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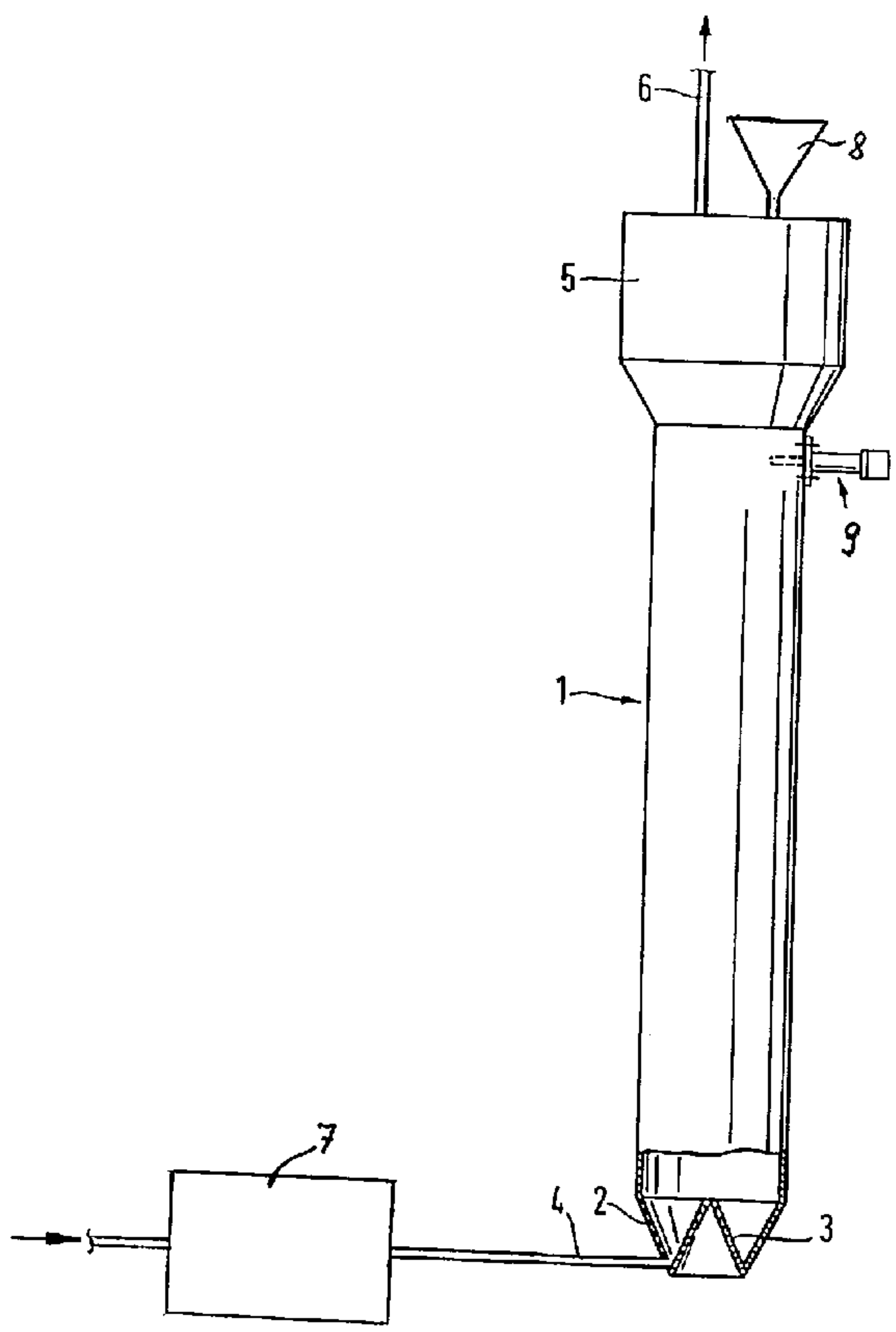
(54) **NOIR DE CARBONE AYANT SUBI UN POST-TRAITEMENT PAR OXYDATION**

(54) **OXIDATIVELY AFTERTREATED CARBON BLACK**



(57) The invention relates to an oxidatively aftertreated carbon black. It is characterised in that its content of volatile constituents is more than 10 wt.%, based on its total weight, and the ratio of its CTAB surface area to the iodine number is greater than 2 m^2/mg. The carbon black according to the invention is used preferably as pigment carbon black for the production of water-based paints, printing inks and as inks for mechanical and manual recording and drawing instruments. The combination of properties imparts to the carbon black an excellent dispersibility in water-based binder systems. The paints, printing inks and printer inks produced from it have an outstanding stability in storage.

