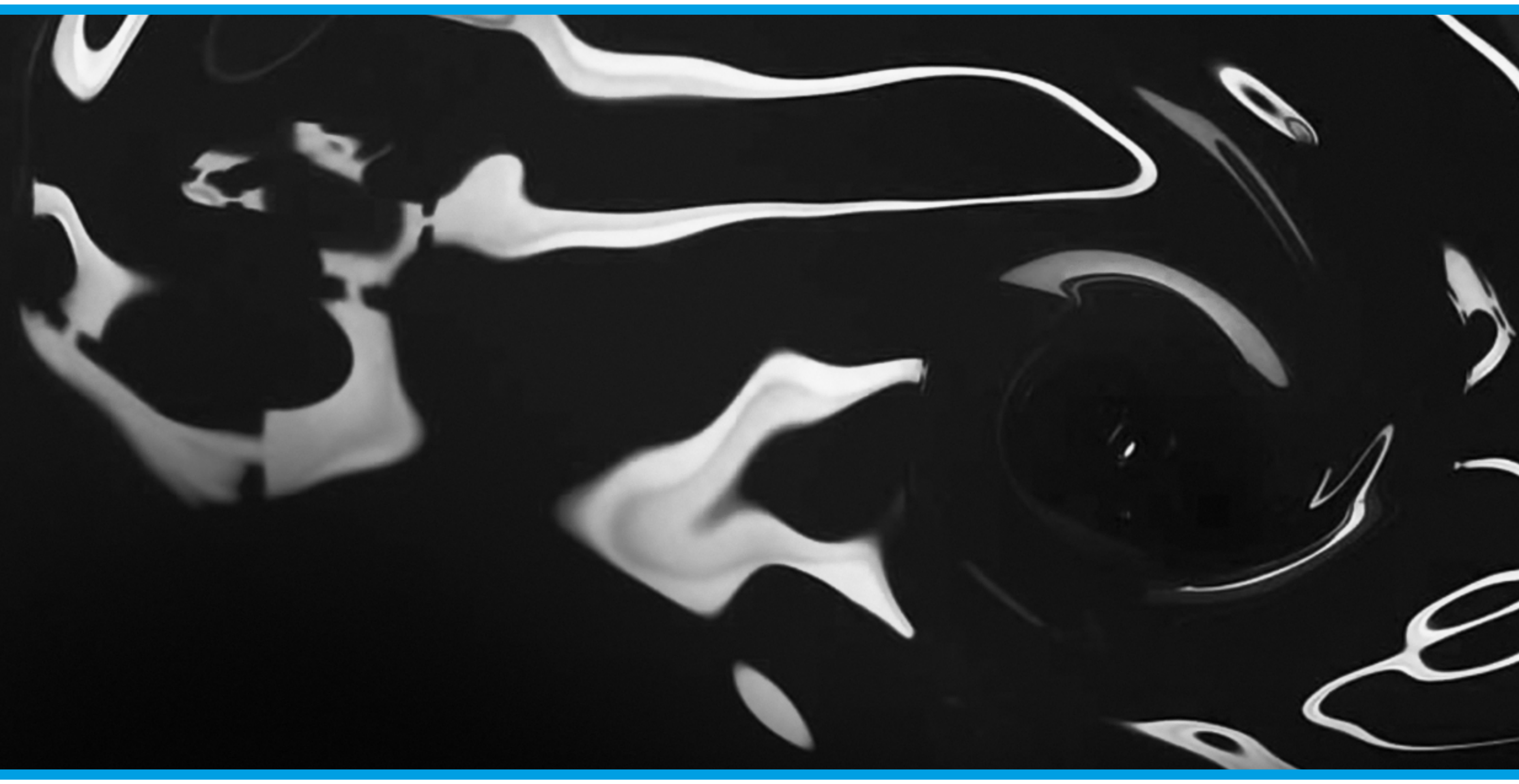
Short dispersion guideline for specialty carbon blacks in coatings

Technical Information 1375



ORION ENGINEERED CARBONS

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Contents

1 Introduction

The process of dispersion includes grinding and distribution of pigment particles evenly into a medium. The maximum colorimetric properties can only be achieved if a pigment is well dispersed and stabilized in a liquid system. Because of the small primary particle size and high surface area specialty carbon blacks are more difficult to disperse than other pigments. Poor pigment dispersion and stabilization can reduce colorimetric properties (jetness, undertone), tinting power and gloss.

