

Lubrizol

PERFORMANCE COATINGS



DISPERSANTS TECHNOLOGY AND BENEFITS



LUBRIZOL DISPERSANTS – A SCIENTIFIC APPROACH TO DISPERSION

Lubrizol dispersants are sold under the **Solsperse™** and **Solplus™** trade names.

Solsperse™ Hyperdispersants cover a wide range of applications. Almost any combination of solid particulate being dispersed into a liquid medium can be catered for.

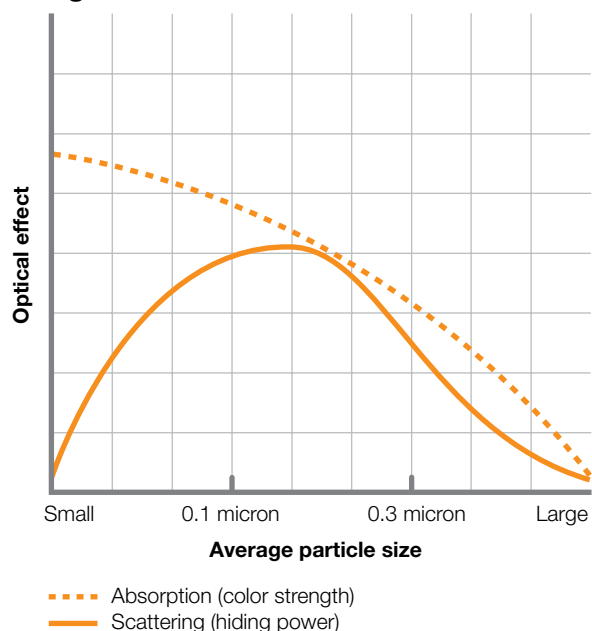
Solplus™ Hyperdispersants have been developed to meet the specific needs of the plastics and composites industries.

The information provided in this document explains the theory behind how dispersants work, the effects produced and how these translate into significant formulating benefits.

DISPERSION OF PIGMENTS AND THE NEED FOR EFFICIENCY

The primary objective of dispersing pigments in a dispersion or grinding medium by mechanical means, is to separate the pigment agglomerates which are formed during the drying processes in pigment manufacture. As particle size is reduced, the surface area so created increases, leading to an improvement in optical properties, such as tinctorial strength, gloss, brightness, opacity or transparency (see figure 1).

Figure 1

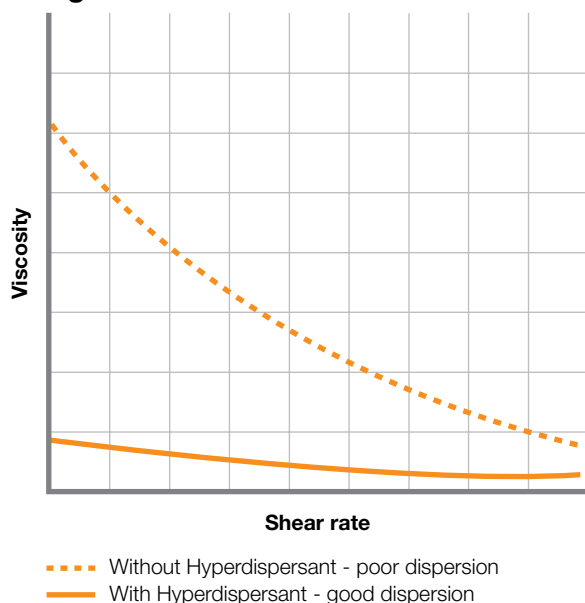


THE ROLE OF HYPERDISPERSANTS

Solsperse™ Hyperdispersants have two fundamental roles in surface coatings: they produce improved pigment dispersion and they reduce inter-particulate attraction within that dispersion.

The improved dispersion means a smaller average particle size (or particle size reduction achieved in a shorter milling time) with a narrower particle size distribution. Small particles are generally more prone to re-agglomeration or flocculation. However, with dispersants reducing inter-particle attraction, dispersions are significantly more stable to flocculation and agglomeration than those produced by conventional means (see figure 2).

Figure 2



SOLSPERSE™ HYPERDISPERSANTS – A SCIENTIFIC APPROACH TO DISPERSION

A reduction in inter-particulate attraction has another important consequence. Among the main contributors to the viscosity of a highly pigmented system (e.g. millbase or high-solids coating) are the forces of attraction between pigment particles. By reducing these forces, Solsperse™ Hyperdispersants lower the contribution to the total viscosity associated with the pigment, thereby producing systems of either lower viscosity or of higher pigment content at equal viscosity. Also, many pigment-containing formulations show a shear thinning or pseudo plastic rheology (often referred to as thixotropy, even if there is no time-dependent factor). Dispersant-based dispersions are generally more Newtonian in behavior than conventional systems. The reduction in inter-particulate attraction can best be understood by considering Potential Energy Curves (a measure of the forces of attraction between particles).

