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Glow and Behold – by Ian Ashdown, P. Eng., LC

When you hear the word "photoluminescence," you might think of toys and novelties such as "glow-in-the-dark" Frisbees and yo-yos. However, there is a more serious side to this complex physical phenomenon.

While you rarely hear about them in the lighting industry, photoluminescent products such as marker tapes and signage are commonly used to delineate emergency escape routes and danger areas, and to mark equipment, pipes, tools, and working and accident prevention clothing.

Photoluminescent products are used in high-rise office buildings, industrial sites, marine environments such as passenger ships and offshore drilling platforms, underground mines, and commercial aircraft.

Their application and use is being recommended, and in some cases mandated, by architectural building codes and international marine and aviation standards.

Perhaps more important is that newly-developed photoluminescent pigments are up to fifteen times more luminous than those used in conventional materials. Even better, newer products remain visible for hours to days instead of minutes.

Their improved luminance characteristics open the door to new opportunities in architectural and entertainment applications. In other words, it is time for lighting designers and architects to give photoluminescent materials serious consideration.

What Is It?

The bases of most photoluminescent products are inorganic pigments that can be incorporated into paint, plastic films, vitreous enamels, and flexible and rigid molded plastics.

Typical products include adhesive vinyl tapes, rigid PVC marker strips, and silk-screened plastic signage. Photoluminescent enamel-coated sheet metal and ceramic products are also available.

A quick search of the World Wide Web using the keyword "photoluminescent" will reveal dozens of manufacturers and distributors for these products. However, it is not enough to simply know that these products exist.

As professional architects and engineers who are ultimately responsible for life safety, we must understand them in detail, and be aware of their performance characteristics and limitations.





Photoluminescence Explained

Many inorganic and organic materials exhibit luminescence, which means that they emit visible or invisible light during and after exposure to a source of excitation energy. For photoluminescent materials, the excitation source is electromagnetic radiation - visible and invisible (typically ultraviolet) light.

The basic principle of photoluminescence is simple: electrons orbiting atoms or molecules absorb energy through collision with photons during excitation. They then emit this excess energy as photons of (usually visible) light at a later time.

Photoluminescence was studied by the British physicist Sir George Stokes in 1852, who noted that the characteristic color of the emitted light is at longer wavelengths than the excitation radiation (Stokes' Law), and that it depends on the chemical composition of the material rather than the spectral distribution of the excitation source.

A few years later in 1859, the French researcher A. Becquerel described the first of many phosphors (photoluminescent materials) that absorb ultraviolet light and emit visible light.

There are two types of photoluminescence;

- Fluorescence and;
- Phosphorescence.

The difference between them is time.

Fluorescent materials emit light within nanoseconds of being excited as the electrons go directly from an excited state to a lower energy level. As such, they require a continuous source of excitation. Fluorescent lamps are a common example, where the ultraviolet light generated by the mercury vapor arc excites the phosphor coating.

The excited electrons in **Phosphorescent materials**, on the other hand, can remain in a "metastable" energy state for minutes to weeks before emitting light. Like fluorescent materials, these materials emit light continuously when they are excited by ultraviolet or visible light.

When the excitation source is extinguished, phosphorescent materials continue to emit light. It is this light (called afterglow) that we perceive as "glow-in-the-dark."

The afterglow decreases (or decays) over time after the excitation source has been extinguished. Some phosphor manufacturers state that the decrease is exponential, but this is usually incorrect.

Most long-persistence phosphors (including those commonly used in commercial products) exhibit what is called hyperbolic decay (see Figure 1). The equation describing this decay is (with apologies for the mathematics); Where t is time in seconds, L_t is the initial luminance (measured in candelas per square meter), L_0 is the luminance at time t , and a and b are constants that depend on the chemical composition and physical properties of the material.





Zinc Sulphide.

Some of the first phosphors to be developed were inorganic zinc sulphide compounds. (German submarine commanders during World War I reportedly rubbed these compounds on their hands to read documents during blackout conditions.)