Orion Engineered Carbons produces different types of specialty carbon blacks, whereof three types are commonly used in the coating industry. Related to their manufacturing process they differ in their properties (see Table 1).

Table 1

Orion types of specialty carbon blacks and their classification

<table>
<tr><th>Gas black pigments[1]</th><th>Furnace black pigments</th><th>Lamp black pigments</th></tr>
<tr><td>small mean primary particle size</td><td>mean primary particle size can be adjusted in a wide range</td><td>large mean primary particle size</td></tr>
<tr><td>narrow particle size distribution</td><td>adjustable particle size distribution</td><td>broad particle size distribution</td></tr>
<tr><td>high structure[2]</td><td>structure can be adjusted in a wide range</td><td>high structure</td></tr>
<tr><th colspan="3">Without oxidative after-treatment</th></tr>
<tr><td>acidic surface oxides</td><td>small quantities of basic surface oxides</td><td>neutral to basic surface oxides</td></tr>
<tr><td colspan="2">without oxidative after-treatment: mainly recommended for water-borne coatings</td><td rowspan="2">mainly recommended for tinting application</td></tr>
<tr><td colspan="2">with oxidative after-treatment: mainly recommended for solvent-borne coatings</td></tr>
</table>

1 By Degussa gas black process

2 Structure: degree of primary particle aggregation

Table 2

General relationship between particle size and coating properties

Small	Mean primary particle size	Coarse
darker	jetness (masstone)	lighter
blue	hue (masstone)	brown
more difficult	dispersibility	easier
higher	viscosity	lower
lower	Specialty carbon black loading	higher

2 Dispersion Process of specialty carbon blacks in general

Dispersion means more than breaking the agglomerates to aggregates, it also includes the wetting procedure with a liquid media, subsequent agglomeration breakup and stabilization of the formed dispersion. These individual steps are closely linked to one another and run simultaneously.

To obtain an optimal performance in a coating several steps are necessary:

- **Incorporation** of specialty carbon blacks into the binder or binder/additive to obtain a homogeneous paste.
- **Wetting:** replacement of the main part of the entrapped air in the specialty carbon black powder by the binder or binder/additive until the complete wetting of the pigment is achieved. The wetting process is influenced by viscosity, surface chemistry and porosity of the pigment.
- **Dispersion:** breaking specialty carbon black agglomerates into aggregates.
- **Stabilization** of the specialty carbon black aggregates by a complete wetting of the specialty carbon blacks with binder or binder/additive to prevent re-agglomeration[3].

The mill base formulation has to be adjusted concerning:

- Sufficient amount of binder/additive for a good wetting and stabilization of the pigment.
- The highest possible amount of specialty carbon black for economic reason.
- Viscosity: if the viscosity of the mill base is too low, abrasion of the grinding media occurs. If the viscosity is too high, the grinding media is immobilized and the shear force decreased. Also excess heat formation can harm temperature sensitive binders in highly viscous systems.

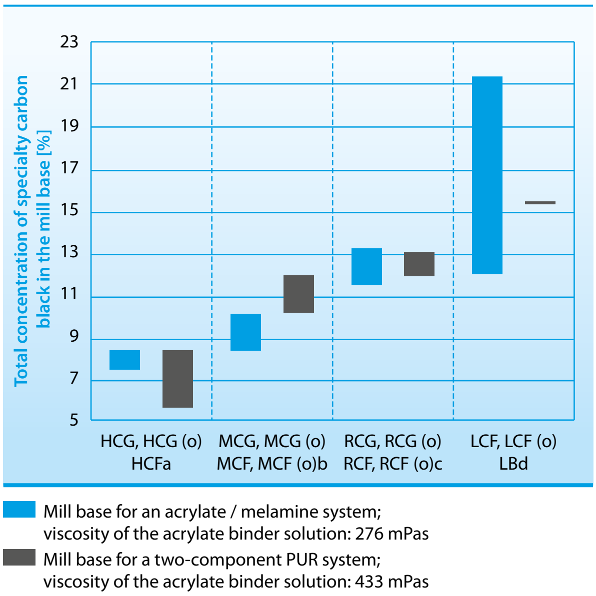
2.1 Dispersion in solvent-borne coatings

In figure 1 the recommended concentration of specialty carbon black is given for the use in two standard solvent-borne mill bases: an acrylate/melamine system and a two-component polyurethane system. Increasing the specialty carbon black concentration in a mill base increases the viscosity of the mill base paste. An optimal specialty carbon black to binder ratio has to be adjusted to obtain high shear forces that can efficiently disperse the pigment.

