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Carbon black, method of producing carbon black, and
device for implementing the method

5 The invention relates to a carbon black, to a method of
producing carbon black, and to a device for
implementing the method.

10 DE 2404536 discloses a method of producing gas blacks
having a low extractables content, wherein hydrogen-
rich mixtures are used as carrier gas for the carbon
black oil vapour, and the carbon black deposited on the
cooling roll is collected. These gas blacks have an
extractables content of less than 0.100% by weight.

15 Furthermore, WO 2005/033217 discloses unscreened,
untreated carbon blacks, having a pH of less than or
equal to 6.0, a residue on ignition of less than or
equal to 0.1%, and a 5 μ m sieve residue of less than or
20 equal to 200 ppm. These blacks are produced by the
method steps of removing the heat from the flame by
thermal conduction and/or radiation, forming a thin gas
boundary layer, and accelerating or expanding the flow
formed by the flame and the boundary layer.

25 A disadvantage of the known blacks is the poor hue
contribution in coatings applications.

30 It is an object of the invention to provide a carbon
black which features a high positive hue contribution
in coatings applications. It is a further object of the
invention to provide a method which removes as much
heat as possible from the flame, without allowing the
resulting black to accumulate on the cold surface.

35 The invention provides a carbon black which is
characterized in that the aggregate size distribution
has a $(d_{90}-d_{10})/d_{50}$ ratio of less than or equal to 1.1,
preferably less than 0.8, more preferably less than



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0.65.

The carbon black of the invention may have a surface oxide content of greater than 50 mmol/kg, preferably greater than 100 mmol/kg, more preferably greater than 120 mmol/kg.

The carbon black of the invention may have an aggregate size distribution with a full width at half-maximum (FWHM) to D_{mode} ratio of less than or equal to 0.6, preferably less than 0.58, more preferably less than 0.56.

The carbon black of the invention may be a gas black.

The pH of the carbon blacks of the invention may be < 7.0, preferably < 6.0, more preferably < 5.0.

The carbon black of the invention can have an STSA value of 20-300 m²/g, preferably of 50-220 m²/g, more preferably of 70-200 m²/g.

The carbon black of the invention may have a volatiles content of 2.0-20.0%, preferably of 3.0-12%, more preferably of 4.0-9.0%.

The carbon black of the invention may have a tint of 90-180%, preferably of 105-106%, more preferably of 120-150%.

The invention further provides a method of producing carbon black of the invention, which is characterized in that a gas mixture comprising a carrier gas and a carbon black feedstock is if desired admixed with hot air, the gas mixture is passed into a burner pipe, the gas mixture burns at the burner pipe openings, and the flames, together with the ambient air drawn in freely under suction from outside, are sucked through a

cooled, narrowing gap and cooled, the cooled, narrowing gap having a height (h) to width (b) ratio of 1-100, preferably 5-50, more preferably 10-40; the width being based on the top edge of the gap, the width (b) being
5 0.5 to 10 mm, preferably 1 to 5 mm, and the flow rate at the narrowest point of the gap being 10 - 200 m/s, preferably 15 - 150 m/s, more preferably 20 - 100 m/s.

The flow rate can be calculated from the ratio of
10 operational gas volume to gap area. The operational gas volume is the volume of gas taken off under suction via the fan. The gap area is given by the product of gap width b and top edge A^1A^2 of the cooled, narrowing gap.

15 The coolant used for the narrowing gap may be water, air, steam and heat-transfer oil.

In a commercially customary thin-film evaporator the carbon black feedstock can be heated and vaporized. The
20 carbon black feedstock vapour is supplied by a stream of carrier gas to a burner pipe. Immediately upstream of the burner pipe (described for example in DE-C 671739) the gas mixture can be admixed with hot air at temperatures of up to 400°C, and supplied to the
25 flames. The carbon black produced can be separated in commercially customary filter systems.

The carbon black feedstock used may comprise carbonaceous gases or vaporizable carbonaceous liquids.
30 Carbon black feedstock used may comprise hydrocarbons, such as acetylene, methane, ethylene, ethane, propane, butane or pentane, or carbon black oil. Carbon black oil may be of petrochemical or carbochemical origin. The carbon black feedstock used may be a mixture of
35 hydrocarbons and/or carbon black oils.

The gaseous or vaporized carbon black feedstock may have a temperature of up to 400°C, preferably 250 -

400°C, more preferably 250 - 350°C.

As carrier gas it is possible to use combustible gases,
preferably gas mixtures having a hydrogen fraction
5 > 50% by volume, more preferably > 60% by volume.

