

**SPECIALTY CARBON BLACKS  
IN MODERN COATING SYSTEMS**

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Industry Information 0402

## FOREWORD

This issue of the Industry Information deals with the use of specialty carbon blacks – the most important black pigment by far – in paints. Priority is given to powder coatings, UV coatings and water-borne systems. Besides the basics relevant for these applications, the incorporation of specialty carbon black in coating systems, as well as their performance and colorimetric properties, are described in detail. Suggested formulations for practical use round out the bulletin.

In addition, the weathering results of some high-jetness black coatings obtained with a new procedure of the Federal Institute of Material Testing (ADF test) in comparison to the established Florida test, are presented.

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## 1 INTRODUCTION

The production of specialty carbon black amounted to approximately 13 million metric/tons worldwide in 2016. Out of this, more than 70% was used as reinforcing filler in rubber products, with automobile tires accounting for the vast majority. The balance was used in printing inks, plastics and coatings. Specialty carbon black manufactured by thermal oxidative degradation of liquid or gaseous hydrocarbons is the predominant specialty carbon black in the coatings industry today. The traditional specialty carbon blacks, also based on carbon, such as vine black, diamond black, bone black or the variants of black tar pigments are practically irrelevant today.

## 2 MANUFACTURE

### 2.1 General

Furnace and lamp black were produced over 4,000 years ago in China and Egypt for inks and dyes by incomplete combustion of organic substances. In ancient Greece, the Roman Empire and during the Middle Ages, these techniques of specialty carbon blacks production were continued. Following the invention of printed books, the demand for specialty carbon blacks rose sharply.

Numerous small businesses arose to satisfy this demand, mostly with specialty carbon blacks from highly resinous pine. In the 19th century, the channel process was developed as the first large-scale industrial process for specialty carbon black production, with abundantly available natural gas being used as a raw material. Production boomed when the reinforcing effect of specialty carbon black in automobile tires was discovered. The processes used today on a large industrial scale for specialty carbon black production and the required raw materials are listed in Table 1 (1), (2). Specialty carbon blacks obtained by thermal decomposition of liquid or gaseous hydrocarbons are of no relevance to the coatings industry.

**Table 1**

**Specialty carbon black manufacturing methods**

CHEMICAL PROCESS	MANUFACTURING METHOD	IMPORTANT RAW MATERIALS
Thermal oxidative decomposition	Furnace black process	Aromatic oils from coal or petroleum, natural gas
	Channel black process	Natural gas
	Gas black process (developed by Orion Engineered Carbons)	Coal tar distillate
	Lamp black process	Aromatic oils based on petroleum or coal
Thermal decomposition	Thermal black process, acetylene black process	Petroleum (oils), acetylene

## 2.2 Processes

Orion produces specialty carbon black by three processes, which are briefly described as follows.

In the gas black process, a hydrogen-containing carrier gas is pumped over hot creosote. The evaporated part of the creosote is burned incompletely by numerous small flames. These flames are directed towards water-cooled rollers on which the majority of the specialty carbon black formed is deposited. The balance is separated by a filter system and merged with the first product stream. The specialty carbon blacks produced by this process feature excellent fineness and a very narrow primary particle size distribution. They have a distinctive agglomerate structure, which facilitates dispersion in liquid systems but also increases viscosity. Other characteristics of gas blacks are their high purity and distinctive hydrophilic particle surface. A precursor of the gas black process was the channel black process developed in the United States. In this process, many small flames were fueled with natural gas, which burned in contact with water-cooled iron channels. The channel process was discontinued because of the very low yield.

The furnace black process is the predominant process used for the production of specialty carbon black. In this process, the liquid raw material is fed through nozzles into a flame of hot air and natural gas, and decomposed by thermal oxidation at high temperatures. The specialty carbon black is separated from the gases by filter systems. The furnace black process is flexible in that it allows for variability in regards to the raw materials and process parameters. The flexibility allows the production of a wide range of specialty carbon blacks having different properties.

Specialty carbon blacks obtained by the lamp black process are unrivaled for some fields of application. So this process, which may seem outmoded, is still indispensable. Core piece in such a plant is a tank that holds the liquid raw material situated under a fireproof hood. The incomplete combustion can be controlled by the gap between the tank and the hood. Lamp blacks feature large primary particles, a wide primary particle distribution and hence low agglomeration and relatively high tamped densities of over 250 g/l.

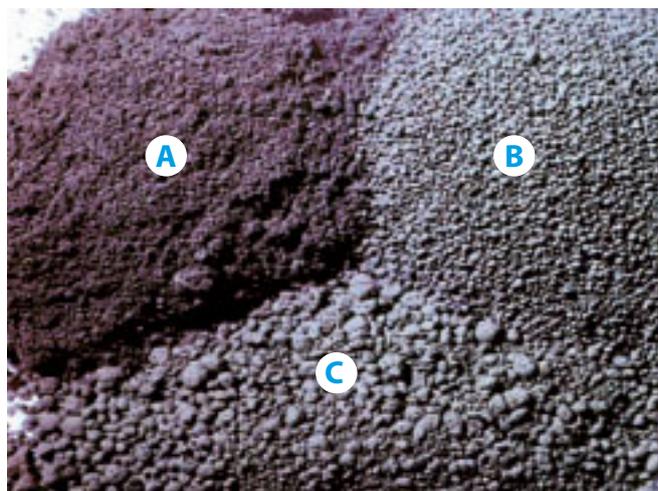
By contrast, gas blacks in powder form have tamped densities between 50 and 200 g/l. The tamped densities for furnace blacks range from 150 to 450 g/l. It is also noteworthy that lamp black is nearly similar in purity to gas black.

## 2.3 Delivery forms

Gas and furnace blacks are produced as very loose powders that are hard to handle. Therefore, they are compressed or granulated. A wet granulation process produces large stable granulates, which also afford easy, almost dust-free handling. However, they are unsuitable for use in the coatings industry because of their high mechanical stability. Besides powdered specialty carbon blacks, dry beaded specialty carbon blacks, which have relatively good dispersion properties, are offered for this application (see figure 1 and table 2).

**Figure 1**

**Delivery forms of specialty carbon black**



A) Powder specialty carbon black, B) Dry beaded specialty carbon black, C) Wet beaded specialty carbon black

**Table 2**

**Comparison of powder specialty carbon black and dry-beaded specialty carbon black**

	ADVANTAGES	DISADVANTAGES
Powder specialty carbon black	More readily dispersible	Dust generation, high volume, poor flow properties
Dry-beaded specialty carbon black	No dust Low bulk volume Easy to handle	Harder to disperse

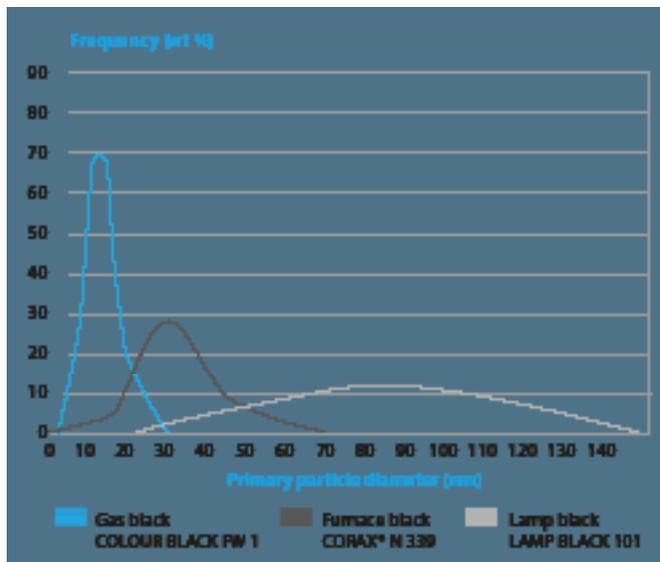
### 3 PROPERTIES OF SPECIALTY CARBON BLACK

#### 3.1 Particles and structure

The primary particle size is mentioned to indicate the application properties of specialty carbon blacks. Specialty carbon black is supplied in the form of tightly bonded aggregates of primary particles, varying in size and shape to impart specific application properties. The average primary particle size of specialty carbon blacks is in the colloidal range and depend to a large extent on the manufacturing process. Average primary particle size can be adjusted with the gas black process, while the lamp black process features relatively large average primary particle size. These coarse specialty carbon blacks also exhibit a very wide primary particle size distribution. The furnace black process affords the greatest range of variation, and the primary particle size can be well adjusted. Generally, the primary particle size distribution curve becomes wider with increasing mean primary particle size (see figure 2). The average primary particle size and the primary particle size distribution are primarily responsible for the performance properties – particularly the colorimetrics of the coating (see table 3).

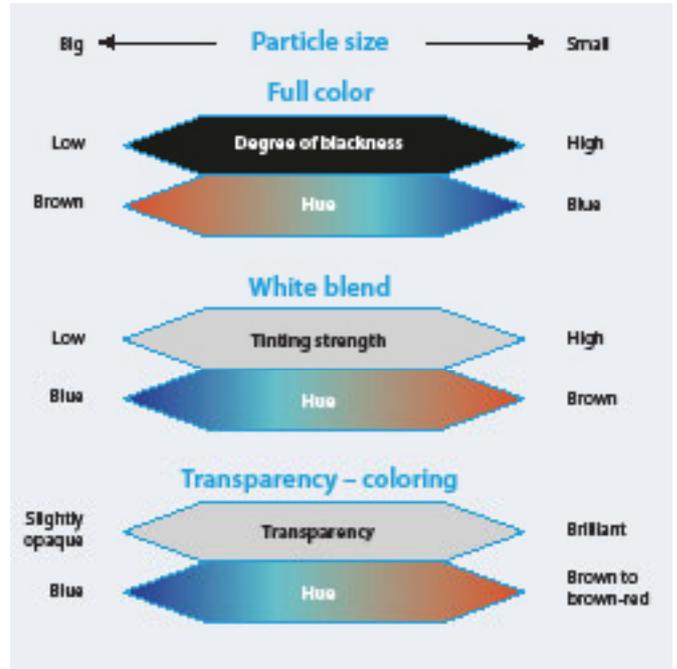
**Figure 2**

Primary particle size distribution curves of three specialty carbon blacks manufactured by different processes



**Table 3**

Influence of the primary particle size of specialty carbon blacks on the colorimetric properties of coatings