The specialty carbon black loading in the mill base is closely related to the mean primary particle size. With increasing mean primary particle size the maximum specialty carbon black content in the mill base can also be increased.

Figure 1

Recommended concentration of specialty carbon black in solvent-borne coatings in relation to the particle size of the specialty carbon blacks. Viscosities were measured with shear rates of 800 s^{-1} with a cone and plate 1 viscometer at 1° contact angle (at 23°C)[4]. At very small concentrations of SCB in the mill base, the viscosity of the binder solution is 168 mPas (acrylate mill base for AY/MF system) and 151 mPas (mill base for two-component PUR system).



[4] Thermo Fischer viscometer VT 550 [a] high color gas blacks (oxidized), high color furnace blacks

[b] Medium color gas blacks (oxidized), medium color furnace blacks (oxidized)

[c] Regular color gas blacks (oxidized), regular color furnace blacks (oxidized)

[d] Low color furnace blacks (oxidized), lamp black

3 To judge the performance of the specialty carbon black in a coating, systems with a minimal number of raw materials are recommended.

2.2 Dispersion in water-borne coatings

Water is a highly polar solvent with high surface tension and insufficient wetting properties for specialty carbon blacks. Thus, for a good dispersion and stabilization of specialty carbon blacks in water-borne coatings, the use of wetting and dispersing additives is absolutely necessary. The specialty carbon blacks and the polymeric dispersion additive and the binder have to be compatible with each other.

Two ways exist for preparing water-borne coatings:

- A mill base consisting of polymeric binder as aqueous dispersion or solution (that is stable against temperature and shear forces), wetting agent, defoamer, amine and pigment.
- A mill base without binder consisting of additives instead of the binder, defoamer, amine and pigment. The advantages of this system are the high specialty carbon black concentration, improved colorimetric properties and the universal applicability.

Much attention has to be paid to the adjustment of the pH value in both systems. For the respective binder the right tune of the pH value is necessary for the ideal performance of the coating.

3 Dispersion process

3.1 Dispersion equipment

There is a variety of existing dispersion equipments. It is important to choose the right equipment for a particular delivery form of specialty carbon black (see table 3).

The delivery forms of specialty carbon blacks cover wet beads, dry beads and powders. Dry beaded specialty carbon blacks are easier to handle because of high bulk density and reduced dust, but they are harder to disperse compared to specialty carbon black powder. The powdered delivery form causes more dust, has a low bulk density and poor flow properties, but it is easier to disperse. Specialty carbon black beads tend to settle out in comparison to the powder delivery form. When the delivery form or the dispersion equipment is changed, an adjustment of the mill base viscosity might be necessary.

3.2 Grinding media

The properties of the grinding media (density, size and material) have a wide influence on the dispersion results. The higher the specific density of the grinding media, the more energy is brought into the system and the better is the dispersion result. Examples for grinding media and their densities are listed below:

Grinding media	
Glass	~ 2.8 g/cm³
Porcelain	~ 3.0 g/cm³
Steatite	~ 2.6 g/cm³
Aluminum oxide (Al_2O_3)	~ 3.5 g/cm³
Zirconium-Silica	~ 3.9 g/cm³
Steel	~ 7.8 g/cm³

Table 3

Dispersion equipment

Dispersion aggregate	Shear force	Suitable for SCB delivered as	Remarks
Dissolver	low	powder	Mainly for premixing.
Rotor-stator (e.g. ULTRA-TURRAX®)	medium	powder, beads	Uses high speed rotation. The fluid is pressed through slits in static rings by centrifugal forces caused by rotating rings.
Ball mill	medium	beads	The assembly contains a rotating drum filled with beads (steel, porcelain, ceramic) which tumble inside the drum. The pigments are dispersed by the high shearing forces between the beads and the impact of the beads. These types of dispersion aggregates need long milling times.
Bead mill	medium	powder	The horizontal milling chamber is filled with grinding media. The grinding media is agitated by a shaft fitted with a number of pins. As the material moves upwards, it is subjected to high shearing forces between the grinding media, which results in the fine grinding of the pigments.
Sand mill	medium	powder, beads	Extra fine grained sand is used. An internal rotating disk causes centrifugal forces that throw the pigment/sand mixture against the mill wall.
Attrition mill	medium	powder	A vertical ball mill with internally agitated grinding media.
Skandex-shakers	medium	powder	For lab scale often shakers ("rüttler") are used. The mill base and grinding media (steel, glass, zr-si- or ceramic beads) are filled in special cups, sealed and shaked.
Three-roller mill	high	powder	A dispersing aggregate for high viscosity pastes that are pressed through a slit between two cylinders. Different rotational speeds of the cylinders generate high shear forces by a gradient in flow velocities in the paste.

