Darren D Bianchi, Brilliant Group, Inc, discusses the use of fluorescent pigments and colourants, and their growing application diversity

Fluorescent pigments and their diverse applications

Fluorescence is a process of photo-luminescence by which light of short wavelengths, either in the ultraviolet or the visible regions of the electromagnetic spectrum, is absorbed and re-radiated at longer wavelengths. The re-emission occurs within the visible region of the spectrum and consequently is manifested as colour.

The commercial development and sale of fluorescent pigments and colourants dates back to the 1940s in the field of graphic arts. Development was initially centred around the application of point-of-purchase displays, advertising, safety and identification. To date, fluorescent materials have gained widespread acceptance in a myriad of applications, including toys, fashions and packaging.

Fluorescent pigments are often used in specific applications where a particular appeal is desired. Studies have been conducted with children and adults showing that fluorescent products are noticed earlier and seen longer than their conventional counterparts. As a result, designers have incorporated the use of fluorescent products in many creative ways to enhance product sales.

The unique brightness of a fluorescent may be employed alone when one is trying to set their product apart from the rest in a competitive situation. Fluorescent pigments can also be used as an accent in contrast to a more drab colour or they may be added to conventional pigments to brighten an otherwise dull colour.

Due to the speciality nature of the pigments themselves and major consolidation in the market, there are a limited number of fluorescent pigment manufacturers that offer a broad range of products, suitable for the many applications where fluorescent pigments and colourants are used.

NATURE OF FLUORESCENT PIGMENTS

As those who have processed fluorescent pigments know, they differ significantly

from conventional pigments not only in colour but in physical properties as well. Conventional pigments can be organic or inorganic substances and are of extremely limited solubility. Their dispersion is usually achieved and enhanced by the application of shear and the pigment particles tend to be more opaque in nature.

Daylight fluorescent pigments, however, comprise a solid-state solution of fluorescent dyes in a friable polymeric resin. Once the dyes are incorporated into the resin, they are ground into a fine powder for use as a pigment or colourant. As these pigments are resinous solutions of dyes, they tend to be transparent in nature.

MANUFACTURING PROCESSES

The techniques employed to make fluorescent pigments have varied over the years. The original method used was a bulk poly-condensation reaction of melamine, formaldehyde and toluene sulfonamide. The resulting products were tailored to various applications by being thermoplastic or thermoset, depending upon the mole ratios of the polymer's raw materials and varying levels of thermal processing. To date, this original technology remains the most popular of all types of fluorescent pigments, largely due to its low cost.

Nevertheless, as fluorescent products evolved and certain shortcomings of the above products were noted, similar bulk condensation polymerisation methods were carried out to make non-formaldehyde polymers, such as polyesters[1] and polyamides.[2] These are currently the most widely used fluorescent colourants for plastics. The polyesters allow for lower processing temperatures (<200°C) for bright, clean colours, while the polyamides allow for higher processing temperatures (>200°C). As these chemistries do not contain formaldehyde, they are particularly well-suited for processing at elevated temperatures.

Another method, developed in the 1970s to manufacture a pigment of similar chemistry to the first example, was that in using suspension polymerisation.[3] This technique offered pigments which combined bright colours and excellent inertness. This was due to the high degree of polymerisation, which was achievable in the droplet state. Initially this technique yielded colourants with poor colour strength and high price. Over time, this technology developed to yield higher performing fluorescent pigments, in terms of solvent resistance and migration resistance, while costs of manufacturing reduced to the point where the product offers good value in use. It is particularly well suited for non-migration applications, such as PVC.

Another important component of fluorescent colourants are the dyestuffs used. Fluorescent pigments, as noted, are solid solutions of fluorescent dyes, which do not fluoresce in an undissolved state. The dyes used are predominately rhodamine (red) and coumarin and naphthalimide (yellow) types. The fluorescent spectrum from yellow to

magenta is achieved by combining the dyes at different ratios.

ENVIRONMENTAL CONSIDERATIONS

We have seen the recent rise of environmental legislation regarding packaging materials, toys, textiles, etc. As a result, designers and users are required to be increasingly more selective about which materials they use, as they incorporate their awareness of environmental issues.