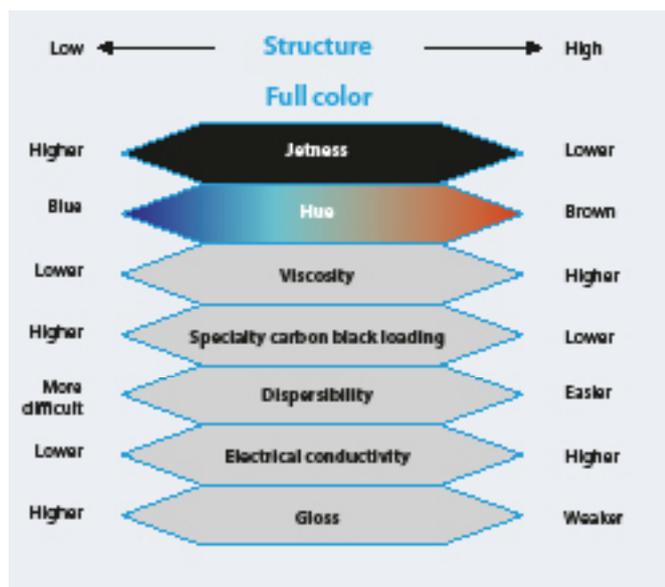


Naturally, specialty carbon black particles are not present in isolated form. They form aggregates by chemical adhesion and agglomerates by physical interactions (see DIN 53206) (3). While the aggregate size of gas blacks and lamp blacks is hard to control, it can be adjusted in furnace blacks by adding alkali metal or ammonium salt solutions to the flame. The degree of aggregation of specialty carbon blacks is known as structure. Specialty carbon blacks with a high degree of aggregation are called high-structured, while those with low aggregation are called low-structured. The agglomerates of specialty carbon blacks show fractal structure (4).

Oil absorption according to ISO 4656 (OAN=Oil absorption number) is a gauge of structure. It is given in ml oil per 100 g of specialty carbon black. Low-structured specialty carbon blacks have values of less than 70 ml oil per 100 g while high-structured specialty carbon blacks have values of over 100 ml oil per 100 g. Middle-structured specialty carbon blacks are an intermediate class. The influence of structure on the performance of a specialty carbon black in coatings is given in table 4.

**Table 4**

**Influence of the structure of specialty carbon blacks on the performance properties of coatings**

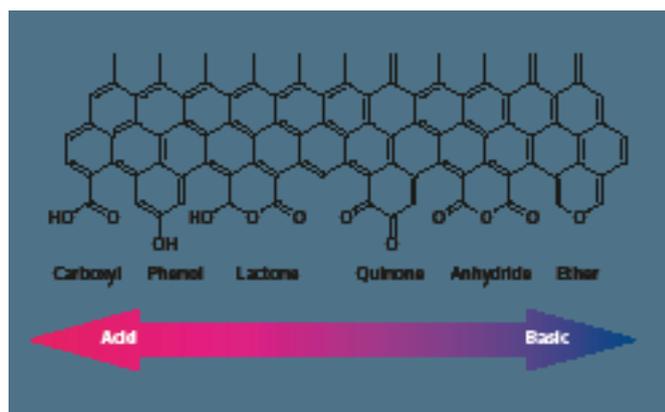


### 3.2 Surface chemistry

Specialty carbon black particles are spherical and consist of paracrystalline carbon layers reminiscent of graphite structure. On the particle surface, the free valences are saturated by different organic groups, which are crucial to the interaction between the specialty carbon black particles and other coating components (see figure 3) (5).

**Figure 3**

**Surface groups of specialty carbon blacks**

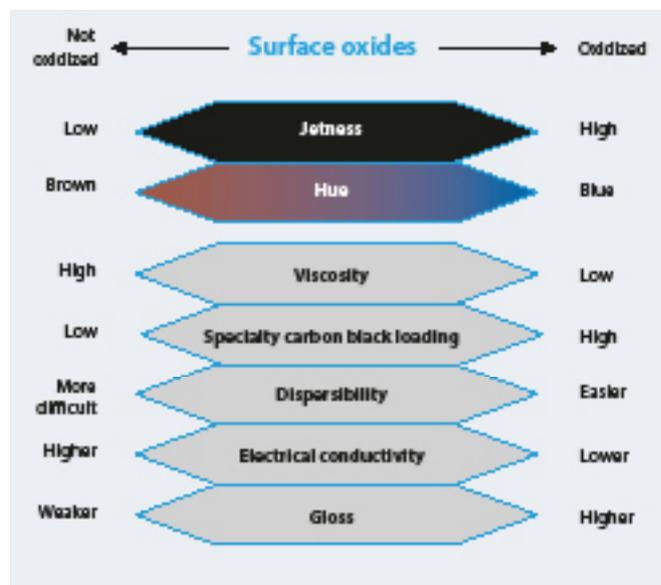


If we consider that a gas black has a specific BET surface of up to 500 m<sup>2</sup>/g and a furnace black has a BET of up to 450 m<sup>2</sup>/g, the significance of surface chemistry of a specialty carbon black for its performance in coatings is quite evident. Untreated gas blacks show a weak acidic reaction while furnace blacks show a weak basic reaction and lamp black has a neutral reaction. To make the particle surface more polar and hence to elevate the interaction with polar solvents and binders, specialty carbon blacks are oxidized. Strong oxidants such as nitrogen oxides, nitric acid or ozone are used for this. This treatment elevates the number of oxygen-containing groups, particularly carboxyl groups. In gas blacks, this reduces the pH by oxidation only slightly, by 1–2. In the case of furnace blacks, the pH drops by approximately 6. This significant difference is naturally due to the definition of the pH.

Another criteria for description of an oxidized specialty carbon black is the content of volatile matter, which is determined according to DIN 53552 by heating for 7 min at 950°C. The content of volatile matter is increased by oxidation from 5 to 20% in very high-grade gas blacks and from 1 to 12% for a high-grade furnace black. The effect of surface oxidation on the performance in coatings is shown in **table 5**.

**Table 5**

**Influence of the surface oxidation of specialty carbon blacks on the performance**



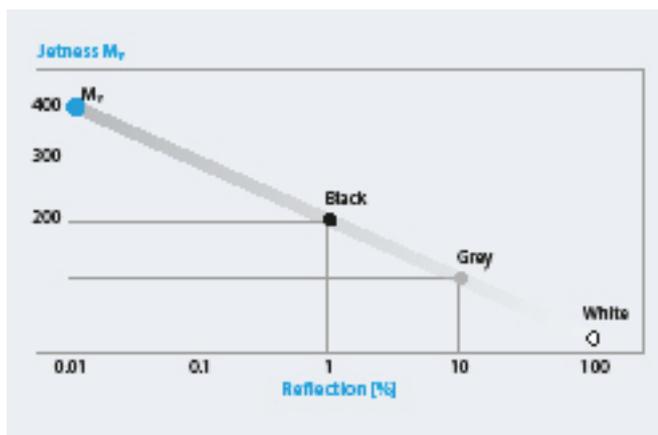
### 3.3 Colorimetric aspects

Generally, with regard to mass tone coloration, a decrease in mean primary particle size of specialty carbon black and of the aggregates leads to an increase in the jetness. The surface appearance of the hue has an increasing bluish undertone, which elevates the visual blackness. In the transparent view, an increase in brownish undertone is observed. However, larger specialty carbon blacks show a brownish undertone on the surface and a blue undertone in the transparent view.

In a white blend with titanium dioxide, the tinting strength of specialty carbon black also increases with decreasing mean primary particle size. In terms of hue, however, the behavior observed is opposite to that of mass tone coloration. The finer the specialty carbon black particles, the more intense the brown tint. Coarser particles provide a more intense blue tint. It must be taken into account that such a white blend generally shows a tendency towards a blue tint, because the red component of the light penetrates more deeply and is therefore absorbed more intensely by the specialty carbon black particles. A decreasing particle size of the titanium dioxide produces an increasing blue tint (6). In the case of transparent colorations, a brown hue is achieved with a fine-particle specialty carbon black, while a coarse-particle specialty carbon black produces a blue hue with reduced transparency.

**Figure 4**

Jetness  $M_Y$  as a function of reflection



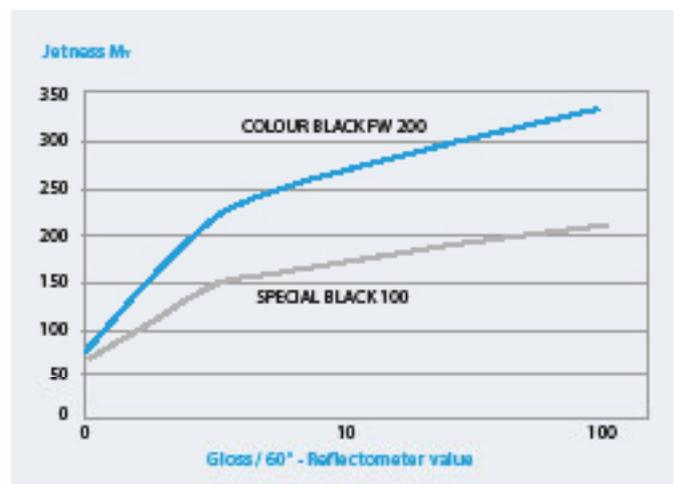
The jetness or “blackness” of specialty carbon blacks can be quantified by the color-independent blackness value as the  $M_Y$  value according to DIN 55979, using a paste of the specialty carbon black with boiled linseed oil. The paste is applied to a glass plate under precisely defined conditions and the reflection of the green component, responsible for the brightness sensation, is measured. The reflected fraction is converted to the  $M_Y$  value (see glossary) (7). Figure 4

illustrates how the decreasing reflection is taken into account in a super-proportional manner, as is usually the case with a logarithmic scale. In black coatings, specialty carbon blacks show  $M_Y$  values between 200 and 300 and even above.

The color-dependent blackness value  $M_c$  can be determined with additional colorimetric tests (see glossary) (8). The hue of the black coloration  $dM$  can be determined from the difference between  $M_c$  and  $M_Y$ . Gloss has a major influence on the measurable jetness of a black paint and on the subjective “black perception” of an observer. As a rule of thumb, the lower the gloss, the lower the jetness (figure 5 illustrates this).

**Figure 5**

Jetness of a black coating as a function of gloss



There are very few exceptions. One of these is top coats for artificial leather, where combinations of highly transparent silica-based matting agents are used. In table 6 the specialty carbon blacks were classified according to their jetness.

