Zeta Potential, Isoelectric Point and Pigment Dispersion Stability

Introduction

Technical publications about pigments and dispersions often make references to the terms "Zeta Potential" and "Isoelectric Point". Some formulators may not be familiar with these concepts. This paper is intended to help explain what these terms mean and how they affect pigment dispersion stability in the simplest terms possible. It also will discuss the Shepherd Color Company's Dynamix® "Stir-In" grade pigments and how Zeta Potential and Isoelectric Point are different with this technology versus conventional pigments.

Background

The three basic states of matter are solids, liquids and gases. If one of these, a solid, is very finely divided within a liquid it may be called a "dispersion". In the case of waterborne coatings or color concentrates, the solid material is pigment (and also possibly polymer particles) suspended in a liquid which is water. The pigment particles may be inorganic, organic, or combinations of both.

The preparation of coatings or color concentrates involves dry powder pigments being introduced into liquid water under mechanical shear in order to wet them out completely. With standard pigments this is generally not possible without the addition of a chemical dispersant to aid in the wetting and de-aerating of the powder. Milling through a high energy media mill is then routinely needed to achieve the optimum particle size. Ideally, the chemical dispersant selected will also provide inter-particle repulsion of the pigments so that the dispersed particles do not re-agglomerate to any extent. Often this is not the case and combinations of dispersant(s) with other surface active ingredients are needed to obtain a stable formulation.

Dispersion Stability & Zeta Potential – Taking a Closer Look

Zeta Potential (ζ) is a property exhibited by particles in suspension. It is a measure of the magnitude of the electrostatic charge repulsion between particles. It is one of the fundamental parameters known to affect dispersion stability, aggregation (flocculation), coagulation, and ultimately sedimentation. Zeta potential is affected by, and will change with, variations in pH. The pH at which the zeta potential equals zero is known as the isoelectric point (IEP). For mixed metal oxide pigments, the isoelectric point is of interest because it is the point where the surface of the pigment shifts from having predominantly $M\text{-}OH_2^+$ present (for pH below IEP) to having $M\text{-}O^-$ present (for pH above the IEP). Theoretically dispersion stability increases as the <u>absolute value</u> of the zeta potential increases. Conversely, dispersion stability would theoretically be weakest at or near the isoelectric point. A commonly used guide is that a zeta potential greater than 30mv or less than -30mv will display good electrostatic stability.

The Dynamix® Breakthrough

The Shepherd Color Company has created a new class of specially treated inorganic pigments called Dynamix®. The Dynamix® pigments require very little or no chemical dispersant in order achieve high concentrations of pigment with relatively low resultant viscosities. Dynamix® also requires minimal energy to achieve optimum dispersion with a Cowles type mixer usually being quite adequate. The Dynamix® products are >99% pigment and the treatment is inorganic in nature.

Formulators of coatings and color concentrates prefer to incorporate the minimal amount of chemical dispersants. This is because these compounds not only bring added cost, but also can result in adverse properties such as product foaming and water sensitivity of the cured coating film. The dispersant / surfactant needs for a Dynamix® containing formulation will depend on the other components of the formulation as well as its inherent rheology and pigment suspending capability. Since Dynamix® is so effective; its mixtures tend to be lower in viscosity than conventional pigments.

While the Dynamix® pigment particles do have inter-particle repulsion, their high specific gravity, and gravity itself can prevail resulting in settling. For this reason it is prudent to incorporate a charge neutral dispersant to afford supplemental steric repulsion to optimize stability in these circumstances (more on this later).

More on Dynamix and the Isoelectric Point

Mixed metal oxides such as complex inorganic color pigments (CICP) will generally exhibit an isoelectric point (IEP) that is an amalgam of the pure metal oxides contained. However the measured IEP is usually slightly different from the exact mathematical prediction based on CICP's composition because the particle surface tends not to have the same exact makeup as the bulk particle. The physical structure changes caused by the calcining process also contribute to this difference. Different color CICP's will exhibit differing IEP's with their varying metal oxide composition.

Dynamix® is different! The proprietary Dynamix® process alters the surface of the CICP making the isoelectric point values more consistent and predictable from pigment to pigment. In addition, through this remarkable process, while the zeta potentials for each Dynamix® will vary with changes in pH as expected, the isoelectric point will stay essentially unchanged.

