The invention relates to a printed media coating, wherein at least one constituent of the ink is bonded to at least one constituent of the media coating via a chemical bond. A process for the production of the printed media coating and the use thereof are furthermore described.
Abstract

The invention relates to a printed media coating, wherein at least one constituent of the ink is bonded to at least one constituent of the media coating via a chemical bond. A process for the production of the printed media coating and the use thereof are furthermore described.
Printed media coating

The invention relates to printed media coating, a process for its preparation and its use.

A media coating as a rule comprises a coating arranged on a medium. The coating is used as an ink uptake layer.

It is known from EP 0514633 that the ink uptake layer, which is arranged on a carrier, comprises a polyvinyl alcohol, a cationic polymer which contains no crosslinking groups, an amorphous silica with a specific surface area of 200 to 400 m$^2$/g and a particle size of 2 to 12 μm and poly(methyl vinyl ether)-maleic acid anhydride and/or a benzotriazole derivative.

EP 0759635 discloses an ink jet recording material which has a carrier and at least one recording layer on the carrier, at least one of the recording layers comprising colloidal particles and a water-soluble resin.

The known inks and coating materials have the disadvantage that they have a low water resistance.

The object of the present invention is to provide a printed media coating of improved print quality, water resistance and high printing speed.

The invention provides a printed media coating, wherein at least one constituent of the ink is bonded to at least one constituent of the media coating via a chemical bond.

The media can be used as carriers for the media coating. The media for the media coating can be glass, ceramic, plastic, textiles, leather or paper. The printed media coating can be bonded to the media via one or more intermediate layers.
The invention also provides an ink, wherein at least one constituent of the ink forms a chemical bond with at least one constituent of the media coating.

The invention also provides a media coating, wherein at least one constituent of the media coating forms a chemical bond with at least one constituent of the ink.

The invention also provides a process for the production of the printed media coating, which comprises spraying, printing or atomizing the ink on to the media coating and reacting at least one constituent of the ink with at least one constituent of the media coating to form a chemical bond.

The chemical bonding of the ink to the media coating can take place according to the following reactions:

(a) The ink can comprise nitrite, preferably zinc, sodium, potassium or lithium nitrite, and carbon black and/or dyestuff and the media coating can comprise a compound containing amino groups.

Furnace, gas, flame, acetylene blacks or inversion blacks, known from DE 195 21 565, can be used as the carbon black. The dyestuffs can be compounds with aromatic systems.

Precipitated or pyrogenic silicas, pyrogenic oxides, chalk, kaolins, mica, zinc oxide, which are modified by a chemical reaction, for example with silanes, such that these contain primary amino groups, preferably aryl-bonded primary amino groups, on the surface, can be used as the compounds containing amino groups.

The reaction can take place in the acid pH range. For this, the media coating is formulated such that after printing of the media coating, a pH of < 6.0, preferably < 3.0, is present.

After the printing, the nitrite of the ink reacts with the primary amine of the media coating to form a
diazonium salt, which then reacts with the carbon black surface or the dyestuff.

The reaction can proceed according to the following equation

\[
\text{NO}_3^- + \text{H}_2\text{N} \equiv \text{R} + \text{H}^+ \rightarrow \text{N}_2 + 2\text{H}_2\text{O}
\]

(b) The ink can comprise a doped carbon black or dyestuff and the media coating can comprise a compound containing hydroxyl groups, the doped carbon black or dyestuff and/or the compound containing hydroxyl groups being modified with a silane. The functional groups of the doped carbon black or dyestuff or silane-modified carbon black or dyestuff can react with the compound containing hydroxyl groups or silane-modified compound containing hydroxyl groups.

