

A Review of Optically Active Coatings

Over a number of years the use of Optically Active Additives, either organic or inorganic, has increased greatly. Their use is specified by a number of fleets, both naval and commercial, around the World and their use is now expanding into concrete substrates as found in wastewater treatment plants, bridges, roadways and infrastructure. There is now an SSPC Technology Up-date (Ref 1) for the technique. 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 paper proposes to identify the differences in chemistry between the two types of OAA and the potential shortfalls in the use of each type under practical working conditions. It will also highlight the proven benefits of these additives in service.

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 or Optically Active Pigments. A coating that can 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) or Optically Active Pigment (OAP) 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 OAA and OAP has for a number of years been restricted commercially to use in coatings for Sea Water Ballast Tanks (SWBT). 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.

A Brief History of Artificial Luminescence

Inorganic:

Luminous materials were known in the times of the Greeks and Romans. Aristotle mentions the sea, meat and fungi as having luminous properties. 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 and called it phosphorous. Hoping to make gold, he took urine, reduced it to a paste, heated this, and condensed the vapour. Amazingly, he did not produce any gold but instead a white, waxy substance that glowed in the dark. He had discovered phosphorus. The word phosphorus comes from the Greek and means light bearer. This gives rise to the term phosphorescence. Scientific investigation of inorganic phosphors only began in the 19th Century. Work was carried out by Becquerel, Lenard, Stokes and Verneuil amongst others. Verneuil, in 1887, identified the contribution which heavy-metal impurities had in the luminescence of inorganic materials (Ref 2).

During the industrial revolution in Germany, galvanised pipes carrying rain water were seen to glow faintly in complete darkness. Chemists eventually discovered that the zinc of the gutters was combining with sulphur deposited from the polluted atmosphere to form zinc sulphide. From that time zinc sulphide phosphors were produced artificially, although they tended to be inefficient due to their low purity.

Towards the end of the twentieth century Albert Krause synthesised a blue phosphor, actually calcium sulphide, in his laboratory from sea shells, but it was forty years before Henry Muller produced a red phosphor by doping calcium sulphide with barium. Later, Henry Muller attempted to produce combination effects by mixing his doped phosphors with conventional pigments such as ultramarine blue and chromium dioxide, but his progress 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.

In 1939 Robert Ruthruff was doping phosphors to produce virtually any shade to order, and his work lead directly to the production of X-ray tubes, and later colour T.V. tubes which today are usually yttrium oxysulphide doped with europium and terbium (red), zinc sulphide doped with silver (blue), and zinc cadmium sulphide doped with copper (green).

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. Aesculin is found in the bark of the horse chestnut tree. 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. Any mechanical action such as washing removed the coumarin from the fabric eliminating the whitening effect.

In 1937 ICI obtained a patent (Ref 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. 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 420-470nm). 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 ($1/10,000^{\text{th}}$ of a second), unlike phosphorescence, where there can be a delayed emission (seconds).

Luminous Technology – The Physics

If a single photon approaches an atom, which is receptive to it, the photon can be absorbed by the atom in a manner very similar to a radio wave being picked up by an aerial. At the moment of absorption 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 have taken no more than 1×10^{-9} seconds. The result is that the substance emits a glow.