**Table 6**

Colorimetric classification of specialty carbon black by jetness

GAS BLACKS	$M_Y$	FURNACE BLACKS	$M_Y$
HCG	> 270	HCF	> 260
HCG (o)	> 270		
MCG	250 – 270	MCF	250 – 260
MCG (o)	250 – 270		
RCG	< 250	RCF	240 – 250
RCG (o)	< 250	RCF (o)	240 – 250
		LCF	< 240

HC = High color, MC = Medium color, RC = Regular color, LC = Low color, G = Gas black, F = Furnace black, o = oxidized

## 4 APPLICATIONS

Specialty carbon blacks are used in paints and coatings for mass tone coloration, tinting of white and colored coatings, including decorative paints, and for transparent coloration. For mass tone coloration of solvent-borne coatings, the use of fine particle sized oxidized gas blacks (HCG (o)/MCG (o)) and oxidized furnace blacks (HCF (o)) are preferred. Untreated fine particle sized gas and furnace blacks (HCG/HCF) are also used in water-borne coatings, for reasons of pH stability. The amount to be added depends on the type of specialty carbon black, the coating system and the required colorimetric properties. As a rule, the concentration ranges from 3 to 6% based on binder. A requirement to optimize the performance of a specialty carbon black is the presence of the smallest possible sufficiently stabilized agglomerates. Oxidized specialty carbon blacks have been found in most cases to have less tendency to flocculate than untreated ones.

The stabilization of specialty carbon blacks in the liquid coating is frequently assured in solvent-containing systems by use of additives. In water-borne coatings, the use of additives is essential. In some cases, 50% or more additive must be added based on specialty carbon black. Whichever of the numerous available additives is best, must be determined experimentally.

The structure and delivery form must also be considered in the processing of specialty carbon blacks. Highly structured specialty carbon blacks, though easier to disperse, have a higher thickening effect. Dry-beaded specialty carbon blacks, though easier to handle, require greater dispersion effort. In any case, it is recommended to use the most intensive possible dispersion to fully utilize the colorimetric properties of the specialty carbon black. In many cases, specialty carbon black preparations facilitate the manufacture of black or tinted coatings. These semi-finished products are commercially available or are manufactured by specialized companies under contract according to customer specifications.

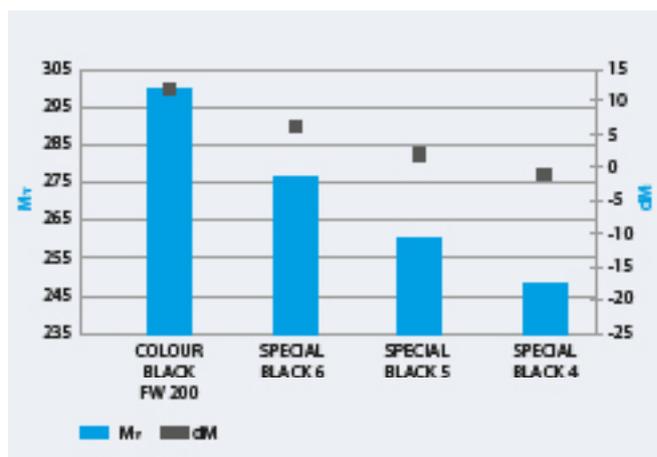
### 4.1 Solvent-borne coatings

#### 4.1.1 Alkyd resin systems

Figure 6 shows the jetness values of four high-grade oxidized gas blacks in an alkyd-melamine stoving enamel. Jetness decreases with increasing mean primary particle size. COLOUR BLACK FW 200 with a small mean primary particle size reaches a jetness  $M_V$  of 300 at a concentration of 5% based on binder, while SPECIAL BLACK 4 with a medium mean primary particle size generates a jetness  $M_V$  of 248. For the preparation of these black coatings, a mill base was premixed 5 min. with a Lab-dissolver (Pendraulic LR 34, tip speed 8.4 m/s) and subsequently dispersed for 1 hour (Skandexdispenser DAS 200 or BAS 20 from LAU® Company). 550 g steel beads: (diameter: 2 mm) were used as a grinding media. As an example, table 7 shows a formulation for a coating with COLOUR BLACK FW 200.

**Figure 6**

Jetness  $M_V$  of oxidized gas blacks (COLOUR BLACK FW 200 and SPECIAL BLACKS 4, 5 and 6) with different mean primary particle sizes in an Alkyd-melamine stoving enamel with a concentration of 5%



**Table 7**

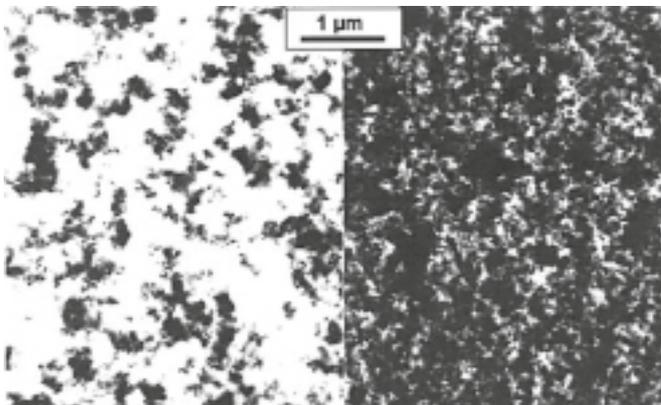
Solvent-borne mill base formulation based on COLOUR BLACK FW 200 (ratio of specialty carbon black o Binder = 20%)

COMPONENTS	PARTS BY WEIGHT, g
Alkydal F 310 60% (Bayer)	55.0
Shellsol A	18.4
COLOUR BLACK FW 200	6.6

Figure 7 shows the differences in tinting capability between a non-oxidized gas black and an oxidized one. The two specialty carbon blacks are COLOUR BLACK S 170 and SPECIAL BLACK 6. The latter is oxidized, and, because of its higher dispersibility, is better distributed in the alkyd-melamine system than the non-oxidized specialty carbon black, COLOUR BLACK S 170. This results in a more homogeneously tinted coating, which looks blacker and also has a bluer undertone. Whether a specialty carbon black has a blue or brown undertone in a coating depends essentially on its stabilization in the system.

**Figure 7**

TEM photo of the coatings surface of an alkyd-melamine stoving enamel with an untreated specialty carbon black (left) and an oxidized specialty carbon black (right). Both specialty carbon blacks have the same mean primary particle size and were used at a concentration of 5%



In a coating with a blue undertone, the interaction of the specialty carbon black with the binder polymer is more intensive. This results in lower-sized specialty carbon black agglomerates, which scatter the blue light more intensively. In a coating with a brown undertone, the dispersion of the specialty carbon black is less than optimal, and the agglomerates are larger than in a coating with a blue undertone. The larger agglomerates result in more intensive Rayleigh scattering of the blue fraction of the light in the forward direction, so more of the red and/or brown fraction persists for the backscattering, and this is responsible for the color impression of coatings with full color.

With an ionized oxygen plasma (9), it is possible to etch the surface of a specialty carbon black tinted coating and subsequently investigate the surface by scattering electron microscopy (SEM). Using this method, the different sizes of agglomerates in a coating can be clearly visualized.

Figure 8 shows the SEM photo of a COLOUR BLACK FW 200 based coating in an acrylate system, treated as described. An optimum state of dispersion was achieved using a dispersion additive. This is evident in the homogeneous distribution of the aggregates (no agglomerates any more) in the system and in the blue undertone of the coating.

**Figure 8**

SEM photo of an oxygen plasma-treated coatings film based on COLOUR BLACK FW 200 and Lioptal A 453 with a dispersion additive

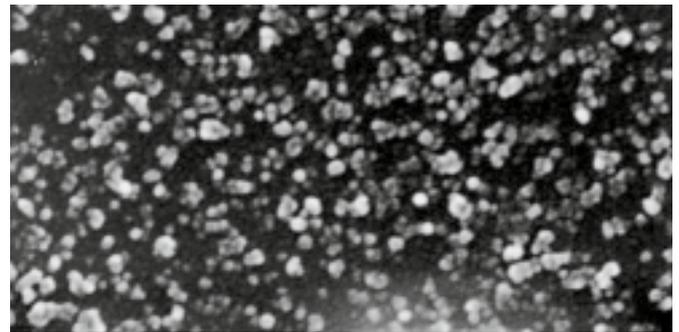
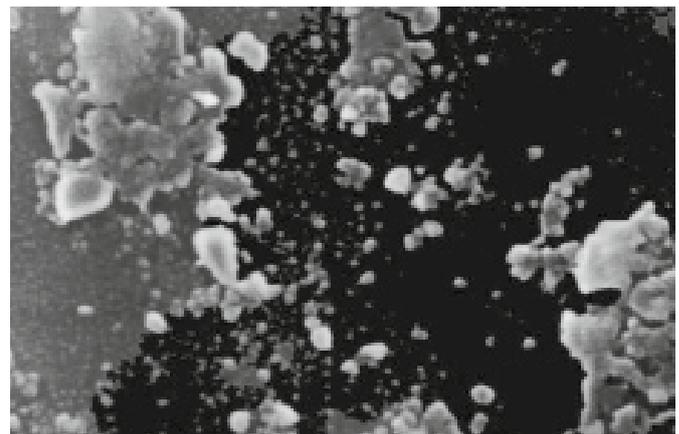


Figure 9 shows the SEM photo of the same coating, with COLOUR BLACK FW 200, without the addition of a dispersion additive. The larger agglomerates are clearly visible and are responsible for the brown undertone of the coating.

**Figure 9**

SEM photo of an oxygen plasma-treated coatings film based on COLOUR BLACK FW 200 and Lioptal A 453 without a dispersion additive



### 4.1.2 Acrylate resin systems

Particularly in the automotive field, acrylate resin systems are frequently used. The elastic-mechanical properties of this binder class are much better in comparison to alkyd binders. However, the wetting properties of specialty carbon blacks in acrylate resins are inferior than in alkyd resins, mandating the use of dispersion additives for some acrylate resins to achieve deep black coating surfaces with a bluish undertone. Various specialty carbon blacks have been investigated in two acrylate systems.

#### Binders and additives used

##### 1. Two-component system:

**Degalan VP 4157** (OH group-containing acrylate), Evonik

**Desmodur N 75** (isocyanate-containing polymer), Bayer, Leverkusen

##### 2. Acrylate/Melamine system 70/30:

**Lioptal A 453** (acrylate polymer); Synthopol-Chemie, Buxtehude

**Maprenal MF 590** (melamine resin), Ineos Melamines GmbH, Frankfurt

**BorchiGen® 0451** (wetting and dispersing additive), Borchers, Leverkusen

In the solvent-containing systems, tinting was done using 5% specialty carbon black.