THEORETICAL BACKGROUND TO EFFECTIVE STABILIZATION

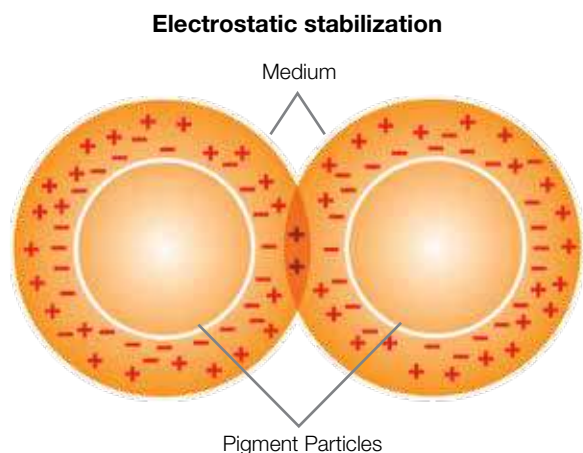
There are two principal mechanisms for the stabilization of pigmented dispersions: electrostatic stabilization and steric stabilization. Both mechanisms require the adsorption of stabilizing molecules on the pigmented surface.

ELECTROSTATIC STABILIZATION

Classic colloidal science explains electrostatic stabilization in terms of an electrical double-layer. A charge is generated on the pigment surface, and a more diffused cloud of oppositely charged ions develops around it. As two particles approach each other the charge effectively provides a barrier to closer particle interactions.

Electrostatic stabilization is effective in media of reasonably high dielectric constant, principally water; although even in water-based systems, steric stabilization, or a combination of steric and charge stabilization will often provide better overall performance. Therefore both mechanisms of stabilization are found in the Solsperse™ Hyperdispersants for use in aqueous systems (see figure 3).

Figure 3



STERIC STABILIZATION

Charge stabilization will not be effective in media of low dielectric constant (the vast majority of organic solvents and plasticizers), and steric stabilization is required to maintain dispersed particles in a stable non-flocculated state.

Steric stabilization relies on the adsorption of a layer of resin or polymer chains on the surface of the pigment. As pigment particles approach each other these adsorbed polymeric chains intermingle and in so doing they lose a degree of freedom which they would otherwise possess. This loss of freedom is expressed, in thermodynamic terms, as a reduction in entropy, which is unfavorable and provides the necessary barrier to prevent further attraction.

Figure 4

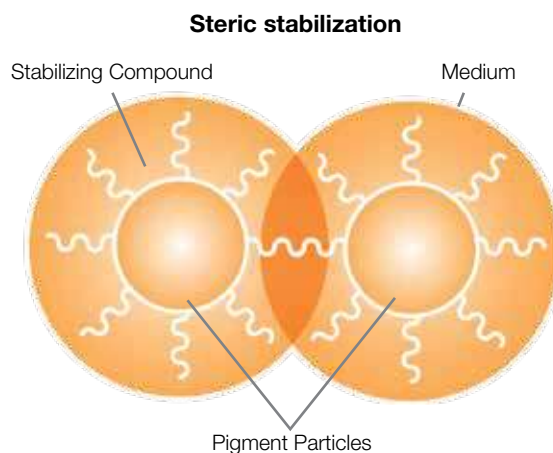
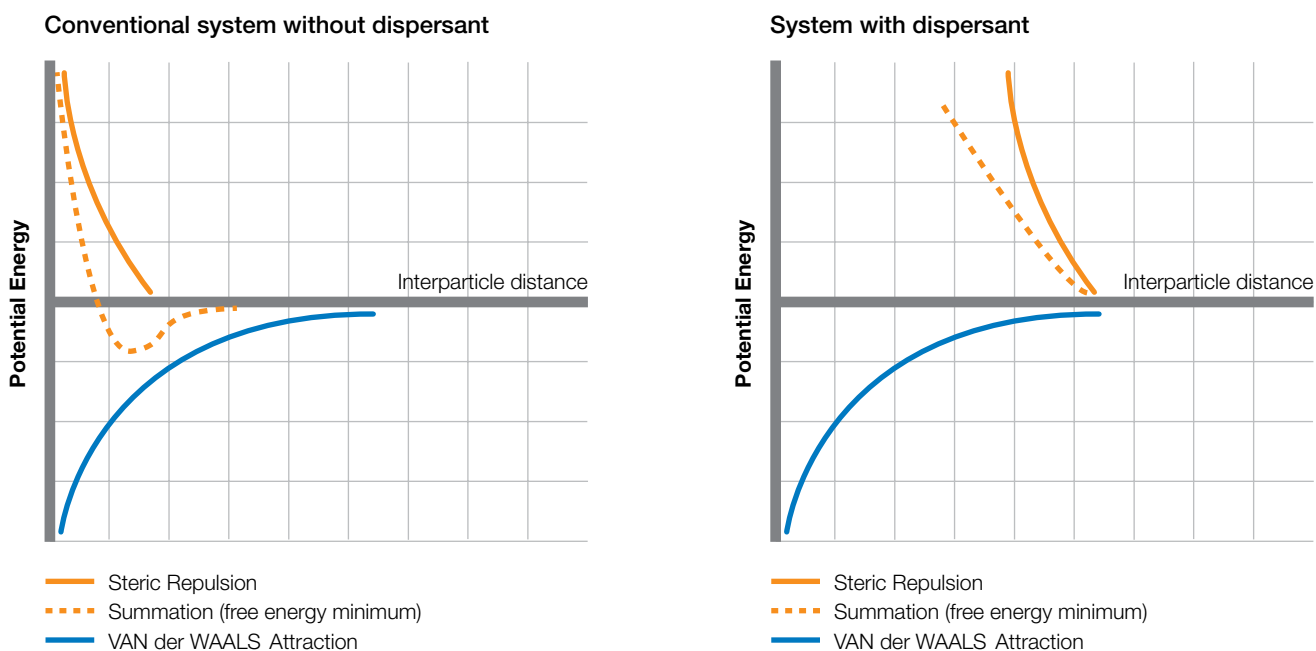