These phosphors typically absorb energy from deep blue and ultraviolet light and emit it as yellow-green light (see Figures 2 and 3). This is useful in that the peak spectral distribution of the emitted light roughly coincides with the peak spectral sensitivity of the human visual system under scotopic (low-level) lighting conditions (which is around 510 nanometers).

Zinc sulphide occurs in crystalline form, but it is not photoluminescent by itself. This requires the addition of activator ions to the crystals, such as copper atoms. These ions absorb the excitation energy of the ultraviolet or visible light and later release it as visible light.

The copper-activated zinc sulphide crystals (identified with the chemical symbol ZnS:Cu) are typically ground into a fine powder with a grain size of 3 to 15 micrometers to avoid light trapping and light piping effects.

This must be done carefully however, because the crystals can darken (or gray) if subjected to heavy pressure or excessive mechanical stress, due to disruption of the crystalline structure.

This photoluminescent powder can be added to many plastics for molding and extrusion, and to acrylic, epoxy, and polyurethane paints. It can also be incorporated in ceramic, glass, and vitreous enamel materials and finishes, which provides excellent protection against graying, abrasion, and environmental damage.

Most manufacturers of zinc sulphide photoluminescent products provide flexible vinyl and rigid polyvinyl chloride (PVC) films and sheets that readily accept silk-screen inks. The plastic materials are typically flame-retardant and designed to withstand salt spray mist, water, and cleaning agents.

Flexible plastic film products are often provided with a white backing material, which reflects the light emitted from the back of the photoluminescent film to the observer. In addition, micro prismatic retro reflective materials can be combined with photoluminescent films to achieve higher on-axis luminance levels (at the expense of reduced viewing angles).

Strontium Aluminate

It is very difficult to perform a theoretical analysis of luminescent materials, and there is no reliable theory that predicts the performance of potential photoluminescent compounds.

Photoluminescent materials research is therefore still both a science and an art, and new compounds are constantly being discovered. Recent research efforts have produced several new inorganic compounds whose photometric characteristics greatly exceed those of zinc sulphide compounds. These materials include oxides of strontium aluminate (identified as SrAl) and other proprietary inorganic compounds.





These compounds offer much brighter and longer-lasting photoluminescence, and they can be formulated (unlike zinc sulphide compounds) to produce a range of colors. While there are many different strontium aluminate compounds, the following is an example of comparative performance characteristics:

Properties	SrAl	ZnS:Cu
Chemical Composition	Compound Oxide	ZnS: Cu
Excitation Color	Pale yellow-green	Pale yellow-green
Emission Color	Yellowish-Green	Yellowish-green
Excitation Spectrum	200-450 nm	200-450 nm
Peak Excitation	360 nm	360 nm
Peak Wmission	520 nm	520 nm
Luminance @ 10 min	150-300 mcd/m ²	10-20 mcd m ²
Afterglow extinction	45 days	200 minutes
Excitation time	30 minutes	4 minutes

Strontium aluminate products are currently available in flexible vinyl and rigid PVC sheets, and can be substituted wherever commercial zinc sulphide products are used for life safety applications.

For the example shown above, it is some fifteen times brighter than commercial zinc sulphide products, and is clearly visible after many hours of total darkness.

Strontium aluminate and other proprietary compounds represent a revolution in the photoluminescent industry, which has relied on zinc sulphide pigments for the better part of a century.

There will undoubtedly be new and better photoluminescent pigments and products introduced in the near future, including those with different emission colors.

How Bright?

You might ask, "How bright are these photoluminescent products?"

Many manufacturers refer to the extinction time of their products, which is defined as the time required for the afterglow to diminish to one masb (0.032 mcd/m², or about 100 times' limit of human perception).

In practice, this is very difficult to see unless your eyes are fully dark-adapted and you are in a completely dark environment.

For practical purposes, luminances of one to two mill candelas per square meter are more appropriate limits for life safety applications, and even this assumes a smoke-free environment.

Thus, zinc sulphide products are useful for perhaps 30 to 45 minutes after their excitation source has been extinguished. The afterglow of strontium aluminate products, on the other hand, can be visible for several days or more.

