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(71) Applicant: **ILFORD Imaging Switzerland GmbH**
1723 Marly 1 (CH)

(72) Inventors:
- **Schär, Meinrad**
  1731 Ependes (CH)
- **Zahnd, Cédric**
  1700 Fribourg (CH)

(74) Representative: **Herzog, Martin**
Herzog Fiesser & Partner Patentanwälte PartG mbB
Immermannstraße 40
40210 Düsseldorf (DE)

(54) Inkjet media for solvent borne inks

(57) The invention relates to inkjet media comprising a substrate layer, a drainage layer wherein the drainage layer comprises a plurality of silicon oxide particles, and a permeation layer which is at least partially superimposed to the drainage layer (3), wherein the contact angle between the permeation layer (6) and an organic solvents, such as diethylene glycol mono-n-butyl ether is 30° or less. The invention also relates to a process for preparing inkjet media, to an inkjet medium obtainable by said process, to a method for applying a liquid phase onto an inkjet medium, and to a printed article which comprises an inkjet medium. The inkjet media of the invention are particularly suited to be printed with solvent-based inks.

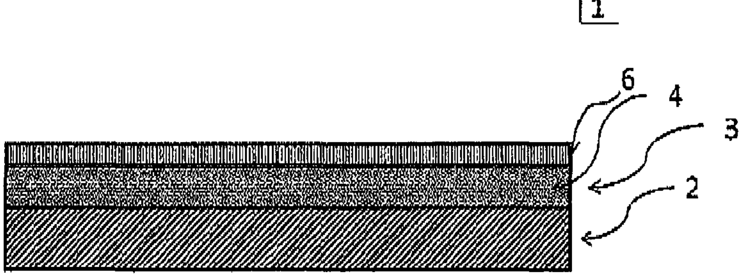


Figure 1

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The invention relates to a layer structure comprising a substrate layer, a drainage layer wherein the drainage layer comprises a plurality of silicon oxide particles, and a permeation layer which is at least partially superimposed to the drainage layer (3), wherein the contact angle between the permeation layer (6) and organic solvents, e.g. diethylene glycol mono-n-butyl ether, is 30° or less. The invention further relates to a process for preparing a layer structure, to a layer structure obtainable by said process, to a method for applying a liquid phase onto a layer structure, and to a printed article which comprises a layer structure. The layer structures of the invention are particularly suited to be printed with solvent-based inks.

[0002] Inkjet printing solutions based on solvent-based inks, also referred to as solvent-borne inks, gain in importance and market share due to their very high weather resistance which is an important feature for outdoor use. These inks usually contain pigments and one or more organic compounds, e.g., organic solvents. Of the organic solvents, often the volatile ones are preferred because of their high evaporation rate. The evaporation rate is often a key factor in the drying process. This process may be accelerated using a heating unit. Another approach to water-fast inks focuses on monomers in the ink which are polymerised using a UV-curing unit. There, polymerisation of the monomers contributes to ink fixation. In both cases, direct printing on a polymer substrate is feasible, especially if the substrate is able to absorb a slight amount of the ink vehicle. Such substrates are usually polyvinylchloride- or polystyrene-based materials.

[0003] The main drawback of UV-curing inks and standard solvent-based pigmented inks is that they contain substances that are dangerous to the health of humans and hazards to the environment. Accordingly, printers must be equipped with a costly air-purging and recycling system when printing such inks. To avoid these difficulties, manufacturers developed inks based on socalled eco-solvents. These inks contain less volatile organic compounds which, however, results in extended drying times after printing and induces tackiness while in undried state.

[0004] Accordingly, there is an ongoing and increasing demand from the market for substrates whose production and recycling is more sustainable. These substrates can be based on paper (with a barrier layer or a resin layer), recyclable polyethylene terephthalate, cellulose-acetate or polylactide, for example. These substrates are considered to be much more environmentally friendly than the standard polystyrene or polyvinylchloride-based substrates. However, these substrates usually do not accommodate the volatile organic compounds of the ink vehicle through absorption.

[0005] An object of the present invention is generally to overcome at least some of, preferably as much as possible the disadvantages of the known processes.

[0006] Another object of the present invention is to provide improved printed articles which show good resistance to water and good weather resistance, both particularly advantageous in outdoor use.

[0007] Another object of the present invention is to provide improved inkjet recording media for printing with solvent-based pigmented inks.

[0008] Another object of the present invention is to provide improved inkjet recording media which further fast drying after being printed, in particular when being printed with solvent-based inks.

[0009] Another object of the present invention is to provide improved inkjet recording media which have no tacky surfaces during drying, in particular when being printed with solvent-based inks.

[0010] Another object of the present invention is to provide improved inkjet recording media for printing with solvent-based pigmented inks wherein the printed surface exhibits good mechanical resistance (rubbing resistance) and good lifetime.

[0011] Another object of the present invention is to provide a recording media for printing which does not contain chlorine-based polymers.

[0012] Another object of the present invention is to provide a recording media which is made from sustainable materials.

[0013] Another object of the present invention is to provide a recording media which is made from readily available and inexpensive materials.

[0014] Another object of the present invention is to provide a recording media for printing, in particular with solvent-based pigmented inks, which has an image quality and a surface feel comparable to those recording media known from silver-halide photography.

[0015] Another object of the present invention is to provide a recording media, in particular for printing with solvent-based pigmented inks, which recording media provide an even and high image quality that does not depend on the chosen substrate.

[0016] Another object of the present invention is to provide a method for applying solvent-based pigmented inks on a substrate, preferably with short drying times.

[0017] Another object of the present invention is to provide a method for applying solvent-based pigmented inks on a substrate resulting in a printed article with good mechanical wear properties.

[0018] Another object of the present invention is a printed article manufactured according to an environmentally friendly process and showing prints of high gloss and color.

[0019] Another object of the present invention is a printed article that is at least partially biodegradable.

[0020] Another object of the present invention is to provide a printed article which has good mechanical wear properties and good weather resistance, in particular in outdoor use.

[0021] Another object of the present invention is to provide a layer structure and a method for applying a solvent-based pigmented ink to a substrate, wherein the layer structure shows only little or no swelling upon contact with solvent-based inks.

[0022] A contribution to the solution of at least one of the above objects is provided by the subject matters of the category-forming claims, whereby the dependent sub-claims of the category-forming independent claims represent preferred aspects of the invention, whose subject matters likewise make a contribution to solving at least one of the objects mentioned above.

[0023] A first aspect of the invention is a layer structure comprising:

(a) a substrate layer;

(b) a drainage layer which is at least partially superimposed to the substrate layer, wherein the drainage layer comprises a plurality of silicon oxide particles, and

(c) a permeation layer, at least partially superimposed to the drainage layer, which is at least partially superimposed to the drainage layer,

wherein the contact angle is 30° or less, preferably 25° or less, or 20° or less, further preferred in the range of from 0° to 10°, or from 0° to 5°, wherein the contact angle is determined between the permeation layer and diethylene glycol mono-n-butyl ether (also referred to as: DEGMBE) according to the method described below.

[0024] Surprisingly, the applicant found that the layer structures of the invention behave very good when being printed with solvent-based inks. It was found that permeation layers based on polymers which permeation layers have low contact angles with organic solvents also absorbs these solvents. It was further found that the layer structure of the above rapidly absorbs organic solvents which migrate through the permeation layer into the drainage layer. It was further found that the layer structure of the above does not suffer from swelling of the layer structure upon exposure to organic solvents. The layer structures of the invention show this behavior with the solvents commonly used in solvent-based inks.

[0025] The term transparent in the context of this invention is used to characterise an article, through which light of a wavelength λ of from 350 nm to 800 nm can pass, whereby the amount of light passed through the item or system is at least 85 % of the amount of light, which amount entered the article.

[0026] The term opaque in the context of this invention is used to characterise an article, through which light of a wavelength λ of from 350 nm to 800 nm can pass, whereby the amount of light passed through the item or system is less than 6 % of the amount of light, which amount entered the article.

[0027] The term biodegradable is used in the present context to characterise an item or system which may be subjected to biodegradation, i.e. which can be broken down, dissolved, or otherwise disintegrated by environmental, in particular biological means, such as by enzymes or microorganisms, e.g. bacteria. The biodegradable properties of an item can be tested according to internationally accepted standards, e.g. ASTM D5511.

[0028] Organic solvents in the context of the present invention are organic compounds which are in liquid state in the temperature range between 5 °C and 40°C.

[0029] A surface of an item, e.g. a silicon oxide particle, is considered positively charged at the surface, when the zeta potential of the item is larger than 0 mV. A surface of an item, e.g. a silicon oxide particle, is considered negatively charged at the surface, when the zeta potential of the item is less than 0 mV. The Zeta Potential can be determined according to the method described below.

[0030] The term superimposed in the context of this invention is used to describe the relative position of a first item, e.g. the drainage layer, with respect to a second item, e.g. a second layer such as a substrate layer. Possibly, further items, e.g. beads or layers may be arranged between the first and the second item. If two items are directly superimposed, no further layer is arranged between both items.

[0031] A drainage layer in the context of the present invention is a layer which is able to accept and retain one or more liquids. There is no particular requirement to the mechanism of accommodation and retention. Retaining a liquid in the present context can mean storing the liquid in the layer to eternity, but also includes a retarded release of the liquid from the drainage layer to a surface of the layer structure and dispensing therefrom. According to a preferred aspect of the present invention, the drainage layer is able to particularly accept and retain organic liquids, in particular organic solvents. To achieve these properties, the drainage layer is preferably porous. Porous is defined in a conventional fashion to involve a structure or a material which has a plurality of pores therein which fluids etc. may pass. The drainage layer is made of a material which is preferably non-swellable in the presence of organic components usually present in solvent-based inks. Non-swellable in the context of the present invention means that the drainage layer does not increase its volume for more than 20 % by volume, when being in contact with an organic solvent, based on the dry volume of the drainage layer prior to contacting with an organic solvent.

[0032] A layer structure according to the invention implies a plurality comprising three or more layers, in which at least a part of a layer is interconnected with at least a part of at least one adjacent layer.

[0033] According to an aspect of the invention, the substrate layer comprises at least one of the following items: paper, card board, metal, such as aluminium, metal foil, metallised substrates, e.g. a polymer, onto which a layer of metal is deposited, glass, flexible glass (e.g.: "Gorilla Glass" manufactured by Coming, Inc., USA), stone paper (a polyethylene composite material containing about 80 wt.-% $CaCO_3$, based on the total composite material) and a combination of two or more thereof.

[0034] According to another aspect of the invention, the substrate layer comprises at least one polymer. Numerous of the known polymers enter into the consideration of those skilled in the art. Preferably, the at least one polymer is the substrate layer. Preferably, the at least one polymer is selected from the group consisting of cellulose esters such as cellulose triacetate, cellulose acetate, in particular cellulose diacetate, cellulose propionate or cellulose acetate/butyrate, polyesters such as polyethylene terephthalate or polyethylene naphthalate, polyamides, polycarbonates, polyimides, polyolefins such as polyethylenes, e.g., low density polyethylene, high density polyethylene and polypropylene, polyvinyl acetals, polyethers, polyvinyl chloride, poly(vinylidene dichloride), polyvinylidenfluoride, polyvinyl sulphones, acrylnitrile, butadiene, styrene, polycarbonates, polyetherimide, polyester ketones, poly(methylmethacrylate), polyoxymethylene and polystyrene, or a combination of two or more thereof.

