Effect of Extenders with Narrow and Broad Particle Size Distributions on the Properties of Coatings

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Extenders are manufactured in a wide range of finenesses enabling paint formulators to influence specific properties of the finished paint. It is necessary to know the "granulometry" or particle size distribution of the extender to select the appropriate one to achieve the desired properties.

Two extenders with practically the same top cut, but one with a broad particle size distribution curve, and the other one with a narrow or "steep" particle size distribution curve, were compared in four different coating systems. The extender with a narrow particle size distribution offered some advantages over the finer one with a broader particle size distribution.

The technical advantages of using such extenders over those with broad curves but similar finenesses, are in particular: ease of dispersion, higher opacity, haze-free gloss, shortening of the drying time, and spacing properties for titanium dioxide.

Extenders are manufactured in a wide range of finenesses and are used in the paint industry to fulfill specific requirements in different coating systems. Products that are used in the coatings industry range from very fine powders in the sub-micron range up to 7-mm chips. To cover the varying requirements of paint manufacturers, a large number of extender grades are manufactured.

Why are there so many different extenders? The paint chemist can influence a wide range of properties, e.g., rheology, density, mechanical and optical properties, corrosion resistance, and durability, by correctly selecting extenders with the appropriate chemical composition and granulometry. The granulometry or particle size distribution of an extender is characterized in general by the particle size distribution curve illustrated in *Figure* 1. The most important points are the "top cut" (d_{98}), which gives the diameter of extender particle so that at least 98% of the particles by weight are finer, i.e., in principle the coarsest particle present, and the "median particle size" (d_{50}), which represents the size of particle so that 50% of the particles by weight are coarser or finer.

These terms are of particular importance when considering fine extenders.

An additional property is the "steepness" of a particle size distribution curve, defined by the "steepness factor" (SF).[1] This is the quotient of the d_{50} and the d_{20} values (corresponding to the size of particle such that 20% by weight of those present are finer). The SF defines certain properties in the finished paint.

The SF can be calculated from the particle size distribution curve of the relevant extender as shown in *Figure* 1 using the following equation:

$$SF = \frac{d_{50}}{d_{20}} \qquad (1)$$

$$SF = \frac{0.85\mu m}{0.45\mu m} = 1.89 \qquad (2)$$

A curve with the SF greater than 2 is described as "broad," and those with the factor of less than 2 as "narrow" or "steep." In other words, a fine extender with a broad particle size distribution curve contains a wider range of different size particles, e.g., from under 0.1 to 3 µm. Such an extender will be referred to in the following text as $CaCO_3$-UF (for ultra-fine). It represents a conventionally manufactured, very fine extender.

An extender with a narrow particle size distribution curve contains particles within a smaller size range. Ideally such an extender would be monodisperse or iso-diametric, i.e., all particles would be of the same size. In the following text, an extender with a very high proportion of particles within a very narrow particle size range will be described as $CaCO_3$-ID (for iso-diametric).

The most important fineness data together with the oil absorption and specific surface area of two fine calcium carbonate extenders are summarized in *Table* 1. *Figure* 2 gives the particle size distribution curves of $CaCO_3$-UF and -ID, representing fine extenders with broad and narrow curves, respectively.
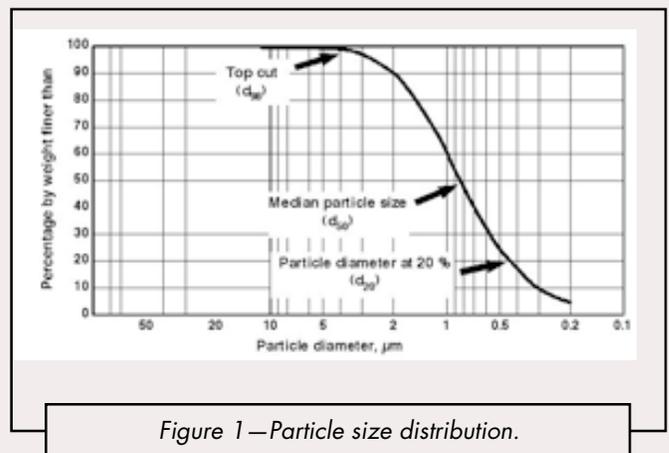

Figure 1—Particle size distribution.