Abstract

The invention relates to an oxidatively aftertreated carbon black. It is characterised in that its content of volatile constituents is more than 10 wt.%, based on its total weight, and the ratio of its CTAB surface area to the iodine number is greater than 2 m^2/mg. The carbon black according to the invention is used preferably as pigment carbon black for the production of water-based paints, printing inks and as inks for mechanical and manual recording and drawing instruments. The combination of properties imparts to the carbon black an excellent dispersibility in water-based binder systems. The paints, printing inks and printer inks produced from it have an outstanding stability in storage.

Oxidatively aftertreated carbon black

Description

This invention relates to an oxidatively aftertreated carbon black for use as pigment in paints, printing inks and inks, for example, for use in ink-jet printers.

Owing to its outstanding properties, carbon black is the main black pigment used in paints and in printing inks. There is available a large selection of pigment carbon blacks having different properties. Various processes are used for the production of pigment carbon black. Production is most frequently by oxidative pyrolysis of carbon-containing raw materials of carbon black. Here the raw materials of carbon black undergo incomplete combustion at elevated temperatures in the presence of oxygen. Examples of this type of process for producing carbon black include the furnace black process, the channel black process and the lampblack process. The carbon-containing raw materials of carbon black used are mainly polynuclear aromatic carbon black oils.

In the furnace black process, the incomplete combustion takes place in a reactor lined with highly refractory material. To this end, a stream of hot waste gas is produced in a preliminary combustion chamber by combustion of a fuel/air mixture and the carbon black raw material is sprayed or injected into this stream of hot waste gas. The carbon black which forms is quenched by water sprayed into the reactor and separated from the stream of gas. The furnace black process permits the production of carbon blacks possessing a very wide range of the properties of carbon black which are useful in practice.

The lampblack and channel black processes are important alternatives to the furnace black process. They yield carbon blacks whose properties overlap to some extent with the useful properties of carbon black which are obtainable through the furnace black process, but they also render possible the production of carbon blacks which cannot be produced through the furnace black process.

The lampblack apparatus consists of a cast-iron shell, which accommodates the liquid or optionally molten raw material, and a fume hood with a refractory lining. The air gap between shell and fume hood and the partial vacuum in the system serve to regulate the air supply and consequently to influence the properties of the carbon black. The raw material vaporises as a result of the heat radiation from the fume hood and undergoes partial combustion, but is mainly converted into carbon black. After having been cooled, the process gases containing the carbon black are passed to a filter to separate off the carbon black.

In the channel black process, the carbon black raw material is first of all vaporised into a stream of carrier gas containing steam and then undergoes combustion in a multiplicity of small flames under a cooled cylinder. A portion of the carbon black formed is deposited on the cylinder and another portion is discharged together with the process gases and deposited in a filter.

The important properties for assessing pigment carbon blacks are the depth of colour M_Y (in accordance with DIN 55979), die colouring power (preparation of a carbon black paste in accordance with DIN EN ISO 787/16 and evaluation in accordance with DIN EN ISO 787/24), the oil requirement (in accordance with DIN EN ISO 787/5), the volatile constituents (in accordance with DIN 53552), the structure, measured as DBP adsorption (in accordance with DIN 53601 or ASTM D2414), the average primary particle size (by assessment of electron micrographs) and the pH value (in accordance with DIN EN ISO 787/9 or ASTM D1512).

Table 1 shows the ranges of properties of pigment carbon blacks obtainable by the above-mentioned production processes. The data in Table 1 were gathered from technical publications by various manufacturers of carbon black regarding the characteristic carbon black values found for carbon blacks which had not been oxidatively aftertreated.