[0035] Further, the at least one polymer of the substrate layer is preferably selected from the group consisting of aliphatic polyesters such as polycaprolactone, poly(β-propiolactone), poly(hydroxyalkanoate), poly(hydroxybutyrate), poly(glycolic acid), poly(β-malic acid), poly(alkylene succinate)s, poly(butylene succinate), poly(lactide)s, starch blends, poly(p-dioxanone), acetyl cellulose with low degree of acylation, poly(vinyl alcohol)s, polyamides, poly(amino acids), pseudopoly(α-amino acids), poly(α-amino acid ester), copolyesters, copolyamides, poly(ester amides), poly(ester ureas), poly(iminocarbonates), polyanhydrides, poly(ethylene glycol)s, poly(orthoester)s, polyphosphazenes, polyurethanes, poly(ester urethane), poly(ether urethane), poly(urethane urea)s, polystyrene, polyolefines such as polypropylene, aliphatic-aromatic copolyesters such as copolyesters of polycaprolactone and poly(ethylene terephthalate), copolyesters of polycaprolactone and poly(butylene terephthalate), copolyesters of polycaprolactone and poly(ethylene isophthalate), copolyesters of adipic acid and terephthalic acid, copolyesters of 1,4-butanediol, adipic acid and terephthalic acid, or a combination of at least two thereof.

[0036] According to another aspect of the invention, the substrate layer is a composite material comprising two or more of the aforementioned substrate layer materials.

[0037] Preferably, the substrate layer is transparent. A transparent substrate layer can be principally obtained by the polymers mentioned above. However, the manufacturing process must be controlled to obtain materials having appropriate structures, such as crystallites, wherein the size of the structures is smaller than a quarter of the wavelength of light passing through, e.g. if the substrate layer is exposed to light of a wavelength λ in the range of from 350 nm to 800 nm, than the structures present in the transparent layer should be smaller than 350/4 nm = 87.5 nm. More preferably, the structures in the transparent layer are smaller than 60 nm, or smaller than 50 nm, or smaller than 40 nm. Usually, amorphous materials meet aforementioned requirements. In this regard, the size of a structure is considered as the longest direct line through the structure which connects two points on the surface of the structure.

[0038] According to another preferred aspect of the invention the substrate layer is opaque. Numerous of the known opaque materials enter into the consideration of those skilled in the art. Preferred materials for opaque substrates are those materials known in the photographic industry, e.g. raw paper, barrier paper, resin coated paper, japanese tissue paper, baryta paper, polyolefin-coated paper or voided white opaque polyester (such as Melinex® manufactured by Du-Pont Tejin films). Particularly preferred substrates of photographic quality are resin-coated paper, baryta paper and voided polyester.

[0039] According to another preferred aspect of the invention, the substrate layer is biodegradable. Yet more preferred the layer structure in whole is biodegradable. Further preferred are all of the layers of the layer structure biodegradable. Sometimes, not all of the layers of the layer substrate are biodegradable. Then, a layer which is not biodegradable fragments due to mechanical failure when the adjacent biodegradable layers are degraded.

[0040] According to a further aspect of the invention, the biodegradable substrate layer has a biodegradability determined according to ASTM D5511 of at least 1% in 45 days, preferably of at least 2% in 45 days, more preferably of at least 3% in 45 days, yet more preferably of at least 3.5% in 45 days.

[0041] Further, the layer structure of the invention comprises a permeation layer. The permeation layer in the context of the present invention is susceptible to organic solvents. This means that the permeation layer can absorb organic solvents, and eventually shows swelling. Further, organic solvents may migrate through the permeation layer if there is a driving force to do so. Without being bound to a theory, it is assumed that if a solvent-based ink comprising binders and pigments is applied onto said permeation layer, the solvent is absorbed or penetrates at least partially through the permeation layer while the binders and pigments of the solvent-based ink remain on the surface of the permeation layer. To achieve these properties, the permeation layer is generally swellable with an organic liquid phase and/or can be penetrated by the organic liquid. Further, the permeation layer is preferably non-porous. Sufficient susceptibility of the permeation layer with regard to an organic liquid phase is achieved when after being brought into contact with said organic liquid phase, the organic liquid phase evaporates from or passes through the permeation layer substantially completely before significant swelling of the permeation layer occurs.

[0042] According to a preferred aspect of the invention the permeation layer is susceptible to organic solvents. Organic solvents are used as organic vehicle in solvent based pigmented inks. An organic vehicle of a solvent based pigmented ink can contain only one single organic solvent. Usually the organic vehicle contains a combination of two or more organic solvents. Numerous of the known organic solvents enter into consideration of those skilled in the art. Suitable organic solvents are preferably selected from the group consisting of ketones, alcohols, hydrocarbons, esters, pyrrolidones and glycols and its derivatives, like acetates and ethers. Preferred ketones are acetone, methyl ethyl ketone, cyclohexanone, 2-heptanone and 2-octanone. Preferred alcohols are methanol, ethanol, isopropanol, n-hexyl alcohol, iso-heptyl alcohol, 2-ethyl hexyl alcohol, n-octyl alcohol, 3-methyl-3-methoxy butanol, and 3-methoxy butanol. Preferred hydrocarbons are toluene, xylene, turpentine, limonene, industrial volatile oil, tetrahydronaphthalene, and decahydronaphthalene. Preferred glycols are ethylene glycol, diethylene glycol, triethyleneglycol, thiodiethylene glycol, tridiethylene glycol, propylene glycol, dipropylene glycol, and tripropylene glycol. Preferred glycol ether acetates are ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, and diethylene glycol monobutyl ether acetate. Preferred glycol ethers are ethylene glycol monomethyl ether, ethylene glycol monoethylether, ethylene glycol monobutyl ether, ethylene glycol monohexyl ether, ethylene glycol-2-ethylhexyl ether, ethylene glycol phenyl ether, propylene glycol monoethyl ether, propylene glycol propyl ether, propylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol hexyl ether, diethylene glycol-2-ethyl hexyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol monobutyl ether, dipropylene glycol propyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol monobutyl ether, and tripropylene glycol monomethyl ether, tetraethylene glycol dimethyl ether, tetraethylene glycol monobutyl ether. Preferred esters are 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, triethylene glycol di(2-ethylbutyrate), propylene carbonate, ethyl lactate, butyl lactate, methyl acetoacetate, ethyl acetoacetate, diacid ester (DBE) and 3-methyl-3-methoxy butyl acetate. A preferred pyrrolidone is N-methyl-2-pyrrolidone. Yet more preferred is a combination of at least two of the aforementioned organic solvents. The combination can comprise two or more solvents of the same group or solvents of different groups.

[0043] Solvents which have a boiling point higher than 250°C at 1013hPa or a vapor pressure of less than 0.27kPa at 25°C, or both, are particularly preferred. Suitable examples include tetraethylene glycol dimethyl ether, tetraethylene glycol monobutyl ether, dipropylene glycol dimethyl ether, ethylene glycol monobutyl ether, diethylene glycol mono-n-butyl ether, ethylene glycol monobutyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate, propylene diglycol acetate, and 3-methoxy-n-butyl-acetate. According to a preferred embodiment of the present invention the combined absorption capacity the drainage layer and the permeation layer together is at least 50 %, preferably at least 70 %, or at least 80 %, or at least 90 %, yet more preferably 100 %, or more than 100 % of the total dry weight of those two layers determined by exposure to diethylene glycol mono-n-butyl ether according to the method described herein. The absorption capacity (AC) of an article with respect to the reference liquid, i.e. diethylene glycol mono-n-butyl ether, is understood as the amount of reference liquid which can be absorbed by the article. The amount of reference liquid that can be absorbed is determined by weighing the article after absorption and then subtracting the weight of the dry article. The absorption capacity (AC) is calculated according to formula (I):

$$AC = \frac{amount\ of\ absorbed\ liquid\ in\ g}{weight\ of\ the\ dry\ layers\ in\ g}\ [wt.-\%] \qquad \text{(I)}$$

[0044] The weight of the dry layers is the sum of all non-volatile compounds of the layers. The absorption capacity is measured at a temperature of 20°C and a standard pressure of 1013hPa. The reference liquid used in the absorption test is diethylene-glycol-mono-n-butyl ether.

[0045] According to another preferred aspect of the present invention the ratio of the thickness of the drainage layer and the thickness of the permeation layer is at least 5:1, preferably at least 6:1, or at least 8:1, or at least 10:1, or at least 12:1, or at least 14:1, each thickness determined in g/m^3. Further, the said ratio of the thickness is preferably in the range of from 5:1 to 14:1, or from 6:1 to 12:1, or from 6:1 to 10:1, each thickness determined in g/m^2.

[0046] According to another preferred aspect of the present invention, the permeation layer comprises less than 5 % by weight, preferably less than 2 % by weight, or less than 1 % by weight, or in the range of 0.1 to 0.5 % by weight of a hydrophilic or water soluble polymer. Yet more preferred, the permeation layer comprises no hydrophilic and no water soluble polymer. Hydrophylic Polymers are polymers which show swelling upon contact with water. Typically, hydrohphilic polymers have an absorption capacity AC of water of at least 50 % of the dry weight of the hydrophilic polymer. Water soluble polymers are miscible with water and can be dissolved therein. Examples of such hydrophilic and/or water soluble polymers are gelatine, starch, polyvinyl alcohol (i.e., partially or completely hydrolysed poly(vinyl acetate)), poly(vinyl pyrrolidone), cellulose and derivatives thereof, poly(alkylene oxide)s such as polyethyleneoxide.

[0047] According to another preferred aspect of the present invention, the contact angle between the permeation layer and deionized water is 65° or more, 70° or more, or 80° or more. Yet more preferred the contact angle between the permeation layer and deionized water is or 90° or more.

[0048] According to a further preferred aspect of the present invention the swell ratio of the swollen layer structure and the layer structure before swelling is less than 1.2, yet more preferably less than 1.15, or less than 1.1, each determined according to the method described herein. Often, the swell ratio of the swollen layer structure and the layer structure before swelling is about 1.0, each determined according to the method described herein.

[0049] According to another preferred aspect of the present invention the BET specific surface area of the silicon oxide particles of the drainage layer is in the range of from 100 - 300 m^2/g, preferably in the range of from 100 to 250 m^2/g.

[0050] Another preferred embodiment of the present invention is a layer structure comprising:

(a) a substrate layer;
(b) a drainage layer which is at least partially superimposed to the substrate layer, wherein the drainage layer comprises a plurality of silicon oxide particles, and
(c) a permeation layer, at least partially superimposed to the drainage layer,
which is at least partially superimposed to the drainage layer,
wherein the contact angle between the permeation layer and diethylene glycol mono-n-butyl ether is 30° or less, preferably 25° or less, or 20° or less, further preferred in the range of from 0° to 10°, or from 0° to 5°, wherein the contact angle is determined according to the method described below,
wherein the absorption capacity both the drainage layer and the permeation layer is at least 50 %, preferably at least 70 %, or at least 80 %, or at least 90 %, yet more preferably 100 %, or more than 100 % of the dry weight of both layers.

[0051] Preferred aspects of the first aspect of the invention are also preferred for this embodiment.

[0052] Another preferred embodiment of the present invention is a layer structure comprising:

(a) a substrate layer;
(b) a drainage layer which is at least partially superimposed to the substrate layer,
wherein the drainage layer comprises a plurality of silicon oxide particles, and
(c) a permeation layer, at least partially superimposed to the drainage layer,
which is at least partially superimposed to the drainage layer,
wherein the contact angle between the permeation layer and diethylene glycol mono-n-butyl ether is 30° or less, preferably 25° or less, or 20° or less, further preferred in the range of from 0° to 10°, or from 0° to 5°, wherein the contact angle is determined according to the method described below, and
wherein the absorption capacity both the drainage layer and the permeation layer is at least 50 %, preferably at least 70 %, or at least 80 %, or at least 90 %, yet more preferably 100 %, or more than 100 % of the dry weight of both layers, and
wherein the swell ratio of the swollen layer structure and the layer structure before swelling is less than 1.2, yet more preferably less than 1.15, or less than 1.1, and yet more preferred about 1.0, the swell ratio always detected as described herein.