Figure 5



Alternatively one can consider that, as the chains intermingle, solvent is forced out from between particles. This leads to an imbalance in solvent concentration which is resisted by osmotic pressure which tends to force solvent back between the particles, thus maintaining their separation (see figure 4).

One fundamental requirement of steric stabilization is that the chains are fully solvated by the medium. This is important because it means the chains will be free to extend into the medium, and possess the above mentioned freedom. In systems where the chains are not so well solvated they will prefer to lie next to each other on the surface of the pigment, providing a very much smaller barrier to inter-particle attraction.

The greater steric repulsion generated by Solsperser™ Hyperdispersants moves the minimum in the Potential Energy Curve, and thus reduces the overall viscosity (see figure 5).

THE DESIGN OF SOLSPERSE™ HYPERDISPERSANTS

Before describing the design of Solsperse™ Hyperdispersants it is useful to understand their chemistry and mode of action.



Dispersants are two-component structures. The anchoring group provides strong adsorption onto the pigment surface. Polymeric chains which are attached to the anchor group provide the stabilization. (The dispersant may also carry ionic charges for those designed for aqueous dispersion).

It is the particular combination of the anchoring group and polymeric chains which leads to the effectiveness of Solsperse™ Hyperdispersants.

POLYMERIC CHAINS

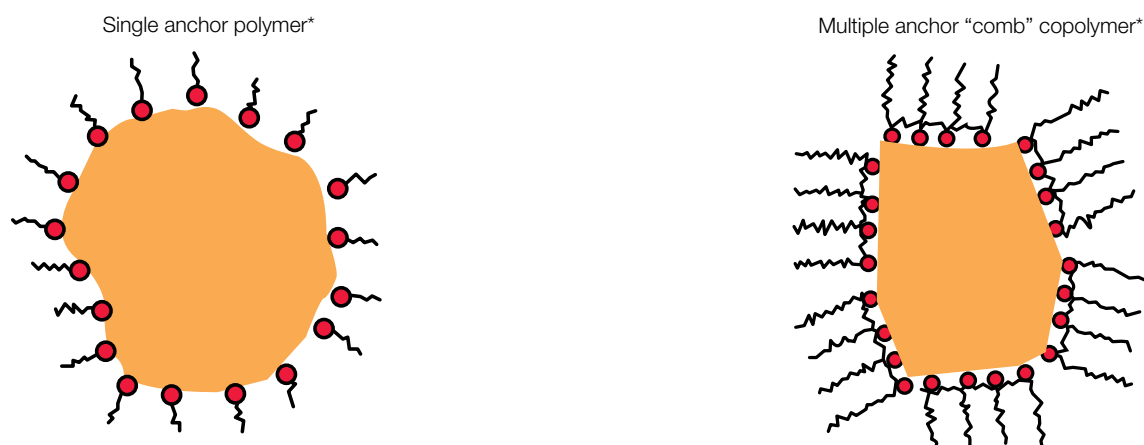
The nature of the polymeric chain is critical to the performance of dispersants. If the chains are not sufficiently solvated then they will collapse onto the pigment surface, allowing the particles to aggregate or flocculate. This need for compatibility with the medium extends throughout the final drying stages of any applied coating and in the dry film. If it ceases to be compatible, flocculation may occur leading to losses in gloss and tinctorial strength. Incompatibility with the binder may lead to haziness in the film.

In order to meet the need for good compatibility, several different polymer chain types are utilized in the Solsperse™ Hyperdispersants range, effectively covering the variety of solvents and binder resins encountered.

The molecular weights of the Solsperse™ Hyperdispersant products are sufficient to provide polymer chains of optimum length to overcome Van der Waals forces of attraction between pigment particles. If the chains are too short, then they will not provide a sufficiently thick barrier to prevent flocculation, which in turn leads to an increase in viscosity and a loss of tinctorial properties.

There is generally an optimum chain length over and above which the effectiveness of the stabilizing material ceases to increase; indeed in some cases, molecules with longer than optimum chains can be less effective. Ideally the chains should be free to move in the dispersing medium. To achieve this, chains with anchor groups at one end only have shown to be the most effective in providing steric stabilization (see figure 6).

Figure 6 Polymeric dispersants with:



*Most Solsperse™ Hyperdispersants utilize one of the structures illustrated above.