At the other end of the time scale, strontium aluminate products can provide surprising amounts of initial afterglow. For example, a four-inch square of material held a few inches away from a magazine page can provide enough light to read by, at least for the first minute or so.





In addition, micro prismatic retro reflectors and other brightness enhancing techniques can increase the material's luminance by several times.

Standards and Codes

The use of photoluminescent materials for life safety applications is recommended or mandated in numerous building codes and transportation standards.

In Europe for example, the characterization and application of photoluminescent materials and products is addressed by the comprehensive DIN 67 510, Phosphorescent Pigments and Products.

Most European countries also mandate the use of photoluminescent materials and products through their building and fire safety codes.

In the United States, the use of photoluminescent materials and products for architectural applications is mandated by the State of California Building Code, and also in building codes for Washington, Illinois, Florida, New York, Wisconsin, Oregon, and other states.

In Canada, Ontario, Alberta, and Manitoba has similar requirements.

Photoluminescent products are also widely used in the maritime industries.

The 1974 Safety of Life At Sea (SOLAS) Convention governs international shipping, and it has adopted International Maritime Organization (IMO) Resolution A752 (18), Guidelines for the Evaluation, Testing and Application of Low-Location Lighting on Passenger Ships, for "low-location lighting" (that is, photoluminescent marker strips) on all ships carrying more than 36 passengers.

Another standard is the International Organization for Standardization ISO/CD 15370, "Ships and Marine Technology - Low-location Lighting on Passenger Ships - Arrangement." This document is intended as a supplement to IMO Resolution A752 (18).

The American Bureau of Shipping (ABS) reportedly intends to use ISO/CD 15370 as an approved test guideline for their ABS Product Type Approval.

In the aviation industry, the US Department of Transportation Federal Aviation Administration Advisory Circular 25-812.2 "provides guidance material for use in demonstrating compliance with the provisions of Part 25 of the Federal Aviation Regulations (FAR) regarding floor proximity emergency escape path marking systems (FPEEPMS) which incorporate photoluminescent elements."

This document is not mandatory, but rather provides guidance for aircraft manufacturers in demonstrating compliance with the safety standards set forth in the rule. Interestingly, zinc sulphide materials are specifically excluded from use. Only strontium aluminate materials are acceptable, although newer materials providing equal or superior performance "may be considered."





Gotcha!

There are many situations where it is important to know about the quirks and limitations of photoluminescent materials. This is especially true when products are being specified for life safety applications and compliance with building codes and standards. Unfortunately, these same documents contribute to the problem.

Many standards specify a minimum afterglow luminance that must be achieved after a certain time. ISO/CD 15370, for example, specifies that photoluminescent materials must exhibit at least 15 mcd/m² at ten minutes after removal of excitation, and at least 2 mcd/m² after 60 minutes.

This is fine, except that the specified ambient temperature for laboratory measurements is 73 degrees Fahrenheit. The initial afterglow luminance of most long-persistence phosphors is highly temperature-dependent.

If a zinc sulphide material is installed outdoors on an offshore oil rig, it is possible that it will not be visible at all in cold weather. On the other hand, it may be brighter than expected in a hot environment such as a boiler room.

A second problem is that photoluminescent pigments require sufficient levels of incident light in order to fully saturate. With lower light levels, the material will emit energy as quickly as it is being absorbed and not reach full brightness when the excitation source is extinguished.

The pigments also have a minimum excitation time that they need to reach full saturation.

Unfortunately, DIN 67 510 specifies an excitation time of five minutes for laboratory tests. This is sufficient for zinc sulphide, but strontium aluminate products may require more time to become saturated. It is therefore important to be somewhat flexible when interpreting DIN 67 510 test requirements for newer photoluminescent pigments.

Setting aside codes and standards, the photometric characteristics of photoluminescent materials are dependent on both the chemical composition of the phosphors and the pigment density.

Lowering the pigment density lowers the manufacturing cost of the product, but it also lowers the initial luminance. If you require specific photometric performance levels to satisfy code requirements, it is advisable to insist on certified photometric test reports from the manufacturers that guarantee compliance.