#### Manufacture of black coatings (Solvent-borne systems)

A 5 min predispersion was done with a Pendraulik LM 34 dissolver at 4000 rpm and a disk diameter of 40 mm (circumferential speed: 8.4 m/sec). The main dispersion was done with a Skandex-disperser (DAS 200 or BAS 20). The grinding medium used was 550 g of steel beads 2 mm in diameter and a 60 min dispersion time. Table 8 shows, as an example, the mill base formulation of an acrylate system with COLOUR BLACK FW 200.

**Table 8**

**Mill base formulation for an Acrylate binder with COLOUR BLACK FW 200**

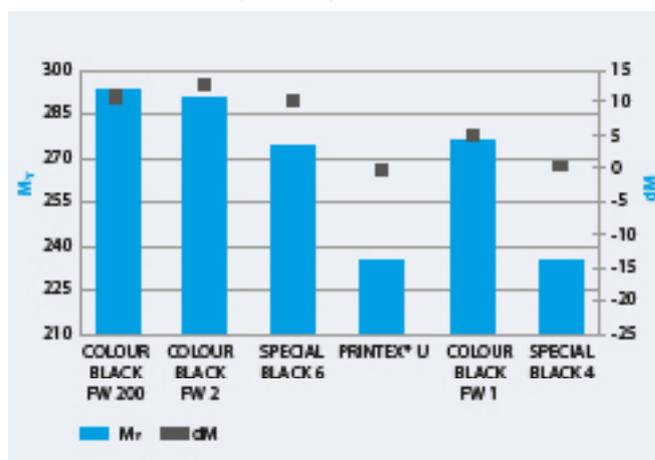
COMPONENTS	PARTS BY WEIGHT
COLOUR BLACK FW 200	8.1
Lioptal A 453, 65%	41.1
Dilution*	25.1
BorchiGen® 0451, 100%	5.7

\* Dilution = 60% Butylacetate (85%), 28% Xylol, 12% Butanol

As we see in figures 10 and 11, the use of COLOUR BLACK FW 200 or COLOUR BLACK FW 2 is recommended for high-jet applications such as coatings for automobile assembly lines. These specialty carbon blacks provide the jetnesses, particularly the blue tints, required by the industry. In both systems, the two-component system Degalan VP 4157 and the acrylate system Lioptal A 453, COLOUR BLACK FW 200 is the superior black.

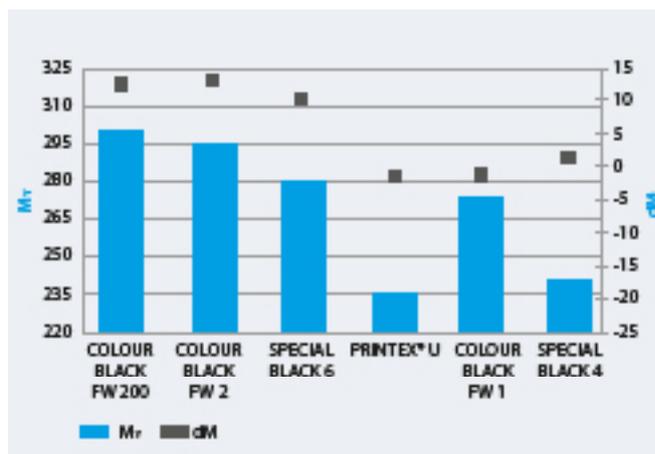
**Figure 10**

**Colorimetric data of the system Degalan VP 4157/Desmodur N 75 at 5%**



**Figure 11**

**Colorimetric data of the system Lioptal A 453/Maprenal MF 590 at 5% without clear coat**



For the most part, specialty carbon blacks with low jetness are used for tinting. Untreated and oxidized gas blacks (RCG), untreated and oxidized furnace blacks (RCF and LCF) and LAMP BLACK 101 can be used. In grey coatings, the coarser specialty carbon blacks produce a blue tint, while the more finely divided ones tend to produce a brown tint. When specialty carbon blacks are used in combination with white or colored pigments, the specialty carbon blacks are more sensitive to the other coatings components than other pigments, because of their complex surface chemistry, extreme fineness and special morphology (10).

#### 4.2 Water-borne coatings

Water-borne coatings will continue to gain importance in comparison to solvent-borne systems. In Germany, more than 90% of all automobile assembly line coatings were water-borne in the year 2000. For the use of specialty carbon black in water-borne coatings, special precautions must be taken, because water is a highly polar solvent with high surface tension and has insufficient specialty carbon black wetting properties. Therefore, the specialty carbon black and also the polymer dispersion additive or binder must be carefully selected and compatible with each other. Table 9 shows coating relevant properties of two organic solvents in comparison to water.

**Table 9**

**Physical properties of solvents**

PRODUCT PROPERTIES	UNIT	BUTYL ACETATE	XYLENE	WATER
Heat of evaporation	kJ/kg	309	342	2453
Boiling point	°C	126	139	100
Evaporation rate		12	13	80
Surface tension	mN/m	29	29	73
Solidification point	°C	-77	-50	0

#### Different processes can be used for dispersion of specialty carbon black in water:

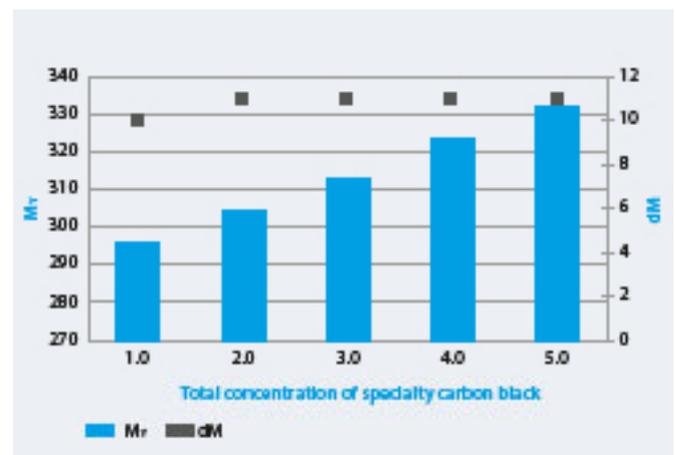
1. The specialty carbon black is dispersed in a binder system, where the polymer is dissolved in water or is present as an aqueous dispersion, for example, a polyurethane dispersion. In addition, wetting agents are added if it is necessary to stabilize the aqueous system.
2. Dispersion is done without binder. Polymeric dispersion additives take the place of the binder and provide the necessary viscosity and stability to the aqueous system. In the subsequent let-down process, the binder of choice is added.

The advantage of the procedure in point 2 is the potential to achieve higher concentrations of specialty carbon black in the mill base. The most important criteria for selection of the specialty carbon black is the jetness to be achieved in the desired coatings system. Oxidized specialty carbon blacks are negatively charged by the carboxyl groups on the surface, at higher pH's, such as those observed in aqueous coating systems.

Figure 12 shows, as an example, the influence of the specialty carbon black concentration in an aqueous polyurethane system on jetness and blue tint. The specialty carbon black used here is the non-oxidized COLOUR BLACK FW 171.

**Figure 12**

**Influence of COLOUR BLACK FW 171 concentration on jetness and blue tone in a water-based coating**



The figure shows that, besides jetness, the blue tint also increases in the beginning with increasing specialty carbon black concentration in the finished product and reaches a stable value.

Table 10 includes an aqueous binder-free formulation with COLOUR BLACK FW 171. For the final let down, Alberdingk U 710® by Alberdingk & Boley was used. The ratio of mill base to binder was 1:5.

**Table 10**

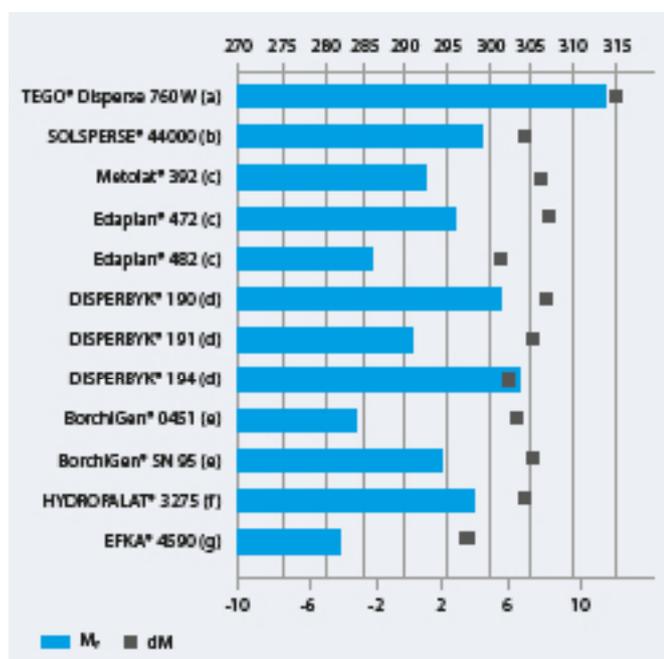
**Binder-free mill base formulation for water-borne coatings based on COLOUR BLACK FW 171**

COMPONENTS	PARTS BY WEIGHT, g
COLOUR BLACK FW 171, Orion Engineered Carbons	10.4
TEGO® Dispers 760 W, 35 wt. %, Evonik	20.8
TEGO® Foamex 830, Evonik	0.2
DMEA	0.1
Water	48.4

The use of dispersion additives is absolutely necessary in water-borne coatings, as mentioned above. In binder-free dispersions, numerous dispersion additives have been investigated, to determine their benefits in terms of jetness and hue. The colorimetric was performed after let down in a PU dispersion, evaluation at a wet film thickness of 200 µm. The results are shown in figure 13. The dispersion additive manufacturers used, are listed in table 11.

