# DuPont Pigment Dispersion in Liquids

The process of dispersing pigments in a liquid can be divided into three phases:

| Phase | Measured by |
|---|---|
| Initial wetting | Mix-in-time |
| Breaking of aggregates and agglomerates | Fineness, gloss, tinting strength, transparency |
| Flocculation | Suspension, consistency, gloss, hiding, fineness under microscope, partial-set rub-up of tints |

This classification is useful because experience shows one pigment may differ from another in one or more of these steps of the dispersion process. However, the three phases are not always taken into consideration by pigment users; consequently, a pigment is frequently described simply as "poor in dispersion properties," regardless of the specific phase in which it is actually deficient.

## Practical Aspects of Dispersion in Liquids

### *Initial Wetting*

It is virtually impossible to disperse a material in a liquid that will not wet the surface of the material, e.g., aluminum stearate in water. However, most commercial pigments are fairly well wet by the vehicles used and differ appreciably only in their rates of wetting. This is usually evident in the latter stages of making a heavy paste; because, at this stage of mixing, there is only a small amount of free liquid available to contact the final additions of dry pigment.

### *Breaking of Aggregates and Agglomerates*

The various types and grades of pigments differ considerably in the toughness of the aggregates and agglomerates that they contain. The lumps in any one pigment are said to break up in a stepwise fashion as the shearing or impact stress on the particles increases. Because of the various combinations of weak and strong fractions in pigments, one pigment may yield superior fineness to another at low shearing stress but be inferior to it at higher shearing stress. For this reason, ratings at several different levels of shearing stress are required for a comprehensive evaluation of ease of dispersion.

A secondary characteristic of a pigment that often enters into its ease of dispersion is its consistency-producing properties. In some mills, the stress on each agglomerate is applied through the medium of the paste itself; consequently, if the paste is thin no large stress can be applied to the agglomerates. For example, it is difficult to obtain good fineness in a heavy duty, dough type mixer with some pigments and vehicles because, even at high pigmentation, a flocculated condition yielding a readily sheared paste prevents application of high stress to the individual agglomerates. The exact application of consistency data to formulating and predicting performance on a particular mill is very complex, but even limited information on consistency is often useful in anticipating or explaining dispersion effects on various mills. In fact, many studies in dispersion are primarily studies in the creation of various consistencies and how these consistencies relate to dispersion on certain mills.

### *Flocculation*

The extent to which pigment particles group into soft clumps, or flocs, after dispersive action is primarily a function of the nature of pigment surface and the polarity of the vehicle. The particular mill used or the fineness of grind obtained does not seem to have any marked effect. As previously mentioned, flocculation can be a potent factor during milling because of its effect on consistency and hence the fineness obtained. Flocculation is classified here as one phase of dispersion, because a pigment is truly "poorly dispersed" when it is not subdivided to its ultimate size (whether the lumps that are present consist of hard aggregates or soft flocculates). Because these two types of poor dispersion have quite different effects, a clear distinction should be made between them. Flocculation may have undesirable effects on hiding and gloss but desirable effects on suspension.

Vehicles of similar composition may vary considerably in pigment deflocculating power, probably because of differences in some minor constituents not noted in the average analysis. The buttery consistency of a flocculated paste makes it easy to handle, but such a paste does not perform well on grinding equipment. The soft, voluminous mass of settled pigment characteristic of a flocculated system is usually more desirable than the hard, thin cake characteristic of a dispersed system; but the clear, supernatant liquid usually present in flocculated systems is sometimes objectionable.

## Determination of Degree of Dispersion in Liquids

The most direct way of determining whether aggregates have been reduced in size to a desirable level is to measure the size of the particles in the finished product. This may be done with a fineness gauge, a microscope, or one of several devices developed for fine particle size measurement.