ANCHOR GROUPS

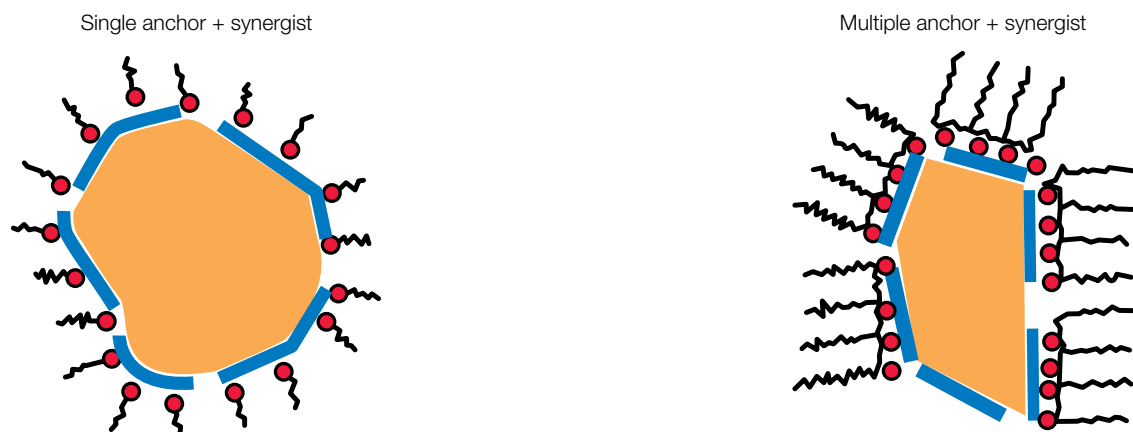
It does not matter whether the previously discussed polymer chains are provided by dispersants containing either single chains or up to many hundreds of chains; indeed both types are available. The essential requirement is that the chains are successfully anchored to the pigment surface, and that the surface of the particles are covered with sufficient density of chains to ensure minimum particle-to-particle interaction.

As the nature of a pigment's surface depends on its chemical type, many different chemical groups are used as anchor groups for dispersants; indeed the Solsperse™ Hyperdispersant range contains several different types of anchor groups. These vary in anchoring ability from products only suitable for inorganic pigments, to products suitable for the whole range of pigments in use today. In dispersants for aqueous systems the anchor group is hydrophobic relative to the rest of the dispersant and also contains specific functionalities to interact with the pigment.

With particularly difficult non-polar pigments, a very successful anchoring approach is the use of Solsperse™ synergists. These synergists are used in combination with a polymeric dispersant. The synergists are pigment derivatives which have a strong affinity for certain pigment types and thereby furnish the pigment surface with anchoring sites for the conventional polymeric Solsperse™ Hyperdispersants (see figure 7).

This versatile approach in the design of dispersants has enabled Lubrizol to produce a range of products which take into account the need for anchoring mechanisms which do not adversely interfere with the cure of reactive systems such as acid catalysed, isocyanate cured or reactive monomer coatings. This is particularly important when one considers the growing importance of dispersants in tinters for mixing schemes, where many different resins are in use.

Figure 7



Generally speaking, the optimum amount of Solsperse™ Hyperdispersant required is dependent on the surface area of the pigment in question. If too little is used then the full benefits will not be realized. If too much is used, it can be shown that the thickness of the protective barrier is actually reduced as a result of overcrowding on the pigment surface (see figure 8).

Therefore the use of an excess of dispersant actually leads to final coating properties which are inferior to those obtained with an optimized dosage. Furthermore, film properties such as adhesion or hardness can be adversely affected by the use of an excess of agent because of the presence of free dispersant molecules in the drying film.

As a general rule 2 mg of polymeric dispersant, per square metre of pigment surface area, will be close to the optimum amount required.

A very simple calculation may be used to determine the amount of dispersant required expressed as percentage Agent On Weight of Pigment (%AOWP) to achieve the 2 mg/m² loading.

$$\% \text{ AOWP} = [\text{pigment surface area (BET)}/5]$$

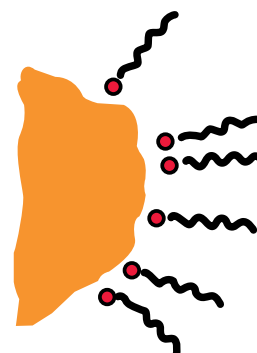
A ladder series of polymeric dispersant levels should be carried out around this 2 mg/m² level. Measurement of millbase viscosity will show a minimum at the optimum dosage; although it is generally more convenient to measure gloss or color strength of the coating which will show a maximum at the same optimum dosage (see figure 9). For digital applications the pigment surface area can often be considerably higher and therefore the dosage of Solsperse™ Hyperdispersant may need to be increased.

The amount of synergist Solsperse™ Hyperdispersant to use, if required, should be additional to the amount of polymeric Solsperse™ Hyperdispersant.