**Figure 13**

**Influence of the dispersion additives on the colorimetric data. 10% COLOUR BLACK FW 171 and 70% dispersion additives related on specialty carbon black. The let down was done with Alberdingk U 710**



**Table 11**

**Dispersion additive manufacturers used**

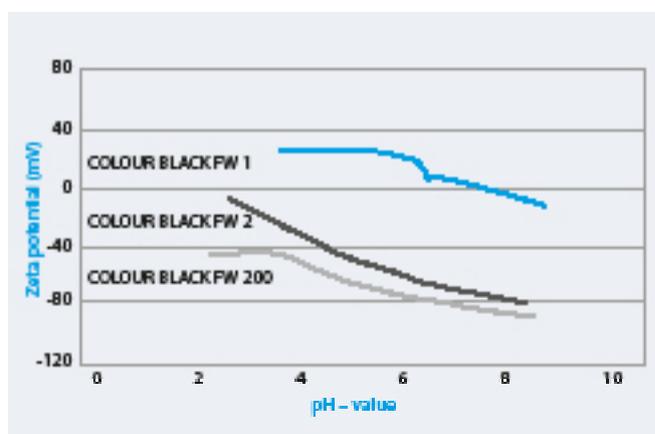
(a)	TEGO®, Evonik
(b)	Avecia
(c)	Münzing-Chemie
(d)	BYK
(e)	Borchers
(f)	Cognis
(g)	Efka

### 4.3 Zeta potential and adsorption behaviour of specialty carbon black

Numerous investigations have shown what types of specialty carbon blacks are best stabilized in water. These specialty carbon blacks have to show a zeta potential only in the weakly negative range over a wide pH range. The zeta potential provides an expression of the charge of the suspended particles in water. Figure 14 shows the zeta potentials of three gas blacks as a function of pH. We see that COLOUR BLACK FW 1 has the lowest negative potential. COLOUR BLACK FW 1 is a non-oxidized specialty carbon black with comparable primary particle size like the other two oxidized specialty carbon blacks COLOUR BLACK FW 2 and COLOUR BLACK FW 200, shown in the figure. Non-oxidized gas blacks can be well stabilized in water-borne coatings and are therefore the alternative of choice for the formulation of water-borne automobile base coat. One explanation for the better performance of non-oxidized gas blacks in water should be their higher pH.

**Figure 14**

**Zeta potential of different gas blacks with the same mean primary particle size**



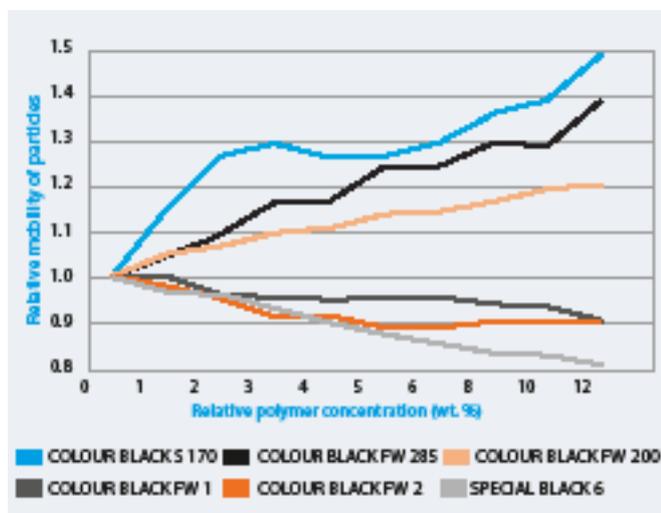
As mentioned above, gas blacks have a pH of 4, that is, weakly acidic. Oxidized gas blacks can have pH's down to approximately 2 and are therefore relatively strongly acidic. Because water-borne coatings are stabilized in the alkaline medium, due to the binders used, a pH between 8 and 9 is usually encountered. The higher the degree of oxidation of the specialty carbon black, the more neutralizer – generally amines such as DMEA or AMP 90 – must be added. This can have negative effects on the other components of the coatings system.

Figure 15 shows mobility investigations with ESA (Electro-kinetic Sonic Amplitude). The adsorption of polymers or polymer dispersion additives on the specialty carbon black surface can be investigated by this method (11) (12). A polymer dispersion additive, Nopcolorsperse 188 A by Henkel, was used for the tests. The change in relative mobility of the specialty carbon black particles can be considered an indication of the adsorption of a binder on the specialty carbon black surface. We see that the non-oxidized specialty carbon blacks show a distinct change in mobility, indicating the adsorption of polymer molecules on the specialty carbon black surface in water. Like the case of the zeta potential measurements, we conclude that the stabilization of non-oxidized or less-oxidized gas blacks is easier to achieve in water.

Figure 16 illustrates the mobility tests with Viacryl SC 303, an acrylate binder by Solutia. Here as well, the non-oxidized gas blacks exhibit greater adsorption of the binder and hence can be better stabilized in water.

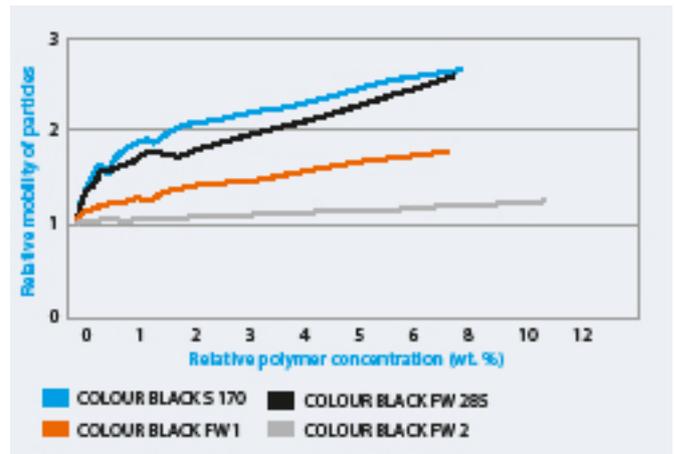
**Figure 15**

ESA Measurements for the adsorption of nopcolorsperse 188 A on the surface of gas blacks



**Figure 16**

ESA measurement of the adsorption of Viacryl SC 303 on the surface of different gas blacks as a function of binder concentration



## 4.4 UV coatings

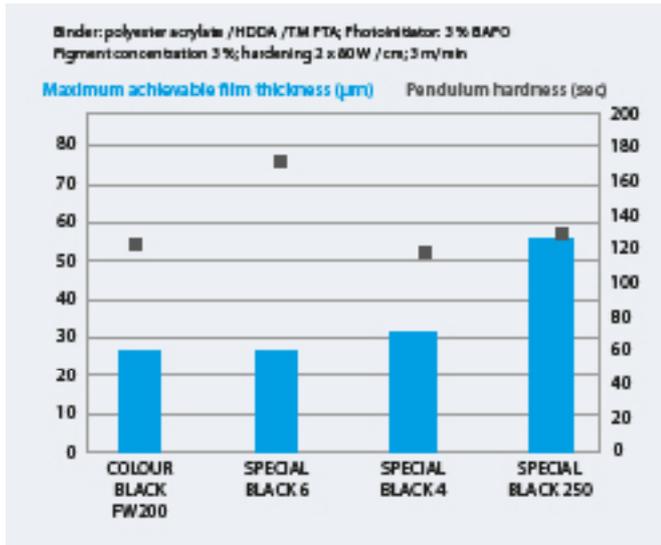
### 4.4.1 UV Liquid coatings

UV coatings will continue to gain importance, particularly from the standpoint of increasingly stringent VOC guidelines. Also, the rapid curing and suitability for temperature-sensitive substrates favor UV coatings. For UV-coatings, the careful selection of specialty carbon blacks is even more essential than with the other applications and processes. This is because specialty carbon blacks absorb light in the UV range as well, so a smaller fraction of the UV light is available for the polymerization process of the binders. Thus, the photoinitiators that start the polymerization by absorption in the UV range “compete” with the specialty carbon black for the energy supplied to the system by the UV light. The substrate on which the UV coating is to be applied is also crucial to the choice of the specialty carbon black.

On a non-reflecting background such as wood, the UV coating is more difficult to cure, because the drying of the entire film thickness of the coating is not additionally supported by reflected light as is the case with a smooth metal surface. For application on non-reflecting substrates, coarser-particle oxidized specialty carbon blacks in combination with fillers have performed best (13). Figure 17 shows the influence of different specialty carbon blacks without additional pigments or fillers on UV hardening (14).

**Figure 17**

**Influence of different specialty carbon blacks on UV curing (14)**



We see that the thinnest films can be obtained with the oxidized COLOUR BLACK FW 200 and SPECIAL BLACK 6. Both specialty carbon blacks belong to the category HCG, which, thanks to their very small particle sizes, have considerably higher jetness than SPECIAL BLACK 250. SPECIAL BLACK 250 has been developed especially for UV coatings and therefore absorbs less UV light. The film thickness achievable with SPECIAL BLACK 250 is almost twice as thick as with COLOUR BLACK FW 200 and SPECIAL BLACK 6.

For application on non-reflecting surfaces, coarser oxidized specialty carbon blacks in combination with fillers perform best. Fillers such as calcium carbonate or barium sulfate not only increase the density of the system and hence the pigment volume concentration, but also act as additional scattering centers for the UV light. This elevates the full hardening density and the specialty carbon black effectiveness. Thus, the hiding power can be elevated by adding approximately 10% barium sulfate based on specialty carbon black. To obtain an opaque layer, at least 0.8% of a coarse-particle specialty carbon black like SPECIAL BLACK 100 must be used. UV coatings with fine-particle specialty carbon blacks have performed poorly for application on non-reflecting substrates. In this case, the fraction of absorbed light is too high to ensure sufficient full curing. Reflective surfaces can always be coated easier with a top coat of a black UV coating. In this case, specialty carbon blacks used in the liquid phase for high-jetness coatings, such as COLOUR BLACK FW 200, can be used.

**In UV coating systems, the following were tested for their applicability:**

- SPECIAL BLACK 250
- COLOUR BLACK FW 285
- PRINTEX® 95
- SPECIAL BLACK 100
- SPECIAL BLACK 200

Based on investigations already conducted, formulations in which specialty carbon blacks were combined with fillers were used to increase hiding power (see table 12).

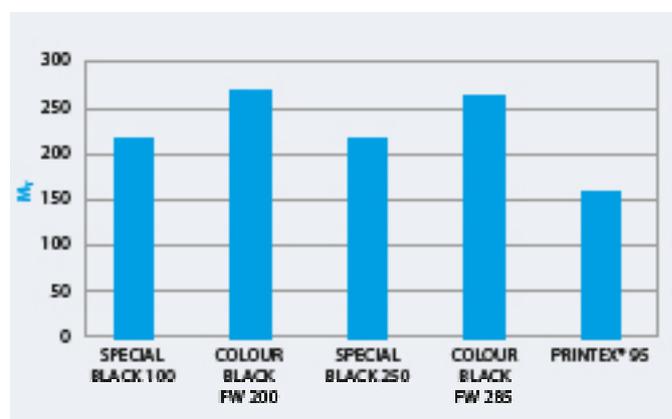
**For the formulation or application of materials, the following was provided:**

- Systems for manual or hot spray application on steel (Q-Panel R-36)
- Systems for manual application on wood (fiberboard with ash veneer primed with colorless UV coating and sanded; paint thinned to roll-on viscosity)
- Full-hardening top coats with a dry film thickness of approximately 50 µm were targeted.

