NAME OF PAPER OR ABSTRACT

Abstract

An essential property of coatings is the ability to hide the substrate. Titanium dioxide (TiO$_2$) is the optimum and essentially the only pigment of choice to provide these properties in white wall paint. Cost-effective extender pigments are typically used to extend or space the TiO$_2$ particles. In certain formulation ranges, TiO$_2$ efficiency and paint performance can be negatively affected by crowding of the TiO$_2$ and other spacing options must be evaluated. Polymeric opacifier is another option to increase TiO$_2$ efficiency. Opacifier can provide increased hiding and tint strength over a wide formulation range without compromising performance. In some formulation spaces there is an opportunity to extend the use of polymeric opacifier beyond traditionally accepted levels. Additionally, advances in dispersant chemistry can also provide improved hiding and much improved tinting strength. New dispersant types and dispersant combinations can provide significant improvements in tinting strength. Using polymer opacifier and new dispersing chemistry together can provide significant cost savings while maintaining paint performance. This presentation will provide formulating techniques and paint performance data demonstrating the optimum use of polymeric opacifier and proper dispersant choice.

Introduction:

The ability to provide hiding depends on the scattering of light, and in coatings light can be bent by surface reflection, refraction and diffraction.$^1$ Among white pigments, the particle size of TiO$_2$ provides the highest refractive index (the measure of the bending of a ray of light when passing from one medium into another). Changes in refractive index promote reflection. The reflection of light will occur from the surface of TiO$_2$ (with a high refractive index of 2.7) in contact with various latexes at a low refractive index of 1.5.$^1$ Opacifiers are voided latex particles with a polymeric shell. The difference in refractive index between the shell and the air void allows for improved light scattering. Dispersants provide improved light scattering by preventing flocculation of pigment particles by adsorbing to the pigment surface and providing steric and ionic repulsion. The repulsive energy maintained between pigment particles is dependent on the nature of the dispersant. Ionic dispersants work by electrostatic repulsion and provide long term stability by preventing flocculation and settling, but as a paint film dries, this repulsion can be overcome resulting in agglomeration in some cases. A steric dispersant maintains steric spacing and provides the best pigment positions for opacity in the late phases of drying. The dispersion in the liquid phase and in the drying phase needs to be optimized which lends to the theory of dispersant blending.
Celocor

Opacifier is considered a pigment when calculating volume solids and pigment volume concentration (PVC). To find the optimum level of CELOCOR, typically 1% PVC of TiO₂ is replaced with 4% PVC of CELOCOR as a starting point. The level of CELOCOR can be increased and the corresponding level of TiO₂ can be decreased to achieve the optimum cost/performance balance. Resulting volume solids and pigment volume concentration will be higher when using opacifier in this way. Extender pigments and/or latex may need to be adjusted to maintain desired performance properties, pigment volume concentration and volume solids.

Dispersants – Bumper Technology

The quality of dispersion and stabilization of TiO₂ particles in diluted conditions depends mainly on the use of well adapted dispersants. Dispersants are required when significant amounts of fine fillers or pigment particles are added to water to make the mill base. Deflocculation is needed because particles of a powdered pigment tend to agglomerate during storage in bulk or big bags, due to the combined compression and remaining moisture. The added dispersant plays the dual role of lubricant and dissociative agent and once the particles are de-agglomerated, it interacts with their surface by forming a protective organic layer. Once wrapped around the particle, it contributes to build an additional layer made of positive charges (Figure 1) that opposes the attraction tendency between the particles. Stability of the particles suspension is ensured by both the reinforcement of the electrostatic repulsion potential, thanks to the double ionic layer and by the steric hindrance effect (Figure 2).

Fig.1: adsorption of a polyacrylic type dispersant on particles of fillers: electrostatic repulsion mechanism
Fig.2: attraction and repulsion forces against distance from the particle surface

When playing on the ionic mechanisms is more difficult or even not possible, the use of nonionic dispersants should be considered. Dispersants adapted for the dispersion of mineral particles in water and showing a reduced ionic character offer new potentials & insights for the formulators. Instead of wrapping the surface of the mineral particles, non-ionic dispersants ensure their spacing due to a comb structure based on long ethoxylated moieties. That way of stabilization can be adapted for titanium dioxide or extenders such as precipitated or natural ultra fine calcium carbonate. Stabilization by spacing also brings advantages for the dispersion of nano-sized mineral particles and gives more flexibility regarding the pH adjustment.