Another issue of concern is that strontium aluminate compounds are more expensive than zinc sulphide, and some manufacturers may use a mixture of both pigments in their products. Again, certified photometric test reports provide assurance that you are getting what you need or expect.

What Light Source?

As can be seen from Figure 2, the ability of a phosphor to absorb energy is dependent on the spectral distribution of the excitation source. ISO/CD 15370 specifies this source to be a "tubular fluorescent lamp" having a color temperature of 2700 degrees Kelvin (2700K).





This looks reasonable, except that the variation of ultraviolet output as a percentage of visible light can vary by a factor of four or more between commercial lamps that satisfy this specification. (This variation is dependent on lamp phosphors and glass composition, and can occur even between lamps with the same ANSI product code.)

A photoluminescent product manufacturer may choose a fluorescent lamp with the highest possible ultraviolet output for ISO/CD 15370 compliance testing in the laboratory. However, the performance of the product under field conditions may not meet ISO/CD 15370 requirements. (DIN 67 510 more usefully specifies a 150 watt xenon lamp with a D65 spectral energy distribution.)

On-site excitation light levels are yet another issue of concern when specifying photoluminescent products. DIN 67 510, for example, specifies an luminance of 1000 lux for laboratory tests. This is far greater than the light levels typically found in building mechanical rooms and ship boiler rooms. It is advisable to perform on-site tests with the manufacturer's product wherever possible if code compliance is an issue. (As a rule of thumb, a minimum of 25 lux from fluorescent lamps is required for sufficient excitation.)

You should also remember that the excitation time and saturation are primarily dependent on ultraviolet irradiance of the material. The best light sources for excitation are those rich in ultraviolet light. These include sunlight, compact and linear fluorescent lamps, "black light" fluorescent lamps, high-intensity discharge (HID) lamps, and (to a lesser extent) quartz-halogen lamps.

Incandescent (tungsten filament) and low-pressure sodium lamps emit insignificant amounts of ultraviolet light, and should be avoided.

When using fluorescent or HID lamps, pay close attention to plastics used in wrap-around diffusers and lenses. They may contain inhibitors that intentionally absorb ultraviolet light. This is good for preventing fabric fading and so forth, but not for photoluminescent excitation.

Finally, you should be aware that zinc sulphide is subject to humidity damage that causes graying of the photoluminescent products.

The elemental zinc separates from the crystals and migrates to the surface of the material, reducing luminance. Ultraviolet inhibitors may be applied to protect the material from direct sunlight while still allowing full saturation. Even so, typical material lifetimes for plastics containing zinc sulphide are eight to ten years for indoor applications, and twelve months for outdoor applications.

Ideas Wanted

So there you have it - an in-depth discussion of photoluminescent products, their performance characteristics, applicable codes and standards, and pitfalls to avoid where possible.

What is missing are new application ideas. Newer products are offering previously unattainable photometric characteristics. Aside from traditional life safety applications, strontium aluminate products immediately bring to mind numerous applications in architecture and entertainment.





Even better, they are competitively priced with zinc sulphide products. Where you use these products is limited only by your imagination.

Definitions:

- **Luminescence:**

The emission of light by a material after it has been exposed to some method of excitation. Includes photoluminescence (electromagnetic radiation), cathodoluminescence (electrons), electroluminescence (stationary or varying electric fields), chemiluminescence (chemical reactions), bioluminescence (biological processes), sonoluminescence (acoustic energy), thermoluminescence (temperature changes), radioluminescence (subatomic particles), and triboluminescence (mechanical energy).

IESNA RP-16-1996: "Any emission of light not ascribable directly to incandescence."

- **Fluorescence:**

Emission which occurs immediately after excitation ceases, and which decays in picoseconds. Due to excited molecule or atom going directly from excited state to lower energy level.

IESNA RP-16-1996: "The emission of light as the result of, and only during, the absorption of radiation of shorter wavelengths (time scale less than approximately 10⁻⁸ seconds)."

- **Phosphorescence:**

Emission that decays slowly (minutes to weeks). Due to excited molecule or atom remaining in a metastable energy state when perturbed by atomic collisions or other causes.