Table 1—Fineness Data of CaCO₃-UF and -ID

		CaCO₃-UF	CaCO₃-ID
Oil absorption (Rub out - method, ISO 787/5)g/100 g		20	21
Specific surface (BET - method, ISO 9277)	m2/g	16	7
Top cut (d₉₈)	µm	3	4
Mean particle size (d₅₀)	µm	0.44	0.90
Particle size (d₂₀)	µm	0.17	0.60
Steepness factor = $\frac{d_{50}}{d_{20}}$	....	2.6	1.5

Table 2—Formulation (C 344) of a Practical Interior Emulsion Paint

Formulation	Pt. Wt.	Lb/100 Gal (U.S.)	Gal (U.S.)
Binder 50% (vinyl acetate, VeoVa, acrylic ester) ...	105.0	138.0	15.32
Rutile TiO₂	60.1	79.0	2.31
Co-extender (5 µm median particle size)	320.0	420.7	18.67
CaCO₃ test extender (density 2.7)	124.9	164.2	7.29
Water + additives	390.0	512.5	56.43
	1000.0	1314.4	100.02

Data
Pigment volume concentration (PVC) 81.5%
Density of the liquid paint .... 13.14 lb/gal
Volume solids 38.2%
Weight solids 61.5%

EXPERIMENTAL EXAMPLES

Opacity of a Heavily Filled Interior Emulsion Paint

The comparison of the optical performance of the ultra-fine CaCO₃-UF with the iso-diametric CaCO₃-ID was made in a practical interior emulsion paint formulation (*Table* 2). The pigment composition consisted of about 6 wt% titanium dioxide and 32 wt% of a co-extender with a mean particle size of 5 µm and in each case 12.5 wt% of the fine extender under test. The pigment volume concentration (PVC) of both paints was 81.5%.

The paints were made using a high speed disperser and allowed to age for about 16 hr. They were applied to black and white opacity charts using a draw bar with a gap of 150 µm. After 24-hr drying time, the optical properties of the dried films were measured. The results are given in *Table* 3.

Virtually no differences between the two extenders were detectable regarding brightness, yellowness index, and low angular sheen. But the contrast ratio was increased by almost one percentage point, although CaCO₃-ID has a higher median particle size diameter (MPD) of 0.9 µm than CaCO₃-UF (MPD 0.44 µm). This difference is clearly visible to the human eye.

This surprising result is attributed to the following properties highlighted in *Figure* 2: CaCO₃-ID contains a high proportion of particles between 0.6 and 1.2 µm—about 55% by weight compared to 22% for CaCO₃-UF— hence, a large number of par-

Figure 2—Particle Size Distribution of CaCO₃-UF and -ID (Sedigraph 5000).

ticles of the right size. The parameters which influence light scattering power are particle diameter, particle size distribution, and refractive index. For high opacity, Burri and Mitton[2,3] calculated that a narrow particle size distribution with a median diameter between 0.6 and 0.8 µm should be the target. All particles having the same size would be ideal.

The second effect is due to the creation of tiny empty spaces between the particles. These can either be filled by air, which increases the opacity, or by the fine pigment particles present. Since the CaCO₃-ID contains virtually no particles below 0.2 µm, these spaces are filled with air. This is called "dry hiding" in the literature.[4] Using an isodiametric extender increases the volume of air in the film markedly. This can be deduced from the oil absorption and the specific surface area (SSA) values given in *Table* 1 and measured using the rub-out method. The SSA of CaCO₃-UF is 16m²/g, double that of CaCO₃-ID (7 m²/g), due to the much higher content of ultra-fine particles.