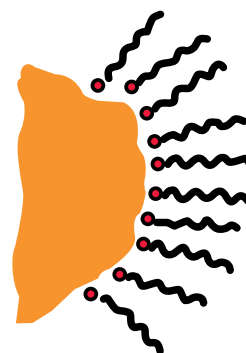
DISPERSANT DOSAGE

Figure 8

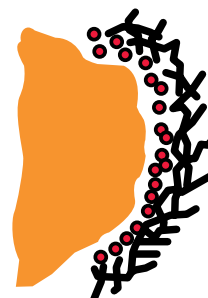
- Too little agent
- Only partial coverage
- Limited performance



- Correct dosage
- Minimum viscosity
- Maximum stability



- Too much agent
- Layer collapses
- Limited performance

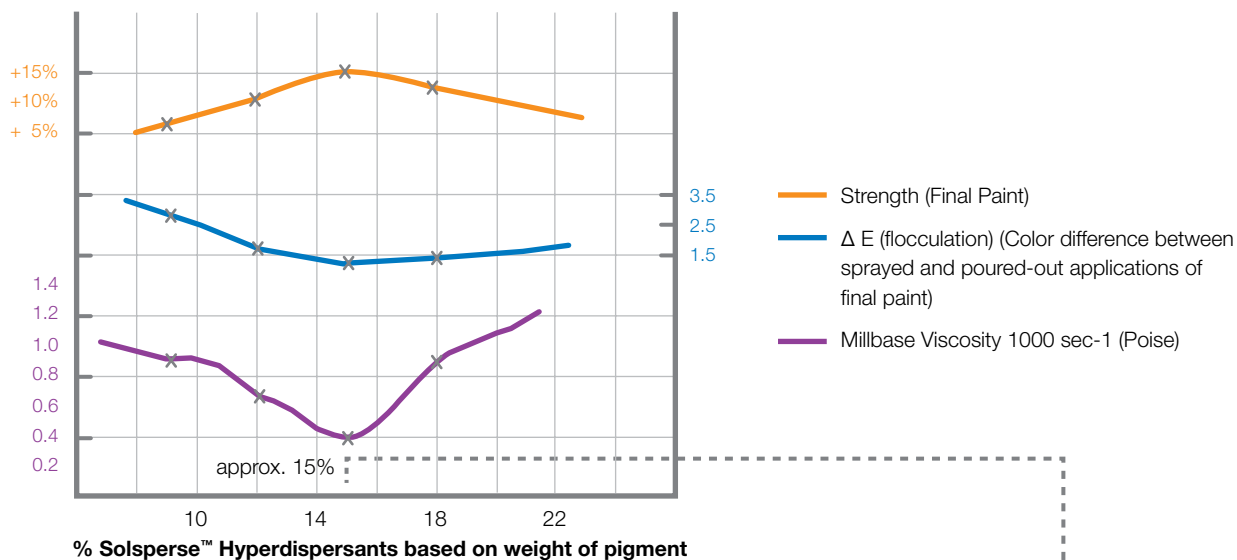


PRACTICAL DEMONSTRATION OF NEED FOR CORRECT DOSAGE

Figure 9

Quinacridone Violet (P.V. 19) in alkyd/MF Surface area: 75 m²/g

Using 2 mg/m² of pigment surface area the theoretical amount of polymeric
Solsperse™ Hyperdispersant = 15% (based on weight of pigment)



MILLBASES	CONTROL	SOLSPERSE™ HYPERDISPERSANT (100% ACTIVE)
QUINACRIDONE Violet	17.5	25.0
20% resin solution	82.5	
10% resin solution		71.2
Solsperse™ Hyperdispersant		3.8
Strength	control	+15%
E Flocculation	3.2	1.5
Gloss	79%	85%

The optimum Solsperse™ Hyperdispersant will not be seen as a “Knife-Edge” change in any optical property but is more likely to be the point at which any further additions would not result in extra improvements and may even give a gradual deterioration in the property.

The important point is that an excess of Solsperse™ Hyperdispersant should be avoided.

FORMULATION GUIDELINES WHEN USING SOLSPERSE™ HYPERDISPERSANTS

In order to obtain the very best from Solsperse™ Hyperdispersants, it is essential that certain guidelines are followed:

MINIMAL RESIN

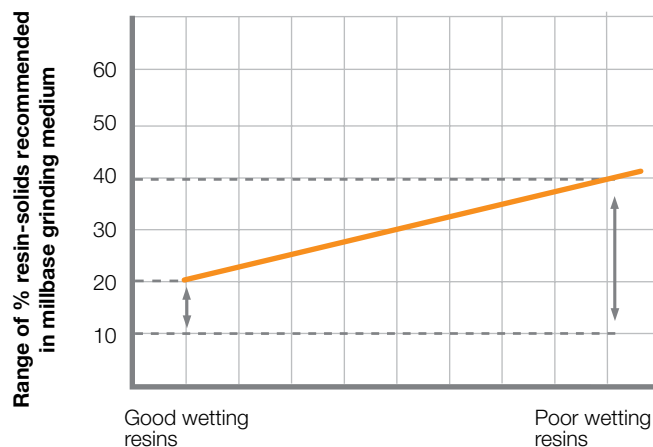
Dispersants are widely used in applications where resins are a component of the millbase e.g. inks and paints.