The hiding power was to be evaluated additionally by application on glass and observation of the samples using contrast charts. Figures 18 and 19 show the jetnesses of some common specialty carbon blacks in UV liquid coating formulations. SPECIAL BLACK 100 and SPECIAL BLACK 250 are especially suited for use in UV liquid coatings. The results of cross cut tests before and after tape removal are also relevant in this field.

**Figure 18**

**Jetnesses of an UV coating on wood with different specialty carbon blacks**



**Table 12****Formulation of a UV wood coating with different specialty carbon blacks (weights listed in g)**

	<b>SPECIAL BLACK 100</b>	<b>SPECIAL BLACK 250</b>	<b>COLOUR BLACK FW 200</b>
Pigment	0.7	0.7	0.7
Ebecryl 1290 <sup>1</sup>	8.0	8.0	8.0
Ebecryl 285 <sup>1</sup>	9.0	9.0	9.0
Ebecryl 6040 <sup>2</sup>	10.7	10.7	10.7
OTA 480 <sup>3</sup>	26.6	26.6	26.6
TMPTA <sup>4</sup>	3.5	3.5	3.5
Laromer PE 44 F <sup>5</sup>	27.0	27.0	27.0
Disperbyk 161 <sup>6</sup>	1.0	1.0	1.0
AEROSIL® R 972 <sup>7</sup>	0.5	0.5	0.5
Blanc Fixe micro <sup>8</sup>	10.0	10.0	10.0
BYK 057 <sup>6</sup>	0.5	0.5	0.5
Irgacure 1700 <sup>9</sup>	2.5	2.5	2.5

<sup>1</sup>Urethane acrylate (UCB) <sup>2</sup>Epoxy acrylate (UCB) <sup>3</sup>Polyether acrylate (UCB) <sup>4</sup>Trimethylol triacrylate (UCB) <sup>5</sup>Polyester acrylate (BASF)<sup>6</sup>Dispersing additive (Byk-Chemie) <sup>7</sup>Hydrophobic fumed silica (Evonik) <sup>8</sup>Barium sulfate (Sachtleben) <sup>9</sup>UV crosslinker (BASF)**Table 13****Formulation of a UV metal coating with different specialty carbon blacks (weights listed in g)**

	<b>SPECIAL BLACK 100</b>	<b>SPECIAL BLACK 250</b>	<b>COLOUR BLACK FW 200</b>
Ebecryl 1290 <sup>1</sup>	5.5	5.5	5.5
Craynor CN 923 <sup>2</sup>	10.0	10.0	10.0
Viaktin VTE 6171 <sup>3</sup>	29.0	29.0	29.0
Sartomer SR 368 <sup>4</sup>	12.0	12.0	12.0
BYK 057 <sup>5</sup>	0.5	0.5	0.5
Disperbyk 168 <sup>5</sup>	1.0	1.0	1.0
AEROSIL® 972 <sup>6</sup>	0.5	0.5	0.5
Finntalc M 10 <sup>7</sup>	5.0	5.0	5.0
Pigment	0.5	0.5	0.5
Irgacure 184 <sup>8</sup>	1.0	1.0	1.0
Irgacure 819 <sup>8</sup>	1.0	1.0	1.0
Benzophenone	1.0	1.0	1.0
TEGO® Rad 2100 <sup>9</sup>	0.5	0.5	0.5
Ebecryl CL 1039 <sup>10</sup>	14.5	14.5	14.5
Laromer LR 8887 <sup>11</sup>	14.5	14.5	14.5
Ebecryl 170 <sup>12</sup>	4.0	4.0	4.0

<sup>1</sup>Urethane acrylate (UCB) <sup>2</sup>Urethane acrylate (Cray Valley) <sup>3</sup>Polyester urethane (Solutia) <sup>4</sup>Isocyanurate triacrylate (Cray Valley)<sup>5</sup>Leveling agent/dispersion additive (BYK) <sup>6</sup>Hydrophobic fumed silica (Evonik) <sup>7</sup>Talc (Omya) <sup>8</sup>UV crosslinker (BASF)<sup>9</sup>Leveling agent (Evonik/Tego) <sup>10</sup>Urethane acrylate (UCB) <sup>11</sup>Acrylate (BASF) <sup>12</sup>Acrylate-phosphoric acid ester (UCB)

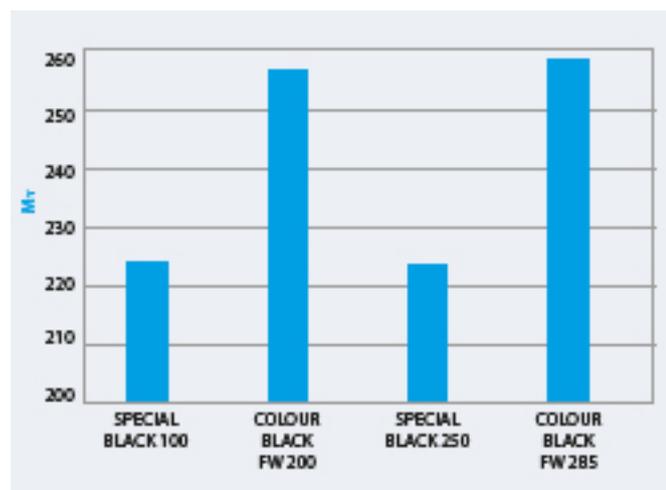
COLOUR BLACK FW 200 and COLOUR BLACK FW 285 are less suitable for UV application, on wood, because products impair full curing and provide negative results in this test. PRINTEX® 95 provides no opaque layers at dry film thicknesses of 40 – 65 µm and is therefore unsuitable for use in the field of wood coatings.

The reflection effect is much bigger on metals, so specialty carbon blacks with high jetness are available for tinting. With the exception of PRINTEX® 85 and 95, however, a wet film thickness of 150 µm must be used to obtain coatings with sufficient hiding power. Table 13 shows formulations for a UV metal coating.

Figure 19 shows the jetnesses for UV metal coatings with specialty carbon blacks. Accordingly, high-jetness metal coatings can be manufactured with COLOUR BLACK FW 285 and COLOUR BLACK FW 200.

**Figure 19**

**Jetnesses of a UV coating with different specialty carbon blacks applied to metal**



#### 4.4.2 UV powder coatings

UV powder coatings with the binders Uvacross by DSM and Uvecoat™ by Cytech were prepared for our tests. The Uvacross resins were a combination of polyesters with maleate/fumarate functionalization using crystalline vinyl ether urethanes. The Uvecoat™ system used consists of an acrylate/methacrylate-functionalized polyester and a crystalline unsaturated polyester resin.

**Table 14**

**Formulation of a UV powder coating based on Maleate/Fumarate functionalized Polyesters (Uracross System) with specialty carbon blacks (weights in g)**

	SPECIAL BLACK 4	SPECIAL BLACK 100
Uracross 3125 <sup>1</sup>	244.0	244.0
Uracross 3307 <sup>2</sup>	26.3	26.0
Uracross 3898 <sup>2</sup>	105.0	105.0
Irgacure 819 <sup>3</sup>	12.0	12.0
Irgacure 2959 <sup>3</sup>	3.0	3.0
Worlée Add. 900 <sup>4</sup>	2.0	2.0
Resiflow PV 5 <sup>5</sup>	4.0	4.0
Pigment	3.2	3.2

<sup>1</sup> Maleate/fumarate-functionalized polyesters (DSM)

<sup>2</sup> Crystallized vinyl ether urethanes (DSM)

<sup>3</sup> UV crosslinker (BASF)

<sup>4</sup> De-aeration agent (Worlée)

<sup>5</sup> Leveling agent (Worlée)

In UV powder coatings 0.8% COLOUR BLACK FW 200, COLOUR BLACK FW 285, SPECIAL BLACK 100, PRINTEX® 95, PRINTEX® 85, PRINTEX® 60 or SPECIAL BLACK 4 were used.

The powder coatings were applied to aluminum and MDF panels, melted, and cured under the conditions prescribed for the binders. To guarantee acceptable full cure and comparability of results, film thicknesses of 50 – 55 µm were targeted. Tables 14 and 15 show examples of powder coatings formulations with SPECIAL BLACK 4 and SPECIAL BLACK 100.

**Table 15**

**Formulation of a UV powder coating based on Methacrylate/Acrylate-functionalized Polyester with specialty carbon black (weights in g)**

	SPECIAL BLACK 4	SPECIAL BLACK 100
Uvecoat 2100 <sup>1</sup>	302.2	308.0
Uvecoat 9010 <sup>2</sup>	75.6	75.5
Irgacure 819 <sup>2</sup>	12.0	12.0
Irgacure 2959 <sup>2</sup>	3.0	3.0
BYK 366 <sup>3</sup>	4.0	4.0
Pigment	3.2	3.2

<sup>1</sup> Urethane acrylate (Cytech)

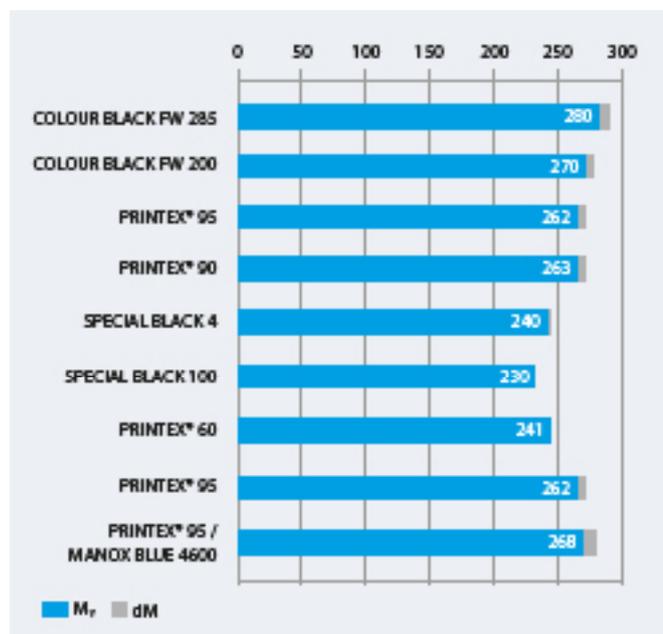
<sup>2</sup> UV crosslinker (BASF)

<sup>3</sup> Leveling agent (BYK)

Figure 20 shows the colorimetric data of specialty carbon black in a UV powder coating system. COLOUR BLACK FW 285 achieves the highest jetnesses. COLOUR BLACK FW 285 provides the much bluer black in the powder coatings system. As in conventional systems, the influence of particle size is evident in UV powder coatings. The more finely divided the specialty carbon black, the greater is the jetness of the UV powder coating produced. The addition of iron blue can elevate the jetness and blue tint of the furnace black PRINTEX® 95.