Table 1:

Property	Furnace black	Channel black	Lampblack
Depth of colour M_Y	210 - 270	230 - 300	200 - 220
Colouring power IRB3=100	60 - 130	90 - 130	25 - 35
Oil requirement [g/100g]	200 - 500	400 -1100	250 - 400
DBP adsorption [ml/100g]	40 - 200		100 - 120
Particle size [nm]	10 - 80	10 - 30	110 - 120
volatile constituents[wt.%]	0.5 - 1.5	4 - 6	1 - 2.5
pH value	8 - 10	4 - 6	6 - 9

For a paint or a printing ink, important properties in use are the stability of the carbon black dispersion in the binder system (stability in storage) and the rheological behaviour of the paint or the printing ink (viscosity and thixotropy). They are influenced crucially by the chemical structure of the surface of the carbon blacks.

The surface chemistry of the carbon blacks depends greatly on the chosen production process. In the furnace black process, the formation of the carbon black takes place in a highly reducing atmosphere, whereas in the channel black process, the atmospheric oxygen has free access to the zone where carbon black formation occurs. Accordingly, even directly after the production, the content of surface oxides in the channel blacks is considerably greater than in the case of the furnace blacks.

The surface oxides are in the main carboxyl groups, lactols, phenols and quinones, which give rise to an acidic reaction in aqueous dispersions of carbon black. To a lesser extent, the carbon blacks also have basic oxides at the surface. The surface oxides form the so-called volatile constituents of the carbon black, as they can be desorbed from the carbon black surface by calcining the carbon blacks at 950°C (DIN 53552).

The content of volatile constituents has a crucial influence on the dispersibility of the carbon blacks, particularly in aqueous systems. The greater the content of volatile constituents in the carbon blacks, the lesser is the hydrophobic character of the carbon blacks and the more readily are they dispersed in water-based binder systems.

For the reasons given above, pigment carbon blacks are generally aftertreated oxidatively in order to increase their content of volatile constituents. Nitric acid, nitrogen dioxide and, to a lesser extent, ozone as well, are used as oxidising agents. The contents of volatile constituents and the pH values given in Table 1 can be increased by oxidative aftertreatment. In this connection, the oxidation behaviour depends crucially on the carbon black production process. In the case of furnace blacks, the content of volatile constituents can be increased to only about 6 wt.%. This is as reported in US 3,565,657 regarding the oxidation of furnace blacks by nitric acid. The highest content of volatile constituents given in the said patent is 7.6 wt.%.

In several patents it has been attempted, by ozone treatment of furnace blacks, to reproduce the advantageous properties possessed by channel blacks due to the high content of volatiles in the latter. Among these are the patents US 3,245,820, US 3,364,048 and US 3,495,999. According to US 3,245,820, the content of volatiles in furnace blacks could be increased to 4.5 wt.% by the ozone treatment.

Another important property of the carbon blacks is their specific surface, which is determined by various adsorption methods. In the determination of the nitrogen surface area (BET surface area in accordance with DIN 66132), one assumes that the surface of the carbon black is covered with nitrogen molecules, the known spatial requirement of the nitrogen molecule rendering possible a conversion into m^2/g. As the small nitrogen molecule can also penetrate into pores and crevices in the carbon black, this method also includes the internal surface area of the carbon black. Cetyltrimethyl-ammonium bromide (CTAB) has a spatial requirement larger than that of nitrogen. The CTAB surface area (measured in accordance with ASTM D-3765) therefore comes closest to the determination of the geometrical surface without pores. Hence the CTAB surface area correlates very well with the particle size and thus allows conclusions as to the behaviour of the carbon blacks in use.

The iodine adsorption, also referred to as the iodine value, is a third method of characterising the surface area of carbon blacks. The iodine value is measured in accordance with ASTM D-1510. It is greatly influenced by surface groups and by adsorbed PAH's (=polyaromatic heterocyclic compounds). The adsorption measured in mg/g is not therefore converted into m^2/g. Generally the iodine adsorption is only given in the case of carbon blacks containing less than 1.5 wt.% of volatile constituents and less than 0.25 wt.% of a toluene extract. Owing to its sensitivity to the volatile surface groups, however, the iodine adsorption can be used especially as a further possible method of characterising oxidised carbon blacks having a high content of volatile constituents.

The object of the present invention is to specify carbon blacks for paints and printing inks, which carbon blacks are distinguished by having an improved dispersing behaviour in water-based binder systems and by the improved stability in long-term storage of the paints and printing inks produced from them.