The carrier gas temperature and hot air temperature may
correspond at least to the temperature of the gaseous
or vaporized carbon black feedstock, in order to
10 prevent condensation.

Figure 1 shows the diagrammatic construction of the
apparatus, where the reference symbols have the
following meanings:

15

A^1A^2 , $A^{1'}$, $A^{2'}$: top edge of the cooled, narrowing gap,

B^1, B^2 , $B^{1'}$, $B^{2'}$: bottom edge of the cooled, narrowing
gap,

20

$A^{1'}$, A^1 , $A^{2'}$, A^2 : narrowest point of the cooled, narrowing
gap,

b: width of the cooling gap = $A^{1'}$, A^1 or
25 $A^{2'}$, A^2

$B^{1'}$, B^1 , $B^{2'}$, B^2 : widest point of the cooled, narrowing
gap,

30 h: height of the cooled, narrowing gap in
the upper region,

h' : height of the uncooled or cooled,
obliquely converging sidewalls,

35

$C^1B^1B^2C^2$: uncooled or cooled, obliquely converging
sidewall,

$C^1B^1B^2C^2$: uncooled or cooled, obliquely converging
sidewall,

5 D^1, D^1 : width of the vertically placed
apparatus,

E: height-adjustable burner pipe.

10 E, A^1A^1 : Burner spacing

The angle α can be 70° to 89° , preferably 80° to 89° ,
more preferably 83° to 88° .

15 The height h can be 0 to 250 mm, preferably 100 to
250 mm, more preferably 140 to 180 mm.

20 The width of the vertically placed apparatus
($C^1C^1 = D^1D^1$) can amount to 100 to 500 mm, preferably
150 to 210 mm.

The exhaust hood may follow the gap directly and may be
connected to a suction withdrawal fan.

25 The apparatus may be manufactured of stainless steel in
order to prevent the typical impurity (grit). In the
case of the method of the invention there is no need
for a rotating cooling roll. The flames of the burner
pipe can be sucked through and cooled by a water-
cooled, narrowing gap.

30 As shown in the sectional drawing of the apparatus of
the invention (Figure 1), the gap may extend over the
entire length of the apparatus and may run parallel to
the burner pipe, i.e. it can be disposed, preferably
35 with centring, above the burner pipe. The sidewalls of
the vertically placed apparatus may initially run
parallel to one another ($C^1D^1D^2C^2$ or $C^1D^1D^2C^2$), then
converge obliquely on one another ($C^1B^1B^2C^2$ or

$C^1B^1B^2C^2$), and end in the cooled, narrowing gap ($A^1B^1B^2A^2$ or $A^1B^1B^2A^2$).

5 The burner spacing with respect to the cooled, narrowing gap can be made variable. This adjustment facility can be provided in order to allow the realization of an optimum burner height.

10 In the conically converging region (h') of the apparatus it is possible for the sidewalls to be water-cooled. In the region (h'), however, this may only serve to protect the material from the flame temperature, since it is only in the upper region (h), the correspondingly named cooling gap, that the cooling
15 of the reaction mixture is to take place.

The construction of the cooling gap may be designed such that, as a result of the generation of a laminar boundary layer at the cooling gap, the accumulation of
20 carbon black can be prevented.

Additives can be added to the carbon black oil. Additives may be a solution of salt in water, alcohol, oil or mixtures thereof. The additives can be converted
25 into an aerosol. The salt used can with preference be potassium carbonate.

The invention further provides a device for implementing the process of the invention, having a
30 burner and a cooling surface against which the flame is directed, which is characterized in that the cooled, narrowing gap has a height (h) to width (b) ratio of 1-100, preferably 5-50, more preferably 10-40, the width being based on the top edge of the gap, the width (b)
35 is 0.5 to 10 mm, preferably 1 to 5 mm and the flow rate at the narrowest point of the gap is 10 - 200 m/s, preferably 15 - 150 m/s, more preferably 20 - 100 m/s.

- The carbon blacks of the invention can be used as non-reinforcing filler, reinforcing filler, UV stabilizer, conductive black or pigment. The carbon blacks of the invention can be used in rubber, plastic, printing inks, liquid inks, inkjet inks, toners, coating materials, paints, paper, bitumen, concrete and other building materials. The carbon blacks of the invention can be employed as a reducing agent in metallurgy.
- 10 The carbon blacks of the invention have the advantage that blacks with a narrow aggregate size distribution can be produced, and the absolute hue contribution (dM) in coatings applications is very high.
- 15 The method of the invention has the advantage that the black does not deposit on the cooled surfaces and can therefore be deposited outside of the device.
- A further advantage is that in the apparatus of the invention there are no longer any rotating parts, which reduces the capital costs and maintenance costs, and that there is no longer separation between roll black and filter black, and hence the product produced is homogenized. As a result of the removal of mechanical conveying, moreover, it is possible to lower the level of impurities in the product.