**Selecting the best adapted dispersants rather than the universal ones**

Acrylic based dispersants are shown to provide decisive advantages in terms of effectiveness, stability and water resistance and therefore often replace the older generation of phosphate based dispersants: tripolyphosphates (TPP), pyrophosphates or hexametaphosphates (HMP). In particular, acrylic based dispersants offer a long lasting stabilization effect when the paint is stored at temperatures higher than room temperature. It is not the case with polyphosphate dispersants which suffer from degradation by hydrolysis in the same conditions. When it is necessary to disperse specific or very fine fillers and pigments such as TiO2, the use of dispersants based on a co-polymeric structure must be considered.
Acrylic based monomers can be combined with esters or monomers showing a hydrophobic character. Side chains bearing hydrophobic end groups can also be grafted to interact in specific ways with hydrophobically modified pigment or binder particles. They can also contribute to an increased hydrophobic character of freshly applied coatings (early rain resistance) and of dried coatings (scrub resistance).

**How to optimize the dispersion of TiO2**

A first way of optimizing the use of TiO2 is to ensure its proper dispersion in water when making the mill base. A powerful stirrer should be preferred and enough time for the operation spent (at least 20 minutes). The dispersant system shall also contribute to better deflocculation and stabilization of TiO2. Therefore, replacing so called “universal” additives is highly recommended, as pure performance on TiO2 is often compromised by the universal character. Using better adapted dispersants can obviously lead to significant amounts of TiO2 savings. The optical effectiveness of TiO2 depends on the design and quality of the grade considered. Selection tables or technical data sheets help choose the proper TiO2 grade. The claimed characteristics and features correspond to the powdered pigment as it is designed and produced. The same should be recovered once the pigment is dispersed in water. Optical effectiveness depends on light scattering, which is enhanced with the use of very fine mineral particles (less than 1 micron). Light scattering efficiency comes from reflected and refracted light onto small particles and diminishes when particles become bigger. It is the case as well for agglomerated particles, which can be assimilated to larger sized particles (Figure 3). Agglomerated particles remain when the powered pigment has not been deflocculated properly at the mill base stage or form when pigment particles begin to flocculate once dispersed in the water phase. In both cases, it is to revert to the deflocculation process whose achievement is based not only on the stirring efficiency and time but also on the proper selection of the dispersing additives.
Fig 3: schematic representation of light scattering potential on poorly dispersed and ideally dispersed pigments

It shows how easy it is to compromise TiO2 optical activity, i.e., opacity, when dispersants chosen are not fully adapted to the specific paint formulations to be made.
New outlook using the co-dispersant approach

The co-dispersant approach combines the use of an acrylic type dispersant (homopolymeric or copolymeric) and a specific additive technology developed by Coatex called Bumper Technology™. Bumper Technology™ is a new proprietary dispersing technology platform developed to help formulators reduce titanium dioxide (TiO2) levels in coatings. This patented additive technology optimizes dispersion and prevents flocculation of particles while using less pigment and maintaining or improving critical optical properties of the paint. Bumper Technology™ is compatible across a wide PVC and binder range. Acrylic type dispersants enable the reinforced electrostatic repulsion potential between the particles and therefore help deflocculate and stabilize TiO2 particles. Bumper Technology™ (Bumper) shows a low ionic character thanks to a reduced acrylic backbone on which long alkoxylated side chains are grafted (Fig. 5). The acrylic backbone ensures the water solubility of the additive. Its accessibility is governed mainly by the spreading rate of the alkoxylated chain (PEG, i.e., polyethylene oxide glycol chains) making it easily accessible or not to the cations.

Polyacrylate electrostatic layer

Fig.4: acrylic dispersant working principle
When the water amount begins to evaporate and the coating starts to dry (high concentration conditions), PEG chains force the polymer to precipitate on the mineral surface as the osmotic pressure becomes too high (Fig 6). PEG chain length can tune the precipitation rate and the molecular weight of the Bumper the spacing distance.