Oil absorption is a measure of the amount of linseed oil adsorbed onto the surface of the extender particles plus the amount needed to fill in the micro-voids between the particles. The higher SSA of CaCO₃-UF results in greater oil adsorption, but the larger number of ultra-fine particles present in CaCO₃-UF fill many of the micro-voids, reducing the amount of oil needed for this purpose. These two opposing effects cancel one another out resulting in virtually identical oil absorption values.

The critical PVC of paints made using CaCO₃-ID is lower than those made with CaCO₃-UF at constant PVC, so more air is entrapped in the dry film, leading to a higher dry opacity.

Manufacture of Eggshell and High-Gloss Oil-Bound Paints Using a High Speed Disperser

High speed mixers are being increasingly used to manufacture the whole range from eggshell to high-gloss synthetic binder-based paints. The aim of saving time and costs can only be achieved when easily dispersible pigments and extenders are available. The CaCO₃-ID is easier to disperse than the conventional ultra-fine calcium carbonate because it contains less particles finer than 0.2 µm. It is these particles that are strongly attracted due to Van der Waals forces and so form hard agglomerates that are difficult to break up.[5] This is illustrated in the following eggshell alkyd paint with a PVC of 34% (*Table* 4).

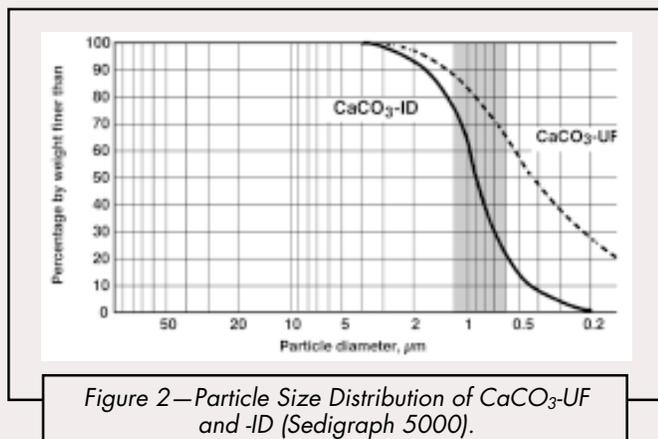A high speed mixer with a saw-toothed disc was used. The peripheral

speed was deliberately kept low at 9.5 m/s (30 ft/s). The fineness of grind was determined using a grindometer according to ISO 1524, comparable with the Hegman gauge. The results, compared to a formulation containing only titanium dioxide as a reference, are given in *Table* 5.

The paints with a PVC of 34% were applied to glass panels using a drawbar with a gap of 150 μm. The films were allowed to dry for four weeks at 23°C and 50% relative humidity (RH). The 60° gloss was 48% for CaCO$_3$-UF and 75% for CaCO$_3$-ID.

The iso-diametric CaCO$_3$-ID with a narrow particle distribution curve, moreover, shows excellent dispersion characteristics, comparable to a very easily dispersible titanium dioxide. The outstanding dispersion properties of CaCO$_3$-ID also explain the markedly smoother film surface and the much higher gloss values compared to CaCO$_3$-UF.

Gloss and Gloss Retention of CaCO$_3$-ID in a Blue Industrial Metal Finish

Air-drying maintenance paints used to coat machinery parts and equipment usually contain small amounts of extenders. These act as bulking agents and also help to lower raw material costs. The extenders must not cause hazing and must be easy to disperse.

Interesting results were obtained when ultra-fine CaCO$_3$-UF was compared with iso-diametric CaCO$_3$-ID, with a steep particle size distribution curve, in a fast-drying blue machine paint. The formulation and data are given in *Table* 6.

The machine paints were made using a high speed disperser (HSD). The phthalocyanine blue pigment was made into a paste concentrate separately using a three-roll mill.

The HSD was run for 10 min with a peripheral disc speed of 18 m/s (60 ft/s). The results are given in *Table* 7.