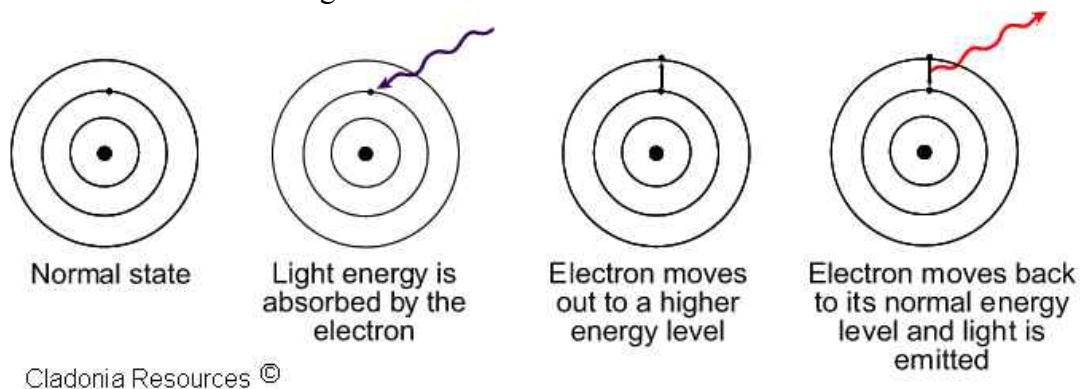


Figure 1

According to Planck (Ref 4), the energy of each photon is given by multiplying its frequency (in cycles per second) by a constant (Planck's constant, 6.62617×10^{-27} erg seconds). It follows that 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 to be of short wavelength (high energy) the gap to be jumped by the electron must be a large one. The numerical relationship between these two aspects is the inverse of Planck's constant.

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 or Optically Active Pigments available commercially, inorganic and organic.

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

Organic OAA's exhibit 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. They are also indistinguishable from old coat-tar epoxy type coatings still seen on some structures and vessels.

Mobility of Organic and Inorganic OAA's



Figure 2

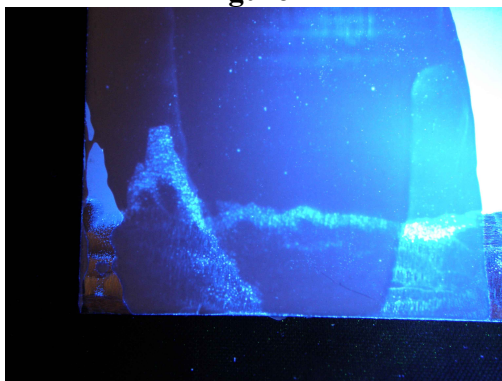


Figure 3

Figure 2: A solvent-free epoxy coating over-coated, after 6 years curing, with another solvent-free coating then over-coated again by the same coating after 7 days curing. The substrate has been mechanically abraded to simulate repair. Viewed under ambient light.
Figure 3: The same system but viewed under UV (Figure 3).

The organic OAA or OAP can be seen to have migrated through each successive coat.