[0053] Further aspects which have been described above are preferred embodiments for the present embodiment.

[0054] According to another preferred aspect of the invention the permeation layer comprises at least one polymer, wherein one or more, or all polymers of the permeation layer have a glass transition temperature Tg of less than 50 °C, preferably less than 40 °C, or less than 30°C, or in the range of from +50 to -50 °C, preferably in the range of from +30 to -50 °C, or in the range of from +20 to -50 °C, or in the range of from +20 to -20 °C.

[0055] According to another preferred aspect of the invention the permeation layer comprises a blend of two or more polymers.

[0056] According to another preferred aspect of the invention the permeation layer comprises less than 40 % by weight, preferably less than 30 % by weight, or less than 10 % by weight of particles, based on the total weight of the permeation layer.

[0057] According to another preferred aspect of the invention the permeation layer is impermeable to water. A substance is impermeable to water in the context of the present invention, when the difference of weight of a test specimen in dry state to a test specimen after 5 minutes in water is less than 2 %, preferably less than 1%, or less than 0.5 %. Sometimes even 0 %, i.e. no difference in weight is observed.

[0058] According to another preferred aspect of the invention the permeation layer of the layer structure has a thickness in the range of from 0.1 to 10 μm, more preferably from 0.5 to 7 μm, or from 0.5 to 4 μm.

[0059] According to a preferred aspect of the invention, the permeation layer comprises a composition comprising at least a polymer, preferably a combination of at least two polymers. Of the numerous polymers known, in principle each polymer can be selected that can form a film which film meets the contact angle requirement described for the first aspect of the invention. Yet more preferred the film shows a contact angle with water of 65° or more, 70° or more, or 80° or more. Yet more preferred the contact angle between the film and water is or 90° or more. Further preferred, the polymer is impermeable to water determined as described in the above.

[0060] The permeation layer can comprise a single polymer or a mixture of polymers. These polymers may be homopolymers, copolymers, random copolymers, block copolymers, graft copolymers, atactic polymers, isotactic polymers, syndiotactic polymers, linear polymers or branched polymers.

[0061] Although the compositions which form the permeation layer of the invention may be solvent-based, water-based compositions are preferred. Of these compositions, water-based emulsions and dispersions are advantageous to reduce solvent emission by employing compositions that are essentially free of volatile organic solvents. Upon evaporation of the solvent or water, the coating typically forms a continuous, solvent permeable, non-porous layer.

[0062] According to another aspect of the invention at least one of the polymers of the permeation layer is selected from the group consisting of an elastomeric polymer and a thermoplastic polymer. Thermoplastic polymers are particularly preferred.

[0063] According to another preferred aspect of the invention at least one of the elastomeric polymers of the permeation layer is selected from the group consisting of a styrene-butadiene rubber, a styrene-butadiene acrylonitrile latex, a natural rubber latex, a synthetic rubber latex, a nitrile butadiene rubber, a silicone latex and a polysiloxane latex.

[0064] Examples of classes of suitable substantially water insoluble thermoplastic polymers include polyolefins, poly(halo-substituted olefins), polyesters, polyamides, polyurethanes, polyureas, poly(vinyl halides), poly(vinylidene halides), polystyrenes, poly(vinyl esters), polycarbonates, polyethers, polysulfides, polyimides, polycaprolactones, polyacrylates, and polymethacrylates. Other examples of specific substantially water-insoluble thermoplastic polymers include thermoplastic high density polyethylene, low density polyethylene, ultrahigh molecular weight polyethylene, polypropylene (atactic, isotactic, or syndiotactic), poly(vinyl chloride), polytetrafluoroethylene, copolymers of ethylene and acrylic acid, copolymers of ethylene and methacrylic acid, poly(vinylidene chloride), copolymers of vinylidene chloride and vinyl acetate, copolymers of vinylidene chloride and vinyl chloride, copolymers of ethylene and propylene, copolymers of ethylene and butene, poly(vinyl acetate), polystyrene, poly(ω-aminoundecanoic acid), poly(hexamethylene adipamide), poly-(ε-caprolactam), and poly(methyl methacrylate).

[0065] According to another preferred aspect of the invention the permeation layer comprises at least one thermoplastic polymer selected from the group consisting of a polyurethane, a polyacrylate, a polyamide, a polyester, a polyvinylacetate, and a polycarbonate. The at least one thermoplastic polymer is preferably substantially water-insoluble.

[0066] In a particularly preferred aspect of the invention, the substantially water-insoluble thermoplastic polymer is selected from the group consisting of a water-dispersible polyurethane, a water-dispersible polyacrilic urethane, a water-dispersible polyacrylate and a water-dispersible styrene-acrylic copolymer.

[0067] A preferred polyurethane can be an aliphatic or aromatic polyurethane, or a mixture of two or more aliphatic polyurethanes or aromatic polyurethanes. Mixtures of aliphatic and aromatic polyurethanes may also be used. The polyurethane is typically the reaction product of the following components: (A) a polyisocyanate having at least two isocyanate (--NCO) functionalities per molecule with (B) at least one isocyanate reactive group having at least two hydroxy groups or an amine.

[0068] In another aspect of the invention, the polyurethane may be an aliphatic acrylic urethane. Suitable acrylic/urethane copolymers are those that are capable of forming stable dispersions in water. In one aspect, the urethane/acrylic copolymers are aliphatic acrylic/urethane copolymers.

[0069] In another aspect of the invention, the permeation layer may be formed from a water-dispersible polyacryl or polymethacryl resin. As used herein, a "polyacryl" includes polyacrylates, polyacrylics, or polyacrylamides, and "polymethacryl" includes polymethacrylates, polymethacrylics, or polymethacrylamides. These resins include those derived from acrylic acid, acrylate esters, acrylamide, methacrylic acid, methacrylate esters, and methacrylamide. The acrylate and methacrylate ester generally contain from 1 to about 30 carbon atoms in the pendant group, or from 1 to about 18, or from 2 to about 12 carbon atoms in the pendant group.

[0070] In one aspect of the invention, the permeation layer may be formed from a water-dispersible styrene-acrylic copolymer. The acryl component is described above. In one aspect, the acryl may be an acrylic acid or ester, an acrylonitrile or their methacrylic analogues. Another useful styrene-acrylic copolymer contains an alkyl acrylate in which the alkyl moiety has 1 to 6 carbon atoms. Butyl acrylate is especially useful as the comonomer of styrene.

[0071] In another aspect of the invention, the permeation layer may be formed from a water-dispersible, thermoplastic copolymer or terpolymer derived from ethylene or propylene and a functional monomer selected from the group consisting of alkyl acrylate, acrylic acid, alkyl acrylic acid, and combinations of two or more thereof. In one aspect, the functional monomer is selected from alkyl acrylate, acrylic acid, alkyl acrylic acid, and combinations of two or more thereof. The alkyl groups in the alkyl acrylates and the alkyl acrylic acids typically contain 1 to about 8 carbon atoms, and, in one aspect, 1 to about 2 carbon atoms. The functional monomer(s) component of the copolymer or terpolymer ranges from about 1 to about 15 mole percent, and, in one aspect, about 1 to about 10 mole percent of the copolymer or terpolymer molecule.

[0072] Examples include: ethylene/methyl acrylate copolymers; ethylene/ethylacrylate copolymers; ethylene/butyl acrylate copolymers; ethylene/methacrylic acid copolymers; ethylene/acrylic acid copolymers; anhydride-modified low density polyethylenes; anhydride-modified linear low density polyethylene, and mixtures of two or more thereof.

[0073] In another aspect of the invention, the permeation layer may be formed from a water-dispersible polyester. Polyesters are prepared from various glycols or polyols and one or more aliphatic or aromatic carboxylic acids. Polyethylene terephthalate (PET) and PETG (PET modified with cyclohexanedimethanol) are useful film forming materials which are available from a variety of commercial sources.

[0074] In another aspect of the invention, the permeation layer may be formed from a water-dispersible homopolymer or copolymer of vinyl acetate. Examples of these polymers include, polyethylene vinyl acetate, acrylic acid or acrylate-modified ethylene vinyl acetate resins, acid-, anhydride- or acrylate-modified ethylene/vinyl acetate copolymers; acid- or anhydride-modified ethylene/acrylate copolymers.

[0075] In one aspect of the invention, the permeation layer may be formed from a water-dispersible terpolymer or copolymer of styrene and substituted styrene such as alpha-methyl styrene. Examples of styrene copolymers and terpolymers include: acrylonitrile-butene-styrene (ABS); styreneacrylonitrile copolymers (SAN); styrene butadiene (SB); styrene-maleic anhydride (SMA); and styrene-methyl methacrylate (SMMA); etc.

[0076] According to another preferred aspect of the invention, the at least one polymer which forms the permeation layer is water-dispersible. Typically, this is achieved by incorporating a compound bearing at least one hydrophilic group or a group that can be made hydrophilic (e.g., by chemical modifications such as neutralization) into the polymer chain. These water-dispersibility enhancing compounds may be of a nonionic, anionic, cationic or zwitterionic nature or the combination thereof. After forming a polymer film, i.e. the permeation layer, the film forming polymers cannot be re-dispersed. Moreover, the polymer film usually has no tendency to absorb water.

[0077] Non-ionic, water-dispersibility enhancing compounds are for example side chain hydrophilic monomers. Some examples include alkylene oxide polymers and copolymers in which the alkylene oxide groups have from 2-10 carbon atoms.

[0078] Anionic moieties may be selected from the group consisting of a carboxylate, a sulfate, a sulfonate, a phosphate or a phosphonate.

[0079] Cationic moieties may be selected from the group consisting of an ammonium salt of a primary, a secondary or a tertiary amine, a quaternary ammonium, a quaternary phosphonium or a ternary sulphonium group.

[0080] Suitable zwitterionic moieties include natural and synthetic amino acid derivatives, choline phosphate derivatives (like phosphatidylcholine), aminophosphate derivatives, aminophosphonate derivatives, betaïnes, aminoalkyl-sulfonate and aminohydroxy-alkyl-sulfonate derivatives, sulfanilic acid derivatives and taurine derivatives.

[0081] A negatively charged polymer has ionic groups which are usually associated with metal cations or small molecule cations. Numerous examples of suitable metal cations or small molecule cations enter into consideration. Preferred examples are cations of these metals: Li, Na, K, Ba, Cs, Mg, Ca, an Sr. A preferred metal cation is Na^+. Preferred examples of small molecule cations are: NH_4^+, H_3O^+, $NR_1R_2R_3R^+$, $PR_1R_2R_3R^+$ and $SR_1R_2R_3^+$, wherein each of R_1, R_2, R_3 and R_4 may be H, an alkyl, an aryl, a substituted alkyl or a substituted aryl. Preferred small molecule cations are NH_4^+ and $N(C_2H_5)_4^+$.

[0082] A positively charged polymer has ionic groups which are usually associated with inorganic or organic anions. Numerous examples of suitable inorganic or organic anions enter into consideration. Preferred examples of inorganic anions are: hydroxide, fluoride, chloride, bromide, iodide, nitrate, sulfate, carbonate, bicarbonate, phosphate, hydrogen phosphate, phosphite, hypophosphite, chlorate, chlorite, hypochlorite and thiocyanate. A preferred inorganic anion is Cl^-. Preferred examples of organic anions include carboxylate derivatives of monocarboxylic acids, like formiate, acetate and propionate, carboxylate derivatives of hydroxy acids, like glycolate, lactate , α or β-hydroxypropionate, or gluconate, carboxylate derivatives of aromatic carboxylic acid, like benzoate or benzylate and substituted analogs, alkyl or aryl sulfonates, alkyl or aryl sulfates, alkyl or aryl phosphonates, alkyl or arly phosphates. Most preferred organic anions are formiate, acetate, lactate and toluenesulfonate.