The following graphs illustrate the zeta potential behavior of conventional CICP pigment examples (FIGURE 1) versus their Dynamix® counterparts (FIGURE 2). Note how the Dynamix® pigment plots all have similar shapes and more closely resemble the curve for the easy disperse grade titanium dioxide used in the testing. The Dynamix® pigments have a consistent and predictable positive charge at the surface.

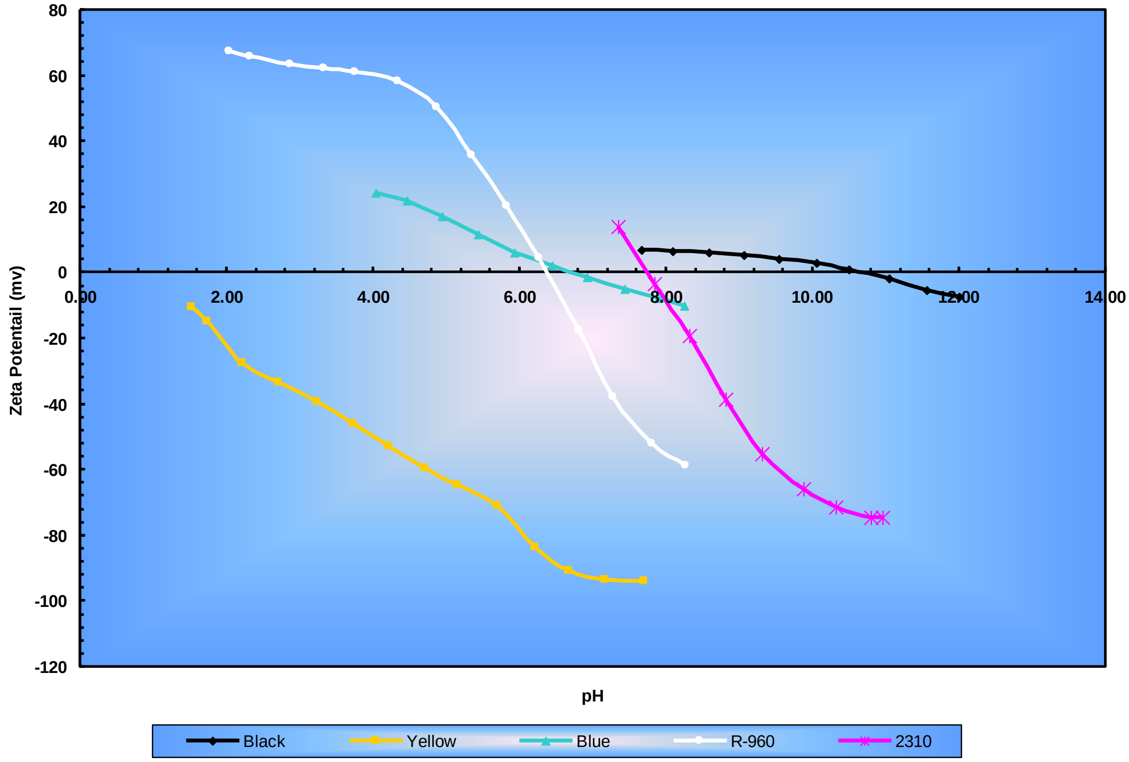

FIGURE 1 – Zeta Potential vs. pH for Conventional CICP

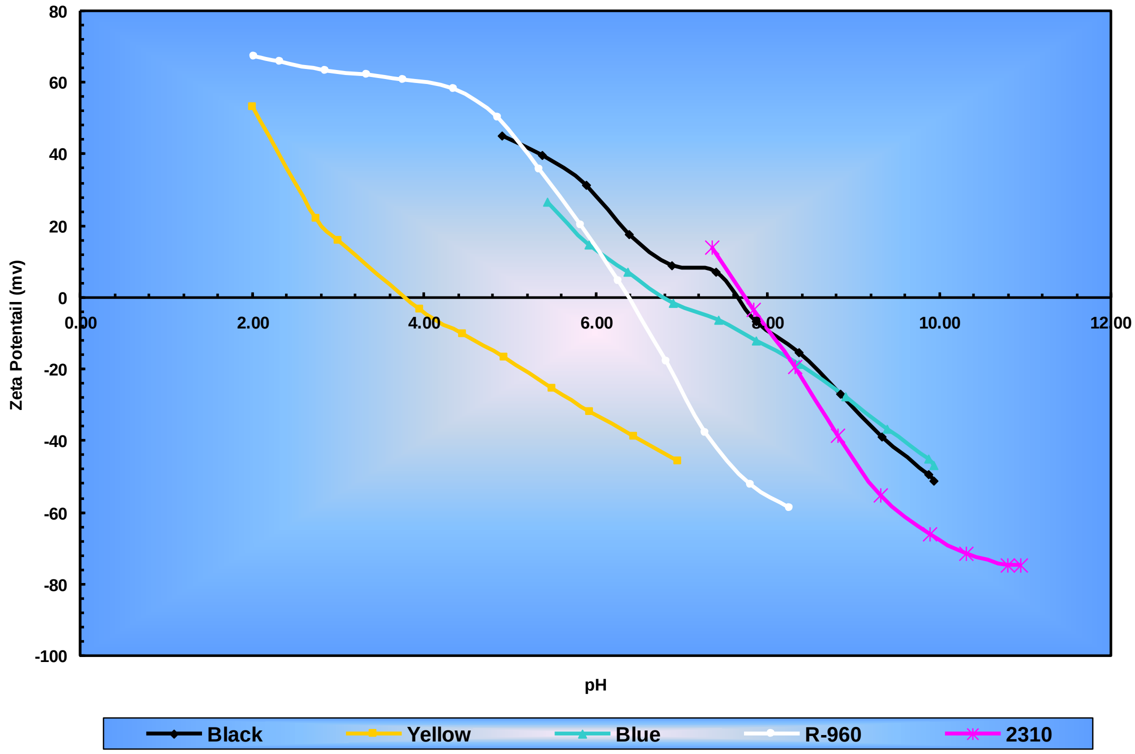

FIGURE 2 – Zeta Potential vs. pH for Dynamix® CICP Pigments

Electrostatic vs. Steric Stabilization

Up to this point the discussion has focused on ionic and electrostatic factors affecting dispersion stability. As mentioned earlier, with conventional pigments the wetting and de-aerating of useful levels of pigment in water is not even possible without the incorporation of a chemical dispersant. However, even with Dynamix® products, electrostatic inter-particle repulsion alone may not be adequate to assure that no stratification or settling will occur, particularly in lower viscosity Newtonian rheology systems. For this reason, specific dispersants may be useful for affording steric inter-particle stabilization to the dispersion.

Laboratory studies have shown that the most beneficial dispersants for CICP stabilization are the “charge neutral” type. These dispersants (such as Disperbyk® 180) have acid values and amine values that are about equal. The amphoteric “head” provides a powerful anchor to the pigment particle while the polymeric “tail” provides steric stabilization to resist particle agglomeration. This can actually allow the replacement of both an anionic dispersant and a nonionic surfactant with a single dispersant.

The dual ionic charge also allows the amphoteric dispersant to function effectively over a broad range of pH values from acid to basic. The key to maximum efficiency at preventing particle agglomeration and possibly settling is determining the proper use level. It is important to understand that more is not better. Dispersant in excess of the amount needed to coat each pigment particle is not just wasteful, it has other adverse effects. The crowding effect on the pigment surface can cause the steric shield to be weakened substantially. Further excess dispersant will remain in the water phase possible causing foaming of the liquid paint and water sensitivity in the cured paint film.

More on Dispersants

It is not just important to know what dispersant to use, but how much to add and when to add it. The dispersant must always be added to the water prior to the start of the pigment addition. Laboratory evaluations show that the key parameter in determining how much dispersant is needed is the pigment’s specific surface area. The surface area for Shepherd pigments may be found on the individual product’s technical data sheet. A description of how to select and determine the best dispersant use levels may be found in a separate Shepherd Color white paper entitled “DISPERSANT **GUIDE FOR SHEPHERD PIGMENTS IN COATINGS**”.