This object is achieved by an oxidatively aftertreated carbon black, which is characterised in that its content of volatile constituents is more than 10 wt.%, preferably more than 15 wt.%, based on its total weight, and the ratio of its CTAB surface area to the iodine value is greater than 2 m^2/mg. The ratio of the CTAB surface area to the iodine value is preferably greater than 4 m^2/mg. In addition, these carbon blacks have no measurable concentration of basic surface oxides.

In this connection, the CTAB surface area and iodine value are measured in accordance with the ASTM standards cited above. It is important here that, prior to the measurement, the carbon blacks are not subjected to a heat treatment for the desorption of the volatile constituents.

It has been found that the consequence of the required combination of properties relating to volatile constituents and to a certain minimum ratio of the CTAB surface area to the iodine value in carbon blacks is that the latter can be very easily dispersed in water and that this dispersion remains stable for days, without the necessity of adding a wetting agent or dispersing additive. This high stability in storage of the aqueous dispersion of carbon blacks renders the carbon blacks according to the invention particularly suitable for use in paints, in printing inks and as inks for mechanical and manual recording and drawing instruments, hence, for example, as inks for ink-jet printers, felt-tip pens and ballpoint pens.

The carbon blacks according to the invention can be obtained by ozone oxidation of channel blacks. Furnace blacks are unsuitable as carbon black starting materials, because their content of volatile constituents cannot be increased to more than about 7 to 8 wt.%, even by ozone oxidation. From appropriate measurements of commercial pigment carbon blacks carried out by various manufacturers, it can be easily shown that the claimed combination of properties was hitherto unknown. Such measurements are reproduced in Table 2.

Table 2: Properties of commercial pigment carbon blacks

Carbon black	Volatile constit-uents [wt.%]	CATB surface area [m^2/g]	Iodine adsorption [mg/g]	CTAB/ Iodine [m^2/mg]
Cabot				
Monarch 1300	11.7	363	479	0.76
Monarch 1000	12.4	255	314	0.81
Mogul L	4.8	132	110	1.20
Columbian				
Raven 5000 UII	15.2	346	302	1.15
Raven 1255	6.2	119	73	1.63
Degussa				
FW 200	24.0	485	255	1.90
FW 1	4.3	236	239	0.99
Printex U	5	99	63	1.57
Printex 90	1	250	350	0.71
SS 550	2.5	120	101	1.19

In this list the commercial channel black FW 200 is noteworthy. This is a channel black which is not oxidised by ozone. Despite its high content of volatile constituents, it does not exhibit the required ratio of CTAB/iodine.

The invention will be explained in more detail with the aid of the following Examples. The Figure is described below.

Figure 1: Apparatus for the oxidation of carbon blacks by ozone

Figure 1 shows a suitable fluid-bed apparatus for the batchwise oxidation of carbon black by ozone. The apparatus consists of a vertically arranged cylindrical treatment vessel (1). This has at its lower end a fluidising section comprising a jacket (2) in the form of a truncated cone passing downwards from the cross-section of the cylinder, a conical upwardly-pointing displacing unit (3) inserted into the truncated cone and, at the lowest point of the fluidising section, at least one substantially tangentially running inlet pipe (4) for the treatment gas. A relieving section (5) with an outlet pipe (6) for the waste gas is mounted above the treatment vessel (1). Carbon black can be introduced into the treatment vessel via the filler necks (8) for the carbon black. (9) indicates a sensor for controlling the height of the fluid bed. To produce the ozone, the treatment gas (air or oxygen) is passed through the ozone generator (7) prior to entry into the treatment vessel. The treatment vessel has an internal diameter of 8 cm and a height of 1.5 m.

The carbon black is oxidised batchwise by means of the apparatus illustrated in Figure 1. However, a continuous mode of operation can also be put into effect by an appropriate arrangement of the fluid bed.

An ozoniser having the following performance data was used for the oxidation tests:

Operating pressure:	max. 0.6 bar
Carrier gas flow:	max. 600 l/h
Cooling water:	40 l/h (15°C)
Operating temperature:	max. 35°C
Generator voltage:	16 kV

The ozone concentration attainable is dependent on the generator voltage, on the flow of carrier gas and on its oxygen content. At a generator voltage of 16 kV, by using air a maximum of 12 g ozone/h is attained and by using oxygen a maximum of 25 g ozone/h is attained.

Example 1:

The channel black FW 1 was oxidised with ozone for different periods of time in the apparatus shown in Figure 1 and then analysed with regard to those properties which are useful in a carbon black.