Anchoring of the dispersant to the pigment surface can be affected by competition between the resin and the dispersant for the surface of the particle. Once the dispersant anchor group is attached to the pigment surface it will remain firmly attached. Molecules of resin, however, are transiently adsorbed on the surface of the pigment, and even though not firmly anchored they can still hinder the dispersant anchoring process. The competition for the pigment surface, resulting from using “good wetting” resins, is the most severe case.

In the presence of Solsperse™ Hyperdispersants, good “wetting” or “grinding” resins need not necessarily be selected for use in the dispersion medium. Other resins, more suitable to end-film properties, can be used, since dispersants will provide the essential pigment wetting function (see figure 10).

We recommend that minimum resin solids are used in the millbase, but present in sufficient quantities to produce the necessary let-down stability; or to produce final coatings with the appropriate resin and solvent contents. If relatively good wetting resins are used, we recommend using 10% to 20% resin solids solution as the grinding medium, and for relatively poor wetting resins, the minimum amount up to the level conventionally used.

Figure 10





SURFACE ACTIVE AGENTS

As with resins, surface active agents may also affect the performance of dispersants; again through competition for the surface of the pigment. Surface active agents such as surfactants and anti-foams may have to be omitted from the millbase and, if still required, added during the let-down. Similarly, matting agents and anti-settling agents should also be added at the let-down stage because dispersants may have adverse effects on them if incorporated in the millbase.

HIGHER PIGMENT CONCENTRATION IN THE MILLBASE

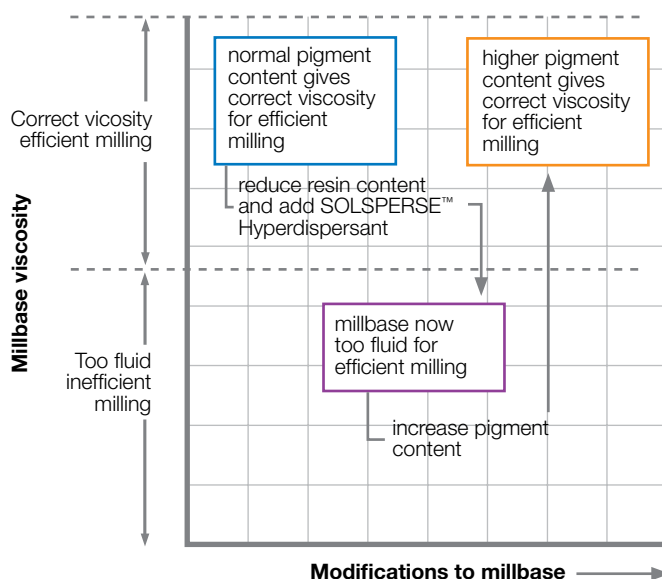
When using Solsperse™ Hyperdispersants, we have described earlier the need to minimise the amount of resin in the millbase. In doing so the contribution from the resin to the viscosity of the millbase is reduced. Furthermore, since dispersants reduce inter-particulate attraction they reduce the viscosity contribution from the pigment.

In low resin or resin-free systems the viscosity may be too low to generate sufficient shear forces for effective dispersion. In these cases, the pigment content should be increased to ensure adequate shear to achieve optimum dispersion.

The effect on pigment concentration of reducing resin and adding dispersant is illustrated diagrammatically (see figure 11).

The Appendix gives guidelines on how to determine the amount of pigment required in a dispersant millbase.

Figure 11



FORMULATION GUIDELINES WHEN USING SOLSPERSE™ HYPERDISPERSANTS

1. BETTER MILLBASE RHEOLOGY

Millbases containing Solsperse™ Hyperdispersants exhibit lower viscosity which allows higher pigment loading whilst maintaining a workable dispersion viscosity, often combined with improved flow (see example 1).

2. REDUCED VOLATILE ORGANIC CONTENT (VOC) IN HIGH-SOLIDS COATINGS

The rheology of a coating is made up of contributions from the solvent, resin and pigment. In “normal” low-solids coatings the contribution from the pigment is dominated by that of the resin solution. However, in high-solids coatings less solvent is present and the resins used are of low viscosity, therefore the contribution from the pigment is far more significant. Solsperse™ Hyperdispersants, by reducing inter-particulate attractive forces, dramatically lower the pigmentary contribution towards viscosity. Therefore when comparing two high-solids coatings, one with, and one without dispersant, the former will have lower viscosity, or more usually, less solvent at equal application viscosity.

3. GREATER PRODUCTIVITY

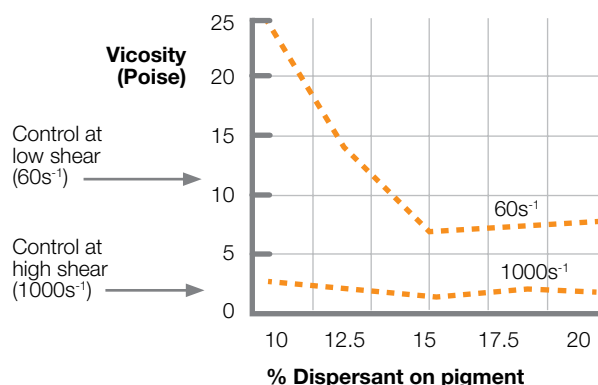
As can be seen in example 2 opposite, productivity gains result from being able to disperse more pigment in a given time and thereby produce more final product from a given weight of millbase (see example 3).