Some effects like low tinting strength can exist at good fineness levels if sufficient flocculation is present. Probably the most common way of measuring relative flocculation in a liquid is noting the differences in the amounts and types of settling on shelf aging. Other methods, such as microscopic examination, can be used. With tints, rubbing a wet film lightly when it is partially set is common practice. A darkening indicates probable deflocculation of the color, while a lightening indicates probable deflocculation of the white. No change would indicate that both pigments were probably well deflocculated before rubbing, but there is a possibility that both pigments may have been equally deflocculated by the rubbing. It is difficult to rate deflocculation quantitatively. Flocculates seldom show as particles on a fineness gauge because they are broken up by the shearing action of the scraper.

The material that follows in succeeding sections briefly describes various types of dispersion equipment and general area of usefulness. In some cases, comments are made on problems connected with the operation of, and the formulation of bases for, a particular type of equipment.

## High Speed Mixer—Cowles Dissolver

A Cowles Dissolver is a mixer with a sufficient power and strength to be run at relatively high speeds using a fairly heavy paste. The laboratory Cowles is usually run at about 5,000 rpm but can be reduced to about 2,000 rpm for reducing pastes or other purposes. The agitator is a flat, circular blade with a saw tooth arrangement at the periphery. A peripheral velocity of about 1,200 m/min is usually recommended for best dispersion. Best results for development of fineness are obtained when conditions cause the paste swirling about the blade to assume a doughnut shape. Although batch temperatures can rise rapidly, cooling jackets on tanks are not often used because maximum fineness obtainable can usually be obtained in 5–10 min or before excessive temperatures are reached. In this type of equipment, the stress on the agglomerates is transmitted by the paste, which must have a high consistency if good fineness is to be obtained.

## High Speed Mixer—Hockmeyer “Discperser”

This mixer is similar to the Cowles, but several types of agitator blades are available. One type has several narrow slots around the periphery. Passage of the paste through these slots is supposed to create considerable shear on the agglomerates. Our laboratory results have indicated that final results are comparable to those obtained with a Cowles, but that a thinner consistency is required.

## Sand Grinder

The sand grinder disperses by stirring a pigment/vehicle mix with disc rotors in the presence of coarse sand. Rotors, usually made of abrasion-resistant metal alloys, are attached to a vertical shaft rotating at 2,400 rpm (for 7.5 cm diameter rotors). Mill base to sand ratio is preferably 1/1 by volume. Consistency is similar to that used in pebble mills.

In laboratory batch processes, pigment and vehicle are premixed for a few minutes in appropriate equipment. Then sand is added and the mixing continued for about 1 min. The batch is then ground with the rotors, with cooling water circulating around the container to keep the temperature fairly constant and not too high. When dispersing $TiO_2$, good fineness is obtained in 5–10 min; longer grinding does not improve it appreciably. The mix is removed and strained through a 40–60 mesh screen to remove sand.

In continuous processes in laboratories or plants, premixed bases are fed continuously into the grinding unit containing the sand and drained continuously from it through a screen to hold back the sand. Most units are bottom fed by a pump and overflow at the top.

In general, pigment mix-in properties are not important because the grind base is not of heavy consistency, but if a pre-mix contains many small lumps, a slightly longer retention time in the grinding unit may be required to obtain a given fineness. Large, hard lumps cannot be ground because they cannot be acted on properly by the small sand particles.

Consistency of $TiO_2$ grinds is not extremely critical, but if the base is too thick or thin because of incorrect formulation or temperature control, poor fineness may result. A thin batch may also be discolored through excessive abrasion of the rotors. In the laboratory batch process, if pigment flocculation exists, it is difficult to separate the sand from the ground mix because the mix will not flow much under the influence of gravity.

## Roller Mills

Three- and five-roll mills are fairly common in the coating industry. Two-roll mills are common in the rubber and plastics industries and are sometimes used in the coating industry for dispersing colors to achieve maximum transparency in lacquers. These mills disperse by passing a pre-mixed paste between closely spaced metal rolls rotating at different speeds. A good pre-mix is essential because any large, dry lumps of pigment broken on the rolls will tend to come through as smaller dry lumps and show up in the finished product. Such dry lumps may score the rolls because of the lack of lubrication normally supplied to the pigment particles by the liquid vehicle. Pre-mixing at a very heavy consistency for a short time before adding enough liquid to obtain the consistency desired for roller milling is one way of getting a good pre-mix.