In all oxidation tests, the ozoniser was operated with a constant flow of air of 310 Nl/h. The fluid bed was loaded each time with 200 g of carbon black. For all tests, the reaction temperature was in the range between 20 and 30°C. Table 3 shows the results obtained after treating FW 1 for different lengths of time, compared with untreated FW 1 and with the commercially oxidised channel black FW 200.

From Table 3, the following are observed to depend on the duration of the ozone oxidation:

- Increase in the volatile content
- Decrease in the pH value
- Increase in the CTAB surface area
- Decrease in the iodine value
- Decrease in the DIN colouring power
- Decrease in the oil requirement
- Significant change in the composition of the surface oxides

The changes in the CTAB surface area and iodine value do not mean that the particle size and therefore the surface are altered by the ozone oxidation, especially as the effects are opposite. Rather, the adsorption of iodine and of CTAB is influenced to such an extent by the modification of the surface of the carbon black, that the values obtained are no longer a measure of the surface. But they are suitable, along with the content of volatile constituents, for obtaining additional evidence regarding the nature of the modification of the surface as a result of the oxidation treatment.

In the highly oxidised carbon blacks, the My value increases to 328. The composition of the surface oxides also changes as the degree of oxidation increases. The carboxyl groups and quinones increase sharply, whereas the phenolic groups and the basic oxides decrease. The lactol content remains virtually unchanged.

Table 3: Analytical data for carbon blacks oxidised by ozone

Property	Unit	Duration of treatment of FW1 with ozone [h]						FW 200
		0	1	2	4	8	16	
Characteristic data for carbon black								
CTAB	m^2/g	236	246	269	311	306	361	485
Iodine number	mg/g	239	198	126	66	67	30	255
CTAB/Iodine	m^2/mg	0.99	1.24	2.14	4.71	4.7	12.03	1.90
BET	m^2/g	264						
My value			279	281	292	295	328	
DIN colouring power		104	106	102	92	92	82	91
Oil requirement	g/100g	995	855	560	390	540	295	620
Volatile content	wt.%	4.3	7.2	10.6	16.0	16.4	22.7	24.0
pH value		4.4	3.8	3.3	3.1	3.0	2.9	2.8
Surface oxides								
Carboxyl groups	mmol/kg	59	97	228	525	550	922	981
Lactols	mmol/kg	50	78	50	50	38	55	78
Phenols	mmol/kg	94	94	60	63	68	23	261
Quinones	mmol/kg	100	175	506	1012	1132	1445	1208
Basic oxides	mmol/kg	59	38	0	0	0	0	0

The channel black FW 200 not oxidised by ozone exhibits a quite different ratio of CTAB surface area to iodine value, a fact which can be attributed to the different composition of the surface oxides.

Example of use:

A particular advantage of the carbon blacks according to the invention is their ready dispersibility in water and the high stability of this dispersion. To investigate this behaviour, so-called settling tests were carried out on the carbon black according to the invention and standard commercial carbon blacks. To this end, in each case 1 gram of carbon black was dispersed ultrasonically in 99 ml water, without a wetting agent, for a period of 5 minutes and the settling of the dispersed carbon black was then observed. The beakers used for these investigations had a volume of 150 ml and a diameter of 5 cm. In the case of the carbon blacks not oxidised by ozone, a settling of the carbon black was already occurring after 15 minutes. A clear layer, free from carbon black, formed at the upper edge of the liquid surface. The settling behaviour found is shown in detail in Table 4.

Table 4: Settling behaviour of various carbon blacks

Carbon black		Oxidation by	Volatile content [wt.%]	Settling after 15 minutes [cm]
SS 550	F[1)]	NO_2	2.5	1
FW 200	G[2)]	NO_2	24.0	0.5
Printex 90	F	---	1	1
Printex U	G	---	5	0.25
FW1	G	---	4.3	0.5
FW1	G	Ozone	15	0

1) F: Furnace black; 2) G: Channel black

In the case of the channel black FW1 oxidised by ozone according to the invention, no settling of the carbon black was to be detected even after a week.

Claims

1. Oxidatively aftertreated carbon black, characterised in that its content of volatile constituents is more than 10 wt.%, preferably more than 15 wt.%, based on its total weight, and the ratio of its CTAB surface area to the iodine value is greater than 2 m^2/mg.

