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Formulating with Pigments: Part 2

For many consumers, a trip to the in-store paint chip aisle can lead to indecisiveness, as choosing the "just-right" color to reflect the personality and mood for a space can be a challenge. Even though many consumers experience doubt when trying to choose the perfect hue, formulators must confidently select the colors they will offer to the marketplace, while also offering a range of finishes and performance features consumers demand for today's paints: high hiding, paint plus primer, low VOC, scrub and stain resistance, light stability, and more.

The technology behind colorants does much more than just deliver color. Part 1 in this series on pigments (*CoatingsTech*, **11** (10) October 2014) focused on the different families and chemistries of pigments and how these impact key properties, such as lightfastness, durability, opacity, and chroma. Equally important for the formulator is the knowledge of how to transform those pigments into a usable form for their application, which is the focus of Part 2.

INTRODUCTION TO DISPERSIONS

Unfortunately, there is no such thing as a true "universal colorant" to deliver the needed performance in all applications and vehicles. Liquid dispersions are the most common means of reliably delivering color in coatings and graphic arts applications. Although pigments may be applied directly to the substrate in applications such as stamped concrete, often the goal of such applications is to deliver a mottled or irregular appearance rather than a uniform surface. In most applications, pigments are handled in a liquid form for both ease of use and consistent color delivery. Dispersions for architectural coatings perform as part of a full-color palette available through in-store dispensing systems or in-plant tinting. A similar palette is utilized in graphic arts for spot color printing, while a smaller CMYK (cyan–magenta–yellow–black) set is used in most other print applications. Consistent strength and color batch-to-batch is critical in all applications. In paints, the color delivery must also be consistent across the various tint base-lines, with strengths ranging from pastels to deep tones.

Properties of pigment dispersions vary widely by targeted application. Dispersions used in waterborne architectural coatings can differ greatly from those used in aqueous stains, solventborne coatings, or today's UV-curable coatings and inks. While the traditional ethylene-glycol-based canister colorant may deliver excellent performance in numerous latex emulsions and alkyd house paints, it will generally fall short in industrial coatings.

Formulation must be tailored to each application's different needs, beginning with pigment selection, as discussed in Part 1. Typical house paints are designed for maximum opacity and often contain relatively large pigment particles to facilitate this. Conversely, an ink formulator needs to use primarily transparent pigments to layer or "trap" colors one over another and create additional colors without the need for another ink base. Transparency is also required in metallic automotive finishes to develop depth of image and sparkle, as well as in high quality furniture stains to showcase wood grain. Many pigments are available in both transparent and opaque grades—often referred to as "ink grade" and "coatings grade"—and are selected according to need.

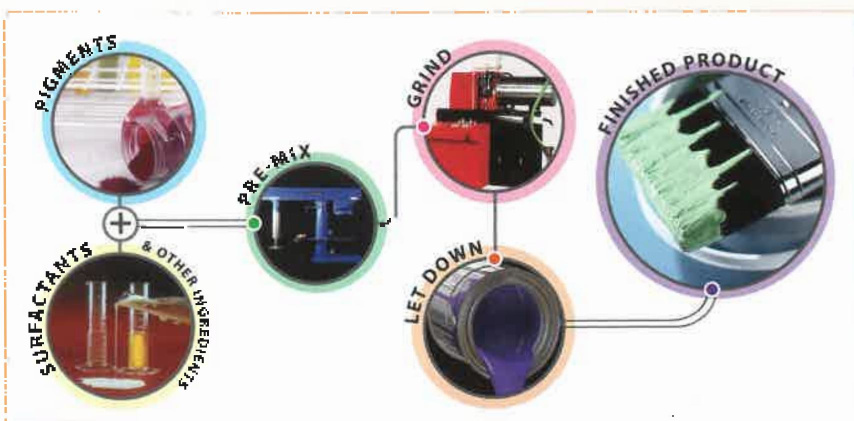

Figure 1—Conventional dispersions are highly engineered and tailored to each ink and coating type, taking compatibility, stability, and other factors into consideration.

GETTING THE PARTICLE SIZE RIGHT

There are numerous critical steps in producing pigment dispersions, and achieving proper particle size is essential. The process involves wetting the pigment, physically reducing the agglomerate size, and stabilizing the particles (*Figure* 1). Obtaining proper particle size is not only important for proper opacity, but also impacts the colloidal stability in-can and during the application process. However, one type of equipment does not meet every requirement for producing a proper pigment dispersion. For example, a basic high speed, saw-tooth Cowles blade mixer sufficiently disperses opaque yellow or red iron oxides for many applications, whereas a high energy media mill is needed to properly disperse and stabilize transparent grades of iron oxides.

Often, the pigment dispersion step is the bottleneck in coatings manufacturing, so manufacturers commonly mill products the minimum amount, as determined by a Hegman grind gauge reading (ASTM D1210 and D1312), then proceed with letdown or finishing. For products with a history of production difficulties, it is often worth the additional time to let down a small portion of the batch in the lab to confirm quality, rather than simply relying on the gauge reading to determine when milling should be stopped. Chroma, transparency, and gloss of a coating will often change substantially as the particle size is reduced (*Figure* 2). Many times, a pigment batch that appears off-shade can be brought in line with additional milling. The other side of the coin is that over-milling can just as easily cause difficulties obtaining the proper chroma, opacity, or viscosity.

