pollution in different parts of Kolkata has been measured by various agencies during normal days as well as during 'Bandhs' when city streets have no vehicular traffic. The idea is to estimate the contribution of vehicular traffic on air pollution. How much is that ?

Q4. There are two elements which are injurious to human health but when combined those become absolutely necessary ingredient of human food. What are those elements ?