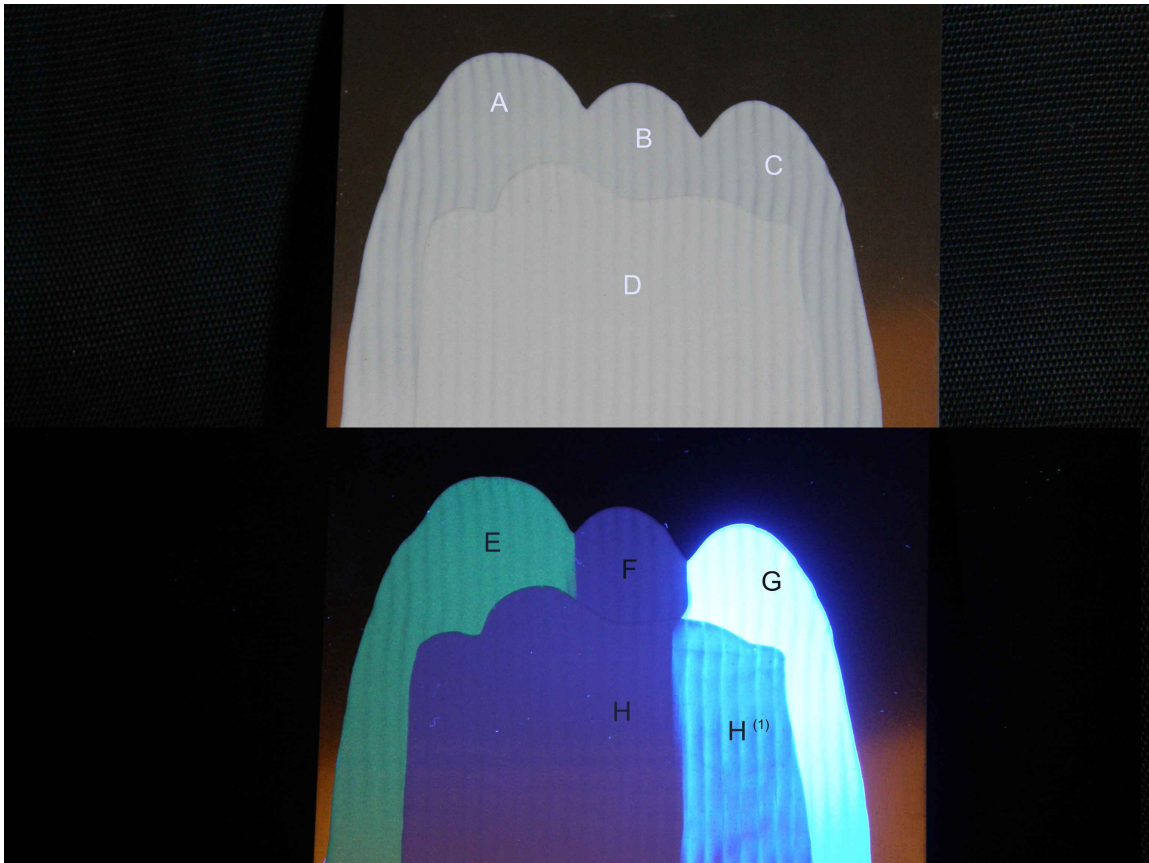


Figure 4

- A: Epoxy with Inorganic OAA under ambient light
- B: Epoxy under ambient light
- C: Epoxy with Organic OAA under ambient light
- D: Epoxy second coat under UV light
- E: Epoxy with Inorganic OAA under UV light
- F: Epoxy under UV light
- G: Epoxy with Organic OAA under UV light
- H: Epoxy second coat under UV light
- H^o: Epoxy second coat under UV light (note migration of Organic OAA through second coat)

Similarly oil, grease, lint and fibres can give false indicators when viewed under UV (Figures 6-7).

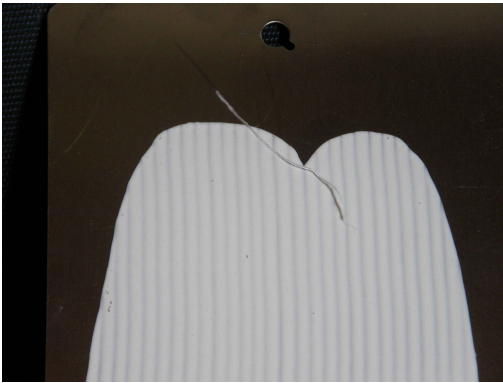


Figure 6 (ambient light)

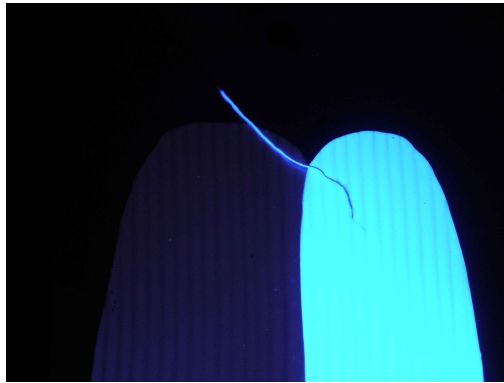


Figure 7 (UV)

Hydroblasted Coal Tar Epoxy under One Coat Epoxy with no OAA

The presence of coal tar epoxy underneath subsequent coatings can give false indications even when no OAA, either inorganic or organic, is present (Figures 8-9).



Figure 8 (ambient light)

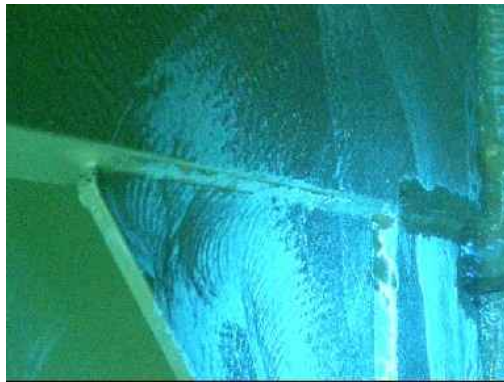


Figure 9 (UV)