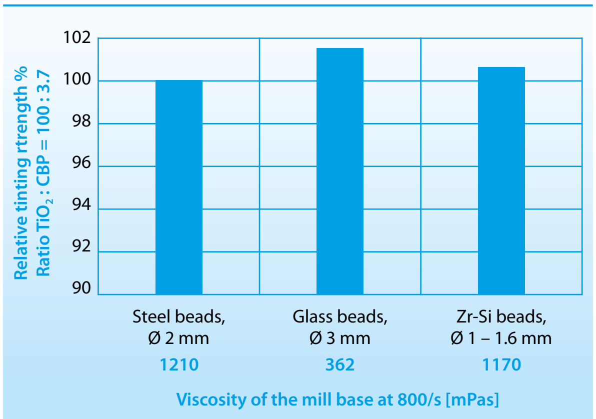
The smaller the grinding media size, the higher is the energy introduced into the system, since the number of collisions increases with $1/d^3$ (d = bead diameter). It is important to know the right relations in size between grinding media and pigment to avoid an excess of unutilized energy and abrasion of the grinding media, which can result in a bad dispersion. Softer conditions (medium dispersing intensity, low circumferential speed in the beginning, right sized grinding medium) lead to an optimum in dispersion.

Also the coating system is important: while steel beads are a possible grinding media for solvent-borne mill bases, in water-borne mill bases the beads would corrode fast.

Figure 2 displays the tinting strength of SPECIAL BLACK 4 in a two-component PUR system using different grinding media (dispersion time 60 min).

Figure 2

Influence of grinding media on relative tinting strength of SPECIAL BLACK 4. Ratio of specialty carbon black to binder solid: 35%.



With Zirconium-Silica and steel beads similar values in relative tinting strength were obtained. The smaller diameter of the Zr-Si beads compared to steel beads increases the number of beads and therefore the number of collisions during grinding. In case of the steel beads the number of collisions is lower, but the impact is higher because of the higher density compared to Zr-Si beads.

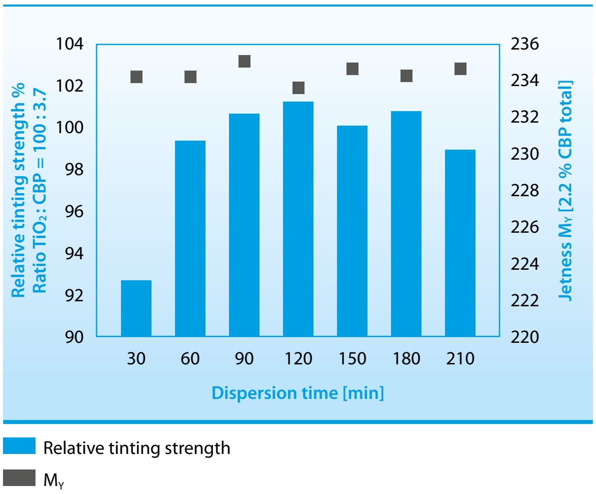
In case of the glass beads, an optimal tinting strength was achieved by lowering the viscosity of the mill base by reduction of the binder concentration.

3.3 Dispersion time

To show the dependency of relative tinting strength and jetness value M_Y on dispersing time, two-component polyurethane coatings with SPECIAL BLACK 4 (mill base dispersed for 30, 60, 90, 120, 150, 180 and 210 minutes) were prepared. Figure 3 illustrates an initial strong increase in tinting strength with dispersing times up to 60 min. The tinting strength finally converges to a maximum value within the error of measurement. In contrast no remarkable change of the jetness value M_Y can be observed.

Figure 3

Relative tinting strength and M_Y of two-component PUR coatings (white blend for tinting strength and 5% let down for M_Y) with SPECIAL BLACK 4 versus dispersing time of the mill base. Grinding media are steel beads with a diameter of 2 mm.