Fig.5 : Bumper configuration

Fig.6: Bumpers positioning in diluted and concentrated conditions
1) Water evaporates
On the following figure, the needed distances for good spacing of TiO2 at the end of the drying process are reported. The targeted dimension for the Bumpers is in the 20-40 nm range.

The first commercially available Bumper is Coadis™ BR 85, in which the particle size is situated at the lower limit of the effective spacing range. Therefore, Coadis™ BR 85 can be considered both as a dispersant and as a Bumper for TiO2. Bumper Technology™ is a flexible technology platform which enables the ability to adapt the Bumper additive’s design for specific spacing of TiO2 particles in various conditions. In particular, starting from the design of Coadis™ BR 85, the molecular weight of the Bumper can be increased in order to cover the full range of spacing distances, or its structure can be modified in order to fine tune possible interactions with TiO2 particles or other ingredients of the paint (e.g., imparting to the Bumper a more or less hydrophilic character). The co-dispersant approach (see Fig.8 and Fig.9) is focused on the pigment stabilization and spacing only and therefore is less formulation dependant than other approaches such as the use of plastic pigments or binders interacting with TiO2.

Fig.7: ideal spacing in concentrated conditions
Fig. 8: TiO$_2$ particles surface configuration in concentrated condition with the co-dispersant approach.

Fig. 9: Stabilization in diluted condition (long distance) and concentrated condition (short distance) addressed by the co-dispersant approach.

The following case studies highlight the benefits that can be achieved with the co-dispersant approach and Bumper Technology™.
Interior Eggshell formulation 1, PVC: 40%
Opacity and tint strength of an Interior Eggshell paint based on a VAE binder is maintained, even with a TiO2 reduction of 10% and replacement of a standard dispersant by a codispersant system. Using the co-dispersant approach, the total amount of dispersant is slightly higher, but with no significant impact on the cost saving corresponding to a reduction of 10% of TiO2. There is no added mineral to compensate the missing TiO2, therefore a slightly lower Pigment Volume Concentration (PVC) after reformulation.

Fig.10: Interior Eggshell reformulation
Fig. 11: Interior Eggshell opacity and tint strength

As can be seen from Fig. 11, opacity and tint strength are maintained despite the 10% TiO2 reduction and the lower PVC. We see better spacing of TiO2 during the latest stages of the drying process of the coating, thanks to the co-dispersant approach and the Bumper Technology™ introduction. Fig. 12 highlights no difference in terms on hiding power and even increased scrub resistance when using the co-dispersant system.

Fig. 12: evolution of scrub resistance and hiding power after the reformulation
Interior Eggshell formulation 2: PVC 40%

Formulation 2 is very similar to formulation 1, but it is based on a vinyl acrylic binder. The reformulation work is deeper due to the extreme high target in terms of TiO2 saving this time: 22%. Therefore, the Coatex co-dispersant approach has been combined with a plastic pigment (opaque polymer) replacement strategy, as shown by Fig. 13.

![Interior Eggshell reformulation](image)

**Fig.13: Interior Eggshell reformulation**
The experimental Bumper XP 1966 has been selected for the synergistic effect it could build with both the copolymeric acrylic dispersant (Coadis™ BR 40) and with the plastic pigment (Celocor™). It’s specifically tuned molecular weight contributes to improve the interfacial interaction between the TiO2 particles and the plastic pigment. As a result, an impressive 22% reduction in TiO2 amount could be achieved while not affecting the opacity and tint strength.

Conclusion
The co-dispersant approach supported by the Bumper Technology™ opens new perspectives for formulators looking for innovative & effective TiO2 savings. Unlike existing strategies, it is focused on the valorisation of TiO2 particles by allowing them to develop their full potential in terms of optical opacity, both in diluted conditions (storage of the paint) and in the highest concentrated conditions (paint during drying). The co-dispersant approach implementation can help save up to 22% of TiO2 or more if it is associated with other compatible strategies such as plastic pigments incorporation.