The superior dispersion properties of this iso-diametric extender compared to CaCO$_3$-UF, which contains many ultra-fine particles that tend to form agglomerates, are evident.

In *Table* 8, the gloss and gloss retention after four-weeks' drying at 23°C and 50% RH are given. Haze was also assessed after 10-weeks' drying time by using visual standards graduated from 0 (no haze) to 10 (very hazy).

The 20° gloss was measured 24 hr after application to the glass panels (starting values) and after four-weeks' drying. The loss of gloss was about 14 per-

Table 3—Brightness, Opacity and Sheen (Gloss at 85° Angle)

	CaCO$_3$-UF	CaCO$_3$-ID
Brightness Y (%)	89.6	89.5
Yellowness index	4.0	3.5
Contrast ratio (%)	95.7	96.6
Sheen at an angle of 85° (%)	3	3

Table 4—Formulation (Q 160) of a White Eggshell Alkyd Paint

Formulation		Pt. Wt.	Lb/100 gal (U.S.)	Gal (U.S.)
Mill base	Long oil soya alkyd 70%	209.2	241.5	30.50
	TiO$_2$ (Kronos 2059)	235.6	271.9	7.96
	CaCO$_3$ extender (density 2.7) ..	235.6	271.9	12.09
	Anti-skinning agent	5.4	6.3	0.82
	Solvent	51.6	59.5	9.16
Let down	Long oil soya alkyd 70%	201.9	233.0	29.43
	Solvent + additives	60.7	70.1	10.04
		1000.0	1154.2	100.0

Data
Pigment volume concentration (PVC) 34.3%
Density of the liquid paint .... 11.54 lb/gal
Volume solids 58.4%
Weight solids 77.5%

Table 5—Results of the Dispersion Trials after Eight Minutes

High speed dispersion (ISO 8780-3)

9.5 m/s (30 ft/s)	**Fineness of Grind**	
Extender:	ISO 1524	Hegman (NS)
CaCO$_3$-UF	40 μm	4.5 - 5.0
CaCO$_3$-ID	10 μm	7.0 - 7.5
For comparison:		
Titanium dioxide	10μm	7.0 - 7.5

Table 6—Formulation (Q 161)—Blue Industrial Metal Finish

Formulation	Pt. Wt.	Lb/100 Gal (U.S.)	Gal (U.S.)
Medium oil alkyd resin (55%)	653.1	601.4	76.71
Phthalocyanine blue	14.2	13.1	0.95
Titanium dioxide, rutile	141.2	130.0	3.90
CaCO$_3$ test extender (density 2.7)	57.6	53.1	2.36
Solvents + additives	133.9	123.4	16.10
	1000.0	921.0	100.2

Data
Pigment volume concentration (PVC) 17.0%
Density of the liquid paint .... 9.21 lb/gal
Volume solids 42.3%
Weight solids 59.6%

Table 7—Results of the Dispersion Trials after 10 Minutes

High speed dispersion (ISO 8780-3)

18.0 m/s (60 ft/s)	Fineness of Grind	
Extender:	ISO 1524	Hegman (NS)
$CaCO_3$-UF	25 - 30 μm	6.0
$CaCO_3$-ID	<10 μm	7.5
For comparison: Phthalocyanine blue paste concentrate	<10μm	7.5

Table 8—Gloss, Gloss Retention, and Hazing of a Blue Industrial Metal Finish

		$CaCO_3$-UF	$CaCO_3$-ID
Gloss (%)	20° Angle		
	Start	66	79
	4 weeks	52	75
Gloss (%)	60° Angle		
	Start	84	87
	4 weeks	79	87
Hazing (visual standards)[a]		6	3
	10 weeks	Marked	Slight

(a) 0 = no haze; 10 = very hazy.

