An Overview of Dispersions for Energy-Curable Applications

By Charles Lubbers and John Erbeck

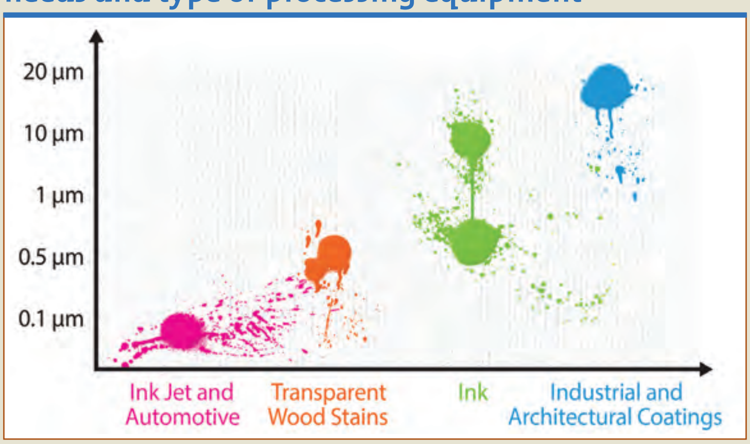
Pigment dispersions can provide an easy route to deliver color into an end-use application. One of the benefits is saving the coatings or ink manufacturer additional—and often messy—processing steps involved in reducing pigment size and placing into a usable formulation, making sure that it has the needed stability and compatibility for processing and application. Energy-curable systems include both ultraviolet (UV) and electron beam (EB) systems. However, UV systems are used predominantly due to the lower cost of capital. While both energy-curable methods are considered to be environmentally friendly, safeguards such as shielding on EB-cured units and ventilation systems for UV lamps to remove ozone emissions should be implemented. This paper will provide an overview of how UV and conventional dispersions differ, including the formulation and processing considerations involved and recent developments in UV-pigment dispersions.

Background

The properties of pigment dispersion will vary widely based upon the end-use application. See Figure 1. A dispersion formulation for a waterborne architectural coating will differ from one used in a stain, solventborne coating and today's energy-curable coatings and ink systems. The dispersion formulation must be tailored to these different needs, starting first with pigment type. For example, typical house paints are designed to hide the substrate and can use relatively larger pigment particles to facilitate this. The ink maker will layer or "trap" colors to create a third color, so they will need a level of transparency in the pigment to achieve this effect. Other applications utilize even more transparency in order to showcase the wood grain or to create the depth of image and sparkle in a metallic automotive finish. In fact, some pigments can be provided in both the transparent or opaque versions. Specifically, transparent iron oxides are chemically identical to their opaque counterparts. It is the crystallization process that creates

FIGURE 1

Particle size requirements vary by application needs and type of processing equipment



either a shape like needles (which are transparent) or a shape like snowflakes (which are opaque).

Equally important is the pigment dispersion vehicle which must be compatible with and, in some cases, must react into the resin system in the end-use application, as is the case for UV and epoxy systems. Examples of vehicles include water, resin, oil-based alkyds, plasticizers, epoxies, monomers and oligomers. In addition, a number of other additives such as dispersants, stabilizers and wetting aids are often required in order to uniformly disperse the pigment in the vehicle. The requirements for these are dictated by differences in density as well as differences in polarity, hydrophobicity/hydrophilicity and chemical nature of the pigment composition and the media. Particle size, shape and surface groups on the particle will also influence whether the particle will disperse easily and remain so—or will easily "settle."

UV Curing

In the case of UV curing and the use of pigments, a review of the physics of light absorption and reflectance is helpful, as this is critical to the process and the color we see. UV curing is a photochemical process in which high irradiance ultraviolet light of a specific wavelength is used to instantly dry and cure inks, coatings or adhesives. UV curing is being increasingly used in these applications over traditional drying methods because of advantages such as increased production speeds, lower processing temperatures, greener technology, zero VOCs, increased scratch, and solvent or chemical resistance.

When light strikes an object, a number of things could happen, including (1) the light wave could be absorbed by the object and its energy converted into thermal energy or a photochemical reaction; (2) the light wave could be reflected by the object; or (3) the light wave could be transmitted through the object.

The selective absorption of light by a particular material occurs because the frequency of the light wave matches the frequency at which electrons in the atoms of that material vibrate. Any visible light which strikes the object and is not absorbed is then available for our eyes and brain to interpret as color. So while the color is not contained within the object per se, it does contain atoms that are capable of selectively absorbing one or more frequencies of the light that shine upon it. The particular color we see depends on the specific frequencies ultimately reaching our eyes.

During the UV-cure process or during atmospheric exposure, the absorbed wavelengths may generate free-radicals and promote a photochemical reaction or photooxidation, which may result in degradation. This has implications for the proper design and selection of materials in a UV formulation.