[0083] In a preferred aspect of the invention, the permeation layer comprises in the range of from 50 to 99 % by weight, preferably from 60 to 98 % by weight, or from 70 to 95 % by weight, or from 90 to 97 % by weight, of at least one polymer, each % by weight based on the total weight of the permeation layer. Preferred embodiments with regard to the nature and properties of the at least one polymer are described in the above.

[0084] Other additives can be added as well to obtain a certain desired characteristic, such as fillers, anti-blocking additives, hardeners, surfactants, waxes, defoamers, plasticizers, surfactants, colourants, anti-oxidants, UV stabilizers, luminescents, cross-linkers etc.

[0085] In one aspect of the invention, the permeation layer contains fillers. Typically the fillers are those that have a BET specific surface area of at least 1 m^2/g. In another aspect, the BET specific surface area of the filler is greater than

5 m^2/g, or greater than 10 m^2/g, or greater than 20 m^2/g. In another aspect, the fillers are those having a BET specific surface area of greater than 100 m^2/g. Often, the introduction of such fillers causes a wanted matte surface.

[0086] Examples of fillers include silica, such as amorphous silica, fumed silica, colloidal silica, precipitated silica and silica gels. Additional fillers include a clay, an alkaline earth metal sulfate or carbonate, an alkaline earth or transition metal oxide or hydroxide, titanium dioxide, bentonites, zeolites, aluminium silicate or calcium silicate. In one aspect, the filler is a silica having a BET specific surface area of at least about 40 m^2/g, or at least 60 m^2/g, or at least about 100 m^2/g. In another aspect, the filler is silica with a BET specific surface area of at least 150 m^2/g, or at least about 200 m^2/g, or at least about 250, or at least about 300 m^2/g.

[0087] In a preferred aspect of the invention, the permeation layer comprises in the range of from 0 to 50 % by weight, preferably from 0 to 40 % by weight, or from 1 to 25 % by weight of aforementioned filler, the % by weight based on the total weight of the permeation layer.

[0088] In one aspect of the invention, the permeation layer contains anti-blocking additives. These additives reduce the tendency of the film to stick together when it is in roll form. The antiblock additives include natural silica, diatomaceous earth, synthetic silica, glass spheres and ceramic particles. Organic inert particles such as polymer beads are particularly preferred. These beads may consist of polyacrylates, polystyrene, polyacrylamides or different copolymers of acrylate and styrene. Preferably, the permeation layer comprises in the range of from 0 to 2 % by weight, preferably 0.1 - 1.5 % by weight of anti-blocking additive, the % by weight based on the total weight of the permeation layer.

[0089] In one aspect of the invention, the permeation layer contains hardeners. Generally, the hardeners are present in an amount from about 0.01 to about 20 % by weight, or from about 0 % to about 6 % by weight, or from about 0.1 % to about 4 % by weight, or from 2 - 4 % by weight, the % by weight based on the total weight of the permeation layer.

[0090] The hardeners may be any of those known in the art. The hardeners may be organic or inorganic. A combination of two or more hardeners may be used. The cross linking agents include such as epoxy compounds, polyfunctional aziridines, methoxyalkyl melamines, triazines, polyisocyanates, carbodiimides, polyvalent metal cations, and the like. In another aspect of the invention, the hardener is a metal containing crosslinking agent. The hardeners include the organometallic catalysts containing metals of group III-A, IV-A, V-A, VI-A, VIII-A, I-B, II-B, III-B, IV-B and V-B. Particularly useful cross linking agents are tin dioctoate, tin naphthenate, dibutyltin dilaurate, dibutyltin diacetate, dibutyltin dioxide, dibutyl tin dioctoate, zirconium chelates, aluminum chelates, aluminum titanates, titanium isopropoxide, triethylene diamine, p-toluene sulfonic acid, n-butyl phosphoric acid, and mixtures thereof.

[0091] In one aspect, the permeation layer is free of one or more of the following materials: gelatin, starch, cellulose and cellulose derived polymers and particles, polyvinyl alcohol, polyalkylneoxides such as polyethyleneoxide, and polyvinyl pyrrolidone.

[0092] Further, the permeation layer comprises preferably in the range of from 0.1 to 2 % by weight, preferably from 0.2 to 1 % by weight of a surfactant, each % by weight based on the total weight of the permeation layer.

[0093] According to another preferred aspect of the invention, the permeation layer comprises less than 1 % by weight, preferably between 0.1 % and 0.7 % by weight of water, each % by weight based on the total weight of the permeation layer.

[0094] According to another preferred aspect of the invention the ratio of the rate of diffusion of the drainage layer rD^1 to the rate of diffusion of the permeation layer rD^2 is more than 1, each determined with diethylene glycol mono-n-butyl ether. More preferred is a ratio of the rate of diffusion of more than 1.5, more than 2, more than 5, more than 100, more than 1.000, or more than 5.000. Often, the rate of diffusion is not more than 10.000, each determined with diethylene glycol mono-n-butyl ether.

[0095] According to another preferred aspect of the invention the absorption capacity of the drainage layer is higher than the absorption capacity of the permeation layer, each determined with diethylene glycol mono-n-butyl ether. Accordingly, the ratio of the absorption capacity of the drainage layer to the absorption capacity of the permeation layer is more than 1, preferably more than 2, more preferably more than 5 each determined with diethylene glycol mono-n-butyl ether.

[0096] In addition, the layer structure according to the invention comprises at least one drainage layer, which is superimposed to the substrate layer. Preferably, the drainage layer is at least partially, e.g. for at least 30 %, 50 %, 70 % or for at least 90 % of the area of the layer structure, superimposed to the substrate layer.

[0097] According to another preferred aspect of the invention, the drainage layer and the substrate layer are connected. The term connected in the context of this invention is used to describe the fact that two superimposed items, e.g. two superimposed layers, are linked. Preferably, the link of the two superimposed items is at least partially, e.g. for at least 30 %, 50 %, 70 % or for at least 90 % with respect to the area of superimposition of the two items.

[0098] In general, numerous means and techniques enter into the consideration of those skilled in the art to connect two layers, which are known and appear proper. Preferably, two layers may be connected by electrostatic interactions, chemical bonding, Van-der-Waals forces, or a combination of at least two thereof. According to another preferred aspect, connecting two layers can be furthered by applying a binder onto at least one of the surfaces of the two layers prior to arranging one layer onto the other layer. According to another preferred method, a liquid phase can be applied to a first layer, the liquid phase forming a further, preferably solid, layer on the first layer by separation of at least a part of the liquid from the liquid phase, e.g. by evaporation of solvent and/or water from a dispersion or a solution. The layer structure according to the invention preferably comprises a plurality of two or more layers, in which at least a part of a layer is connected with at least a part of at least one adjacent layer.

[0099] The at least one drainage layer comprises a plurality of silicon oxide particles. Two major processes are widely used to produce silicon oxide particles of small particle size. In the first process, a precipitation in a wet process (precipitated silicon dioxide) is performed. In the second process, a gas phase reaction yields the desired silicon oxide particles (fumed silicon dioxide). The fumed silicon dioxide is generally prepared by flame pyrolysis, for example by burning silicon tetrachloride in the presence of hydrogen and oxygen. A variety of commercial products of fumed silicon dioxides is offered under the tradename Aerosil® from Evonik Industries AG, Essen, Germany. Another commercial product is Cab-O-Sil® M-5, available from Cabot Corporation, Billerica, USA.

[0100] According to a further aspect of the invention, at least 75 % by weight, preferably at least 80 % by weight, or at least 90 % by weight of the silicon oxide particles, which are present in the drainage layer, have an average particle diameter, preferably determined in a liquid phase, in the range of from 1 to 499 nm, preferably in the range of from 200 - 300 nm, or from 150 to 290 nm, or from 150 to 250 nm, wherein each % by weight is based on to the total weight of the silicon oxide particles. Further preferred is a range of from 10 to 200 nm, preferably in the range of from 30 to 150 nm, more preferably in the range of from 30 to 120 nm, yet more preferably in the range of from 30 to 90 nm, even more preferably in the range of from 30 to 80 nm, or in the range of from 35 to 75 nm, most preferably in the range from 40 to 70 nm. Silicon oxide particles like those mentioned above are aggregates. These silicon oxide particles of aforementioned size ranges are often referred to as "nanoparticles". The average particle diameter of such aggregates d_{50} is defined as the diameter, where 50 mass-% (of the aggregates) of the sample have a larger diameter, and the other 50 mass-% have a smaller diameter. The diameter of the aggregates can be measured using various techniques, e.g. using a centrifugal sedimentation particle size analyzer, as in the test method given below.

[0101] According to another aspect of the invention, the silicon oxide particles, which are present in the drainage layer, have an average particle diameter d_{50} in the range of from 0.5 to 1000 μm, preferably in the range of from 1 to 800 μm, more preferably in the range of from 1 to 500 μm, yet more preferably in the range of from 1 to 300 μm, even more preferably in the range of from 1 to 200 μm, or in the range of from 1 to 100 μm, most preferably in the range of from 1 to 50 μm. Particles of aforementioned size ranges are often referred to as "microparticles". The average particle diameter d_{50} is defined as the diameter where 50 mass-% (of the particles) of the sample have a larger diameter, and the other 50 mass-% have a smaller diameter. The particle diameter can be measured using various techniques, e.g. using a centrifugal sedimentation particle size analyzer, as in the test method given below.

[0102] According to a preferred aspect of the invention, at least 75 % by weight, or at least 80 % by weight, or at least 90 % by weight, of the silicon oxide particles have an average particle diameter as described before, the weight being based on the total weight of the silicon oxide particles in the drainage layer.

[0103] According to another aspect of the invention, the drainage layer has a pore volume in the range of from 55 to 80 %-Vol., preferably in the range of from 60 to 75 %-Vol, each based on the total volume of the drainage layer. The pore volume can be determined by the method described below.

[0104] According to a further aspect of the invention, the silicon oxide, which is present in the drainage layer, has a BET specific surface area in the range of from 20 m^2/g to 600 m^2/g, preferably in the range of from 50 m^2/g to 550 m^2/g, more preferably in the range of from 70 m^2/g to 500 m^2/g, yet more preferably in the range of from 100 m^2/g to 400 m^2/g.

[0105] According to a preferred aspect of the invention, the silicon oxide particles, which are present in the drainage layer, have a negatively charged surface. Preferably the surface of suitable silicon oxide has a zeta potential of less than -10 mV, less than -20 mV or less than -30 mV. Accordingly, preferred ranges of the Zeta Potential are in the range of from 0 to -50 mV, from 0 to -40 mV, from -10 to -40 mV, from - 20 mV to -40 mV, or from - 30 mV to -40 mV. Preferred negatively charged silicon oxide particles are selected from fumed silica and precipitated silica.

[0106] According to a another preferred aspect of the invention, the silicon oxide particles, which are present in the drainage layer, have a positively charged surface. Preferably the surface of suitable silicon oxide has a zeta potential of more than +20 mV, more than +30 mV or more than +40 mV. Accordingly, preferred ranges of the Zeta Potential are range from 0 to +100 mV, from 0 to + 70 mV, from 0 to +50 mV, from 20 mV to 50 mV, from 25 mV to 50 mV, from 30 mV to 50 mV, from 35 mV to 50 mV or from 35 mV to 45 mV.

[0107] According to a further aspect of the invention, the silicon oxide particles which have a positively charged surface further comprise at least a compound selected from the group consisting of trivalent aluminium compounds, tetravalent zirconium compounds, aminoorganosilane compounds, reaction products of at least one trivalent aluminium compound with at least one aminoorganosilane compound, reaction products of at least one tetravalent zirconium compound with at least one aminoorganosilane compound, reaction products of at least one trivalent aluminium compound and at least one tetravalent zirconium compound with at least one aminoorganosilane compound and combinations thereof.