IESNA RP-16-1996: "The emission of light as the result of the absorption of radiation, and continuing for a noticeable length of time after excitation."

- **Afterglow:**

Phosphorescent or fluorescent light **Time constant:** Time required for afterglow luminance ("photometric brightness") to become 1/e (approximately 37 percent) of the initial luminance value.

- **Excitation time:**

Time required for saturation with standard D65 illuminant at 200 lux.

- **Extinction time:**

Time required for afterglow to diminish to one masb (0.32 mcd/m², or about 100 times limit of human perception). (Referred to as the light decay "period" in DIN 67 510 standard.)

- **Saturation:** Ultraviolet irradiance required to excite photoluminescent material to its maximum capacity.



- **Phosphors:**

Luminescent materials, consisting of two general groups. The first group (mostly organic materials) has molecules which absorb excitation energy; the molecules enter an excited energy state, and emit radiation as they return to a lower state. The second group (mostly inorganic compounds) derives their luminescence from perturbations in their crystal lattice structure or the presence of foreign atoms (called activators).

The activators become ionized, and release their energy when the free electrons combine with the ionized atoms.

Typical inorganic materials are sulphides and oxides or silicates and phosphates of metals such as zinc, calcium, magnesium, cadmium, tungsten, and zirconium. Small amounts (0.01 to 1.0 percent) of metal impurities are added as activators.

- **Quantum efficiency:**

Number of visible photons emitted divided by number of UV photons absorbed depends on chemical composition of phosphor, method of construction or deposition, and kind of excitation.

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About the Author

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Figure 1 - Typical hyperbolic afterglow decay

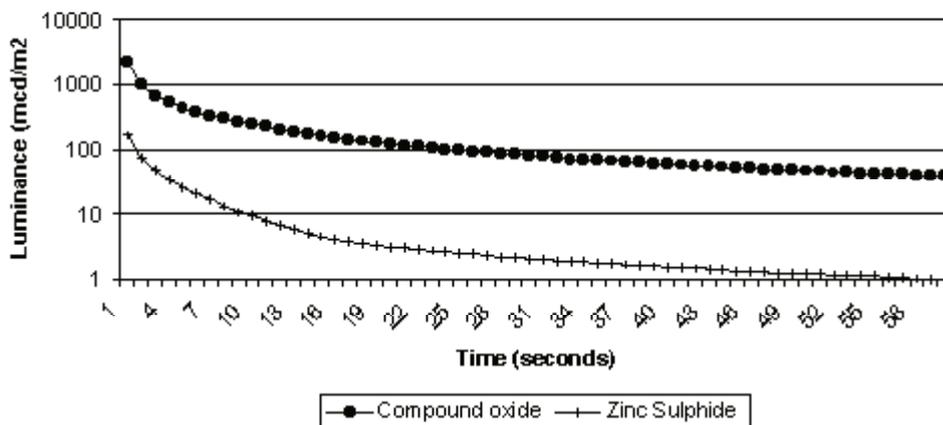


Figure 2 - Typical excitation spectral distribution (relative)

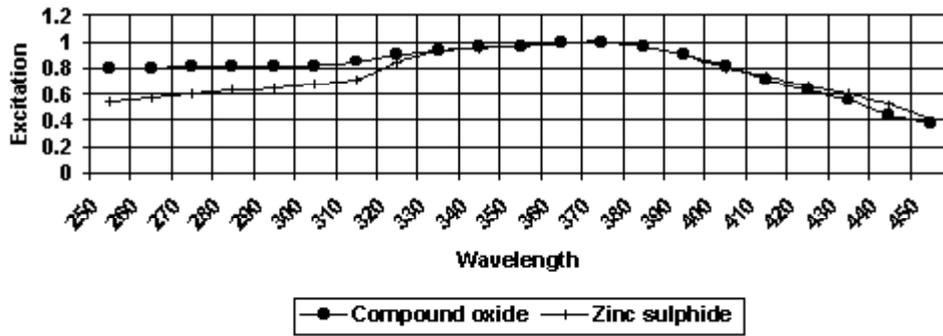


Figure 3 - Typical emission spectral distribution (relative)