Dispersions used in UV curing have a unique set of challenges for both the choice of pigment and the vehicle, or matrix of oligomers and monomers. Either transparent or opaque pigments may be chosen for UV-curable applications. Two central factors come into play—(1) the pigment must be lightfast/durable and not fade due to photooxidation from the UV exposure; and (2) the pigment must not absorb the UV light such that the UV light would not be transmitted and available to adequately cure the resin matrix. (This issue goes away when utilizing electron beam for a cure mechanism.) For this same reason, the more opaque the pigment is, the more difficult it tends to be to cure, and adjustments to the photoinitiator packages can be made to overcome variations in lamp irradiance and can further be adjusted by the use of higher functioning oligomers.

Pigment Overview

Fading can make a critical difference in the perceived value of an item. It can make a product change from looking new and appealing to looking old and out-of-date. In the case of more durable items such as flooring and cabinets, consumers place value on those that have long-lasting product warranties.

What makes one pigment more durable and lightfast versus one that will fade on exposure to UV light? The chemical structure and type of bonds present in the pigment molecule are critical to understanding its relationship to these key properties.

Pigments fall into two main categories—organic (petroleum-based) and inorganic (metal-based). In general, organic pigments have a more vibrant hue and higher tint strength than inorganic pigments. On the other hand, inorganic pigments are known for their complete insolubility, which prevents bleed and migration in coatings and inks and, generally, have outstanding light fastness, though they may require higher concentrations to achieve the desired tint strength. Their lower cost certainly favors the inorganics. Within the organic and inorganic pigment classes are a number of families as shown in Table 1.

Generally, pigments based upon inorganic compounds are much more stable against photodegradation than organic-based dyes and pigments, which are susceptible to a wider array of photocatalyzed oxidation and other reactions that can result in color fade or color shift with environmental UV exposure over time, or even from UV exposure during curing. Among the various chemical families used in commercial organic pigments, certain classes are more light stable than

Table 1

Pigment families

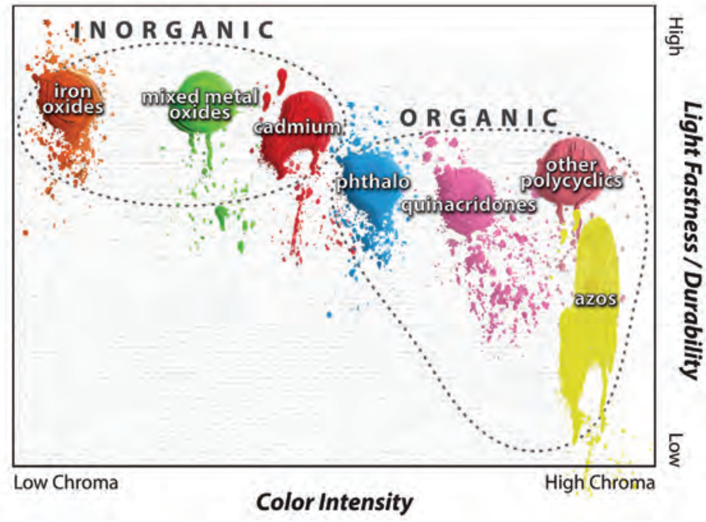
Organic Pigment Families		
Type	**Structure**	**Typical colors**
Phthalocyanine	Macrocyclic structures with varying type and degree of halogenation, few carbon-hydrogen bonds	Blues, greens
Quinacridone	Heterocyclic structures based on succinic acid esters and/or substituted or unsubstituted aniline	Magenta, reds, maroon, violet, gold
Azo (mono & disazo)	Contains at least one nitrogen double-bonded to another nitrogen in the structure	Orange, violet, yellows, reds
Other polycyclic	Non Azo organics	Perylenes, DPP Red
Inorganic Pigment Families		
Type	**Structure**	**Typical colors**
Iron oxides	Based from ore or synthetically produced pigments	Black, brown, sienna, red, yellow, gold, blue
Cadmium	Calcium sulfides/mercury cadmium compounds	Yellow, orange and red
Other single and mixed metal oxides	Titanates, aluminates, chromates, molybdate compositions (nickel, copper, manganese, chromium, lead etc.)	Violet, green, blue, yellow, orange

others, and even within classes the light stability can vary widely from one pigment to another. For example, the azo-based classification contains more than 100 pigments with a wide range of chemical structures that vary in UV durability from very good to poor. Figure 2 shows some of the general properties of various classes of pigments with respect to light stability/pigment durability and color irradiance.

For this reason, it is important to consider light stability and your specific application requirements in the selection of pigment. The "wool scale" is a common rating for light stability. Though originally developed for the textile industry, the test has been adopted by the printing and coatings industry as measure of light fastness and permanence of colorants. As background in this test, two

Figure 2

General properties of various classes of pigments with respect to light stability/pigment durability and color irradiance



identical samples are created. One is placed in the dark as the control and the other is placed in the equivalent of sunlight for a three-month period. The amount of fading of the sample is then assessed by comparison of the sample placed in sunlight to that with no sunlight exposure. A standard fading test card is also placed in the same light conditions as the sample under test as a control. A rating between 0 (extremely poor) and 8 (permanent, no fade) is awarded by identifying which one of the eight strips on the standard card has faded to the same extent as the sample under test.