[0108] Preferably, the modification of the silicon oxide particles into silicon oxide particles which have a positively charged surface is performed at least on the surface of the particles. Accordingly, the silicon oxide particles which have a positively charged surface and are present in the drainage layer, comprise at least one of the aforementioned compounds at least on the surface of the particles. Another preferred aspect of the invention relates to such a modification, which can be performed on the surface and in cavities of the particles, particle agglomerates or both. Accordingly, the silicon oxide particles, which have a positively charged surface and are present in the drainage layer, comprise at least one of the aforementioned compounds at least on the surface and in at least some cavities of the particles.

[0109] Of the available types of silicon oxide particles, fumed silicon oxide particles, which are also known as fumed silicon dioxide, are preferred. Accordingly, aforementioned silicon oxide particle having a positively charged surface are preferably based on fumed silicon oxide particles.

[0110] In the preparation of such surface modified silicon oxide particles, fumed silicon dioxide, for example, is added at high shear rates to a mainly aqueous solution containing the reaction products of a compound of trivalent aluminium (e.g., aluminium chlorohydrate), preferably reacted with at least one aminoorganosilane. Under suitable conditions, a dispersion of surface modified fumed silicon oxide particles is obtained that does not coagulate. The riiixture containing the reaction products of a compound of trivalent aluminium (such as aluminium chlorohydrate) with at least one aminoorganosilane has a high buffer capacity. The alkaline aminoorganosilane neutralizes hydrochloric acid formed during hydrolysis of the compound of trivalent aluminium (e.g., aluminium chlorohydrate). The required quantity of the compound of trivalent aluminium (e.g., aluminium chlorohydrate) for the surface modification of silicon dioxide is much lower in comparison to a modification with aluminium chlorohydrate only. These surface modified dispersions of silicon oxide particles have a much lower salt content in comparison to dispersions where the surface has been modified with aluminium chlorohydrate.

[0111] The reaction products used in the surface modification step of a compound of trivalent aluminium (e.g., aluminium chlorohydrate) with at least one aminoorganosilane may be prepared by the addition of the aminoorganosilane to an aqueous solution of the compound of trivalent aluminium (e.g., aluminium chlorohydrate) or vice versa. The reaction of the compound of trivalent aluminium with the aminoorganosilane is usually carried out at temperatures from 10° C. to 50° C. for 5 minutes to 60 minutes. Preferably, the reaction is carried out at room temperature for 10 minutes to 15 minutes.

[0112] The modification of the surface of the silicon oxide particles with the reaction products of a compound of trivalent aluminium (e.g., aluminium chlorohydrate) with at least one aminoorganosilane is a faster process than the surface modification of silicon oxide particles with aluminium chlorohydrate. Accordingly, the modification time may be shortened or the modification temperature may be lowered in the case where the surface of the silicon dioxide is modified with the reaction products of a compound of trivalent aluminium (e.g., aluminium chlorohydrate) with at least one aminoorganosilane.

[0113] Of the silicon oxide particles available, particles of fumed silicon dioxide are particularly preferred for the surface modification with the reaction products of a compound of trivalent aluminium (e.g., aluminium chlorohydrate) with at least one aminoorganosilane.

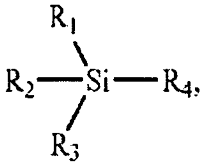
[0114] Instead of a single fumed silicon dioxide powder, a mixture of different silicon dioxide powders having different sizes of the primary particles may be used. The modification step with the reaction products of a compound of trivalent aluminium (e.g., aluminium chlorohydrate) with at least one aminoorganosilane may be carried out individually for each silicon dioxide powder or simultaneously with the mixture of the different silicon dioxide powders.

[0115] If the modification step is carried out at high shear rates, the reaction products are regularly distributed on the surface of the silicon dioxide. Furthermore, the rheological behaviour of the dispersion is improved.

[0116] Preferred compounds of trivalent aluminium are aluminium chloride, aluminium nitrate, aluminium acetate, aluminium formiate, aluminium lactate and aluminium chlorohydrate.

[0117] According to a further aspect of the invention, the silicon oxide particles may further comprise at least an aluminium-zirconium hydrate complex. Preferably, in the aluminium-zirconium hydrate complex, the ratio of zirconium to aluminium is from 1:1 to 1:7. Preferred aluminium-zirconium hydrate complexes are selected from the group consisting of aluminium zirconium trichlorohydrate (CAS 98106-53-7), aluminium zirconium tetrachlorohydrate (CAS 98106-52-6), aluminium zirconium pentachlorohydrate (CAS 98106-54-8) or aluminium zirconium octachlorohydrate (CAS 98106-55-9). These complexes may be synthesized according to the procedures provided in US 3,903,258 or US 5,179,220, or purchased commercially (Rezal 67, Summit Reheis Co or Zirconal L540, BK Giulini GmbH, Ludwigshafen, Germany). According to a further aspect of the invention, the silicon oxide particles may comprise at least a compound selected from the group consisting of the reaction products of at least one of the aforementioned aluminium-zirconium hydrate complexes with at least one aminoorganosilane.

[0118] Suitable aminoorganosilanes are aminoorganosilanes of formula (I)



(I)

wherein R_1, R_2, R_3 independently represent hydrogen, hydroxyl, unsubstituted or substituted alkyl radicals having from 1 to 6 carbon atoms, unsubstituted or substituted aryl radicals, unsubstituted or substituted alkoxyl radicals having from 1 to 6 carbon atoms or unsubstituted or substituted aryloxyl radicals. R_4 represents an organic moiety substituted by at least one primary, secondary or tertiary amino group.

[0119] Condensation products of aminoorganosilanes may also be used in place of aforementioned monomeric aminoorganosilanes. The condensation reactions may occur between identical or different aminoorganosilanes.

[0120] Numerous of the known aminoorganosilanes enter into the consideration of those skilled in the art. Preferred aminoorganosilanes for the surface modification of fumed silicon dioxide resulting in silicon oxide particles having a positively charged surface are 3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, (3-triethoxysilylpropyl)-diethylentriamine, 3-aminopropyltriethoxysilane, N-(2-amino-ethyl)-3-amino-propyltriethoxysilane, (3-triethoxysilylpropyl)-diethylenetriamine, n-butylaminopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane and mixtures of at least two of these aminoorganosilanes. More preferred aminoorganosilanes are n-butylaminopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane or a combination of the two.

[0121] In a further preferred aspect of the invention, the aminoorganosilane is reacted in solution with CO_2 under formation of an ammoniumorganosilane (i.e., protonated species of an aminoorganosilane) and hydrogen carbonate, before it is added to the solution of the trivalent aluminium compound (e.g., aluminium chlorohydrate). In this way, the pH of the reaction mixture containing the reaction products of a compound of trivalent aluminium (e.g., aluminium chlorohydrate) with at least one aminoorganosilane is lowered and the buffer capacity of the mixture is increased. The formation of undesirable, partially insoluble aluminium byproducts of very high molecular weight can be reduced using this procedure.

[0122] A silicon oxide particle, the surface of which has been modified by a treatment with the reaction products of at least one tetravalent zirconium compound (e.g., zirconium oxychloride, zirconium carbonate, zirconium acetate, zirconium lactate), preferably at least one tetravalent zirconium compound reacted with at least one aminoorganosilane, or at least one tetravalent zirconium compound combined with at least one trivalent aluminium compound of the above and both reacted with at least one aminoorganosilane, is another preferred silicon oxide particle having a positively charged surface according to the invention.

[0123] The preparation of such surface modified silicon oxide particles is performed similar to the aforementioned preparation of surface modified silicon oxide particles modified with the reaction product of a trivalent aluminium compound, but instead of the trivalent aluminium compound a tetravalent zirconium compound, or at least one tetravalent zirconium compound reacted with at least one aminoorganosilane, or at least one tetravalent zirconium compound combined with at least one trivalent aluminium compound of the above and reacted with at least one aminoorganosilane, is used.

[0124] According to a further aspect of the invention, the drainage layer comprises an amount of silicon oxide particles having a positively charged surface in a range of from 0.5 g/m^2 to 25 g/m^2, preferably from 1 g/m^2 to 20 g/m^2, or from 2 g/m^2 to 15 g/m^2, or from 3 g/m^2 to 10 g/m^2, or from 3 to 8 g/m^2. Aforementioned amounts are usually determined at 50 % relative humidity and 20 °C.

[0125] According to a further aspect of the invention, the drainage layer has a thickness of from 0.5 μm to 100 μm, preferably 2 μm to 50 μm, or from 5 μm to 40 μm, or from 20 μm to 40 μm. The thickness of the drainage layer is determined perpendicular to the plane of the drainage layer at 50 % relative humidity and 20 °C.

[0126] According to a further aspect of the invention, the drainage layer comprises in the range of from 50 to 90 % by weight, preferably from 65 to 85 % by weight, or from 70 to 80 % by weight of fumed silica, the % by weight based on the total weight of the drainage layer. Yet more preferred, the fumed silica is positively charged.

[0127] According to a further aspect of the invention, the drainage layer comprises in the range of from 0 to 10 % by weight, preferably from 1 to 5 % by weight of at least a compound comprising trivalent aluminium, tetravalent zirconium or both, the % by weight based on the total weight of the drainage layer. Preferred compounds comprising trivalent aluminium, tetravalent zirconium or both are those described above.

[0128] According to a further aspect of the invention, the drainage layer comprises in the range of from 0 to 10 % by weight, preferably from 1 to 5 % by weight of at least an aminoorganosilane, the % by weight based on the total weight of the drainage layer. Preferred aminoorganosilanes are those described above.

[0129] According to a further aspect of the invention, the drainage layer comprises at least one binder. Numerous types of the binders known in the art enter into the consideration of the skilled person. Suitable Binders are often water-soluble polymers. Especially preferred are film-forming polymers. A preferred group of binders are water-soluble polymers that are natural polymers and modified products thereof, such as gelatin, starch, hydroxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, or combinations of at least two of these polymers. Further, a combination of at least two of the aforementioned natural binders may be used.

[0130] A second preferred group of binders are water-soluble polymers that are synthetic binders. Of these, the following synthetic binders are preferred: polyvinyl alcohol, polyvinyl pyrrolidone, completely or partially saponified products of copolymers of vinyl acetate with other monomers; homopolymers or copolymers of unsaturated carboxylic acids such as maleic acid, (meth)acrylic acid or crotonic acid and the like; homopolymers or copolymers of sulfonated vinylmonomers such as vinylsulfonic acid, styrene sulfonic acid; homopolymers or copolymers of vinylmonomers of (meth)acrylamide; homopolymers or copolymers of other monomers with ethylene oxide; polyurethanes; polyacrylamides; water-soluble nylon type polymers; polyesters; polyvinyl lactams; acrylamide polymers; substituted polyvinyl alcohol; polyvinyl acetals; polymers of alkyl and sulphoalkyl acrylates and methacrylates; hydrolysed polyvinyl acetates; polyamides; polyvinyl pyridines; polyacrylic acid; copolymers with maleic anhydride; polyalkylene oxides; copolymers with methacrylamide and copolymers with maleic acid. Derivatives of the aforementioned polymers are also preferred.

[0131] A preferred synthetic binder is polyvinyl alcohol. Polyvinyl alcohol with a degree of hydrolysis between 70% and 99%, in particular between 88% and 98%, and a weight average molecular weight between 14,000 g/mol and 300,000 g/mol, in particular between 100,000 g/mol and 200,000 g/mol, is preferred; another preferred aspect of the invention are mixtures of at least two polyvinyl alcohols which differ in at least one of the properties selected from the group consisting of: degree of hydrolysis, weight average molecular weight, or both. Properties, such a weight average molecular weight and degree of hydrolysis are provided as technical information by the manufacturer of the polyvinyl alcohol.