Examples

- 30 The apparatus of the invention used in the examples in accordance with Figure 1 has a sidewall distance (D^1D^1) of 177 mm and a height (D^1C^1) of 600 mm. Above a height of 600 mm, the sidewalls converge obliquely on one another and end in the cooled, narrowing gap. In the examples which follow, the length A^1A^2 of this cooling gap amounts to 2000 mm and the height (h) amounts to 50 mm. The height (h') of the gap in the examples below

amounts to 159 mm. The angle α is 87°.

Methods of determination

5 pH

The pH is determined in accordance with DIN EN ISO 787-9 20.

10 Volatiles

The volatiles are determined at 950°C in accordance with DIN 53552.

15 BET surface area

The BET surface area is determined in accordance with ASTM D-6556-00.

20 STSA surface area

The STSA surface area is determined in accordance with ASTM specification D-6556-00.

25 Tint

The tint strength is determined in accordance with ASTM specification D-3265.

30 Aggregate size distribution

The aggregate size distribution curves are measured using a Brookhaven BI-DCP disc centrifuge with red-light diode. This instrument is a development specifically for determining aggregate size distribution curves of finely divided solids from absorbance measurements, and is equipped with an

automatic measuring and evaluation program for determining the aggregate size distribution.

To carry out the measurements, first of all a
5 dispersion solution is prepared from 200 ml of ethanol,
5 drops of ammonia solution and 0.5 g of Triton X-100,
made up to 1000 ml with demineralized water.
Additionally a spin fluid is prepared from 0.5 g of
Triton X-100 and 5 drops of ammonia solution, made up
10 to 1000 ml with demineralized water.

Subsequently 20 ml of dispersion solution are added to
20 mg of carbon black, which are suspended in the
solution for a period of 4.5 minutes in a cooling bath
15 with 100 watts of ultrasound (80% pulse).

Prior to the beginning of the actual measurements, the
centrifuge is operated for 30 minutes at a speed of
11 000 min^{-1} . With the disc spinning, 1 ml of ethanol is
20 injected, and then a bottom layer of 15 ml of spin
fluid is carefully laid down. After about a minute,
250 μl of the black suspension are injected, the
instrument's measuring program is started, and the spin
fluid in the centrifuge is overlaid with 50 μl of
25 dodecane. A duplicate determination is performed on
each sample for measurement.

The raw data curve is then evaluated using the
instrument's arithmetic program, with correction for
30 scattered light and with automatic baseline adaptation.

The ΔD_{50} value (FWHM) is the width of the aggregate size
distribution curve at half the peak height. The D_{mode}
value (modal value) is the aggregate size having the
35 greatest frequency (peak maximum of the aggregate size
distribution curve). The values d_{10} , d_{50} and d_{90} are the
aggregate sizes determined from the cumulative curve
with a volume fraction of 10%, 50% and 90%,

respectively.

Surface oxides

- 5 Regarding the characterization and quantification of surface oxides on the carbon black's surface, i.e., here, functional groups containing oxygen, such as carboxyl, lactol and phenol groups:
- 10 The initial mass of carbon black, m_i , is guided by the number of surface oxides anticipated. As a starting point for the initial mass, the volatiles content of the carbon black can be employed (Table 1).

15 Table 1:

Volatiles content in % by weight	Initial mass of carbon black, m_i in g	Volatiles content in % by weight	Initial mass of carbon black, m_i in g
1	5	16-17	1
2	4.5	18-19	0.9
3-6	4	20-23	0.8
7-9	3	24	0.7
10-11	2	25	0.6
12-15	1.5	26	0.5

- The quantity of carbon black specified in Table 1, dried at 105°C, is weighed out to an accuracy of 0.1 mg
- 20 into a glass centrifuge tube, and 25 ml (volume V_1) of 0.05 M aqueous sodium hydroxide solution are added. The air in the centrifuge tube above the sample is displaced by nitrogen, and the tube is tightly sealed, inserted into a holder, and mixed overnight in a
- 25 rotation machine.

After the end of the mixing procedure, the contents are

transferred to another centrifuge tube and centrifuged for at least 1 minute.

10 ml (volume V_2) of the supernatant solution are withdrawn by pipette and transferred to a glass beaker, 20 ml of 0.025 m sulphuric acid are added, and the mixture is boiled briefly in order to expel carbonate.