As already mentioned, some fluorescent pigments are made without formaldehyde. In addition, if properly made, fluorescent pigments typically do not contain any of the commonly regulated heavy metals (cadmium, lead, mercury, chromium, etc) and can comply with regulations, such as EN71-3, AP (89)1, ROHS, etc. Users should confirm this with their supplier and request certifications appropriate for the intended use.

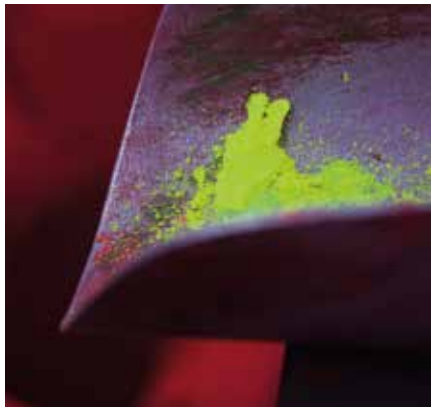
Finally, many of the fluorescent products have been tested for skin irritation and acute oral toxicity. As a result, those that have been tested are classified as 'essentially non-irritating' with a Draize Score of 0 and 'essentially non-toxic' with an oral LD50 (rat) >5000mg/kg.

QUALITY CONTROL

The quality control testing of fluorescent colourants by the manufacturers has been based upon attempted simulation of the end user's testing. Fluorescent pigments are commonly tested by the manufacturer in solvent-based coating, plastisol screen ink, textile ink, flexo ink, lithographic ink or in plastics. In most cases, they are tested in both masstone and tint. In plastics, the colourants are commonly injection moulded in HDPE for observation. Carefully trained technicians perform visual observations, while those in the fluorescent industry await the development of technology, which will allow for adequate computerised colour measurement of materials with greater than 100% reflectance.

INCORPORATION INTO PAINTS, INKS AND PLASTICS

Once the fluorescent colourant passes quality control testing, it is then made useful for more specific applications by industrial users. The industrial users are commonly ink makers, paint manufacturers, masterbatch manufacturers, paper coaters and crayon manufacturers, to name a few. By use of these methods and materials, one is allowed to create products for markets, such as crafts, toys, detergent



boxes and bottles, traffic cones and safety equipment. There is not a great deal of work done with fluorescents in architectural or automotive applications due to the inherently poor light fastness and low tinting strength of these materials.

PROCESSING CHALLENGES

There are some challenges that processors may face when handling fluorescent colourants. Because they are polymeric in nature, unlike organic and inorganic pigments, they do not tolerate high shear. In this situation, the polymer will heat and fuse, causing unusably large agglomerates. Further, many fluorescent pigments are not resistant to highly polar solvents and the dyes used can migrate out of the article. There are certain grades, which are resistant to these phenomena and should be sought out if these specific properties are desired. Also, as mentioned, fluorescent pigments are inherently poor in terms of light fastness. The best way to prolong the life of a fluorescent article is to colour it with high loadings of fluorescent pigment, with as thick a film as possible and then follow with an over-coat of clear containing UV absorber. The addition of UV absorbers into the system is not a terribly effective way to improve the performance in this regard.

In plastics, many grades of fluorescent pigments suffer from the occurrence of plate-out. This phenomenon occurs when organic material, such as oligomeric species containing fluorescent dyestuffs, thermally decompose and separate from the compounding mixture. Thus, these materials deposit on screws and other metal processing equipment.

Steps have been taken to address this problem by both the colourant manufacturers and the compounders. Manufacturers have worked to alter the polymer composition of the colourants and reduce the lower molecular weight species[4], thus, reducing the likelihood of separation and decomposition. Compounders and additive suppliers have developed additive packages to reduce plate-out.[5]

Other challenges in processing fluorescents may be heat instability or incompatibility of the colourants with the various resins. The manufacturers of fluorescent colourants are continually looking at ways to improve their processability in these areas. In the end, fluorescent pigment manufacturers are available as resources to the product users to assist in the selection of the most appropriate grade for the application and the most appropriate processing to get optimal results.

CONCLUSIONS

The use of fluorescent pigments and colourants in a broad range of applications has experienced sustained growth over the past few decades. Research and development efforts continue in the pursuit of more thermally stable, more light fast and plate-out resistant fluorescent colourants, with greater tinting strength and opacity. As these qualities are achieved and improved upon, we should see the use and growth of fluorescent pigments and colourants into more diverse applications well into the future. **PPCJ**

References

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