**Figure 20**

**Jetness of UV powder coatings based on Uracross with specialty carbon blacks**



#### 4.5 Powder coatings

Another application process with big growth rates is powder coatings. In 2006, the worldwide production was about 1.1 million metric tons. The advantages of powder coatings in comparison with conventional coating processes are:

- The loss of material on application can be held below 5 % thanks to the recycling potential.
- No decomposition products are formed.
- As a rule, these coatings have high chemical resistance.

If we consider the manufacturing process for powder coatings, the most important differences with regard to the specialty carbon black dispersion, in comparison to the other previously introduced systems, become evident. The components resin (e. g., carboxy functional polyester), hardener (amines, isocyanates, e. g.,  $\beta$ -hydroxyalkylamide (HAA), triglycidyl isocyanurate, carboxyfunctional polyesters), specialty carbon black and fillers are mixed in a heated mixer. All components are solids. The temperature in the subsequent extrusion process during which the components are dispersed must not exceed the critical temperature at which a reaction occurs between resin and hardener. The dispersion of the pigment in a medium of molten polymer with a viscosity of over 100,000 mPa·s is subject to different natural laws, in comparison to those of a liquid in a bead mill. Essentially higher shear forces occur, benefiting jetness development of the specialty carbon black. However, homogenization is more difficult to achieve. The typical specialty carbon black concentration in a powder coating is 1–3% based on polymer concentration.

Systematic studies have shown that fine particle furnace blacks can generate high jetness and hue in epoxy hybrid systems.

In blends with titanium dioxide, fine particle sized furnace blacks provide more jetness than fine particle sized gas blacks.

**Table 16**

**Formulation of an Epoxy Hybrid powder coating (Epoxy and Carboxyl functional Polyester Resins)**

RAW MATERIAL	CONCENTRATION [%]	CONCENTRATION [%]
Uralac® P 3560 <sup>1</sup>	68.4	68.0
Araldite® GT 7004 <sup>2</sup>	29.3	29.2
Benzoin <sup>3</sup>	0.5	0.5
Resiflow® P V 5 <sup>4</sup>	1.0	1.0
Specialty carbon black	0.8	1.3
Total	100.0	100.0

<sup>1</sup> hybrid resin consisting of polyester and epoxy (70/30), DSM

<sup>2</sup> epoxy resin, Omya GmbH

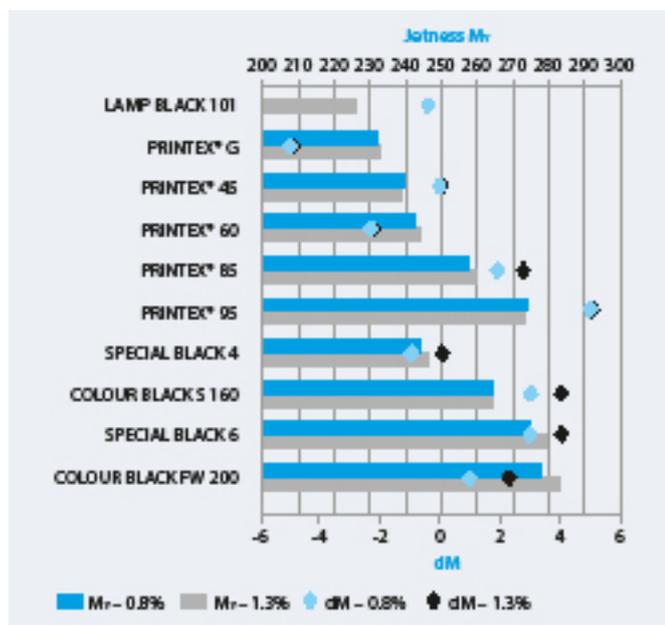
<sup>3</sup> aromatic hydroxy ketone, degassing aid, Merck

<sup>4</sup> flow and wetting additive, Worlée

Figure 21 shows the jetnesses and blue tints of various furnace and gas blacks in a conventional powder coating system (see table 16). The fine particle sized furnace blacks PRINTEX® 95 and PRINTEX® 85 show high jetness in the epoxy hybrid system. Due to the concentration of specialty carbon black the gas blacks COLOUR BLACK FW 200 and SPECIAL BLACK 6 show the highest jetness values. In general gas blacks and furnace blacks with small primary particle size have high bluish undertone dM values that can't be achieved by COLOUR BLACK FW 200 in this system.

**Figure 21**

**Colorimetric properties of specialty carbon blacks in an epoxy resin powder coating at different specialty carbon black loadings**



## 5 WEATHERING BEHAVIOR OF BLACK COATINGS

Besides the coloristics, weathering resistance is a fundamental quality criteria in black coatings. An example is an automobile coating. With gas blacks, these coatings generally show less loss of gloss and less haze than those with furnace blacks. The oxidized specialty carbon blacks also provide better properties than untreated ones (15). This positive effect is attributable to the fineness and excellent degree of dispersion, and to the marked UV absorption of the specialty carbon black.

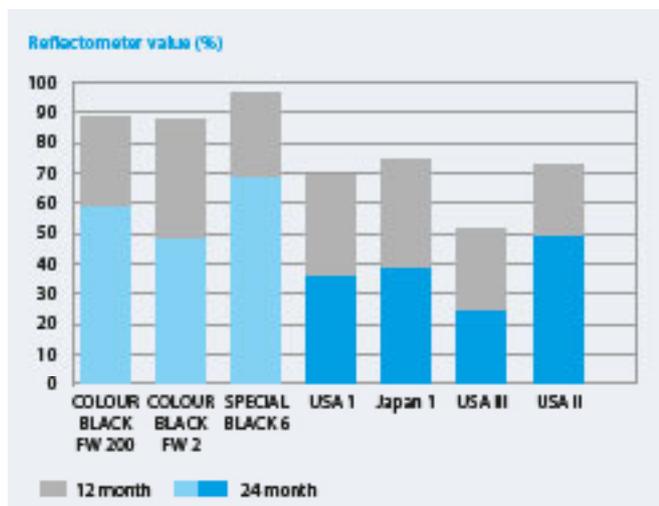
The radiation energy is transformed to thermal energy, limiting radical degradation reactions of the binder. The larger the specialty carbon black surface area exposed to UV radiation, the more significant is the protective action.

The quantitative weathering stability of a specialty carbon black is a major criteria for selection. The known Florida weathering test is an accelerated open-air weather test with relation to Central European conditions. The literature indicates that one year of Florida weathering corresponds to approximately 2.5 years in Europe (16). Because modern weather-proof coatings are generally permitted by the user only after a two-year test in Florida, the performance for approximately 5 years in Central Europe can be predicted without taking influences such as angle of inclination into account. Assuming a 90° arrangement, which is relevant for coated facade cladding, in comparison to a 45° exposure, factor two can be used with regard to weathering. The weathering results after 24 months in Florida can then be extrapolated to 8–10 years in Central Europe.

Detailed information on the Florida tests are contained in (15). Figure 22 shows the residual gloss values for some oxidized gas blacks and some competitive specialty carbon blacks. It is evident here that the oxidized gas blacks COLOUR BLACK FW 200, COLOUR BLACK FW 2 and SPECIAL BLACK 6 provide considerably higher residual gloss values in comparison to furnace blacks of Class HCF and ox. HCF (USA I, USA II, USA III, Japan I) after 12 and 24 months of open-air weathering in Florida. For this reason, oxidized gas blacks have always been preferred in the coatings industry.

**Figure 22**

**Residual gloss in % of black-coated panels after 12 and 24 months of Florida test**



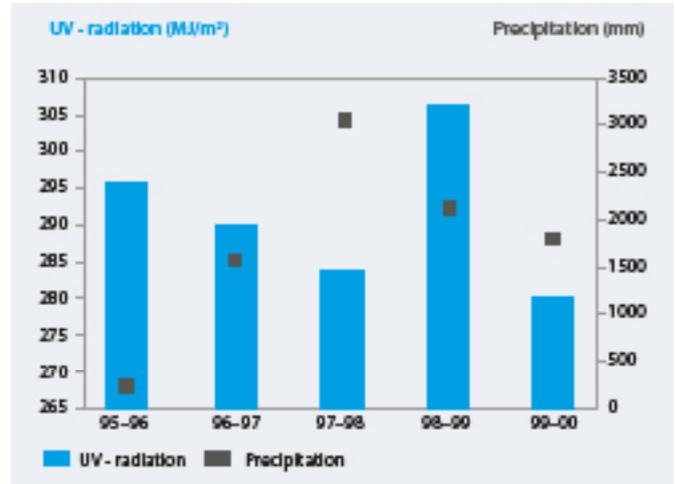
Besides the incontestable advantages of a test affording near-field conditions under intensified conditions, open-air weathering in Florida also has some significant drawbacks. The result of the evaluation depends to a great extent on the season of the year in which exposure started. If the panels are exposed in the springtime in Florida, intensive post-curing occurs in the months of March through August before the actual rainy season begins, and the coating is exposed to acid rain more extensively. However, if the panels are sent to Florida at the end of summer or the beginning of fall for open-air weathering, the panels are immediately exposed to intensive rain at the start of testing, entailing distinctly negative results in terms of residual gloss and haze.

In addition, the probability that panels will also be exposed to storms during exposure entailing additional heavy stress on the coatings surface of the panels, is very high. Subsequently, no evaluation as to which scratches are attributable to storms and which ones to the actual influence of rain, sun, and a combination thereof can be conducted.

Figure 23 represents the climatic data in Florida for several years. Both UV radiation and precipitation quantity fluctuate widely, resulting in imponderables in the evaluation of panels that have been stored for the same duration in Florida but at different times (17).

