"Recent trends in Glow-In-the-Dark Coloration"

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Abstract

Glow-In-The-Dark colorants used to be limited to novelty and toy applications. Older ZnS based pigments have limited glow and are not light fast. Today's new pigment technology delivers bright longer lasting luminescence with good light fastness, making possible applications that avoid expensive electronics, provide greater reliability and open exciting new avenues for the technology.

This paper tells how phosphorescence works, reviews the latest colorants available and should stimulate the designer to re-think ways to use phosphorescent materials as well as provide molders with a look at the pitfalls of processing plastics formulated with these new colorants.

Technical Details

First, which ….essence?

We can't see light go through the air, but we can detect it. It might feel warm to the skin (particularly a bald pate); we see its reflection from a surface or are blinded by on-coming headlights.

Light (visible radiation) is a form of electromagnetic radiation able to be detected by the human eye.[1] Light that is emitted from hot surfaces (above 900 ° K) is called **Incandescence**. All non-thermally produced light, hence the term "cold light" is called **Luminescence**.

When referring to glow-in-the-dark (GITD), some people mistakenly use the term fluorescence. **Fluorescence** is a form of luminance that it is rapid short duration luminescence. *Fluorescence* is the instantaneous production of light when a substance is exposed to any type of radiation.[2] As soon as the radiation is stopped, the fluorescence ceases.

Phosphorescence (a.k.a. glow-in-the-dark) is distinguished from fluorescence by the fact that the emitted radiation continues for some time after the source of excitation has been removed. This afterglow can last minutes, hours or even days after the excitation radiation is stopped.

There are many forms of luminescence. Some of the more common include:

Form	Induced by
Bioluminescence	Natural system such as glow-worms, fireflies
Cathodoluminescence	Cathode-Ray electrons
Chemiluminescence	Chemical reaction(s)
Electroluminescence	Bombardment by electrons or electric fields
Photoluminescence	Absorption of other electromagnetic radiation
Radioluminescence	Radioactive materials or particles
Thermoluminescence	Raising the temperature
Triboluminescence	Friction in or between materials

How does **phosphorescence** work?

GITD materials have to be "charged or activated"; excited in order for them to emit light. Electrons in the uncharged pigment are mostly paired electrons in ground state (called **singlet)** where the electrons are nonradiative. Excitation is generally achieved by irradiating the phosphorescent pigments with high-energy light, which leads to an excited vibrational state or excited *singlet* state.

The “charged” pigment can lose vibrational energy to its surroundings and return to some sort of ground state by nonradiative dissipation of its excess electronic energy, or by decay through a lower energy **triplet** state.

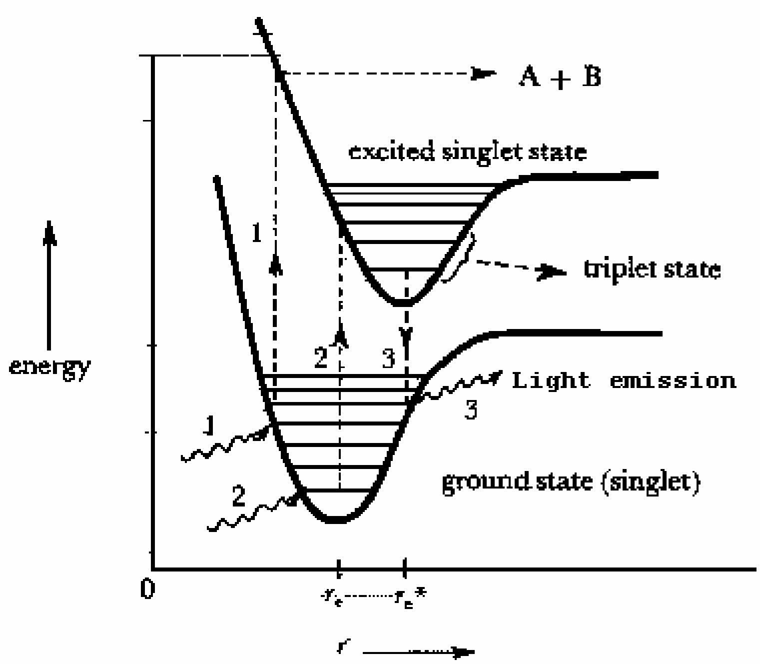
A triplet state has two *unpaired* electrons and is normally more stable than corresponding singlet state because less interelectronic repulsion is expected with unpaired than paired electrons. The name “triplet” arises from the fact that two unpaired electrons turn out to have *three* possible energy states in an applied magnetic field.[3]

The processes involving a triplet state, even though of high energy, are often long-lived, up to a second or more. The triplet state can return to the ground state by nonradiative means, but in many cases the transition results in emission of electromagnetic radiation or **photons**.