Grinding efficiency is quite dependent on millbase consistency, but the exact characteristics of consistency required have never been defined. Such indefinite properties as "tack" and "visco-elastic effects" must be considered along with yield value, pseudoplasticity, dilatancy, and other common measures of consistency. Highly flocculated pastes slip on the rolls and grind poorly. Dilatant pastes may overload the mill and blow fuses protecting electric drive motors. Our laboratory tests have shown that pigment concentration can be critical. This may be related to consistency changes, but grinding of one pigment particle against another may also be involved.

It is not easy to set the clearance between the rolls to give the desired results. In the laboratory, shims are sometimes used before starting the mill. Some rolls are controlled by hydraulic pressure, and gauge pressure with the mill loaded and operating is used to reproduce settings. Probably most settings are made by an operator, depending on his/her eyes, ears, and past experience to achieve the desired results. If reproducible results are to be obtained, the temperature of the cooling water running through the rolls must be controlled. It is a good idea to use a temperature above the dew point to avoid moisture condensation on the rolls.

The fineness obtained varies considerably, depending on the setting and the number of passes used. Sometimes one grade of $TiO_2$ is superior to another at a tight setting, but inferior to it at a loose setting.

## Pebble Mills

Pebble mills are in common use today, even though they are one of the oldest type mills used. They have the ability to produce a fine grind at low cost with minimum labor. A variety of jars and shells with various linings are available. The grinding media may be natural flint pebbles or synthetic porcelain "balls" made in various sizes, shapes, and densities.

Fastest grinding is obtained with the mill half full of pebbles (including the voids surrounding them), with just enough charge to fill these voids. The charge will occupy only about 20% of the total mill volume. The pebbles should be as small and heavy as possible from a practical standpoint; a good average diameter is about 1 in. A mixture of sizes is not desirable. The rotational speed should be 50–80% of the critical speed, that is, the speed at which the pebbles, with no charge, are held against the shell by centrifugal force. Slight overcharging does not retard grinding radically and may be advisable if the mill can be opened only at certain intervals, such as every 24 hr.

Over the years, much work has been done on the formulations of pebble mill grind bases because the results obtained are definitely a function of the consistency and other factors related to the grind base formulation. The best general practice, at least for $TiO_2$, is to use only enough polymer to deflocculate the pigment and the amount of solvent required to produce a consistency, about 60–80 K.U. that will cause cascading of the pebbles. One of the advantages for using high pigment to binder ratios in pebble mills is the high yield of ground pigment per batch.

Good fineness can be obtained with $TiO_2$ in 2 hr, but batches are sometimes run for 72 hr if exceptional fineness is desired. Gloss does not always parallel fineness. It is conceivable that vehicle degradation, such as incipient resin precipitation through oxidation, may affect gloss as well as the degree of pigment dispersion. Flocculation can cause trouble because the resultant puffy body will usually not permit proper pebble action.

Mix-in rate is seldom a factor. However, dry pigment bulking can be critical when there is not enough room in the mill to load all of the pigment in a batch without wetting it down by turning the mill over a few times. If a similar pigment with lower dry bulking can be obtained, this wetting down process can be eliminated.

## Reduction of Millbases

When the vehicles and solvents required to make a finished product are added to a ground millbase, it is best to add the reducing liquids slowly with appropriate agitation. Rapid reduction may cause the stiff millbase to break into small or large chunks that cannot be broken by the agitator because of the relatively thin liquid surrounding the chunks.

Sometimes, even with slow reduction and good agitation, numerous coarse and fairly tough particles are created when a millbase is reduced. This phenomenon is frequently called "shock." The reducing liquid, instead of blending into and diluting the millbase, seems to suck the vehicle, or possibly just the solvent, from the millbase—leaving the pigment relatively dry. This effect can be observed by smearing a layer of millbase on a panel and covering it with a layer of reducing liquid. In a few minutes, if the tendency to “shock” is present, the millbase will become stiff and dry; often cracks, like those seen in dried mud, will form. Vulnerability to “shock” appears to be independent of pigment type or grade.