Si-containing carbon blacks known from WO 98/45361 or DE 19613796 or metal-containing carbon blacks known from WO 98/42778 can be used as the doped carbon black. Inorganic and organic dyestuffs can be employed as the dyestuff. Inorganic dyestuffs can be metal oxides, such as, for example, (Zn,Co). \( \text{Al}_2\text{O}_3 \), \( \text{ZnO.(Al, Cr)}_2\text{O}_3 \), (Zn,Co)O.(Al,Cr)\(_2\)O\(_3\), ZnO.(Al,Cr,Fe)\(_2\)O\(_3\), MnO.Cr\(_2\)O\(_3\), (Mn,Co)O.(Cr,Fe)\(_2\)O\(_3\), CuO.Cr\(_2\)O\(_3\), spinels or doped oxides, or silicates, such as, for example, olivine, 2Co.SiO\(_2\), 2(Ni,Zn).SiO\(_2\), vanadium blue or Turkish blue. Precipitated silicas, pyrogenic silicas, pyrogenic oxides, silica sols, silica gels or naturally occurring pigments can be used as the compounds containing hydroxyl groups.
If only the doped carbon black or dyestuff or the compound containing hydroxyl groups is modified with silane, bifunctional silanes, such as, for example, 3-chloropropyltrialkoxyisilane, isocyanate-silane, tetraethyl orthosilicate (for example Dynasil® A), tetramethyl orthosilicate (for example Dynasil® M), tetra-n-propyl silicate (for example Dynasil® P), tetrabutylglycol silicate (for example Dynasil® BG), ethyl polysilicate (for example Dynasil® 40), 3-aminopropyltrimethoxysilane (for example Dynasylan® AMMO), 3-aminopropyltriethoxysilane (for example Dynasylan® AMEO), N-aminoethyl-3-aminopropyltrimethoxysilane (for example Dynasylan® DAMO), triamino-functional propyltrimethoxysilane (for example Dynasylan® TRIAMO), 3-mercaptopropyltrimethoxysilane (for example Dynasylan® MTMO); 3-glycidyloxypropyltrimethoxysilane (for example Dynasylan® GLYMO), 3-glycidyloxypropyltriethoxysilane (for example Dynasylan® GLYEO), 3-methacryloxypropyltrimethoxysilane (for example Dynasylan® MEMO), 3-acryloxypropyltrimethoxysilane, vinyltrichlorosilane (for example Dynasylan® VTC), vinyltrimethoxysilane (for example Dynasylan® VTMO), vinyltriethoxysilane (for example Dynasylan® VTEO), allyltrichlorosilane, allyltrimethoxysilane, allyltriethoxysilane, N-(n-butyl)-3-aminopropyltrimethoxysilane (for example Dynasylan® 1189), or 3-ureidopropyltriethoxysilane (for example Dynasylan® 2201/2220), can be used. For this, the doped carbon black or dyestuff or the compound containing hydroxyl groups is reacted with the silane. The reaction can proceed according to the following equation
The functional group A can be a halogen, alkoxy, epoxy or isocyanate group. If the doped carbon black or dyestuff and the compound containing hydroxyl groups are modified with silane, both the doped carbon black or dyestuff and the compound containing hydroxyl groups contain, after the modification, functional groups which can react with one another. For example, the doped carbon black or dyestuff and the compound containing hydroxyl groups can be modified with the following combinations of silanes:

- alkoxyaminosilane, for example 3-aminopropyltrimethoxysilane (for example Dynasylan® AMMO), 3-aminopropyltriethoxysilane (for example Dynasylan® AMEO), or N-aminomethyl-3-aminopropyltrimethoxysilane (for example Dynasylan® DAMO),
- alkoxysilane, for example 3-glycidyloxypropyltrimethoxysilane (for example Dynasylan® GLYMO) or 3-glycidyloxypropyltriethoxysilane (for example Dynasylan® GLYEOL),
- alkoxyammonium chloride-silane, for example (3-triethoxysilylpropyl)dimethyloctadecylammonium chloride or (3-triethoxysilylpropyl)trimethylammonium chloride, and sulfonatohydroxysilane, for example 3-sulfonatopropyltrimethoxysilane,
• alkoxyaminosilane, for example 3-aminopropyltrimethoxysilane (for example Dynasylan® AMMO), 3-aminopropyltriethoxysilane (for example Dynasylan® AMEO), or N-aminoethyl-3-aminopropyltrimethoxysilane (for example Dynasylan® DAMO) and isocyanate-silane. The reaction can proceed according to the following equation

![Chemical equation diagram]

The functional groups A and B can be anionic and cationic groups, amino and epoxy groups or amino and isocyanate groups.