Photon. – A photon is a quantum of electromagnetic radiation which has zero rest mass and an energy of h (Plank’s constant) times the frequency of the radiation. Photons are generated in collisions between nuclei or electrons and in any other process in which an electrically charged particle changes its momentum.[4]

GITD pigments are crystalline phosphors that are produced in such a way that many defects or holes are created in their crystal lattice. These defects or holes trap electrons. The charging by high-energy light leaves many triplet state electrons trapped in these defects or holes.

As each of these triplet state electrons moves downward they emit a photon. The light we see radiating from GITD pigments thus is the result of many trapped triplet state electrons emitting a photon as it escapes and moves down to the ground state.



Phosphorescent Pigments

Phosphorescent pigments consist of an ultra-pure crystalline base, activator(s) or dopants and generally a co-activator. These carefully controlled impurities create defects in the crystal lattice where the electrons can be trapped. Other impurities, called *killers or poisons*, can quench the phosphorescence entirely. They do this by shunting the excitation energy to nonradiative decay mechanisms such as heat.

Nickel (Ni), Iron (Fe) and Carbon (C) are particularly potent in this regard. Knowing this is of particularly importance in successfully processing the newer high performance phosphorescent pigments because of their abrasiveness.

Good Old ZnS

The most widely used phosphorescent pigment base has been zinc sulfide (ZnS) doped with copper, Cu or ZnS:Cu. Manganese (Mn) or silver (Ag) has also been used to activate ZnS phosphorescence. Afterglow of ZnS:*x* phosphorescent pigments range in color from pink to yellowish green and blue. Some of this glow color is achieved by blending in small amounts of dye with the ZnS:*x,* but this can have negative effect due to quenching that generally diminishes the glow intensity.

ZnS:Cu pigment is quickly activated. Just 4 to 5 minutes of bright room light is sufficient to fully activate ZnS:Cu. Producers claim as much as 200 minute's afterglow for ZnS:Cu. That represents ideal conditions and is based on extrapolation of instrumental measurement to 0.3 mcd/m^2 of brightness.

Light of 0.3 mcd/m^2 is the lowest Luminance level an average person acclimated to total darkness can detect. Plastics formulated with ZnS:Cu pigment typically only glow brightly for about 1 hour and they decay to 0.3 mcd/m^2 in about 2 hours.

Rare Earth Pigments

What is creating all the excitement today are the new rare earth ion activated phosphors. Virtual alphabet soups of chemistries are showing up. Non-radioactive aluminates and silicates activated with Europium (Eu), Dysprosium (Dy) and Neodymium (Nd) are being produced which have as much as 10 times brighter luminance and 40 times longer afterglow than the ZnS:*x* based phosphors.

Some of these new pigments are not suitable for plastics (at least not all plastics) and a few of them have become embroiled in patent infringement claims. The worldwide patent situation on these compounds is a complex situation and beyond the scope of this paper. Care should be taken to assure you don't unwittingly get caught up in the legal minefield.

Eu and Dy doped Strontium Oxide Aluminate and Alkaline Earth Metal Silicate Aluminate Oxide phosphorescent pigments work best in plastic and are compatible with a wide range of polymers.

These pigments take longer to activate ~ 30 min. vs. 4 min. for ZnS:Cu. But, they glow for 2,000 min or more and the glow brightness is as much as 20 times greater than ZnS:Cu , depending on how you compare results.