The pigment's primary particle size, shape, and surface groups also influence whether the particle will disperse easily and remain so or will rapidly re-agglomerate, potentially causing problems with strength, shade, and settling. For many pigments, manufacturers have developed easily dispersed grades, incorporating surface treatments that greatly reduce the milling time required versus non-treated grades. As an example of the latest technology coming to market, several manufacturers now offer "self-dispersed pigment," dispersions where the surface groups directly on the pigment have been modified, providing extremely stable dispersions without the use of traditional formulating aids such as surfactants or dispersants. Also available are surface-modified "easy to disperse" pigments that simplify formulating and may completely eliminate certain process steps such as milling. These premium technologies can offer substantial benefits in demanding applications, such as inkjet printing, where agglomerated particles will cause both quality problems and equipment issues, or certain industrial coatings applications, potentially streamlining processing and reducing waste.

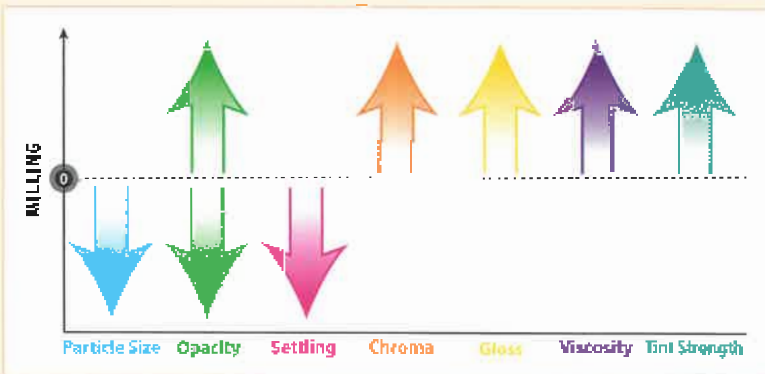

Figure 2—As particle size decreases due to milling, chroma, gloss, viscosity, and tint strength increase, while settling decreases. Opaque pigments tend to behave differently than transparent pigments with additional milling. For example, opacity/hiding tends to increase with additional surface area.

FORMULATING TO ADDRESS CURRENT REGULATIONS

Following particle reduction, the remaining formulation steps are necessary to ensure compatibility with the coating, obtain other important properties such as viscosity and freeze/thaw stability, inhibit microbial growth—and meet the needed VOC level.

When formulating dispersions, the vehicle type is the next component to consider after pigment. The vehicle must be compatible with and, in some cases, react into the resin system in the end-use application. Examples include coatings based on traditional two-component systems such as urethanes and epoxies, as well as the latest UV/EB-cured materials. Vehicle components can include acrylic resins, alkyds, polyesters, plasticizers, epoxies, monomers, and oligomers. In addition to VOC limits, other health and safety regulations have forced changes in raw material selection, such as the current emphasis on the elimination of certain phthalates, with bisphenol A (BPA) possibly next in the crosshairs.

In addition to the primary vehicle, a number of additives—such as wetting aids, dispersants, various stabilizers, and defoamers—are often required to satisfactorily disperse the pigment. The requirements for these are dictated by the differences in pigment density, polarity, hydrophobicity/hydrophilicity, and chemical nature of the pigment composition and media. For example, a dispersant that may be a workhorse in interior house paints would likely be unsuitable in industrial maintenance

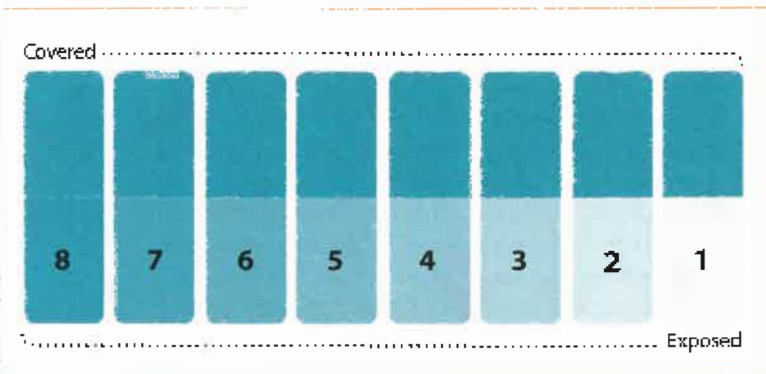

Figure 3—The wool scale measures lightfastness of a formulation by comparing a covered "control" swatch with a swatch exposed to light. The level of fading corresponds to the wool scale rating, with 1 being most faded and least lightfast. For more on the wool scale and how to increase lightfastness, see Part 1 of this series.

applications, where durability requirements are higher. As with all ingredients, achieving acceptable performance at minimal cost is an overarching consideration.