Productivity is also improved by having a significantly faster rate of dispersion. This can be seen in the example showing a difficult-to-disperse class of pigment (see example 4).

Increased productivity arises with less machinery wear, lower energy consumption and most importantly, lower labour and fixed costs for every kilogram of final product produced.

Example 1

Quinacridone Violet (P.V. 19) in alkyd/MF



→ Viscosity of control millbase containing 17.5% pigment in 20% resin solids solution

--- Viscosity of Solsperse™ Hyperdispersant millbase containing 35.0% pigment in 10% resins solids solution

At twice pigment loading with optimum dosage of Solsperse™ Hyperdispersant (15%) millbase exhibits less shear thinning



4. GREATER MILLBASE FLEXIBILITY

Solsperse™ Hyperdispersants will permit higher pigment loadings in the millbase, not only improving productivity, but also reducing the amount of potentially incompatible medium which is carried through from the millbase to the final coating formulation. Solsperse™ Hyperdispersant millbases therefore have wider “acceptance” in a range of base finishes, especially if a “wide compatibility resin” can be used; important for the production of tinters for mixing schemes.

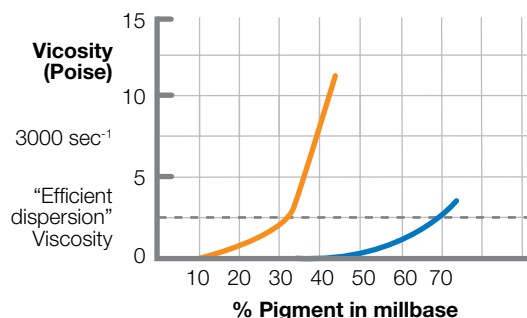
In addition, since dispersants act as wetting agents there is less need to select grinding media purely for their wetting power. The formulator can therefore be more flexible in the choice of dispersing medium (see example 5).

5. HIGHER COLOR STRENGTH

Increases in color strength arise from a reduction in the average size of pigment particles. A higher pigment content in the millbase increases the number of particle collisions, giving faster reduction of particle size. Dispersants will permit milling at higher pigment concentrations, leading to more rapid break down of particles; at the same time they will prevent viscosity building up in the system during the grinding process. Finally they will impart colloidal stability to the finer particles so that they do not flocculate and their full intrinsic color strength is utilized. This is illustrated in example 6 with rapid and ultimately increased color strength development.

Example 2

Yellow iron oxide millbases in alkyd resin



- Control millbase in 20% alkyd resin solution
- Solsperse™ Hyperdispersant millbase in 10% alkyd resin solution

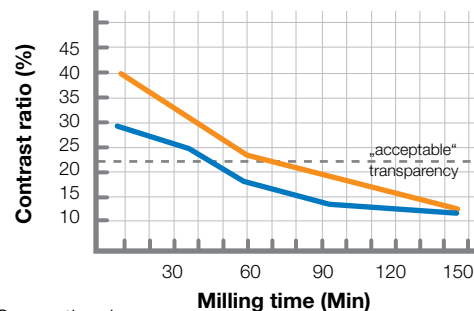
Example 3

Milbases	conventional	Hyperdispersant	
20% Resin-solids solution	64% solvent	58.5% solvent	10% Resin-solids solution containing SOLSPERSE™ Hyperdispersant
	16% resin	6.5% resin	
	20% pigment	35% pigment	

Letdown			
Millbase	100	100	Millbase
Resin or binder	84	168.5	Resin or binder
Solvent	216	431.5	Solvent
Total paint	400	700	
Pigment content	5%	5%	
P:B	0.2:1	0.2:1	

Example 4

Transparent yellow iron oxide in long-oil alkyd



- Conventional
- Dispersant

FORMULATION BENEFITS WHEN USING SOLSPERSE™ HYPERDISPERSANTS

6. HIGHER GLOSS

A maximum particle size greater than 5 microns is generally considered unacceptable for gloss paint finishes, whilst in high quality gloss coatings, 3 microns is the acceptable limit. Most inks contain particles dispersed to less than 1 micron.

Large particles, present in the coating, may occur either through a failure to disperse effectively or through flocculation or “shock-seeding” during let-down.

Solsperse™ Hyperdispersants will aid the efficiency of the grinding process, directly through their ability to wet-out newly created pigment surface, or indirectly through their ability to increase the millbase pigment concentration.

Dispersants will also reduce the incidence of large particles due to flocculation effects.