The samples are subsequently back-titrated with 0.05 m aqueous sodium hydroxide solution to a pH of 6.5 (pH electrode). The amount of sodium hydroxide solution consumed is V_3 .

A blank sample must be prepared accordingly. To determine the blank value, the amount of NaOH consumed, Bl_3 , is obtained similarly.

On the basis of the initial carbon black mass m_i , the volumes V_{1-3} and Bl_3 , the amount of surface oxides, G , in mmol/kg, is calculated in accordance with the following equation:

$$G = \frac{V_1 \cdot (V_3 - Bl_3)}{V_2 \cdot m_i} \cdot 0,05 \left[\frac{\text{mol}}{\text{l}} \right] \cdot 1000$$

In this formula the symbols have the following meanings:

m_i : Initial carbon black mass in g,

V_1 : Volume in ml of the reagent solutions (= 25 ml) added to the carbon black,

V_2 : Volume in ml of sample solution withdrawn by pipette (= 10 ml),

V_3 : Amount of sodium hydroxide solution consumed for titration, in ml,

Bl₃: Amount of sodium hydroxide consumed, in ml, for the blank value titration.

5 **Relative black value My and absolute hue contribution dM**

Description/Procedure

10 1. Preparation of reagents

Diluent formula

Ingredients	in g	in % by wt.
Xylene	1125	68.20
Ethoxypropanol	225	13.63
Butanol	150	9.09
Baysilon OL 17, 10% in xylene	75	4.54
Butyl glycol	75	4.54
Total	1650	100.00

15 Baysilon formula

Ingredients	in g	in % by wt.
Baysilon OL 17	10	10
Xylene	90	90
Total	100	100

Component A

Ingredient	in g	in % by wt.
Alkydal F 310, 60%	770	77
Diluent	230	23
Total	1000	100

Component B

Ingredient	in g	in % by wt.
Maprenal MF800, 55%	770	77
Diluent	230	23
Total	1000	100

The ingredients of the 4 formulas are mixed and are
5 kept in a suitable vessel.

2. Preparation of the black coating

Formula of the black coating for determining the black
10 value My:

Ingredient	in g	in % by wt.
Standard clearcoat component A	27.3	65.3
Standard clearcoat component B	12.7	30.4
Carbon black pigment	1.8	4.3
Total	41.8	100

First of all the coating components A and B are weighed
out into a PTFE beaker, then the carbon black pigment,
15 dried at 105°C, is weighed in, and 275 g of steel beads
($\varnothing = 3$ mm) are added as grinding media. Finally the
sample is dispersed in a Skandex mixer for 30 minutes.

After the dispersing procedure, approximately 1 - 2 ml
20 of black coating are taken for the drawdown and applied
to the support plate in a stripe 5 cm long and
approximately 1 cm in width. Care should be taken to
ensure that there are no air bubbles in the coating
stripe. The film drawing bar is placed over the stripe
25 of coating and drawn uniformly across the plate. A
drawdown is produced which is approximately 10 cm long
and 6 cm wide. The drawdown must be air-dried (in a
fume cupboard) for at least 10 minutes.

Subsequently the sample is baked at 130°C in a drier for 30 minutes. The samples can be subjected to measurement immediately after cooling or later. The
5 measurements can be carried out using the Pausch Q-Color 35 instrument with WinQC+ software. The measurement takes place through the glass.

3. Calculations

10

3.1. Formulae and constants

3.1.1 Hue-independent black value M_y and hue-dependent black value M_c

15

First of all the hue-independent black value M_y is calculated (Equation 1) from the tristimulus value Y of the measurement (illuminant D65/10):

$$(1) \quad M_y = 100 \cdot \log\left(\frac{100}{Y}\right)$$

20

Subsequently the hue-dependent black value (Equation 2) is calculated:

$$(2) \quad M_c = 100 \cdot \left(\log\left(\frac{X_n}{X}\right) - \log\left(\frac{Z_n}{Z}\right) + \log\left(\frac{Y_n}{Y}\right) \right)$$

25

X_n / Z_n / Y_n (DIN 6174) = tristimulus values of the coordinate origin, based on the illuminant and the observer (DIN 5033 / part 7, illuminant D65/10°)

30

$$X_n = 94.81 \quad Z_n = 107.34 \quad Y_n = 100.0$$

X / Y / Z = tristimulus values calculated from the measurements of the samples.