(c) The ink can comprise a doped carbon black or dyestuff, optionally modified with a silane, and the media coating can comprise a polymer with functional groups. The functional groups of the doped carbon black or dyestuff or silane-modified carbon black or dyestuff can react with the functional groups of the polymer.

If the doped carbon black or dyestuff is not modified with silane, the polymer can contain functional groups which can react with the doped carbon black or dyestuff. The abovementioned compounds can be employed as the doped carbon black or dyestuff. The polymer can contain functional groups, such as, for example, epoxy,
isocyanate, alkoxy or hydroxyl groups. The reaction can proceed according to the following equation

\[ \text{Si-OH} + \text{polymer-A} \rightarrow \text{Si-O-polymer} \]

Si-doped carbon black  Media coating

If the doped carbon black or dyestuff is modified with silane, both the modified doped carbon black or dyestuff and the polymer contain functional groups which can react with one another. For example, the doped carbon black or dyestuff can be modified with the following silanes, it being necessary for the polymer to have corresponding functional groups:

- alkoxysilicon chloride-silane, for example (3-triethoxysilylpropyl)dimethyloctadecylammonium chloride or (3-triethoxysilylpropyl)trimethylammonium chloride, and polymer with sulfonate groups,

- sulfonatohydroxysilane, for example 3-sulfonatopropyltriethoxysilane, and polymer with ammonium chloride groups,

- alkoxysiliconamine, for example 3-aminopropyltrimethoxysilane (for example Dynasylan® AMMO), 3-aminopropyliethoxysilane (for example Dynasylan® AMEO), or N-aminomethyl-3-aminopropyltrimethoxysilane (for example Dynasylan® DAMO)

and polymer with epoxy groups,

- alkoxysiliconamine, for example 3-glycidyloxypropyliethoxysilane (for example Dynasylan® GLYMO), or 3-glycidyloxypropyliethoxysilane
(for example Dynasylan® GLYEO), and polymer with amino groups,

- alkoxyaminosilane, for example 3-aminopropyltrimethoxysilane (for example Dynasylan® AMMO), 3-aminopropyltriethoxysilane (for example Dynasylan® AMEO), or N-aminoethyl-3-aminopropyltrimethoxysilane (for example Dynasylan® DAMO)
and polymer with isocyanate groups or

- isocyanate-silane,
and polymer with amino groups.

The reaction can proceed according to the following equation

\[
\text{Si-OH} + \text{C-silane-A} \rightarrow \text{Si-O-silane-A} \in \text{ink}
\]

\[
\text{Si-doped carbon black} \downarrow \text{Media coating}
\]

\[
\text{Si-O-silane-polymer}
\]

The polymer can be a copolymer, block copolymer, polyampholyte or comb polymer. The polymers are built up here such that the abovementioned functional groups are present or can be incorporated by polymer-analogous reaction. The molecular weight Mw of the polymer can be less than 100,000 g/mol, preferably less than 10,000 g/mol.

Copolymers based on (meth)acrylic acid with basic (meth)-acrylates, such as dimethylaminoethyl (meth)acrylate and dimethyaminopropyl (meth)-acrylamide and quaternary ammonium compounds thereof and further alkyl or aryl (meth)acrylates (for example C_{4-30}-alkyl (meth)acrylates, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, phenylethyl (meth)acrylate),
heterocyclic (meth)acrylates (for example morpholinoethyl (meth)acrylate, N(2-
methacryloyloxyethyl)ethyleneurea) or hydroxy esters (for example 2-hydroxyethyl (meth)acrylate,
hydroxypropyl (meth)acrylate) or alkyl polyethylene glycol (200-2000) (meth)acrylates (for example methoxypolyethylene glycol 750 methacrylate), can be used. Water-soluble polymers based on (meth)acrylic acid, which have dispersing or pigment-stabilizing properties and moreover, by interaction with the carbon black pigment, should prevent diffusion into the paper surface, can be used as the polyampholytes. Graft polymers with emulsifier properties, which are obtained by copolymerization of hydrophobic macromonomers with functionalized end groups with hydrophilic monomers (EP 0 728 780 B1), can be used as the comb polymers. The macromonomers with a (meth)acyloyl end group are prepared, for example, from C₈-C₁₀ alkyl methacrylates, cyclohexyl methacrylate or benzyl methacrylate and then with hydrophilic (meth)acrylates (for example (meth)acrylic acid, (meth)acrylamide, 2-hydroxyethyl (meth)-acrylate, hydroxypropyl (meth)acrylate, dimethylaminoethyl (meth)acrylate and dimethylaminopropyl(meth)acrylamide and quaternary ammonium compounds thereof).