**Figure 23**

**Climatic data for Florida in 1995 – 2000 (16)**



The Bundesanstalt für Materialforschung und Prüfung (Federal Institute for Materials Research and Testing (BAM)) in Berlin has developed a process that reproduces the weather conditions in Florida and ensures exactly reproducible conditions (18). The development work was done jointly with well-known automobile and coatings manufacturers. In the ADF (acid dew and fog) test, coated panels are subjected to weathering in chambers. Heat, rain and UV radiation continuously alternate. Water corresponding to the pH and NO<sub>x</sub>/SO<sub>2</sub> contents of the rain and dew in Florida is used as rain. The process can provide reliable data on the weathering stability of coated metal panels within only 42 days. The results of open-air Florida weathering were reproduced with the ADF method, in many cases. This is important particularly to the automobile industry, which depends on accelerated accurate test procedures for launching new products on the market.

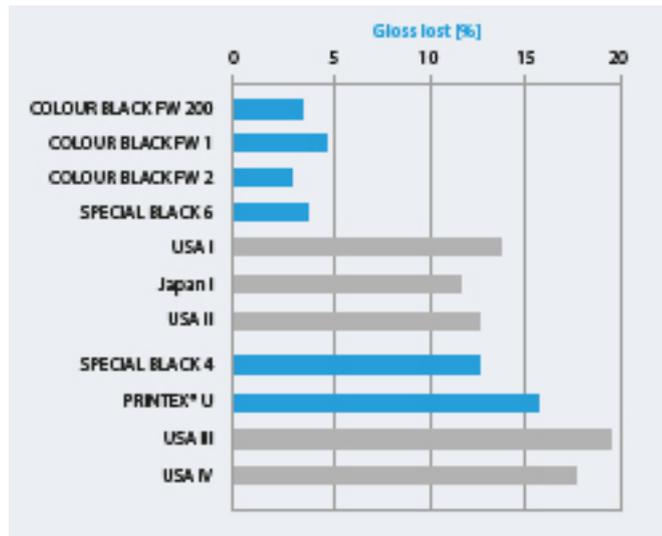
Various specialty carbon blacks have also been tested with the ADF process. As in the open-air weathering tests in Florida, gas blacks showed their superiority over specialty carbon blacks manufactured by the furnace black process.

Figures 24 and 25 show the gloss losses or haze values after 42 days of weathering of metal panels coated with specialty carbon black tinted coatings. As we see from the figures, both the gloss losses and the haze values of the panels treated with gas black containing black coatings are lower than with coloristically comparable furnace blacks (USA I, USA II, USA III, USA IV, Japan I). Figure 26 shows the comparison of coated panels during and at the end of weathering.

These panels were coated with systems containing the specialty carbon blacks COLOUR BLACK FW 200 and HCF (USA I). It is clearly evident that the panels show considerably less wear, in the case of gas blacks, after 42 days of weathering. This is explained by their better pigment distribution in the binder system and hence absorption of a larger fraction of the UV light, in comparison to the furnace blacks.

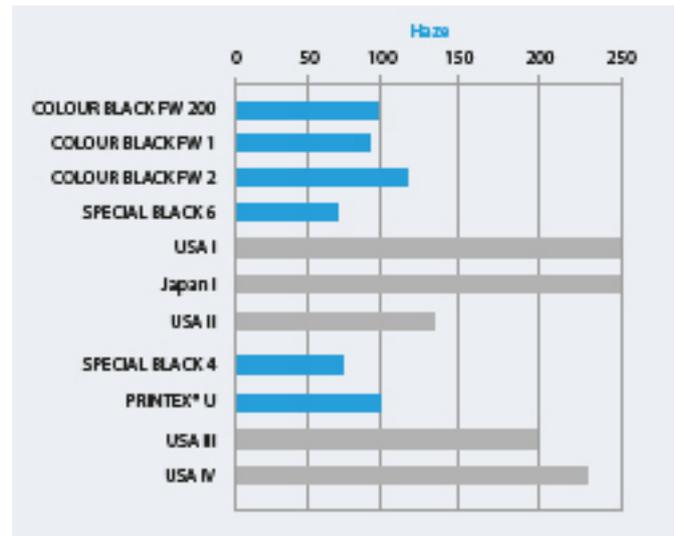
**Figure 24**

**Gloss losses of black-coated panels after 42 days of ADF testing (5% specialty carbon black based on Lioptal A 453)**



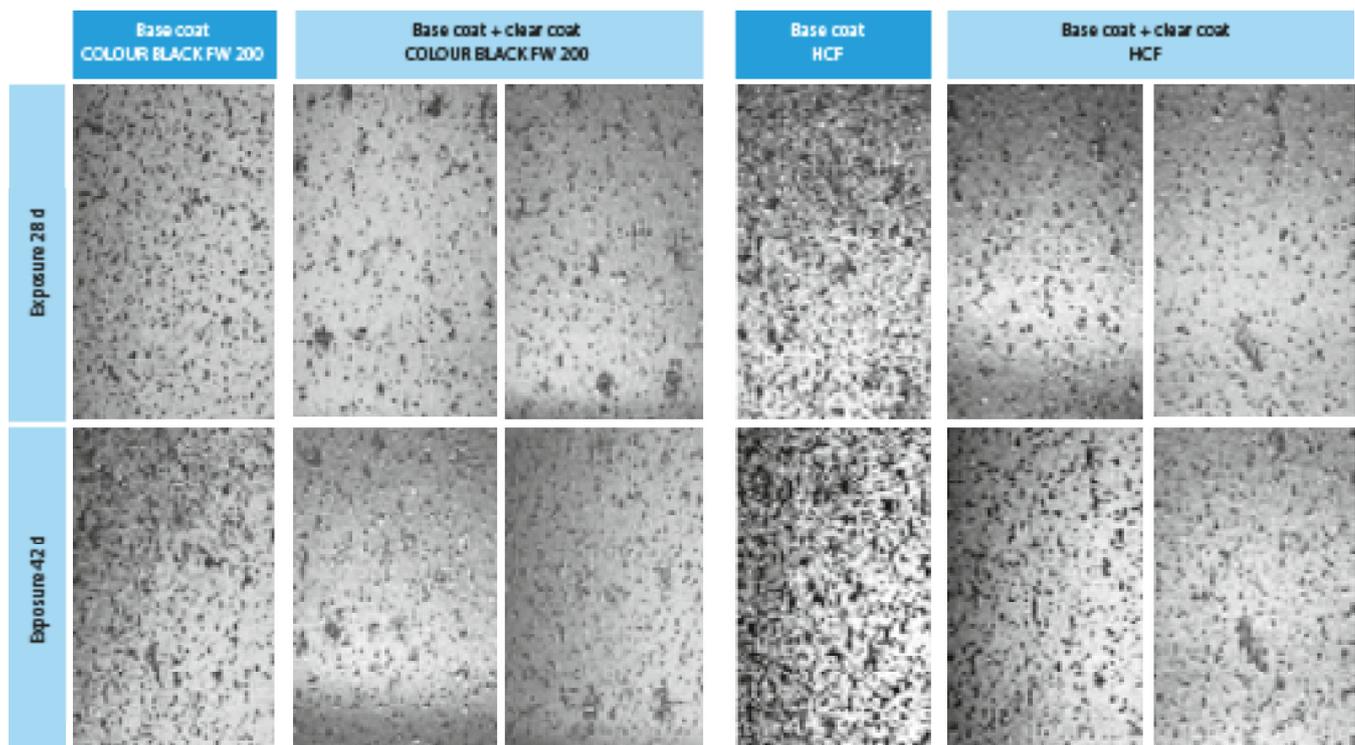
**Figure 25**

**Haze of black-coated panels after 42 days of ADF testing (5% specialty carbon black based on Lioptal A 453)**



**Figure 26**

**Weathering results of coated panels by ADF test**



## 6 PRODUCT SAFETY

Specialty carbon blacks are used in a wide range of applications. In the decades of specialty carbon black production and processing, no significant hazards have been observed in humans. Toxicological studies showed no acute toxicity after oral or dermal uptake.

Specialty carbon black is regarded as safe from the viewpoints of skin irritation, skin sensitization, mutagenicity and reproductive toxicity. Also, repeated dose exposure to skin and repeated oral uptake did not give any critical result. In 1996 specialty carbon black was classified by IARC in group 2B (possibly carcinogenic to humans). This evaluation was upheld by IARC in early 2006. This classification is based on long-term experiments on rats. However, mice and hamsters do not develop lung tumors under similar testing conditions. Here, the significance of the animal species and the tumor triggering mechanism has not yet been determined. High-quality investigations on large groups of workers at specialty carbon black facilities in Germany (Kalscheuren), the UK and the USA were carried out on behalf of the International Carbon Black Association (ICBA). The ICBA is an association of leading carbon black producers. The result of these mortality studies do not show any evidence of a link between exposure to specialty carbon black and higher lung cancer mortality rates in humans.

Ultra-fine particles were also investigated as part of these studies. Ultra-fine particles are particles measuring less than 100 nanometers. The ICBA commissioned a systematic evaluation of exposure to ultra-fine particles in the workplace at three specialty carbon black facilities. The results show that workplace exposure to fine particles is well below the regulatory limits. The proportion of ultra-fine particles found in the air at the facilities was not higher than normal in areas outside the facilities. Thus, specialty carbon black manufacturing did not increase the amount of ultra-fine particles in the air.

Information concerning the safety of our products are listed in the corresponding Safety Data Sheets, which will be sent with the first delivery or upon updating.

## 7 GLOSSARY

### Aggregate

Aggregated composite or clustered → primary particles, the surface of which is smaller than the sum of the surfaces of the primary particles involved (DIN 53206)

### Agglomerate

Non-aggregated composite of → primary particles and/or → aggregates clustered, for example, at corners and edges, the total surface of which does not deviate significantly from the sum of the individual surfaces (DIN 53206)

### BET-surface

The specific surface of a finely divided substance as determined by nitrogen adsorption on the basis of DIN 6131

### Jetness

A measure of the intensity of a color sensation (DIN 53235)

### Hue

Describes the kind of chromaticity (DIN 5033)

### Contribution of Hue dM

$$dM = M_C - M_Y$$

$dM > 0$  blue undertone

$dM < 0$  brown undertone

### Primary Particles

Particle identifiable as an individual by suitable physical processes (e. g., with the light-optical microscope, electron microscope, etc.), (DIN 53206)

### Blackness Value $M_Y$ , color-independent

$M_Y = 100 \cdot \log (100/Y) Y$ ; ( $Y$  = standard color value, green) or

$$M_Y = 100 \cdot D_{vis} (D_{vis} = \text{visual density})$$

### Blackness Value $M_C$ , color-dependent

$$M_C = 100 (\log X_n/X - \log Z_n/Z + \log Y_n/Y)$$

$X_n, Z_n, Y_n$  = standard color values of the illuminating light type (DIN 6174)

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