[0132] According to another preferred aspect of the invention, a combination of at least two of the aforementioned synthetic binders may be used. Further, a combination of at least one of the aforementioned synthetic binders and at least one of the aforementioned natural binders may be used.

[0133] According to another aspect of the invention, the binder may be blended with water insoluble natural or synthetic high molecular weight compounds, such as acrylate latices or with styrene acrylate latices. Accordingly, water insoluble polymers may be used as binder, or at least as part of a binder of the invention.

[0134] According to another preferred aspect of the invention, the drainage layer comprises at least one binder which at least one binder is selected from the group of reactive polymers. Reactive polymers in the context of this invention are polymers having functional groups, which functional groups are capable of forming covalent bonds with at least one of the items selected from the group consisting of: neighboring polymer molecules, the surface of nanoparticles, or with a combination of both thereof. An advantage of using these binders is improved scratch resistance and weather resistance. Particularly preferred reactive polymers are silanol-modified polyvinyl alcohols, e.g. Poval R-polymers (such as R-1130, R-2105 and R-3109, all provided by Kuraray Europe GmbH, Frankfurt, Germany), carbonyl-modified polyvinyl alcohols, e.g. Poval D-polymers (such as DF-05, DF-17, DF-20 and DF-24, all provided by Kuraray Europe GmbH), carboxyl-modified polyvinyl alcohol, e.g. Poval A-polymers (such as AP-17, AT-17 and AF-17, all provided by Kuraray Europe GmbH), or a combination of at least two of the aforementioned reactive polymers. Further, a combination of at least one of the aforementioned reactive polymers and at least one of the aforementioned natural or synthetic binders may be used.

[0135] Preferably, the binder is selected from the group consisting of polyvinyl alcohol and its derivatives, gelatine and its derivatives, polyvinyl pyrrolidone and its derivatives and mixtures of at least two aforementioned binders.

[0136] According to another preferred aspect of the invention, the drainage layer comprises in the range of from 1 to 30 % by weight, preferably from 5 to 20 % by weight, or from 10 to 20 % by weight, of at least a binder, each % by weight being based on the total weight of the drainage layer. Preferred binder are those described above.

[0137] According to another preferred aspect of the invention the layer structure of the invention further comprises at least an intermediate layer which is arranged between to the drainage layer and the permeation layer. An intermediate layer is particularly preferred when each of the permeation layer and the drainage layer contain at least one charged species, e.g. an ion or a polymer, which charged species are electrically oppositely charged. Preferably, the intermediate layer does not comprise any charged species. That way, the drainage layer can be electrically positively charged whereas the permeation layer is electrically negatively charged. In this case, the intermediate layer separates these layers of opposite charge. In an alternative aspect, the drainage layer is electrically negatively charged whereas the permeation layer is electrically positively charged. Preferably, the intermediate layer again does not comprise any charged species. It is yet more preferred to arrange an intermediate layer in the above mentioned way when all layers are applied to the substrate at the same time, e.g. by a single-pass multilayer coating. If the layers are prepared in individual sequential steps layer-by-layer, there is often no need to arrange an intermediate layer between the drainage layer and the permeation layer. Further, there is usually no need to arrange an intermediate layer between the drainage layer and the permeation layer, when the permeation layer is not electrically charged.

[0138] According to a further preferred aspect of the invention the intermediate layer is not a continuous layer. An intermediate layer which is not a continuous layer comprises gaps in the layer area. At the gaps, the layers which are adjacent to the intermediate layer, e.g. a drainage layer and a permeation layer, are in direct contact. Preferably, the intermediate layer has an area weight in the range of from 50 to 150 mg/m^2, or from 70 to 120 m^2/g, or of 100 mg/m^2. Such intermediate layer may be not a continuous layer, i.e. has gaps in the layer, as described above.

[0139] According to another aspect of the invention the layer structure has

α) a drainage layer which comprises at least:

(i) 50 - 90 % by weight, preferably 65 - 85 % by weight, or 70 -80 % by weight of fumed silica, which silica is preferably positively charged;
(ii) 0 - 10 % by weight, preferably 1 - 5 % by weight of at least a compound comprising trivalent aluminium, tetravalent zirconium or both;
(iii) 0 - 10 % by weight, preferably 1 - 5 % by weight of at least an aminoorganosilane;
(iv) 1 - 30 % by weight, preferably 5 - 20 % by weight, or 10 - 20 % by weight, of at least a binder;
(v) 0.1 - 6 % by weight, preferably 0.5 - 4 % by weight, or 2 - 4 % by weight of at least a hardener;
(vi) 0.1-2 % by weight, preferably 0.2 - 1 % by weight of a surfactant
(vii) less than 1 % by weight, preferably between 0.1 % and 0.7 % by weight, of water;

β) a permeation layer which comprises at least:

(viii) 50-99 % by weight, preferably 60 -98 % by weight, or 70 - 95 % by weight, or 90 - 97 % by weight, of at least one substantially water-insoluble polymer
(ix) 0-50 % by weight, preferably 0 - 40 % by weight, or 1 - 25 % by weight of a filler
(x) 0 - 6 % by weight, preferably 0.1 - 4 %, or 2 - 4 % by weight of a hardener,
(xi) 0-2 % by weight, preferably 0.1 - 1.5 % by weight of an anti-blocking additive
(xii) 0.1-2 % by weight, preferably 0.2 - 1 % by weight of a surfactant
(xiii) less than 1 % by weight, preferably between 0.1 % and 0.7 % by weight of water

wherein the fractions (i) - (vii) sum up to 100 %, with respect to the total weight of the drainage layer; and wherein the fractions (viii) - (xiii) sum up to 100 %, with respect to the total weight of the permeation layer.

[0140] With respect to preferred aspects for each of the components (i) to (xii), reference is made to the aspects of the first aspect of the invention which are described in the above.

[0141] A hardener in the context of the present invention is a chemical component that crosslinks the binder to improve the strength of the layer.Suitable hardeners for the permeation layer are described above.

[0142] Suitable hardeners for use in the drainage layer are preferably selected depending on the type of water-soluble polymers to be hardened. Preferred hardeners are either organic hardeners or inorganic hardeners.

[0143] Organic hardeners are preferably selected from the group consisting of aldehydes, e.g. glyoxal, formaldehyde or glutaraldehyde; dioxanes, e.g. 2,3-dihydroxydioxane; reactive vinyl compounds; reactive halogen compounds; epoxydes; aziridines; N-methylol compounds, e.g. dimethylhydantoin; and dihydrazides, e.g. adipoyl dihydrazide; or a combination of two or more thereof.

[0144] Inorganic hardeners are preferably selected from the group consisting of chromium alum, aluminium alum, zirconium compounds, bivalent metal cations and boron compounds, e.g. borax or boric acid. A preferred boron compound is boric acid.

[0145] According to another aspect of the invention, a combination of at least two of the aforementioned organic or inorganic hardeners may be used, e.g. one organic and one inorganic hardener, or two organic hardeners, or two inorganic hardeners, each depending on the water-soluble polymers used in the drainage layer.

[0146] According to another aspect of the invention, the drainage layer comprises in the range of from
0.1 to 6 % by weight, preferably of from 0.5 to 4 % by weight, or from 2 to 4 % by weight of at least a hardener, preferably selected from those described above with respect to the drainage layer, the % by weight are based on the total weight of the drainage layer.

[0147] Further, the drainage layer comprises preferably in the range of from 0.1 to 2 % by weight, preferably from 0.2 to 1 % by weight of a surfactant, the % by weight based on the total weight of the drainage layer.

[0148] According to another preferred aspect of the invention, the drainage layer comprises less than 1 % by weight, preferably between 0.1 % and 0.7 % by weight of water, the % by weight based on the total weight of the drainage layer.

[0149] According to another aspect of the invention, the hardeners used in the permeation layer and in the drainage layer are the same or different hardeners.

[0150] According to a further aspect of the invention, the layer structure comprises one or more adhesion promoting layers. Numerous types of adhesion promoting layers are known in the art enter into the consideration of the skilled person. Preferably at least one, yet more preferably all of the adhesion promoting layers of the layer structure comprise one or more of the binders mentioned above. According to another preferred aspect of the invention, an adhesion promoting layer may be arranged on the substrate layer. Numerous types of adhesion promoting layers are known in the art enter into the consideration of the skilled person, in particular those, which are used in the photographic industry. Preferably, adhesion to the substrate may be improved by a corona discharge treatment or a corona-aerosol treatment.

[0151] A further aspect of the invention is a process for preparing a layer structure having a substrate layer, a drainage layer and a permeation layer comprising at least the process steps:

(I) providing a substrate layer;
(II) superimposing to the substrate layer a drainage layer, wherein the drainage layer comprises a plurality of silicon oxide particles,
(III) superimposing at least partially at least one permeation layer onto the drainage layer,
wherein the contact angle between the permeation layer and diethylene glycol mono-n-butyl ether is 30° or less.

[0152] Preferred aspects of the process of the invention for preparing the layer structure are incorporated herein, which aspects relate to the properties of components of the layer structure, such as the substrate layer, the drainage layer, its components and any other aspects that are described above in the context of the inventive layer structure according to the first aspect and further aspects of the invention.

[0153] If a further layer is superimposed to the substrate layer, the further layer can be arranged in different ways relative to both, the substrate layer and the drainage layer. Accordingly, the further layer which is superimposed to the substrate layer can be arranged

(i) so that the further layer is arranged between the substrate layer and the drainage layer;
(ii) so that the further layer is arranged between the drainage layer and the permeation layer; or
(iii) so that the further layer is arranged on the permeation layer on the side opposite to the drainage layer
(iv)so that the further layer and the drainage layer are arranged on opposite sides of the substrate layer.

[0154] Preferably, the further layer is arranged so that the further layer and the substrate layer are arranged on opposite sides of the drainage layer.

[0155] In a further aspect of the invention, step (II) is performed by at least the following steps:

i. preparing a liquid phase comprising a plurality of silicon oxide particles and at least one liquid A;
ii. coating the liquid phase with amount in the range of from 5 to 300 g/m^2, or from 50 to 250 g/m^2, or from 200 to 300 g/m^2 onto the substrate layer; and then
iii. drying the coating formed in step ii. resulting in the drainage layer.

[0156] By performing step ii. in step (II), a drainage layer is obtained which comprises an amount of silicon oxide particles in a range of from 0.5 g/m^2 to 25 g/m^2, preferably from 1 g/m^2 to 20 g/m^2, or from 2 g/m^2 to 15 g/m^2, or from 3 g/m^2 to 10 g/m^2, or from 3 to 8 g/m^2. Aforementioned amounts are usually determined at 50 % relative humidity and 20 °C.

[0157] According to a further aspect of the invention, the further layer is applied in step (II) of the process from a liquid phase, preferably a dispersion comprising the silicon oxide particles and a liquid. In the context of this invention, the term dispersion describes a system, in which a discontinuous phase of at least a first component is dispersed in a continuous phase of at least a further component. Often, the at least one component contributing to the discontinuous phase is particulate. The continuous phase is often not in the same physical state as the discontinuous phase. Both, the continuous and discontinuous phase can independently of each other comprise one or more components.

[0158] The liquid phase comprising a plurality of silicon dioxide particles having a positively charged surface according to step i. can be accomplished, for example, by means of a conventional dispersion device such as Nanomizer®, Ultimizer®, Manton-Gaulin®, Ystral Conti®, Dyno-Mill® and the like. The aforementioned devices may be used alone or two or more types may be used in combination, in a parallel or sequential array.

