

UPDATE

Optically Active Coatings – additives vs light sources.

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The challenges faced by owners, managers and operators as well as paint manufacturers and applicators is how to properly protect key structures and survey them for three key criteria, coating integrity, corrosion and early failure. Many structures contain relatively large spaces that are difficult to inspect and exhibit defects, which are very hard to detect. This need has led to the development of coatings containing Optically Active Additives, OAAs (or Optically Active Pigments). A coating that can be more easily inspected will improve coating integrity and aid safety. Improved coating integrity will result in improved through-life performance resulting in reduced maintenance and repair.

The purpose of an Optically Active Additive (OAA) is to make a coating react to ultra violet light. This effect enables quick, non-invasive inspection of very large coated areas during the application process allowing the inspector to identify and concentrate on defective areas, thus reducing inspection time, while assuring the probability of good application and coverage. It works by highlighting holidays and pin-holes, areas of over and under application, as well as giving the opportunity for defect detection and identification of early coating deterioration through life. It can be said that improved first time coating quality will improve coating performance.

The use of OAAs has for a number of years been restricted commercially to use in coatings for sea water ballast tanks. However, they are being increasingly used in coatings for the protection of offshore structures, waste-water treatment plants, oil storage tanks, bridges and the like. There is now an SSPC Technology Up-date [1] for the technique. However, there is a body of evidence that shows there can be limitations in their use under certain circumstances. These can include false positives, cost, migration, and system limitations.

This article discusses the results of a research project carried out by Luminous Technologies Ltd and a number of paint manufacturers worldwide on the use of the two types of OAA, organic and inorganic, and identifies the differences in chemistry between them and the potential shortfalls in the use of each type under practical working conditions.

A Brief History of Artificial Luminescence

Inorganic

Luminous materials have been known since the times of the Greeks and Romans and in 1602, Vincentus Casciorolo, a Venetian alchemist, discovered that barium sulphide became luminous when heated.

In 1609, Brand (or Brandt) discovered a substance, which glowed in air. Hoping to make gold, he took urine, reduced it to a paste, heated this, and condensed the vapour. Un-surprisingly, he did not produce any gold but instead a white, waxy substance that glowed in the dark, which he called phosphorus, from the Greek word meaning light bearer. This gave rise to the term phosphorescence. Scientific investigation of inorganic phosphors only began in the 19th Century and by 1887, the contribution of heavy-metal impurities to the luminescence of inorganic materials was identified [2]. Also by the end of 19th century, a blue phosphor (calcium sulphide), and a red phosphor (calcium sulphide doped with barium) had been synthesised. Later, an attempt to produce combination effects by mixing doped phosphors with conventional pigments such as ultramarine blue and chromium dioxide, was limited by severe quenching of the phosphorescent emissions. This quenching of luminescence by non-luminescent colourants can present a serious barrier to producing economic phosphors with a daylight colour.

Organic

In 1929, Kraus demonstrated that fabric appeared much whiter after immersion in a solution of aesculin. The solution of aesculin was colourless but was highly fluorescent. This proved the theory that whitening of fabric could be brought about by fluorescent blue light compensating for the blue light absorbed by the yellow contaminants in fabric. The optically active part of the molecule is a dihydroxy coumarin. This will not bond with fibres and was physically deposited onto the fibres during immersion and any mechanical action such as washing removed the coumarin from the fabric eliminating the whitening effect.

In 1937 ICI obtained a patent [3] which mentions that textiles treated with stilbenes fluoresce under ultraviolet radiation. At the same time German chemists investigating the use of stilbenes observed that some of these compounds had compatibility with cellulose materials and produced a whitening effect. Subsequently I. G. Farben started to produce these

products commercially. Dyestuff manufacturers continued to develop these products in the late 1940's and the term Optical Brighteners came about.

Optical brighteners are classed as dyes which absorb light in the ultraviolet spectrum and re-emit visible light in the blue region (typically 420-470 nm). Therefore, a white surface treated with an optical brightener emits more visible light than shines on it and will appear brighter. Fluorescent activity is very rapid ($1/10,000$ th of a second), unlike phosphorescence, where there can be a delayed emission (seconds).