7. INCREASED BRIGHTNESS

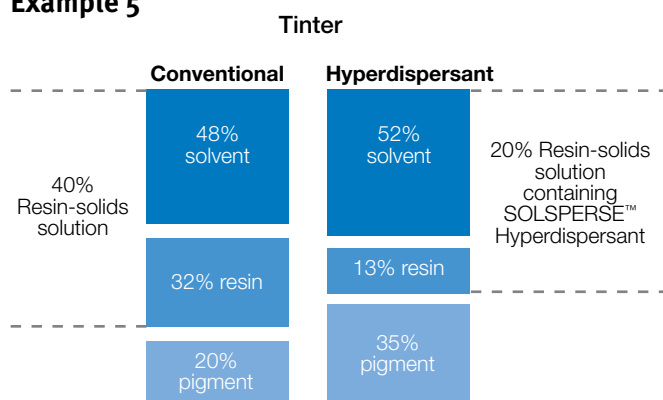
The particle size distribution in a dispersed pigment system influences the brightness of a surface coating, and in particular, the presence of large particles tends to introduce a “dulling” effect. Solsperse™ Hyperdispersants, because of their ability to produce a narrower particle size distribution, give brighter colors.

8. BETTER FLOCCULATION RESISTANCE

Flooding and flotation of surface coatings are dependent on the relative densities, sizes and state of dispersion of pigment particles in a system. As a result of this latter factor, flooding and flotation are adversely affected by pigment flocculation. Although dispersants cannot affect the relative densities of pigments, they are able, through effective stabilization, to prevent

flocculation. This improvement in flocculation resistance not only leads to better optical properties, as outlined previously, but also to improved flooding and flotation properties; and thereby a general improvement in the reproducibility of a coating by different application methods.

Example 5

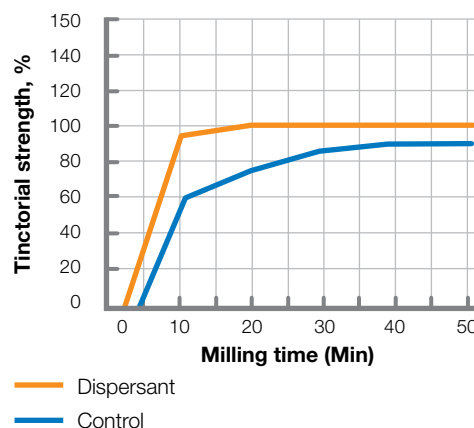


If above tinters are used to tint a white base to give 5 parts colored pigment in the finished paint then the amounts of solvent and resin transferred are:

Solvent	12	7.43
Resin	8	1.86
Pigment	5	5

Example 6

Indanthrone blue (P.B. 60) in alkyd/MF



APPENDIX

Formulating a Solsperse™ Hyperdispersants millbase

The amount of dispersant is expressed as % agent on weight of pigment (% AOWP). To optimize a Solsperse™ Hyperdispersant millbase, four formulating steps are recommended:

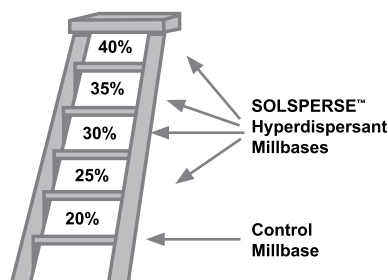


Stage 1: Calculation of % AOWP of polymeric dispersant

The theoretical amount of polymeric Solsperse™ agent required in a millbase is 2 mg of polymeric agent per square metre of pigment surface area.

Example: Pigment surface area - 70 m²/g. Therefore 140 mg polymeric agent/1g pigment are required = 14 g agent/100 g pigment i.e. 14% AOWP. Synergists (if required) are used with the polymeric agent in ratios between 4:1 and 9:1 polymeric : synergist.

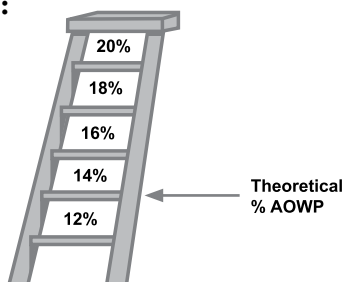
Example:



Stage 2: Determines the higher pigment content required

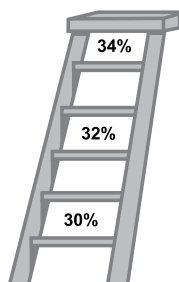
(Can be performed on lab. shaker e.g. Red Devil) Using the % AOWP of polymeric agent (calculated above) + synergist (if required) prepare a series of millbases with increasing pigment contents in a grinding medium containing approximately 10% solid resin. Note: the ratio of dispersant to pigment must be maintained. The pigment concentration giving the same viscosity as the control should now be used in Stage 3.

Example:



Stage 3: Determines the optimum amount of Solsperse™ Hyperdispersant

(Can be performed on lab. shaker e.g. Red Devil) Using the higher pigment content established in Stage 2. Carry out a series of polymeric agent dosages around the theoretical % AOWP (+ any synergist required) to optimize the required agent dosage. Determine best dispersant dosage by measuring desired property.



Stage 4: Optimizes the final pigment concentration

(Should be done in equipment representative of bulk production) Using the % agent on weight of pigment established in Stage 3. Prepare final ladder series of pigment contents - maintaining agent : pigment ratio determined in Stage 3 to determine optimum amount which gives best final product.

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