2. Carbon black according to claim 1, characterised in that the ratio of its CTAB surface area to the iodine value is greater than 4 m^2/mg.

3. Oxidatively aftertreated carbon black, obtainable by oxidation of a channel black by ozone.

4. Use of the carbon blacks according to one of the preceding claims in paints, in printing inks and as inks for mechanical and manual recording and drawing instruments.

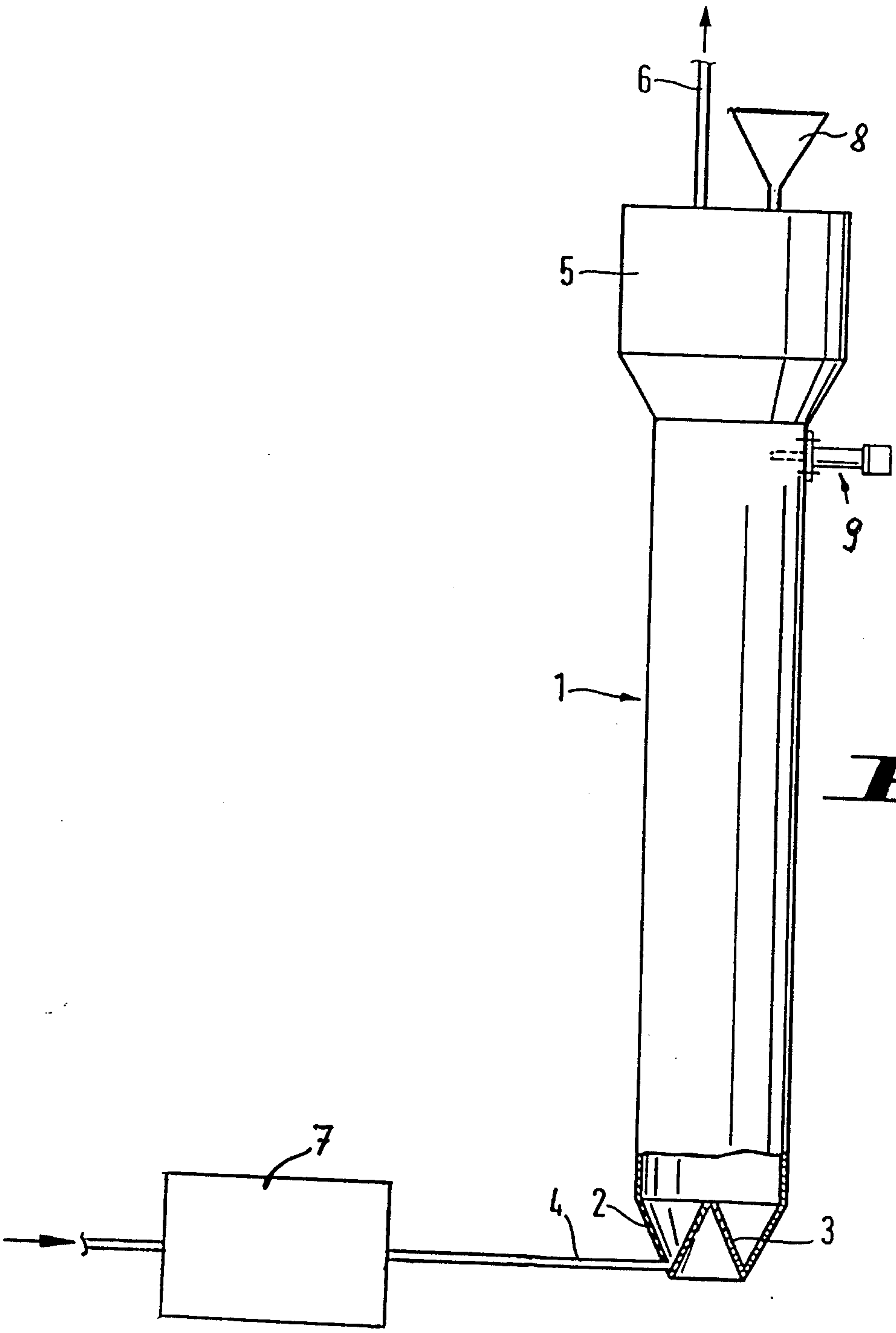


Fig. 1