4 Stabilization with additives

The stabilization of specialty carbon blacks in coatings is mainly influenced by following parameters:

- Kind of specialty carbon black (e. g.: surface area, surface chemistry, manufacturing process)
- Kind of binder, whereas binder systems with integrated pigment affine groups are more efficient stabilizers
- Additives and solvents
- Dispersion conditions (milling equipment, grinding time and the viscosity of the mill base).

Poor specialty carbon black dispersion and stabilization typically result in flocculation, flooding/floating and sedimentation of the pigment, which finally reduces the colorimetric properties (e. g. masstone and tinting strength) and the gloss of the coating film. The attractive forces responsible for re-agglomeration of the pigments are effective only over relatively short distances. Dispersing additives are added to prevent this distance from dropping below a critical value. Plenty of wetting and dispersing additives exist, that enhance pigment wetting and stabilize the specialty carbon blacks in the coating formulation.

In solvent-borne coatings specialty carbon blacks are mainly stabilized sterically (see figure 4). Most of these wetting additives are bifunctional molecules with pigment affinic groups and solvent soluble parts. The solvent soluble part extends into the medium and separates the particles. Also the binder interacts with the pigment surface and stabilizes additionally. The grade of interaction between binder and pigment depends on the structure and polarity of the binder.

Electrostatic pigment stabilization is important in water-borne coatings (see figure 4). A mutual repulsion of the pigment particles results from the equally charged surfaces. The pigment surface is coated with ionic wetting and dispersing agents or non-ionic agents with segments of different polarity. The choice of ionic or non-ionic additives depends on the properties of the used pigment (e. g. grade of oxidation of specialty carbon black).

In coating systems with solubilized binder molecules, there is interaction between the pigment surface and the binder. In water-borne dispersions, where the binder exists as polymer lattices (binder in micelle) there is almost no interaction between binder and pigment surface, the stabilization and dispersion of the pigments has to be assured only by the wetting and dispersion agents.

To demonstrate the difference between poorly and well stabilized specialty carbon blacks in an acrylic coating film, Figure 5 shows two films: without and with additive. The jetness of the optimal dispersed and stabilized COLOUR BLACK FW 200 is higher compared to the not sufficiently stabilized pigment. The dM value, as a degree of stabilization of specialty carbon blacks in the coating, is higher with a good stabilization (bluish undertone).

Figure 4

Differences in stabilization in solvent- or water-borne coatings[5]

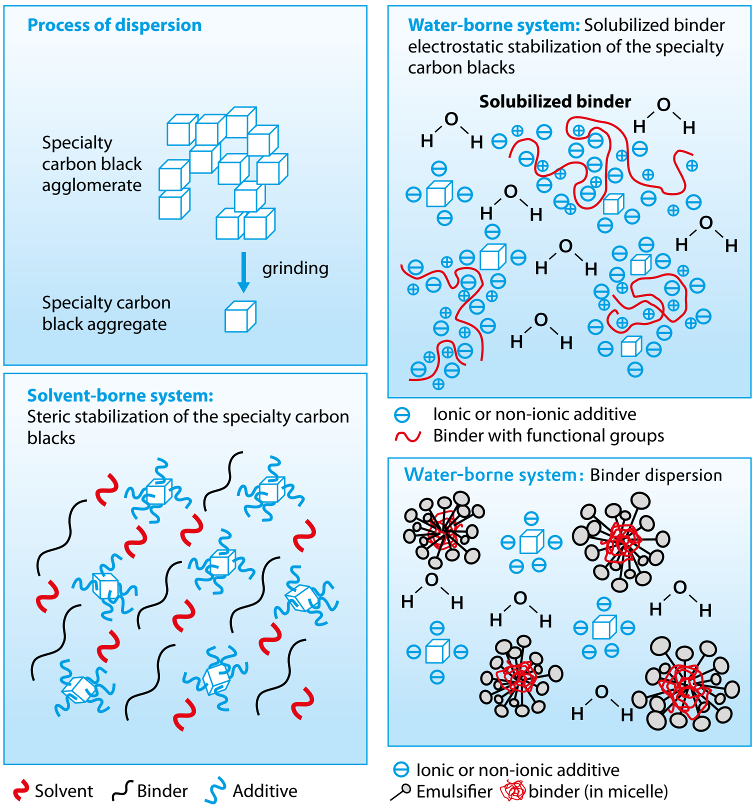
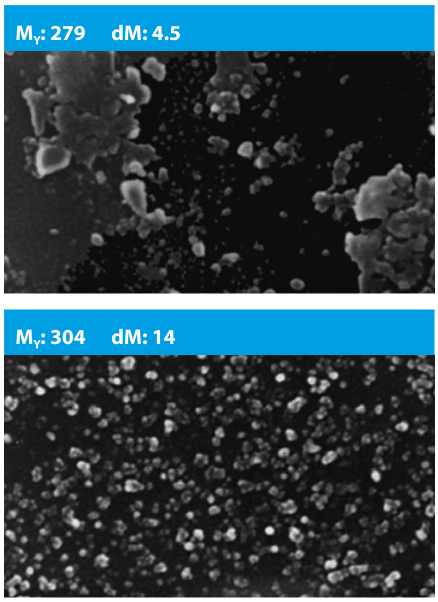