3.1.2 Absolute hue contribution dM

The absolute hue contribution dM (Equation 3) is
5 calculated from the black values Mc and My:

$$(3) \quad dM = M_c - M_y$$

Examples 1-10:

10

The settings for the production of the examples for the inventive carbon blacks, and of Comparative Example 6, are listed in Table 2. A device as per Figure 1 is used.

15

For the inventive examples and for Comparative Example 6 the hot air temperature is 310°C and the hydrogen content of the carrier gas is 92-99% by volume.

20

The burner spacing reported in Table 2 is the distance from the top edge of the burner pipe, in other words the point at which the oil vapour-carrier gas mixture emerges, to the top edge of the cooled, narrowing
25 cooling gap.

In the subsequent table, Table 3, the analytical data of the inventive carbon blacks and of a comparison black are shown. The comparison black used (Example 7)
30 is that of Example 3 from WO 2005/033217.

Table 2:

Example	Gap dimensions height: width	Gap width b mm	Burner spacing [mm]	Hot air [m ³ /h(stp)]	Carrier gas volume [m ³ /h(stp)]	Oil vapour quantity [m ³ /h(stp)]	Operational gas volume [m ³ /h(stp)]	Flow rate [m/s]
1	12.5	4	171	9	3	3	650	22.6
2	25	2	181	14	4	3.2	650	45.1
3	25	2	171	14	3	3.2	650	45.1
4	25	1.5	181	18	4	3.2	650	45.1
5	33	4	181	17	4	3.2	650	60.2
6	12.5		171	9	4	3	250	8.7
(Comparative Example)								

Table 3:

Example	BET [m ² /g]	STSA [m ² /g]	Volatiles (950°C) [%]	pH	Tint [%]	Surface oxides [mmol/kg]	Coating My	Coating dM	(d ₉₀ -d ₁₀) /d ₅₀	FWHM /D _{mode}
1	93.1	76.1	4.8	3	120.5	130	251	4.2	0.57	0.55
2	142.9	118.7	4.3	3.6	141.3	170	284	15	0.58	0.55
3	169.5	132.2	4.5	3.4	142.6	200	293	18.5	0.60	0.54
4	274	190.9	8.76	3.07	146.6	320	282	2.3	0.64	0.60
5	274.8	192.3	7.75	3.1	141.3	290	284	4.4	0.64	0.58
6 (Comparative Example)	Experiment discontinued owing to deposition of black in the cooled, narrowing gap									
7 (Comparative Example)	316.6	244.2	4.62	3.9		220	291	-0.8	1.35	0.63

The results show that the carbon blacks of the invention (Examples 1-5) have an aggregate size distribution with a $(d_{90}-d_{10})/d_{50}$ ratio of less than or equal to 1.1. The advantage of the carbon blacks of the
5 invention is manifested in a dM value of > 0.5 and in a resulting higher blue hue.

Claims

1. Carbon black characterized in that the aggregate size distribution has a $(d_{90}-d_{10})/d_{50}$ ratio of less than
5 or equal to 1.1.
2. Carbon black according to Claim 1, characterized in that the aggregate size distribution has a full width at half-maximum (FWHM) to D_{mode} ratio of less than
10 or equal to 0.6.
3. Carbon black according to Claim 1 and 2, characterized in that the surface oxide content is greater than 50 mmol/kg.
15
4. Method of producing carbon black according to any one of Claims 1 to 3, characterized in that a gas mixture comprising a carrier gas and a carbon black feedstock is if desired admixed with hot air, the gas
20 mixture is passed into a burner pipe, the gas mixture burns at the burner pipe openings, and the flames, together with the ambient air drawn in freely under suction from outside, are sucked through a cooled, narrowing gap and cooled, the cooled, narrowing gap
25 having a height (h) to width (b) ratio of 1-100, the width being based on the top edge of the gap, the width (b) being 0.5 to 10 mm, and the flow rate at the narrowest point of the gap being 10 - 200 m/s.
- 30 5. Device for implementing the method according to Claim 4, having a burner and a cooling surface against which the flame is directed, characterized in that the cooled, narrowing gap has a height (h) to width (b) ratio of 1-100, the width being based on the top edge
35 of the gap, the width (b) is 0.5 to 10 mm, and the flow rate at the narrowest point of the gap is 10 - 200 m/s.

6. Use of the carbon blacks according to any one of Claims 1 to 3 as non-reinforcing filler, reinforcing filler, UV stabilizer, conductive black, pigment or reducing agent.

5

7. Use of the carbon blacks according to any one of Claims 1 to 3 in rubber, plastic, printing inks, liquid inks, inkjet inks, toners, coating materials, paints, paper, bitumen, concrete and other building materials.