New Options for UV Color Dispersions

UV dispersions differ from other types of dispersions with respect to the choice of vehicle and consideration of pigment. Like other dispersion types, in addition to the pigment and vehicle, there are stabilizers, dispersants, wetting aids and perhaps other additives. However, rather than an aqueous, alkyd, plasticizer or solvent vehicle, UV dispersions utilize oligomers and/or monomers as a vehicle for a 100% actives system, which will range from 30 to 75% colorant content depending upon the pigment. The coating or ink manufacturer then formulates the dispersion into a coating or ink, adding additional monomers, oligomers and photoinitiator, all of which are designed to cure upon exposure to a certain wavelength and irradiance of UV light in their process.

It is important that the ingredients in the additive package in the dispersion react into the final cured film to achieve the desired physical properties and expected benefits associated with a fully cured product. A high unreacted content, known as a "soft cure," results in the presence of species that could migrate, interfere with adhesion or potentially cause odor problems associated with certain low molecular weight species.

It should be noted that while there are many similarities between UV- and EB-cured systems, there are a couple key differences in formulation and processing considerations. First, EB formulations do not require a photoinitiator in order to cure. In addition, the electron beam generally penetrates the coating layers completely, achieving full "through-cure." Nonetheless, the selection of a pigment with good light fastness characteristics is still very important in EB systems as the final articles are subject to powerful radiation during the cure process and will also be subject to fading from UV exposure in the environment.

Careful consideration to both pigment and vehicle was a key factor in the design of a new line of energy-curable dispersions. The choice of vehicle results in a high flash point and emitting no organic or hazardous air pollutants (HAPs). Nonetheless, optimization of the choice of oligomer and monomer, as well as making sure that full through-cure is achieved, will minimize odor that is sometimes associated with UV curing. Through-cure and odor are a special concern with packaging or industrial applications where the end use is flooring or cabinetry.

The UV dispersions for ink applications consist of the four process colors (CMYK) and several spot colors. Coatings applications tend to utilize oxides or Trans-Oxide® colors combined with specialized pigment colors typically used in industrial coatings. Products for both applications utilize high-performance, durable pigments, rating 8 on the wool scale. The typical, non-energy-cured dispersions made with traditional pigments and used in most packaging applications will tend to have light fast properties that are on the low end of the blue wool scale, as shown in Table 2.

The line of energy-curable dispersions includes white pigments and black, yellow and red Trans-Oxide®

Table 2

Comparison of CMYK colors in standard versus UV applications

Color	Standard Dispersion	Wool Scale (8=no color change, 0=complete fading)	New UV Dispersion	Wool Scale (8=no color change, 0=complete fading)
Cyan	Blue 15:4	8	Blue 15:4	8
Magenta	Red 57:1	5	Red 122	7-8
Yellow	Yellow 14	4-5	Yellow 74	7-8
Black	Black 7	8	Black 7	8

Figure 3

Transparent UV dispersions

Transparent iron oxides are chemically identical to their opaque counterparts; it is the crystallization process that creates the transparent effect. Extremely durable, light-fast pigments, the UV-curable pigment dispersions shown here showcase the wood grain.

pigments, which are extremely durable inorganic pigments noted to produce a transparent effect (particularly desirable in wood coatings), as shown in Figure 3. All of these have a rating of 8 on the wool scale. Additional spot colors include other shades of red, blue, yellow and orange, ranging from 4 to 8 on the wool scale.

The opaque pigments are particularly difficult to cure, as they act as diffusing agents and make light more difficult to penetrate. For this reason, black and white pigments are particularly challenging. The product line includes both the black and white UV dispersions. However, the formulator must select the right photoinitiator/monomer/oligomer package to optimize results. The black and white UV dispersions have optimized functionalized oligomer packages to assist the formulator in achieving the needed through-cure properties.

While Trans-Oxides® are extremely durable pigments, they are also known to be a natural UV absorber, which one would typically expect to interfere with cure in UV systems. However, these dispersions have been formulated to have the needed characteristics and stability to be able to cure and still have the high level of performance associated with this pigment family.

Viscosity and viscosity stability are also important. The viscosity for coatings and flexographic printing applications needs to be designed so materials are easy to handle and, in many cases, pumpable. Offset inks have a significantly different rheology requirement. While the products have been tailored to meet the different rheology requirements of each application, the systems need to be stable, resist settling and exhibit minimal drift regardless of the rheology in order to obtain predictable and repeatable results.

Conclusion

Pigment dispersion selection is critical to the success of a UV-curable system and can make the difference between an item that maintains its appearance and one that quickly looks old and outdated. Achieving the right balance of light fastness and durability in a pigment—while making sure that these beneficial properties do not interfere with through-cure, adhesion and other properties—can be a challenge. The new line of UV dispersions is based on some of the most durable pigment types, such as transparent iron-oxides, burnt sienna, black and white pigments, as well as offering highly functional vehicle packages. Our CMYK for inks has been developed for the specialized requirements of the graphic arts market. Such products have the highest rating on the wool scale, indicating complete color retention and no fade by optimizing key ingredients such as monomer, oligomer and stabilization package, and have been selected to minimize odor and maximize stability.

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