Figure 5

SEM Images of oxygen plasma treated acrylic coating films based on COLOUR BLACK FW 200 in LIOPTAL A 453 (Synthopol).

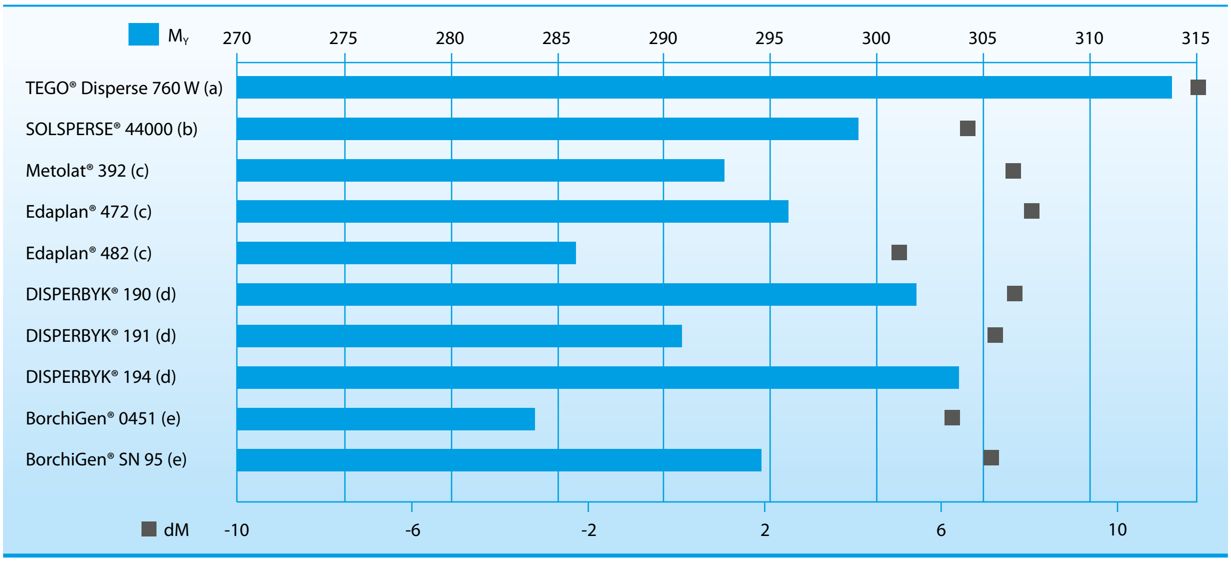


[5] Figure 4 is a modification of a picture of H.-G. Schulte (Cognis) presented at a VILF seminar. By courtesy of Mr. Schulte.

In water-borne coatings the usage of dispersing additives is essential. The dispersing additive concentration is recommended to be in the range of 0.5 – 2 mg per m^2/g particle surface. An overview about the jetness values of COLOUR BLACK FW 171 in a water-borne one-component PUR coating resulting from different dispersion agents is given in figure 6.

Figure 6

Influence of the dispersion additive on the colorimetric data of COLOUR BLACK FW 171 in water-borne PUR coating. 70% wetting agent (solid) based on specialty carbon black. (a) TEGO® Chemie, (b) Avecia, (c) Münzing-Chemie, (d) BYK, (e) Borchers.