Table 9—Formulation (I 145) Use of $CaCO_3$-ID in a Road Marking Paint

Formulation	Basis (pt. wt.)	$CaCO_3$-ID (pt. wt.)
Styrene acrylate emulsion 40%	223.0	223.0
Titanium dioxide, rutile	148.0	100.0
$CaCO_3$ 5 μm	189.0	189.0
$CaCO_3$ 15 μm	377.0	377.0
$CaCO_3$-ID (test extender)	—	48.0
Water + additives	63.0	63.0
	1000.0	1000.0
Data		
Pigment volume concentration	73.8%	74.1%
Density of the liquid paint	15.52 lb/gal (U.S.)	15.37 lb/gal (U.S.)
Volume solids	63.1%	63.4%
Weight solids	80.3%	80.3%

Table 10—Formulation (L 131) of a Short-Oil Baking Enamel

Formulation	Pt. Wt.	Lb/100 Gal (U.S.)	Gal (U.S.)
Short-oil castor oil alkyd 60%	432.8	455.0	53.45
Highly reactive melamine resin 55%	146.0	153.5	19.16
Rutile titanium dioxide, enamel quality	294.5	309.5	9.05
Additives + solvents	126.7	133.2	18.34
	1000.0	1051.2	100.0
Data			
Pigment volume concentration (PVC)	19.4%		
Pigment:binder (100% solids)	0.87:1		
Alkyd:melamine resin ratio	76:24		
Baking conditions	30 min/120°C		

centage points for $CaCO_3$-UF and only 4 for $CaCO_3$-ID.

This can be explained by the shrinkage of the film as the last traces of solvents evaporate. The surface of the paint film takes up the contours of the underlying pigment and extender particles. As already noted, the $CaCO_3$-UF contains more, larger agglomerates than $CaCO_3$-ID resulting in a "rougher" surface. Paints manufactured with the easy dispersible $CaCO_3$-ID have not only a high initial gloss but also superior gloss retention. This makes such an extender of particular interest to the paint industry, including manufacturers of glossy filler-surfacers for automotive OEM coatings and glossy powder coatings. In the latter case, the easy dispersion of $CaCO_3$-ID helps to disperse the white and colored pigments during the extrusion process.

Two additional examples illustrate the advantages offered by an extender with a steep particle curve such as $CaCO_3$-ID; further interesting properties of a steep particle size distribution curve become evident.

Drying Time of Waterborne Coatings

The speed of drying such systems depends on the ease with which water molecules can escape to and evaporate from the surface of the coating. This is one of the most important criteria in physically drying waterborne road marking paints.

When the extenders contain ultra-fine particles, these block the micro-capillaries hindering the passage of water molecules. In contrast, the $CaCO_3$-ID does not contain such particles leaving the micro-capillaries free. This phenomenon is comparable to the passage of water in trees from the roots to the crown or with the flow of liquid wax in the wick of a burning candle.

The partial replacement of titanium dioxide by an iso-diametric extender can reduce the drying time of a road marking paint by 50% as shown in *Table* 9. The simple addition of $CaCO_3$-ID can shorten the drying time of a waterborne road paint from 17 to 7 min, a reduction of more than 50%. This was measured under ambient conditions using the drying-time-wheel according to ASTM D 711.

Shortening the drying time of water-reducible paints offers further opportunities for $CaCO_3$-ID, especially in primers. In wood primers, the fibers swell less since there is less time for them to absorb water. In anti-corrosion primers, it reduces the risk of flash-rusting during the drying process.

CaCO₃-ID as a Spacing Extender for the Partial Replacement of TiO₂

In North America, the paint industry used about 775,000 tons of TiO_2 in 1997.[6] Assuming that perfect dispersion and optimum formulation allows a saving of 10%, then 78,000 tons of this valuable, expensive raw material could have been saved. Evidently it is of great importance to the paint industry to use the technical properties of this raw material to the utmost by optimizing the formulation.