The exact mechanism of “shock” has not been clearly established. It generally occurs only when the resin content is considerably higher in reducing liquid than it is in the millbase vehicle. Addition of straight solvent to a millbase will seldom, if ever, produce “shock.” The specific solvents used in the grinding and reducing vehicles may also have some effect. “Shock” is most likely to be a problem when the vehicle in the millbase is very low in resin solids. Such millbases are likely to be used in pebble milling to obtain fast grinding. This grinding technique is sometimes called “slush grinding.”

“Shock” can usually be avoided by employing a millbase vehicle no lower in resin solids than the reduction vehicle. If avoiding “shock” is not feasible, some sort of milling after reduction can usually be used to disperse the agglomerates formed in reduction. This is usually not difficult when pebble milling because it can be done by adding the reducing liquids to the mill and continuing milling for a half hour or so before emptying. Because in many operations it is very inconvenient to mill after reduction, it is best to avoid “shock” if possible.

**Fineness Gauge Scales***

| PC** Gauge Scale | Hegman Gauge Scale | Channel Depth (approx. particle diameter) | | PC** Gauge Scale | Hegman Gauge Scale | NPIRI Grind-Ometer Scale | Channel Depth (approx. particle diameter) | |
|---|---|---|---|---|---|---|---|---|
| | | mil | µm (approx.) | | | | mil | µm (approx.) |
| 0.00 | 0.0 | 4.0 | 100 | 5.25 | 4.2 | | 1.9 | |
| 0.25 | 0.2 | 3.9 | | 5.50 | 4.4 | | 1.8 | 45 |
| 0.50 | 0.4 | 3.8 | 95 | 5.75 | 4.6 | | 1.7 | |
| 0.75 | 0.6 | 3.7 | | 6.00 | 4.8 | | 1.6 | 40 |
| 1.00 | 0.8 | 3.6 | 90 | 6.25 | 5.0 | | 1.5 | |
| 1.25 | 1.0 | 3.5 | | 6.50 | 5.2 | | 1.4 | 35 |
| 1.50 | 1.2 | 3.4 | 85 | 6.75 | 5.4 | | 1.3 | |
| 1.75 | 1.4 | 3.3 | | 7.00 | 5.6 | | 1.2 | 30 |
| 2.00 | 1.6 | 3.2 | 80 | 7.25 | 5.8 | | 1.1 | |
| 2.25 | 1.8 | 3.1 | | 7.50 | 6.0 | 10 | 1.0 | 25 |
| 2.50 | 2.0 | 3.0 | 75 | 7.75 | 6.2 | 9 | 0.9 | |
| 2.75 | 2.2 | 2.9 | | 8.00 | 6.4 | 8 | 0.8 | 20 |
| 3.00 | 2.4 | 2.8 | 70 | 8.25 | 6.6 | 7 | 0.7 | |
| 3.25 | 2.6 | 2.7 | | 8.50 | 6.8 | 6 | 0.6 | 15 |
| 3.50 | 2.8 | 2.6 | 65 | 8.75 | 7.0 | 5 | 0.5 | |
| 3.75 | 3.0 | 2.5 | | 9.00 | 7.2 | 4 | 0.4 | 10 |
| 4.00 | 3.2 | 2.4 | 60 | 9.25 | 7.4 | 3 | 0.3 | |
| 4.25 | 3.4 | 2.3 | | 9.50 | 7.6 | 2 | 0.2 | 5 |
| 4.50 | 3.6 | 2.2 | 55 | 9.75 | 7.8 | 1 | 0.1 | |
| 4.75 | 3.8 | 2.1 | | 10.00 | 8.0 | 0 | 0.0 | 0 |
| 5.00 | 4.0 | 2.0 | 50 | | | | | |

(1.25)(Hegman) = PC

10–(0.25)(NPIRI) = PC

10–(0.25)(mil) = PC

10–(0.1)(µm) = PC (approx.)

*See ASTM Standard Methods for test D-1210

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