Block copolymers with the same monomer composition can equally suitably be used.

Copolymers which are prepared from acrylamide monomers and at least one of the monomers chosen from acrylic acid, dimethylaminopropylamine, dimethylaminopropylacrylamide (basic, neutral, quaternized), dimethylaminoethyl acrylate or dimethylaminoethyl methacrylate, can be used as the polymers.
(d) The ink can comprise a polymer with functional groups and the media coating can comprise a compound which contains hydroxyl groups and is optionally modified with silane. The functional groups of the polymer can react with the functional groups of the compound containing hydroxyl groups or silane-modified compound containing hydroxyl groups. Precipitated silicas, pyrogenic silicas, pyrogenic oxides, silica sols, silica gels or naturally occurring pigments can be used as the compound containing hydroxyl groups.

The polymer with the functional groups can bond the carbon black or dyestuff physically or chemically. The abovementioned compounds or metal sulfides, selenium sulfides, metal powders, pigments or coloured pigments can be employed as the carbon black or dyestuffs. If the compound containing hydroxyl groups is not modified with silane, the polymer can contain functional groups which can react with the compound containing hydroxyl groups. The polymer can contain functional groups, such as, for example, epoxy, isocyanate, alkoxy or hydroxyl groups.

The reaction can proceed according to the following equation:

\[ -\text{Si-OH} + \text{Polymer-A} \rightarrow -\text{Si-O-polymer} \]

<table>
<thead>
<tr>
<th>Compound containing hydroxyl groups</th>
<th>Media coating</th>
</tr>
</thead>
</table>

If the compound containing hydroxyl groups is modified with silane, both the compound containing hydroxyl groups and the polymer contain, after the modification,
functional groups which can react with one another. For example, the compound containing hydroxyl groups can be modified with the following silanes, it being necessary for the polymer to have corresponding functional groups:

- alkoxyammonium chloride-silane, for example (3-triethoxysilylpropyl)dimethyloctadecylammonium chloride or (3-triethoxysilylpropyl)trimethylammonium chloride, and polymer with sulfonate groups,

- sulfonatohydroxysilane, for example 3-sulfonatopropyltrihydroxysilane, and polymer with ammonium chloride groups,

- alkoxyaminosilane, for example, 3-aminopropyltrimethoxysilane (for example Dynasylan® AMMO), 3-aminopropyltriethoxysilane (for example Dynasylan® AMEO) or N-aminoethyl-3-aminopropyltrimethoxysilane (for example Dynasylan® DAMO), and polymer with epoxy groups,

- alkoxyepoxysilane, for example 3-glycidyloxypropyltrimethoxysilane (for example Dynasylan® GLYMO) or 3-glycidyloxypropyltriethoxysilane (for example Dynasylan® GLYEO), and polymer with amino groups,

- alkoxyaminosilane, for example 3-aminopropyltrimethoxysilane (for example Dynasylan® AMMO), 3-aminopropyltriethoxysilane (for example Dynasylan® AMEO) or N-aminoethyl-3-aminopropyltrimethoxysilane (for example Dynasylan® DAMO), and polymer with isocyanate groups or
• isocyanate-silane,  
  and polymer with amino groups.

The abovementioned compounds can be employed as the polymers.