Luminescence

The Physics

When a single photon of light is absorbed by an atom, in a manner very similar to a radio wave being picked up by an aerial, the photon ceases to exist and the total energy contained within the atom increases. This increase in energy is usually described symbolically by suggesting that one of the outermost electrons "jumps" to a "higher orbit".

This new configuration the atom finds itself in is unstable and the tendency is for the electron to fall back to its lower orbit or energy level, emitting a new photon as it goes (Figure 1). The entire process may take no more than 1×10^{-9} seconds. The result is that the substance emits a glow.

The wavelength of a photon emitted from a luminescent system is directly related to the difference between the energy of the two levels involved. In terms of wavelength this relationship is an inverse one so that if an emitted photon is of short wavelength (high energy) the gap jumped by the electron must be a large one. Chemical Engineers are able to devise molecules with these energy levels in mind, so as to adjust the wavelength of the emitted photons to produce a specific colour.

Inorganic vs Organic OAA's

There are two common types of Optically Active Additives available commercially, inorganic and organic.

Inorganic OAA's have relatively large particle size: 5-10µm (no mobility), are light stable, available in a choice of colours, are useful in a wide range of coating systems, but are expensive.

Organic OAA's have low addition level, are soluble in solvents and organic liquids (mobile), are blue under UV (same colour as lint, oil, grease etc), can fade quickly, have limited use in a range of coating systems and are less expensive. The light emitted by organic OAA's is also indistinguishable from that from old coal-tar

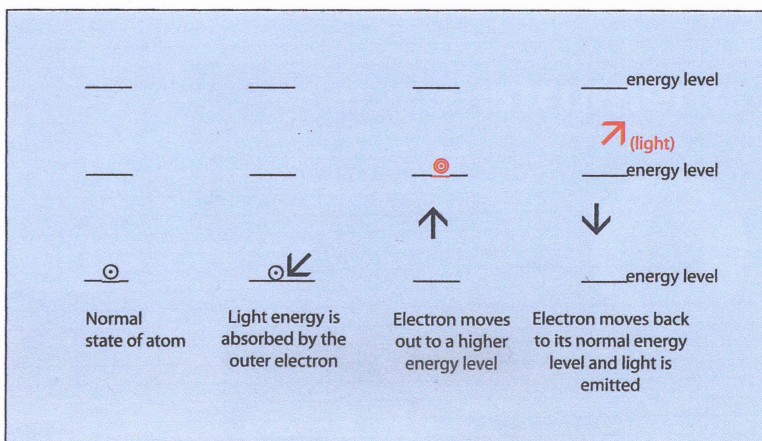


Figure 1

epoxy type coatings still seen on some structures and vessels.

In general, inorganic OAA's phosphorescence and organic OAA's fluorescence, and essentially all organic OAA's are optical brighteners.

Mobility of Organic and Inorganic OAA's

Due to the solubility of organic OAA's they can migrate to successive coats thus confusing the inspection. This can be seen in the following set of photographs of epoxy coatings. (Figure 2)

The top view shows an epoxy coating with inorganic OAA (A), an unmodified epoxy (B), an epoxy with an organic OAA (C) and a second coat of unmodified epoxy (D) all under ambient light. The lower view shows the same systems under UV light, which clearly shows the migration of the organic OAA into the epoxy

second coat (H(1)), but no movement of the inorganic OAA.

In the laboratory organic OAA's were shown to bleed into a drop of xylene placed on top of a cured epoxy coating. The migration has even been noted in subsequent topcoats containing white spirit. This effect means that the organic OAA can migrate into any successive coating which contains solvent. Xylene has no migratory effect on films containing inorganic OAA.

Reaction to UV

Organic OAA's have a more pronounced reaction to UV (under both 365 and 405 nm light) than inorganic OAA's, i.e. are clearer to see (figure 3). However, the wavelength of irradiated light also affects the usefulness of OAA's. Typically, 365 nm or 405 nm is used.