Table of actual test data:

Color Code	Polymer	Afterglow * 1 min (mcd/m^2)	Decay time to .3 mcd/m^2 in seconds	Pigment Type
SSC-63023	Clear Nylon	1396	1121	SrOAl
SSC-62921	Clear ABS	611	928	SrOAl
SSC-79733	PC/ABS	53	310	SrOAl
SSC-41663	Clarified PP	733	1160	SrOAl
SSC-62924	Clarified PP	971	1411	SrOAl
SSC-63124	PC	1061	1281	SrOAl
SSC-62754	Santoprene	586	825	SrOAl
SSC-62899	pp	75	60	ZnS
SSC-75148	Santoprene	34	35	ZnS

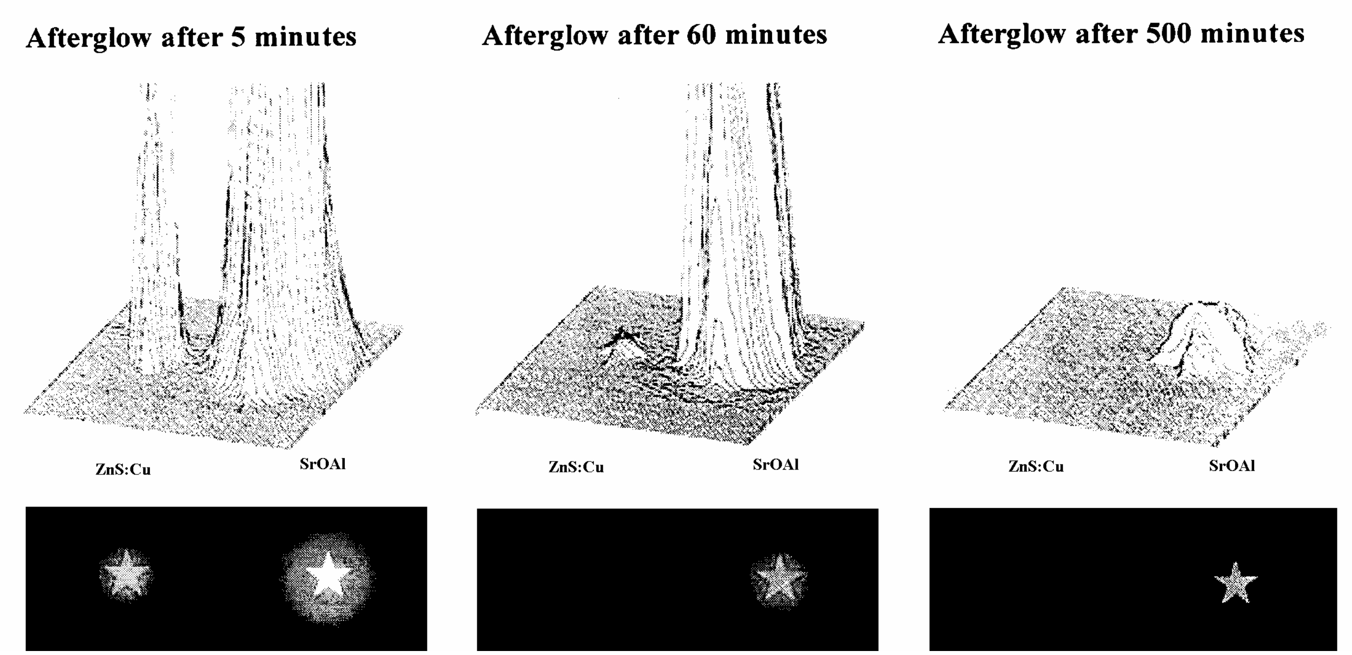
Note: The clearer resins have better brightness and within a pigment type give longer afterglow.

Formulating

Coloration with GIDT pigments is limited by several factors;

1. Killer impurities are easily introduced when adding any dye or processing aid to a GITD system. Extremely small amounts of another colorant or additive can be very deleterious to the glow intensity.
2. Even with the new high performance GITD pigments, you are still dealing with rather low light levels. Use of dyes to change the daytime color of the material or to shade the afterglow color can filter away substantial amounts of the glow brightness. Since most of the strong glow phosphors are green to yellow, use of blue and red are particularly limiting to the brightness.
3. Polymer opacity plays a key role in glow brightness. Just as your headlights can't penetrate a heavy fog, the glow of phosphorescence can't penetrate a cloudy polymer.