The reaction can proceed according to the following equation

\[ \text{Compound containing hydroxyl groups} \rightarrow \text{Media coating} + \text{Polymer-B} \]

\[ \rightarrow \text{Si - O-silane-polymer} \]

(e) The ink can comprise a modified carbon black with \(-\text{SiR}_{(3-a)}(\text{O-(CH}_2\text{)}_n\text{-CH}_3)_a\) groups \(n = 0 - 5\), \(a = 1-3\), \(R = \text{alkyl}\) and the media coating can comprise a compound containing hydroxyl groups. The alkoxy groups of the modified carbon black can react with the compounds containing hydroxyl groups. The modified carbon black with \(-\text{SiR}_{(3-a)}(\text{O-(CH}_2\text{)}_n\text{-CH}_3)_a\) groups can be obtained by reaction of the carbon black with

• the corresponding azido compound,

• a corresponding compound \(R-S_y-R\), where \(y = 2-10\) (DE 10012784.3) or

• a corresponding compound which contains C-C double or triple bond which is not a constituent of an aromatic system, the C-C double or triple bond of which is activated by at least one substituent, for example \(-\text{COOR}, -\text{CO-R}, -\text{CN}, -\text{SO}_2\text{R}, -\text{SO}_2\text{OR or -CO-X-CO-},\) (DE 19931314.8).
Precipitated silicas, pyrogenic silicas, pyrogenic oxides, silica sols, silica gels or naturally occurring pigments can be used as the compound containing hydroxyl groups.

The alkoxy groups of the modified carbon black can react with the compound containing hydroxyl groups after the printing.

The reaction can proceed according to the following equation

\[
\text{Carbon black} + \text{N}_3\text{-(CH}_2\text{)_mSi(O-(CH}_2\text{)_n-CH}_3\text{)}_3 \rightarrow \text{NH-}(\text{CH}_2\text{)}_m\text{Si(O-CH}_2\text{)}_n\text{CH}_3\text{)}_3
\]

or

\[
+ S_i[(\text{CH}_2\text{)}_m\text{Si(O-(CH}_2\text{)_n-CH}_3\text{)}_2]
\]

or

\[
+ R-(\text{CH}_2\text{)}_m\text{Si(O-CH}_2\text{)}_n\text{CH}_3\text{)}_3
\]


(f) The ink can comprise an oligomer or polymer and a crosslinking agent and the media coating can comprise an oligomer or polymer, optionally a crosslinking agent. The crosslinking agent can crosslink the oligomer or polymer of the ink and additionally react with the oligomer or polymer of the media coating.

Compounds with functional groups, for example C-C double bonds, can be used as the oligomer or polymer.
The functional groups can react with the crosslinking agent. The crosslinking agent can be activated by air, heat, light or UV.

(g) The ink and the media coating can comprise one or more monomers and the ink and/or media coating can comprise a polymerization initiator. The ink and the media coating can be bonded by the polymers prepared by the polymerization.

The polymerization initiator can be activated by air, heat, light or UV. In a particular embodiment of the invention, the polymerization can be carried out by autocatalysis, without a polymerization initiator. Dimers, trimers or tetramers can be used as the monomers.

The ink can also comprise further constituents, such as, for example, water, solvents, polymer, cationic additives, binders, such as, for example, starch, cellulose, gelatine, casein, polyvinyl alcohol, polyvinylpyrrolidone, styrene/butadiene copolymer or ethylene/vinyl acetate copolymer, glass frit and other auxiliary substances.

The media coating can also comprise further constituents, such as, for example, binders, pigment, wetting agents, tinting dyestuffs, antistatics and other auxiliary substances.

The ink jet process, for example, can be used as the process for the production of the printed media coating.

The printing can be carried out at temperatures of 10 °C to 200 °C. A heat treatment, for example by a heated roller, at 10°C to 300°C can optionally take place after the printing, in order to allow the reaction or to bring it to completion.
The printed media coatings can be used for the production of books, journals, posters, newspapers, textiles, articles of glass, metal or ceramic, depending on the medium.