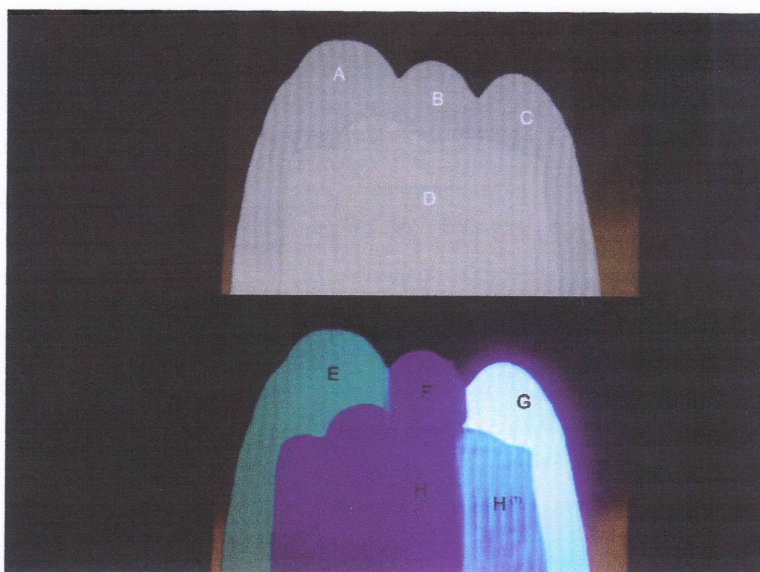


Figure 2

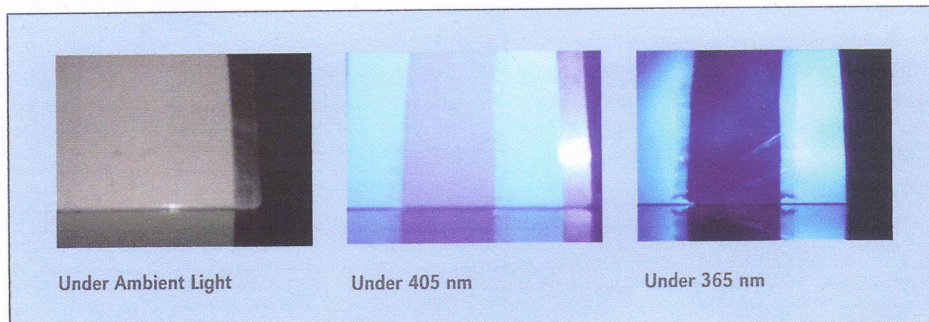


Figure 3

405 is less efficient than 365, since 405 nm lamps operate within the visible spectrum a proportion of visible light illuminates the coating under examination. This results in a lowering of contrast making it difficult, at times, to identify small defects on the coating. As no visible spectrum is emitted from lamps at 365 nm this lowering of contrast does not occur. This can result in defects being difficult to detect with organic OAAs at 405 nm. Inorganic OAAs do not react sufficiently at 405 nm, and currently only work at 365 nm irradiation.

Safety

All wavelengths within the spectrum of 100 nm to 3000 nm have the potential to cause damage to the human organism, including thermal skin burns, retinal or cornea burns and cataracts. The topic itself is too complex to discuss in any detail. This is the reason that, all light sources should be considered potentially dangerous and appropriate PPE should be worn regardless of what wavelength is used. However it is worth noting that the band from 365 nm to 405 nm appears to be the least injurious.

Conclusions

Inorganic OAA's, are useful in a wide range of coating systems, although they are expensive, whereas organic OAA's are most useful in single coat applications although care should be taken when over-coating due to possible migratory effects. Organic OAAs are also indistinguishable from old coat-tar epoxy type coatings still seen on some structures and vessels.

The reduced contrast when using 405 nm sources makes the identification of small defects difficult. Similarly, the presence of lint, grease, oil etc can give rise to false positives.

The use of 405 nm lamp sources with organic OAAs, while suggesting efficiencies in inspection techniques on paper, can give rise to serious complications during real time on-site inspections due to false positives and lower contrast. 365 nm lamp sources with inorganic OAAs do not present the same challenges.

References

- (1) Technology Up-date 11 – Inspection of Fluorescent Coating Systems (SSPC, Pittsburgh 2006)
- (2) Newton Harvet. A History of Luminescence (until 1900), Academic press New York 1996.
- (3) T. Forster: Fluoreszenz organischer Verbindungen, Vandenhoeck und Ruprecht, Göttingen, 1951.