Which factors inhibit the perfect use of TiO_2? What can $CaCO_3$-ID do to improve its efficacy? These questions can be answered by the following example of the partial replacement of TiO_2 in a white baking enamel. The most important factors that hinder the optimum efficacy of TiO_2 in a paint system can be summarized as follows[7]: incomplete dispersion of TiO_2 agglomerates during the mixing process; flocculation caused by incomplete wetting of TiO_2 and unsuitable stabilization; and imperfect spacing of the TiO_2 particles in the dry film due to too high a TiO_2 volume concentration and crowding caused by shrinking of the film during drying, which forces the TiO_2 particles to pack too closely together.

What can a suitable extender do to improve the optical efficiency of titanium dioxide?[8] The main requirements are: good dispersion to break up TiO_2 agglomerates and hinder flocculation during drying[9,10]; suitable separation of TiO_2 in particular in the dry film (also referred to as spacing[11]; any single particle of a 0.8 μm spacing extender (e.g., $CaCO_3$-ID, replaces 64 particles of a 0.2 μm TiO_2 on an equal volume basis[12]); and good dried film appearance (i.e., maintain the gloss of the dried film and not cause hazing).

The results of trials with $CaCO_3$-ID as a partial replacement of titanium dioxide are given in the following example. The trials were carried out in a critical, short-oil baking enamel; the formulation is given in *Table* 10.

The partial replacement of titanium dioxide was carried out in two steps: on a volume basis, 6.25% and in a second step, 12.5% of the titanium dioxide was replaced. The enamel was made using a high speed disperser with a saw-tooth disc. It was dispersed for 15 min and the peripheral speed of the disc was 11 m/s (36 ft/s). The results are given in *Tables* 11 and 12.

The outstanding results can be explained by the narrow particle size distribution curve with practically no

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Table 11—Results—Dispersion, Gloss, and Hazing

TiO₂ (%)	100.00	93.75	87.50
CaCO₃-ID (%)	0 (basis)	6.25	12.50
Fineness of grind			
ISO 1524 (0 - 25 μm)	< 10 μm	< 10 μm	< 10 μm
Hegman (NS)	7.5	7.5	7.5
Gloss at 25° angle			
Goniophotometer	99%	97%	97%
Hazing (visual standards)a	0	0	1
	None	None	Virtually none
Gloss reduction after overbaking (60 min at 150°C)			
Percentage points	10	11	11

(a) 0 = no haze; 10 = very hazy.

Table 12—Results—Brightness and Opacity

Volume Replacement of TiO₂		Brightness (%)			
TiO₂ (%)	: CaCO₃-ID (%)	RX (red)	Ry (green)	Rx (blue)	Opacity (%)
100.00 :	0 (basis)	92.6	92.4	90.4	98.8
93.75 :	6.25	92.5	92.2	90.4	98.7
87.50 :	12.50	92.4	92.2	90.4	98.4

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ultra-fine particles below 0.2 μm. This is anther example of the excellent dispersion properties of $CaCO_3$-ID with a fineness of grind of under 10 μm measured using the 25 μm gauge. This ease of dispersion is comparable to that of a top quality titanium dioxide which is sold for the manufacture of industrial enamels using a high speed disperser.

There was scarcely any difference in the brightness, gloss, gloss retention after over-baking, or hazing compared to the original formulation that contained only titanium dioxide.

The values given in *Table* 12 show that virtually identical optical properties were achieved even when up to 12.5 vol% of the titanium dioxide was replaced on a volume basis by $CaCO_3$-ID.

SUMMARY

The examples given have shown that "still finer" does not necessarily mean "still better." Fineness as defined by top cut and median particle size must be supplemented by the steepness factor (SF) of the particle size distribution curve. A narrow particle size distribution extender (SF 1.5) – offers the following advantages over a product with a broad particle size distribution (SF 2.6): improved opacity of emulsion paints; easier dispersion; higher gloss and no hazing in oil-bound systems; shortening of the drying time, especially of water-borne systems, due to the capillary effect; and partial replacement of titanium dioxide by spacing and preventing reagglomeration.

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