The printed media coatings according to the invention have a higher water resistance, fastness to light, fastness to wiping and an improved print quality. The printing can be carried out at a higher printing speed.
Examples

To evaluate the interactions between inks and coating materials, coloristic measurements are carried out and the improved fastness to wiping is evaluated.

For the inks described by way of example which are based on pigment carbon blacks, the optical density D is determined with a densitometer from Macbeth of the type RD 918.

The fastness to wiping of an ink - coating material combination is estimated by the following method.

A modified K Control Coater from Erichson is used for the newly developed test method. An ink according to the invention described by way of example is knife-coated on to the medium to be coated (paper, film etc.) and dried, wetted with a defined amount of water and the water is wiped over the area to be tested by operating the slide.

The optical densities before and after wiping are determined as measurement values and a standardized rating of the pigment discharge is given with a figure from 0 (complete discharge) - 9 (no discharge). The data of the media coatings selected are assigned to the corresponding example.

Example 1

Preparation of a carbon black dispersion

Distilled water is initially introduced into a dispersing vessel and 7.5 % Lutensol AO 30 from BASF is slowly added with the Ultra-Turrax running. When the Lutensol has dissolved completely, 2.1% Hypomer CG6 from ICI Surfactants and 0.3% AMP 90 from Angus Chemie are added. 15% carbon black FW18 from Degussa are then added in portions, the dispersion is dispersed with the Ultraturrax (level 10) and
thereafter the coarse contents are separated off in a centrifuge.

A bead mill is employed for further homogenization of the dispersion. The amount flowing through is 31/h at 3000 rpm. To separate off bead fragments, the mixture is filtered over a sieve of 100μm mesh width and centrifuged at 4000 rpm.

Preparation of an ink

10 g 2-pyrrolidone, 5 g 1,2-propanediol and 4 g 1,5-pentanediol are topped up with 65 ml water. 35 g of the dispersion described above are then added, while stirring. The ink obtained in this manner is then deaerated and introduced into the cartridge.

Production of the media coating

15 0.8 g NaNO₂ are added to 50 g ink, while stirring. The ink is investigated in respect of its fastness to wiping and optical density by the test methods mentioned.

A paper which is modified with amino-functional groups by the following process is used as the medium to be coated.

20 To prepare the brushing paints for the paper, polyvinyl alcohol (PVA) is dissolved in the total amount of water at approx. 95°C, the pigment (precipitated silica + Dynasilan® AMEO from Sivento) is then incorporated at 500 to 1000 rpm and the components are dispersed for half an hour at 3000 rpm. The brushing paints are adjusted to a solids content of 18%. The example recipe comprises 100 parts of pigment and 50 parts of Mowiol 28-99 (PVA from Clariant GmbH). The solids content is 18%, the application weight is approx. 10 g/m². The viscosity is determined by the Brookfield method, after stirring up. Thereafter, all the brushing paints are used to knife-coat in each case 10 sheets by hand on an 80 g/m² wood-free base paper, and the
coated papers produced are calendered, weighed and then subjected to the individual tests. The tests for determination of the quality of the paper include a printing test (printing a test image on an EPSON Stylus color 800 and HP Deskjet 550) and a drying test (determination of the drying time of 1 µl water on the paper coated with ink).

The optical density of the ink coating according to the invention described above is 1.11. The difference from the optical density after the wiping operation is 0.05. The pigment discharge is rated as 8.

Example 2

Functionalization of a pigment carbon black

15 g of a carbon black doped with silicon (according to EP 0799866) are stirred into 100 ml methyl ethyl ketone, 1.5 g Dynasylan® Glymo from Sivento are added, and the mixture is stirred for 12 hours at room temperature and then filtered with suction. The carbon black obtained is then dried in a drying cabinet at 100 °C for eight hours.

The functionalized carbon black is incorporated into a dispersion by the process described in example 1 and this is converted into an ink. The ink is investigated in respect of its fastness to wiping and optical density by the test method mentioned.

A paper which is coated by the process described in example 1 is used as the medium to be coated.