The Effect of VOC or Solvents

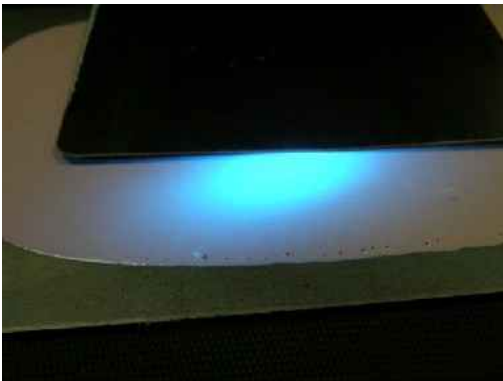


Figure 10



Figure 11

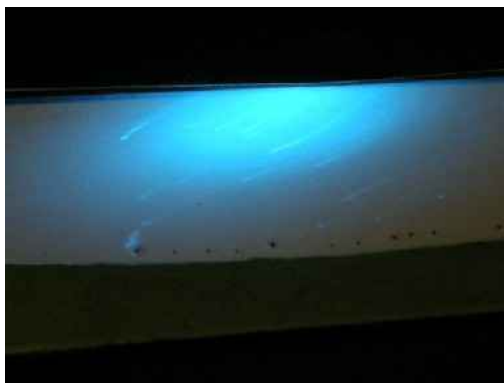


Figure 12

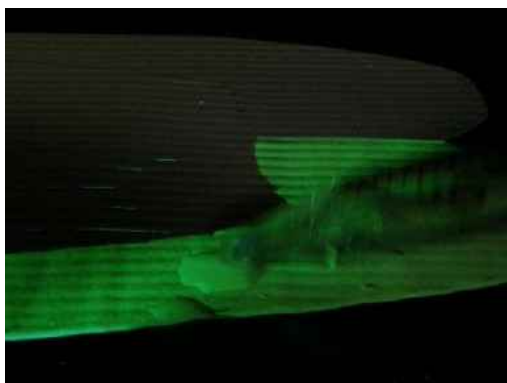


Figure 13

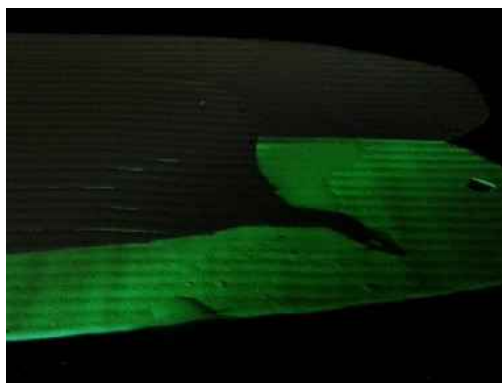


Figure 14

The addition of a small amount of xylene on aged epoxy shows the organic OAA bleeding into the xylene (Figures 10-12). This effect will allow the organic OAA to migrate into any successive film which contains solvent. The migration has even been noted in subsequent topcoats containing White Spirit. Xylene has no migratory effect on films containing inorganic OAA (Figures 13-14). All viewed under UV.

Reaction to UV

Organic OAA's have a more pronounced reaction to UV than Inorganic OAA's.

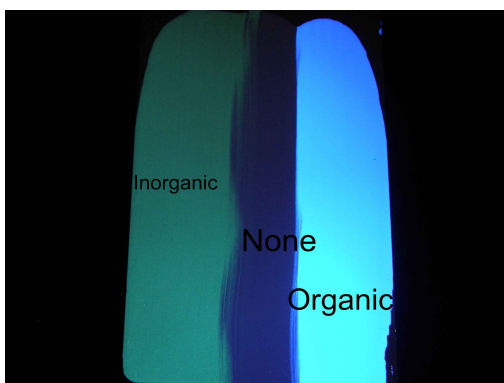


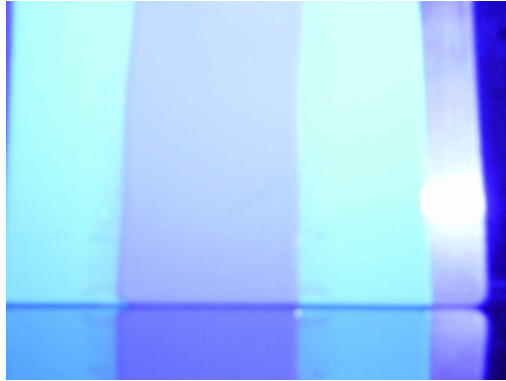
Figure 15

This makes them more suited to single coat applications. However it should be noted that Inorganic OAA's can bleed through into subsequent coats which may be used in maintenance and repair.