[0159] Numerous of the known liquids enter into consideration of those skilled in the art to be used as liquid A. Preferably, liquid A in aforementioned liquid phase is water, an alcohol or a glycol, for example methanol, ethanol, *n*-propanol, iso-propanol or ethylene glycol. According to another preferred aspect of the invention, the liquid phase comprises a mixture of more than one liquid, preferably at least two of the liquids, wherein, yet more preferred, more than 50 wt.-% of the liquid phase is water, the wt.-% based on the total weight of the liquid phase.

[0160] According to another preferred aspect of the invention, the liquid phase, which comprises at least two liquids selected from the aforementioned group, comprises at least 75 % by weight, preferably at least 80 % by weight, or at least 90 % by weight, or between 94 and 99.5 % by weight of water, each of the percentages based on the total weight of liquids in the liquid phase.

[0161] Step ii. can be accomplished by means of extrusion coating, air knife coating, doctor blade coating, slot bead coating, slide bead coating and curtain coating. Preferred methods are slide bead coating and curtain coating. Preferably, step ii. is at least partially performed at temperatures of from 20°C to 60°C, or from 25°C to 50°C, or from 30°C to 40°C. Preferably, the coating process is carried out at a speed of about 20 to about 400 meters/min.

[0162] Step iii. can be performed at a temperature of from 2°C to 90°C, with a relative humidity of from 10% to 80%, for a time of from 30 seconds to 10 min. If step iii. comprises two or more sub-steps, the temperature, relative humidity and time may vary from step to step, each of them independently within the aforementioned temperature range, humidity range and time range.

[0163] According to another aspect of the invention, the silicon oxide particles of the process comprise at least a compound selected from the group consisting of trivalent aluminium compounds, tetravalent zirconium compounds, aminoorganosilane compounds, reaction products of at least one trivalent aluminium compound with at least one aminoorganosilane compound, reaction products of at least one tetravalent zirconium compound with at least one aminoorganosilane compound, reaction products of at least one trivalent aluminium compound and at least one tetravalent zirconium compound with at least one aminoorganosilane compound, and combinations thereof. Further preferred aspects are described with regard to the first aspect and further aspects of the invention and are incorporated herein. This applies also to the way, according to which the modification of silicon oxide particles can be performed.

[0164] Numerous of the known liquids and mixtures thereof enter into the consideration as continuous phase of the aforementioned liquid phase. According to an aspect of the invention, the liquid is selected from the group consisting of water, alcohols, and mixtures thereof. Preferably, water is selected as liquid. Yet more preferred, the dispersion obtained from the surface modification of silicon oxide particles is used directly for the preparation of that dispersion, which is applied to form the further layer in step (II) of the process.

[0165] According to another aspect of the invention, the liquid phase contains less than 5 % by weight, preferably less than 2 % by weight of volatile organic compounds. Volatile organic compounds in the context of this invention are organic compounds, which are liquid at 20 °C, 1013 hPa, and either have an initial boiling point of less than 250 °C at 1013 hPa or a vapor pressure of more than 0.27 kPa (2 mm Hg) at 25 °C, or both.

[0166] According to another aspect of the invention, the liquid phase comprises at least one binder. Further preferred aspects are described with regard to the first aspect of the invention and incorporated herein.

[0167] According to a further aspect of the invention, the liquid phase of the process may comprise additional components, such as pH regulating substances, antioxidants, stabilizers, antifouling agents, preservatives, plasticisers, rheology modifiers such as thinners and/or thickeners, film forming agents, fillers. Aforementioned additional components of the liquid phase of the process may be added to the liquid phase as aqueous solutions. If one or more of these compounds are not sufficiently water-soluble, they may be incorporated into the liquid phase by other common techniques known in the art, e.g., these compounds may be dissolved in a water miscible solvent such as lower alcohols, glycols, ketones, esters, or amides. Alternatively, the compounds may be added to the liquid phase of the process as fine dispersions, as emulsion, or as cyclodextrine inclusion compounds, or incorporated into latex particles yet forming a further group of particles in the liquid phase of the process.

[0168] According to a further aspect of the invention, step (III) is performed by at least the following steps:

i) preparing a liquid phase comprising at least one of the polymer which can be used in a permeation layer as described above, preferably at least a polymer selected from an elastomeric polymer and a thermoplastic polymer, or two or more thereof, and
at least one liquid B;
ii) coating the liquid phase with amount in the range of from 1 to 50 g/m^2, preferably 2 to 40 g/m^2 oder 5 to 30 g/m^2, or 5 to 20 g/m^2, onto the drainage layer; and then
iii) drying the coating formed in step ii) resulting in the permeation layer.

[0169] In principle, liquid B can be selected from the same items as liquid A. Preferably, liquid B is water.

[0170] By performing step ii) in step (III), a permeation layer is obtained which has a weight in a range of from 0.1 g/m^2 to 5 g/m^2, preferably from 0.2 g/m^2 to 4 g/m^2, or from 0.5 g/m^2 to 3 g/m^2, or from 0.5 g/m^2 to 2 g/m^2. Aforementioned amounts are usually determined at 50 % relative humidity and 20 °C.

[0171] According to a further aspect of the invention process steps (II) and (III) of the above are performed by at least the following steps:

1) preparing a liquid phase comprising a plurality of silicon oxide particles and at least a liquid A;
2) preparing a liquid phase comprising at least one of the polymer which can be used in a permeation layer as mentioned above, preferably at least a polymer selected from an elastomeric polymer and a thermoplastic polymer, or two or more thereof,
and at least a liquid B;

3) coating the liquid phase of 1) with amount in the range of from 5 to 300 g/m^2, preferably in the range of from 50 to 270 g/m^2, or from 200 to 300 g/m^2, onto the substrate layer (2);
4) coating the liquid phase of 2) with amount in the range of from 1 to 50 glm^2, preferably 2 to 40 g/m^2 oder 5 to 30 g/m^2, or 5 to 20 g/m^2, onto the drainage layer (3); and then
5) drying the coatings formed in step 3) and step 4), whereby the drainage layer (3), and the permeation layer (6) are formed.

[0172] Liquid A and liquid B can be same or different. The preferred items for liquid A and liquid B are same as mentioned above. Preparing, coating and drying steps can be performed as mentioned above. Preferred aspects regarding the steps of preparing, coating and drying are as mentioned above.

[0173] In the art, numerous techniques are known to apply a layer comprising particles to a substrate layer. Accordingly, those skilled in the art will identify appropriate techniques for applying a drainage layer comprising a plurality of silicon oxide particles to the substrate layer in step (II) of the process.

[0174] According to a further aspect of the invention, the drainage layer, the permeation layer and optionally further layers, are applied in process step (II) by extrusion coating, air knife coating, doctor blade coating, cascade coating or curtain coating. The drainage layer, the permeation layer, and optionally further layers, may also be applied using spray techniques. It is further possible to coat the substrate layer on more than one surface with a drainage layer, a further layer or additional layers, or a combination of at least two thereof. It is further preferred to coat an antistatic layer or an anti-curl layer on the side of the substrate layer, which is facing away from the drainage layer. Preferred coating procedures to apply the drainage layer, and optionally further layers, in step (II) are cascade coating or curtain coating, wherein the drainage layer, optionally further layers and possibly other additional layers are coated simultaneously onto the substrate layer. It is further preferred to perform the coating step in the inventive process either in a single-layer coating, to coat two or more single-layer coatings performed in series, but also to perform a simultaneous multilayer coating in one-pass. The cited coating methods, however, are not to be considered limiting the invention.

[0175] A further aspect of the invention is a layer structure obtainable by the process for preparing a layer structure as described above which layer structure preferably comprises layers as described in the first aspect of the invention.

[0176] According to a further preferred aspect of the invention the drainage layer of the layer structure is a transparent layer.

[0177] Another aspect of the invention is a method for applying a liquid phase onto a layer structure comprising at least the following steps

α) Providing a layer structure as described above, and
β) Providing a reservoir comprising a liquid non-aqueous phase,
wherein the liquid phase comprises

1) at least 75 % by weight, or from 80 to 99 % by weight, or from 85 to 95 % by weight of an organic solvent, preferably selected from those used on organic vehicles of solvent-based pigmented inks; and
2) from 0.1 to 10 % by weight, or from 1 to 5 % by weight of a pigment,
3) from 0.1 to 10 % by weight, or from 1 to 5 % by weight of a at least a binder, preferably a resin binder
4) less than 1 % by weight, preferably less than 0.5 % by weight of water;
wherein the sum of all weight-% is 100;

γ) Transferring of at least a part of the liquid phase from the reservoir to the permeation layer of the layer structure,
δ) Removing of at least a part of the liquid phase from the permeation layer.

[0178] By performing this method, a printed substrate is obtained, which printed substrate is at least partially covered by a layer of at least a pigment and at least a resin binder, or which printed substrate has at least partially absorbed the solvents of the ink, or a combination of both. Suitable and preferred resin binders are known to the person skilled in the art of solvent-based pigmented inks.

[0179] According to a further aspect of the invention, steps β) and γ), or steps β) to δ) of aforementioned method are repeated one or more times on the same substrate, wherein in each step of repetition a liquid phase is provided, which liquid phase comprises another composition of pigments than any liquid phase provided onto the sample prior to said repetition step.

[0180] Numerous of the known substrates are considered suitable for the aforementioned method. Preferred substrates are those mentioned above when describing the substrates of the layer structure of the invention. Preferably, aforementioned method of applying a liquid phase comprising one or more pigments of the invention is used to print text or images onto any one or more of the aforementioned substrates.

[0181] Another aspect of the invention is a printed article which comprises a layer structure

which layer structure is as defined for above,
wherein the pigment which was applied in form of a solvent-based pigmented ink is positioned on the side of the permeation layer which faces away from the drainage layer.

[0182] Preferred is a layer structure as mentioned above wherein the drainage layer is able to absorb aforementioned liquid phase comprising aforementioned pigment and aforementioned resin binder at least partially, in particular the liquid. Then, the permeation layer of the layer structure is partially covered with pigment and resin binder.

[0183] Another aspect of the invention is a use of a substrate layer as described above for receiving solvent borne inks for inkjet printing, for writing utensils or in ink solutions for printing advertisement, signs, banners, posters, sheets, labels, particularly preferred for outdoor use.

[0184] The following Examples serve for exemplary elucidation of the invention and are not to be interpreted as a restriction.

DESCRIPTION OF THE FIGURES

[0185] The subject matter of the invention is exemplified in the figures. The figures, however, are not intended to limit the scope of the invention or the claims in any way.

[0186] Referring to Figure 1, a layer structure (1) is shown. The layer structure comprises a substrate layer (2) a drainage layer (3) and a permeation layer (6). The drainage layer (3) comprises silicon oxide particles (4).

[0187] Referring to Figure 2, another layer structure (1) is shown. As in Figure 1, the layer structure comprises a substrate layer (2), a drainage layer (3) and a permeation layer (6). The drainage layer (3) comprises silicon oxide particles (4). In a preferred aspect (optional), an intermediate layer (5), such as an adhesion promoting layer, can be arranged between the substrate layer (2) and the drainage layer (3).

[0188] In Figure 3, the process of the invention is shown.

[0189] In Figure 4, a printed article (9) is shown where pigments (10) are affixed to permeation layer (6) (not shown) of a layer structure (1).

TEST METHODS

A. Glass Transition Temperature

[0190] The glass transition temperature of polymers was determined with a Mettler TA3000 system equipped with a Mettler DSC30 differential scanning calorimetry unit and a Mettler TC10 temperature controller. The temperature range was -100°C to +100°C and the temperature changing rate was 10°C/minute for heating and cooling

[0191] A sample of 15-20mg was put in a 40µl crucible with pin, and gaseous nitrogen at a rate of 100cm^3/min. was used for the low temperature range. Each sample was measured twice to eliminate the thermal history of the sample.

[0192] The glass transition temperature was automatically calculated by the system software (Graphware TA72.2/5) based on the second heating cycle.