The optical density of the corresponding coating is 1.23. The difference from the optical density after the wiping operation is 0.11. The pigment discharge is rated as 7.
Example 3

Functionalization of a pigment carbon black

15 g of a carbon black doped with silicon (according to EP 0799866) are stirred into 100 ml methyl ethyl ketone, 1.5 g Dynasylan® 1161 (based on the active compound) from Sivento are added, and the mixture is stirred for 12 hours at room temperature and then filtered with suction. The carbon black obtained is then dried in a drying cabinet at 100 °C for eight hours.

The functionalized carbon black is incorporated into a dispersion by the process described in example 1 and this is converted into an ink. The ink is investigated in respect of its fastness to wiping and optical density by the test method mentioned.

A paper which is coated by the process described in example 1 is used as the medium to be coated. In addition to the constituents described, Polystabil S312 from Stockhausen was added.

The optical density of the corresponding coating is 1.20. The difference from the optical density after the wiping operation is 0.04. The pigment discharge is rated as 9.

Example 4

Preparation of a carbon black dispersion

The dispersion is prepared analogously to example 1. Tego ABIL soft AF 100 from TEGO is used as the polymeric wetting agent.

The dispersion is converted into an ink as described in example 1.

A paper which is coated by the process described in example 1 is used as the medium to be coated. Instead of Dynasilan®
AMEO, Dynasilan® Glymo is incorporated into the paper coating.

The optical density of the corresponding coating is 1.25. The difference from the optical density after the wiping operation is 0.03. The pigment discharge is rated as 9.

Example 5

Functionalization of a pigment carbon black

Variant 1:

A solution of 2 ml azidosilane Si250 from Degussa in 150 ml acetone is added to 10 g carbon black FW1 from Degussa, the mixture is stirred for 30 minutes at RT and the solvent is then stripped off in vacuo. The carbon black is heat-treated for two hours at 180°C. It is then washed with acetone and dried in a drying cabinet at 105°C for eight hours.

Variant 2

A solution of 2 ml azidosilane Si250 from Degussa in 150 ml acetone is added to 10 g FW1 from Degussa and the solution is stirred for six hours under irradiation from two laboratory heating lamps and while cooling with water (temp<50°C). It is then filtered with suction and the residue is dried in a drying cabinet at 105°C for eight hours.

The functionalized carbon blacks are incorporated into dispersions by the process described in example 1 and these are converted into inks. The ink is investigated in respect of its fastness to wiping and optical density by the test method mentioned.

Copy office paper from Kompass is used as the medium to be coated.
The optical density of the corresponding coating is 1.45 (variant 1) or 1.42 (variant 2). The difference from the optical density after the wiping operation is 0.02 (variant 1) or 0.04 (variant 2). The pigment discharge is rated as 9 (variant 1) or 8 (variant 2).

Example 6

Functionalization of a pigment carbon black

2 g Si69 (bis(triethoxysilylpropyl)tetrasulfane) from Degussa are dissolved in 150 ml toluene, 10 g FW1 are added and the mixture is boiled under reflux for five hours. The carbon black is then filtered off with suction and dried in a drying cabinet at 105°C for eight hours. The yield is determined with the aid of the amount of carbon black obtained.

Yield: 75%

The functionalized carbon black is incorporated into a dispersion by the process described in example 1 and this is converted into an ink. The ink is investigated in respect of its fastness to wiping and optical density by the test method mentioned.

Copy office paper from Kompass was used as the medium to be coated.

The optical density of the corresponding coating is 1.42. The difference from the optical density after the wiping operation is 0.04. The pigment discharge is rated as 9.

The inks described are investigated for their printability. Printing tests are carried out by means of commercially obtainable office inkjet printers. Printing takes place on in each case one side on four different commercially available ink jet papers and on copying paper immediately and after a 5 min, 10 min, 20 min, 30 min and 60 min
printing pause. A long-term test (printing of 20 pages without a pause) and a refire test (investigation of the writing properties of the ink after a 1, 3 and 7 day printing pause) is furthermore carried out. The printed images correspond to or exceed the results of the corresponding original inks.
Patent claims

1. A printed media coating, wherein at least one constituent of the ink is bonded to at least one constituent of the media coating via a chemical bond.