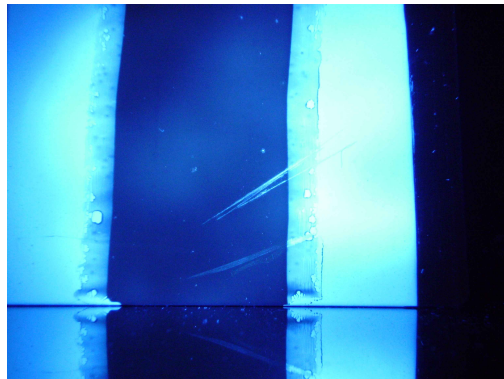
365nm vs 405nm



Under Ambient Light



Under 405nm



Under 365nm

Figure 16

The difference in the amount of visible light generated by 365nm and 405nm sources can have an effect on the degree of conversion to visible light. This can result in defects being difficult to detect at 405nm (Figure 16).

One of the problems that arise when viewing under 405nm is the lack of contrast between the activation source and the emitted energy. At 405nm the organic additive is only functioning at 40% efficiency and the difference in wavelength between the activation source and the emitted energy is only 45nm at best. Using inorganic additives the efficiency is almost 100% and the difference in wavelength is almost 180nm (Figure 17).

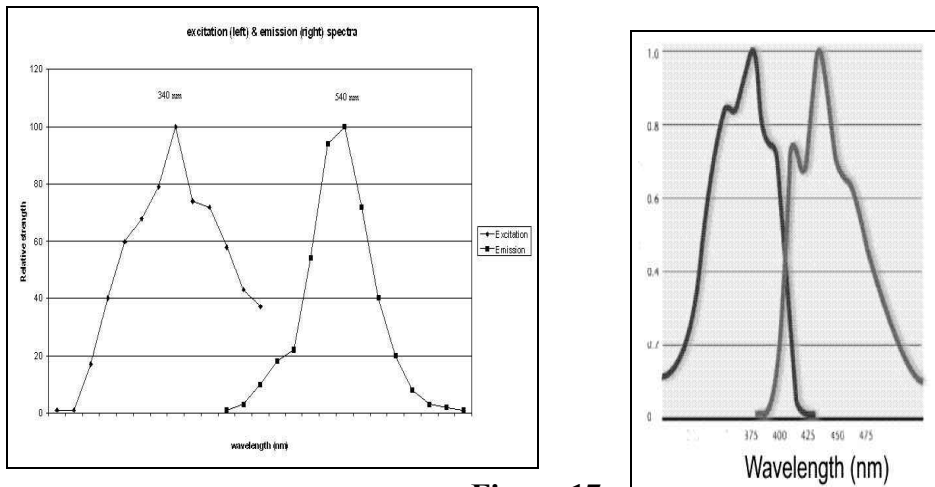


Figure 17

Safety

All wavelengths within the spectrum of 100 nm to 3000 nm have the potential to cause damage to the human organism. The topic itself is too complex to discuss in any detail. The diagram below (Figure 18) (Ref 5) outlines possible adverse effects at particular wavelengths. It is worth noting that the band from 365 nm to 405 nm appears to be the least injurious. However, all light sources should be considered potentially dangerous and appropriate PPE should be worn regardless of what wavelength is used.

CIE band	UV-C	UV-B	UV-A	VISIBLE	IR-A	IR-B	IR-C
	100	280	315	400	700	1400	3000
Adverse Effects	Photokeratitis		Retinal Burns		Corneal Burns		
	Cataracts				Cataracts		
	Erythema		Colour Vision Night Vision Degradation				
			Thermal Skin Burns				

Courtesy J. W. Herrington, Ohio State University

Figure 18

Conclusion

Inorganic OAA's exhibit relatively large particle size: 5 – 10um (no mobility), are light stable, can have a choice of colours, are useful in a wide range of coating systems, and are more expensive.

Organic OAA's can exhibit lower addition levels, 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. They are also indistinguishable from old coat-tar epoxy type coatings still seen on some structures and vessels. Organic OAA's are most useful in single coat applications although care should be taken when over-coating.

References:

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