The new high performance GITD pigments are as much as 10 times the cost of the ZnS:*x* based phosphors. Fortunately the new types are more potent so you can get by with lower loadings than needed for ZnS:*x* based phosphors and achieve equivalent brightness. The gain is ~ 10X glow brightness and 40X afterglow persistence.



Compounding and Testing

These newer high performance pigments have high hardness and are abrasive which makes plastic compounding a challenge. Once compounded into plastic and thoroughly wetted out with polymer, this abrasiveness is diminished by polymer encapsulation. However, the pigment can still scour contaminants out of processing equipment and cause quenching of glow properties.

Formulating with special additives that lubricate barrel & screw can aid in reducing this problem. It is easy to unwittingly introduce quenching contaminants, so Compounders must frequently test afterglow properties to assure quality products are being generated. Performance of these tests requires a highly sensitive microprocessor-based photometer that utilizes a photomultiplier tube detector for maximum sensitivity at low light levels.

Processing GITD material

GITD plastics can be extruded into sheet and profiles, or molded into parts like any other colored product. Desiccant drying of pellets prior to processing is more important than with normal colored plastics. These new pigments are somewhat hygroscopic and processed when wet diminishes glow performance. Molding good clean GITD parts can be more crucial to maintaining glow properties than keeping the plastic pellets free of contamination during compounding. Any residual material in the molding machine can introduce killer impurities and turn perfectly good material into scrap parts. Because of the abrasive nature of the Strontium Aluminate pigment, it is essential that the non-return valves be in good condition. The combination of a worn contact surface on a slip ring with the abrasiveness of the pigment can turn pale yellow plastic into dark gray parts. A build-up of carbonized residue in the barrel will do the same dirty deed. Purging the machine with glass filled material before molding GITD compounds sometimes does a good job of cleaning out lingering contaminants.

Molding conditions should be low shear and short residence time. High stock temperatures generally work better than low temps, and of course; the tool surfaces should be hardened.

Designing with GITD

This is the fun part. The brightness and persistence of these new high performance pigments opens up a whole new variety of applications. Before launching into a laundry list of the many applications you must first understand this; you can literally read by the light generated from a plaque molded out of this new material and it glows all night long!

Applications include:

Safety Road worker vests, traffic signs, rail crossing markers
Dials, buttons & switches in Autos & Aircraft

Rescue
Fire & Ambulance handles & latches,

Emergency
Emergency signage, Low-level lighting of escape routes
Life rafts & vests, Trunk releases, Fire Extinguisher Pins & Hangers.

Sports
Diving markers, camping gear, Hunting vests, Boating markers & Bicycle parts.

Convenience
Cell phone buttons, Light switch covers, Doorbell buttons, Appliance Dials/Buttons
Electrical breaker switches, Commode seats, House Numbers, TV Remote buttons

Military
Dials, Buttons and Switches in ships, tanks, trucks & planes. Gun sites.

Cost factors are an important consideration. These newer phosphors are expensive and loadings must be higher than normal colorants, so coloring costs for GITD plastics are high. However, the bottom-line cost of many applications ends up lower and the resulting products are more reliable.

Take emergency EXIT lighting for example. The typical electric unit requires expensive electrical apparatus, wiring to a power source, and a constant supply of electricity. When the power goes off it must have battery backup and most important, installation costs are outrageously high. The GITD equivalent can be made from extruded sheet, stamped out and quickly laser marked. Often as thin as a piece of poster board, they are easy to mount (double-stick tape works for most exits) and they require no backup power. When the power goes off they are ready to go as is, “on” all the time running off of ambient light!

Acknowledgements

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[1] John Daintith, “The Facts On File Dictionary of Physics”, Intercontinental Book Productions Ltd. 1981.

[2] Kurt Nassau, “The Physics and Chemistry of Color”, John Wiley & Sons, Inc. 1983.

[3] John D. Roberts and Marjorie C. Caserio, “Basic Principles of Organic Chemistry”, W.A, Benjamin, Inc., 1965

[4] “Handbook of Chemistry and Physics”, The Chemical Rubber Publishing Company.