In efforts to reduce or eliminate VOCs over the years, formulators have looked to change nearly every component of their coatings formulation, evaluating alternative resins, coalescents, defoamers, and colorant dispersion systems. The formulator faces constant challenges to balance reduced VOCs with the desired performance features of the paint. For instance, many of the solvents used in the past imparted beneficial features with respect to dry time, stability, dirt pick-up, and hardness development. Reducing those solvents to reduce VOCs requires the use of highly engineered resin systems and additives to achieve comparable performance. In response to demand for low/zero-VOC coatings systems, resin and additive manufacturers have overhauled their product lines and now offer highly functional additives and resins, often tailored for specific applications.

UV systems are another low-VOC option. Dispersions used in UV curing have a unique set of challenges, for both choice of pigment and vehicle. Like other dispersion types, in addition to pigment and vehicle, there are stabilizers, dispersants, wetting aids, and perhaps other additives to consider. However, rather than emulsion, alkyd, plasticizer, or solventborne vehicles, UV dispersions utilize oligomers and/or monomers as a vehicle for a 100% solids system, containing 10–45% pigment. The manufacturer formulates the dispersion into a finished coating or ink, adding additional monomers and oligomers and a photoinitiator, all designed to cure on exposure to UV light or electron beam (EB). In many cases, the photoinitiator selection is vitally important and has a direct relation to the color being cured. For instance, black and white are very difficult to cure, as light will not easily penetrate the coating due to reflection or absorption by the pigment. Utilizing highly functional oligomers and the proper photoinitiator allows the coating to obtain proper through-cure. This also has other benefits, such as improving adhesion to difficult substrates.

Either transparent or opaque pigments may be chosen for UV-curable applications; however, as covered in Part 1, lightfastness is a major criterion in pigment selection. Typically, a rating of 7–8 of 8 on the "wool scale" is desired for superior color durability (*Figure* 3). More opaque pigments may offer greater light stability, but are also more difficult to cure (*Figure* 4.) As mentioned previously, challenges encountered in curing—whether due to pigment or variations in lamp intensity—can sometimes be overcome through adjustments to the photoinitiator packages and/or substitution of higher-functioning oligomers in the formulation.

When formulating to comply with regulations, viscosity and viscosity stability can be major issues. The viscosity for coatings and flexographic printing applications must be designed so materials are easy to handle. For in-store coatings, colorant dispersions are incorporated into the paint base volumetrically from dispensing equipment. In-plant coatings generally meter in colorants by weight, but must be pumpable and easily incorporated into the batch with minimal agitation. Although dispersions are tailored to meet the different rheology requirements of each application, all systems need to resist settling or separation and be stable and suitable for use with the dispensing/application equipment, exhibiting minimal drift on aging regardless of the rheology to obtain repeatable results.

COLOR MATCHING AND QUALITY CONTROL

Consistent lot-to-lot color for various tint-bases and strengths is critical. So, when color variations occur, where does the formulator begin to address the issue?

Figure 4—Transparent iron oxides are chemically identical to their opaque counterparts; it is the crystallization process that creates the transparent effect. Extremely durable, lightfast pigments, the UV-curable Lucida Colors™ Trans-Oxide® pigment dispersions shown here in black, yellow, and red (10% dispersion on left, 5% on right) have a 7–8 wood scale rating and showcase the wood grain.

The first step is to "rub-up" or shear the applied wet film. If the sheared film's color shifts compared to the control, poor color acceptance or compatibility issues could be to blame. Color acceptance issues include the three F's: *floating*, resulting in an uneven film appearance; *flooding*, meaning the film's surface does not match the body of the film; and *flocculation*, balls of isolated dispersion formed in the film that have not been completely dispersed. As color acceptance issues are a common problem, manufacturers have developed numerous additives to address these defects. For example, floating and flooding can be resolved with the use of surfactants or dispersants, while flocculation may require reformulation or utilizing additional mechanical shear.

Assuming there is no compatibility problem, the next step is to examine the individual colorants used to determine how the current lot compares to previous lots that were successful. The range of acceptable color variation batch-to-batch is largely determined by application requirements, but generally falls between 0.5 and 2.5 delta E to minimize perceived shade variation to the eye. Each product will have its own specification range that will include an acceptable limit for color properties such as strength, tint shade, and masstone shade, all of which are measured versus the manufacturer's standard lot. Pre-testing a sample of each colorant is highly recommended when manufacturing a coating with tight color specifications, particularly products high in chroma, which leave little room for color correction. Even then, a problem can occur if the manufacturer has chosen a particular colorant lot as the internal standard without checking to see how that lot compares to the colorant manufacturer's standard.

CONCLUSION

Dispersions are the most common way to reliably deliver reproducible color for coatings or graphic arts applications. They can either be purchased in a ready-to-use form or the manufacturer can custom-produce his/her own dispersions in-house. By purchasing ready-to-use dispersions or "stir-in" pigment types, companies can minimize inventories and avoid costly capital and maintenance expenses associated with milling equipment. Consistent color and pigment optimization also offers improved throughput and helps to eliminate production snags, a common cause of last-minute scheduling changes and down time. There are also environmental benefits gained by reducing exposure to pigment dust and to the solvents and cleaners for milling equipment after use.