2. A printed media coating as claimed in claim 1, wherein the media are glass, ceramic, plastic, textiles, leather or paper.

3. A printed media coating as claimed in claim 1, wherein the ink comprises nitrite and carbon black and/or dyestuff and the media coating comprises a compound containing amino groups.

4. A printed media coating as claimed in claim 1, wherein the ink comprises a doped carbon black or dyestuff and the media coating comprises a compound containing hydroxyl groups, the doped carbon black or dyestuff and/or the compound containing hydroxyl groups being modified with a silane.

5. A printed media coating as claimed in claim 1, wherein the ink comprises a doped carbon black or dyestuff, optionally modified with a silane, and the media coating comprises a polymer with functional groups.

6. A printed media coating as claimed in claim 1, wherein the ink comprises a polymer with functional groups and the media coating comprises a compound which contains hydroxyl groups and is optionally modified with silane.

7. A printed media coating as claimed in claim 1, wherein the ink comprises a carbon black with $-\text{SiR}_{(3-a)}(\text{O-}(\text{CH}_3)_n-\text{CH}_3)_a$ groups ($n = 0 - 5$, $a = 1 - 3$, $R = \text{alkyl}$) and the media coating comprises a compound containing hydroxyl groups.
8. A printed media coating as claimed in claim 1, wherein the ink comprises an oligomer or polymer and a crosslinking agent and the media coating comprises an oligomer or polymer, optionally a crosslinking agent.

9. A printed media coating as claimed in claim 1, wherein the ink and the media coating comprise one or more monomers and the ink and/or media coating comprise a polymerization initiator.

10. An ink, wherein at least one constituent of the ink forms a chemical bond with at least one constituent of the media coating.

11. A media coating, wherein at least one constituent of the media coating forms a chemical bond with at least one constituent of the ink.

12. A process for the production of a printed media coating as claimed in claim 1, which comprises spraying, printing or atomizing the ink on to the media coating and reacting at least one constituent of the ink with at least one constituent of the media coating to form a chemical bond.

13. A process for the production of a printed media coating as claimed in claim 12, wherein an ink jet process is used.

14. A process for the production of a printed media coating as claimed in claim 12, wherein the printing is carried out at temperatures of 10°C to 200°C.

15. A process for the production of a printed media coating as claimed in claim 12, wherein the ink comprises nitrite and carbon black and/or dyestuff and the media coating comprises a compound containing amino groups.
16. A process for the production of a printed media coating as claimed in claim 12, wherein the ink comprises a doped carbon black or dyestuff and the media coating comprises a compound containing hydroxyl groups, the doped carbon black or dyestuff and/or the compound containing hydroxyl groups being modified with a silane.

17. A process for the production of a printed media coating as claimed in claim 12, wherein the ink comprises a doped carbon black or dyestuff, optionally modified with a silane, and the media coating comprises a polymer with functional groups.

18. A process for the production of a printed media coating as claimed in claim 12, wherein the ink comprises a polymer with functional groups and the media coating comprises a compound which contains hydroxyl groups and is optionally modified with silane.

19. A process for the production of a printed media coating as claimed in claim 12, wherein the ink comprises a carbon black with \(-\text{SiR}_{(3-a)}(0-(\text{CH}_2)_n\text{-CH}_3)_a\) groups \((n = 0-5, a = 1-3, \text{R} = \text{alkyl})\) and the media coating comprises a compound containing hydroxyl groups.

20. A process for the production of a printed media coating as claimed in claim 12, wherein the ink comprises an oligomer or polymer and a crosslinking agent and the media coating comprises an oligomer or polymer, optionally a crosslinking agent.

21. A process for the production of a printed media coating as claimed in claim 12, wherein the ink and the media coating comprise one or more monomers and the ink and/or media coating comprise a polymerization initiator.

22. The use of a printed media coating as claimed in claim 1 for the production of books, journals, posters,
newspapers, textiles, articles of glass, metal or ceramic.