5 Suggested formulations

To support proper formulation steps with specialty carbon blacks, we provide guideline formulations for several coating systems with different specialty carbon black grades. The coating formulations recommended here, are a testing standard formulation for different specialty carbon black types and therefore prepared with a minimum number of raw materials. We highly recommend to adjust the formulation to become a fully developed coating system, for example with addition of wetting and dispersion additives.

5.1 General dispersion procedure

Binder, solvent (and additive) are added one after another and mixed with a spatula. Finally the specialty carbon blacks is added and also mixed with a spatula. Premixing is done with a dissolver, (e.g.) Pendraulik, LR 34, tip speed: 8 – 10 m/sec. 5 min premixing with a dissolver ensures the complete wetting of the specialty carbon black with binder (and additives). For the dispersion step a dispersion cup is filled with one-third (volumetric) grinding media and one-third mill base. The cup is sealed and the mill base is dispersed for one hour with a "Skandex" Disperser, (e.g.) DAS 200 or BA S-20.

5.2 Solvent-borne mill base formulation

Table 4

Different mill base formulations based on COLOUR BLACK FW 200.

Mill base for alkyd/melamine stoving enamel		Weight /g
	ALKYDAL® F 310 SN, 60% (from Nuplex Industries)	55.0
	Shellsol A	18.4
	COLOUR BLACK FW 200	6.6
	Total	80.0
Grinding media	Steel pearls, Ø = 2 mm	550.0
(Ratio of specialty carbon black to binder (solid) = 20%)		

Mill base for two-component PUR system		Weight /g
	DEGALAN® VP 4157 L, 60% (from Evonik Industries)	55.0
	Butylacetat (98%)	18.4
	COLOUR BLACK FW 200	6.6
	Total	80.0
Grinding media	Steel pearls, Ø = 2 mm	550.0
(Ratio of specialty carbon black to binder (solid) = 20%)		

Mill base for acrylate/melamine stoving enamel		Weight /g
	Lioptal A 453, 65% (from Synthopol)	41.4
	Diluent*	25.2
	BorchiGen® 0451 (from Bochers)	5.7
	COLOUR BLACK FW 200	8.1
	Total	80.0
Grinding media	Steel pearls, Ø = 2 mm	550.0

(Ratio of specialty carbon black to binder (solid) = 25%)

* Diluent: butylacetate (85%)/xylole/butanole: 60%/28%/12%

Table 5

Different mill base formulations based on PRINTEX® G.

Mill base for alkyd/melamine stoving enamel		Weight /g
	ALKYDAL® F 310 SN, 60% (from Nuplex Industries)	50.8
	Shellsol A	17.0
	PRINTEX® G	12.2
	Total	80.0
Grinding media	Steel pearls, Ø = 2 mm	550.0
(Ratio of specialty carbon black to binder (solid) = 40%)		

Mill base for two-component PUR system		Weight /g
	DEGALAN® VP 4157 L, 60% (from Evonik Industries)	50.8
	Butylacetat (98%)	17.0
	PRINTEX® G	12.2
	Total	80.0
Grinding media	Steel pearls, Ø = 2 mm	550.0
(Ratio of specialty carbon black to binder (solid) = 40%)		

Mill base for acrylate/melamine stoving enamel		Weight /g
	Lioptal A 453, 65% (from Synthopol)	35.7
	Diluent*	24.8
	BorchiGen® 0451 (from Bochers)	7.3
	PRINTEX® G	12.2
	Total	80.0
Grinding media	Steel pearls, Ø = 2 mm	550.0

(Ratio of specialty carbon black to binder (solid) = 40%)
* Diluent: butylacetate (85%)/xylole/butanole: 60%/28%/12%

5.3 Water-borne mill base formulation

Table 6

Binder-free mill base formulation based on COLOUR BLACK FW 171.

		Weight /g
	Water, dest.	36.2
	TEGO® Dispers 760 W, 35% (from TEGO® Chemie)	28.8
	TEGO® Foamex 830 (from TEGO® Chemie)	0.4
	DMEA (neutralization agent)	0.2
	Specialty carbon black e.g. COLOUR BLACK FW 171	14.4
	Total	80.0
Grinding media	Chromanit steel pearls, Ø = 3 mm	540.0

(Specialty carbon black total =18%; ratio of wetting agent (solid) to specialty carbon black = 70 %): The let down is done with a clear coat containing the 1-component PUR binder Alberdingk U9800® from Alberdingk & Boley®.

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