B. BET Specific surface area

[0193] The BET specific surface area was determined by the BET isotherm method, as described by S. Brunauer, P.H. Emmet and J. Teller in "Adsorption of Gases in Multimolecular Layers", Journal of the American Chemical Society 60, p. 309-319 (1938).

C. Particle Size

[0194] Particle size distribution was determined with a disc centrifuge CPS DC24000, using a gradient from 8wt.-% to 24wt.-% sucrose. After the gradient was established, a calibration standard *(PVC calibration standard 0.377 µm in deionised water,* provided by CPS Instruments, Inc.) was injected into the centrifuge disc rotating at 20000rpm.

[0195] Once the calibration was done, the investigated dispersion was injected into the centrifuge disc (20000rpm) at a concentration of 0.5wt.-%. The graph indicates the particle size (in µm) on the *x*-axis and the weight distribution in wt.-% on the γ-axis. The median particle size d_{50} (in nm) was obtained from the integral of the weight distribution curve. The polydispersity index (PDI) of the sample was calculated from the ratio between the weight average diameter (D_w) and the number average diameter (D_n):

$$PDI = \frac{D_w}{D_n} \text{ with } D_w = \frac{\sum D_i^2 N_i}{\sum D_i N_i} \text{ and } D_n = \frac{\sum D_i N_i}{\sum N_i}$$

[0196] N_i being the number of particles of diameter D_i.

[0197] The calculations of the d_{50}-diameter and the polydispersity index are performed automatically by the CPS software.

D. Thickness of an item, e.g. a layer, a layer structure

[0198] For each sample, a thin cut was obtained with a Leica RM2245 rotary microtome equipped with a low profile blade Leica 819. The width of the thin cut is 35 μm. The thin cut was then examined with an optical microscope Zeiss Axiophot and a Zeiss Epiplan Neofluar 20x objective. Pictures were taken with a JVC KY-F70B Tri-CCD camera (1360x1024 pixel resolution) and the layer thickness was determined with the software analySIS 3.1 provided by Soft Imaging System. The precision of the thickness measurement is ±1μm. Among several samples for each example, only those with a layer thickness in the range 14-17μm qualified for further evaluation.

E. Zeta Potential and Isoelectric Point

[0199] The zeta-potential titration was carried out on a Dispersion Technology DT1200 instrument. The "sample chamber" consists of a 100ml-beaker, a magnetic stirrer, two injection pipes and five sensors: acoustic, cvi (colloid vibration current), temperature, pH and conductivity. The zeta-potential was obtained by the cvi and acoustic sensors. The measurement was performed at room temperature and the silica dispersions were diluted to 2wt.-% SiO_2 to avoid gelation around the isoelectric point. The starting point of the titration curve is the dispersion pH, and depending on it, either hydrochloric acid 0.1mol/L or sodium hydroxide 0.1mol/L were added via the injection pipes. The titration was carried out from the starting pH to around pH 11 for the dispersions of positively-charged silica, and from the starting pH to around pH 3 for the dispersions of anionic silica. The zeta-potential in mV at the dispersion pH and the isoelectric point are read from the graph of the zeta-potential as a function of pH.

F. Viscosity

[0200] Viscosity measurements were performed with a Bohlin Visco 88 BV rotational viscosimeter equipped with a C25 system (measurement head 25cm, external cylinder 27.5 mm, capacity 15ml), at a shear rate of $225s^{-1}$ (speed 5) and at a temperature of 40°C.

G. Measurement of swell by solvent absorption

[0201] This test was performed with pure DEGMBE (diethylene glycol-mono-n-buthylether).

[0202] The apparatus used to measure swell consists of a metallic support holding the sample to measure, a pressure-sensitive head having a diameter of 1.2cm, a voltmeter and a Dosimat dosimeter containing the solvent or the mixture of solvents to absorb. The pressure head, the voltmeter and the dosimeter are connected to a computer that controls the process and reads the values provided by the voltmeter. The voltmeter is further connected to the pressure-sensitive head, and sends to the computer a signal that is proportional to the vertical position of the head.

[0203] A 3 x 5cm piece of each example was inserted with the coated side up between the pressure-sensitive head and the metallic holder. Every second, the pressure-sensitive head lowered towards the sample. As soon as the head contacted the sample, it sent a position signal to the voltmeter and returned to its start position. The signal sent from the voltmeter was automatically adjusted to 0V (0μm swell). After 10 seconds, the dosimeter began to drop the solvent onto the sample at a constant rate of 1.5 ml/min for 180 seconds.

[0204] The data recorded by the computer were sent to a printer. The printed graph indicates the absorption time on the x-axis and the amount of swelling in μm on the γ-axis. The swell thickness in μm was determined by interpolating the 10 last values.

[0205] The swell thickness [μm] was converted in swell ratio [%] with the following formula:

$$Swell\ ratio = \frac{Swell\ thickness\ [\mu m]}{Thickness\ of\ all\ layers\ [\mu m]} * 100$$

[0206] The tendency to swell of the sample was then quoted according to the following scale:

A: ≤5% swell ratio *B*: 5 to ≤10% swell ratio *C*: 10 to ≤15% swell ratio*D*: 15 to ≤20% swell ratio *E*: 20% swell ratio and more.

[0207] An *A* means that there is no significant tendency of the investigated material to swell. An *E* means that there is a strong tendency to swell.

H. pH

[0208] The pH was measured at 40°C with a standard combined glass pH-electrode.

I. Minimum drying time after printing

[0209] A roll of the material to be tested was printed with a 4K solid block measuring 28cm x 8.0cm, at a temperature of 19°C and a relative humidity of 48%, with an ink jet printer Roland VS-300 (GPPM: Photo Matte Paper, High Quality, 1440dpi Pre-Press Europe, +5CMYK, Bi-direction), using Eco-Sol Max inks. The temperature of the printing plate and of the drying plate were set at 40°C.

[0210] Directly after printing, the printed area was cut from the roll as a sheet of about 35cm x 15cm. An unprinted sheet of the same material and the same dimension was then put on the printed sample, in such a way that the back side of the unprinted material is in contact with the front side of the printed material. The two sheets were inserted together between two soft PVC rolls having a diameter of 3cm, one fixed and the other allowed to move vertically in order to adapt to the media thickness. The pressure applied to the two sheets is due only to the weight of the second roll, which is 594g. The rolls are slowly rotating at a linear speed of 270mm/h, until the whole sample has passed through the rolls.

[0211] Then the two sheets were separated. The length of the zone where ink has been transferred to the backside was measured with a ruler in cm, and converted into minutes. The damage occurred to the printed surface was assessed in the same way. To the determined times was added the time taken between the end of the printing process and the beginning of the test. The extent of the damage to the printed zone was assessed visually and quoted from "none" to ,,very strong".

J. Gloss Value (unprinted)

[0212] Gloss was measured according to norms ISO 2813 and ISO 15994 with a glossmeter Micro-TRIGloss®, available from BYK Gardner, Columbia, USA. Values are given for three geometries at 20°, 60° and 85°.

K. Volume of Color Space (Gamut)

[0213] Patches of the colors yellow (Y), red (R), magenta (M), blue (B), cyan (C), green (G) and black (4K) at 100% print were printed at 21°C and 55%rH onto a roll of each example with an ink jet printer Roland VS-300 (GPPM: Photo Matte Paper, High Quality, 1440dpi Pre-Press Europe, +5CMYK, Bi-direction), using Eco-Sol Max inks. The temperature of the printing plate and of the drying plate were set at 40°C. The printed area was cut from the roll as an A4 sheet. The media sheets were left during 24 hours at 21°C and 55%rH to allow the ink to dry. Then the L*a*b* color coordinates of the colors yellow, red, magenta, blue, cyan, green, black and white were measured with a X-Rite 310X densitometer and the volume of the color space L*a*b*formed by these eight colors was calculated using the formulae of G. Wyszecki and W. Stiles in "Color Science Concepts and Methods, Quantitative Data and Formulae", John Wiley & Sons, 2nd edition 1982, ISBN 0-471-02106-7, pages 164-169 and page 829.

L. Dry pigment adhesion

[0214] This test reproduces the conditions endured by a wide format print wound into a roll directly after printing. 2cm x 0.3cm patches of the colors cyan (C), magenta (M), yellow (Y), red (R), blue (B), green (G) and black (4K) at 100% print density were printed at 21°C and 55%rH onto a roll of each example with an ink jet printer Roland VS-300 (GPPM: Photo Matte Paper, High Quality, 1440dpi Pre-Press Europe, +5CMYK, Bi-direction), using Eco-Sol Max inks. The temperature of the printing plate and of the drying plate was set at 40°C. Directly after printing, the printed area was cut from the roll as an A4 sheet. This A4 sheet was sticked onto the tray of a Mettler PM-15 balance with a Tesa 4104 white tape. Each of the color patches was then rubed with a 2kg pressure of the thumb across the width of each color patch, until a distance of about 3cm from the patch was reached. The extent of pigment transfer to the adjacent unprinted area and the damage at each color patch was assessed visually using the following rating:

Partial Value 1: The color patch shows no damage, and there is no pigment transfer to the adjacent unprinted area.
Partial Value 0.5: The color patch shows some damage visible to the naked eye, but there is no pigment transfer to the adjacent unprinted area.
Partial Value 0: The color patch shows some damage visible to the naked eye, and there is visible pigment transfer to the adjacent unprinted area.

[0215] Subsequently, all the partial values were added for the 7 color patches. This sum is a measure of dry rub resistance and is called here "Dry Pigment Adhesion Value". Samples with high pigment adhesion have a Dry Pigment Adhesion Value of 7, which means that printed samples will be immune to rubbing applied under the conditions of the test, and that no damage is likely to occur upon winding of the print into a roll. Samples with very bad pigment adhesion have a Dry Pigment Adhesion Value of 0, which means that the printed samples will be very sensitive to rubbing applied under the conditions of the test, and that strong damage is likely to occur upon winding of the print into a roll.

M. Wet pigment adhesion

[0216] This test reproduces the conditions endured by a wide format print when the image is contacted with water. 2cm x 0.3cm patches of the colors cyan (C), magenta (M), yellow (Y), red (R), blue (B), green (G) and black (4K) at 100% print density were printed at 21°C and 55%rH onto a roll of each example with an ink jet printer Roland VS-300 (GPPM: Photo Matte Paper, High Quality, 1440dpi Pre-Press Europe, +5CMYK, Bi-direction), using Eco-Sol Max inks. The temperature of the printing plate and of the drying plate were set at 40°C. After 24hrs drying time at 21°C and 55%rH, the printed pattern was cut as an A4 sheet and a drop of deionised water was put over each of the color patch. The A4 sheet was sticked onto the tray of a Mettler PM-15 balance with a Tesa 4104 white tape. Each of the color patches was then rubed with a 2kg pressure of the thumb across the width of each color patch, until a distance of about 3cm from the patch was reached. The extent of pigment transfer to the adjacent unprinted area and the damage at each color patch was assessed visually using the following rating:

Partial Value 1: The color patch shows no damage, and there is no pigment transfer to the adjacent unprinted area.
Partial Value 0.5: The color patch shows some damage visible to the naked eye, but there is no pigment transfer to the adjacent unprinted area.
Partial Value 0: The color patch shows some damage visible to the naked eye, and there is visible pigment transfer to the adjacent unprinted area.

[0217] Subsequently, all the partial values were added for the 7 color patches. This sum is a measure of wet rub resistance and is called here "Wet Pigment Adhesion Value". Samples with high wet pigment adhesion have a Wet Pigment Adhesion Value of 7, which means that printed samples will be immune to spilling with water, and that no damage is likely to be visible once the water has evaporated. Samples with very bad wet pigment adhesion have a Wet Pigment Adhesion Value of 0, which means that the printed samples will be very sensitive to spilling of water, and that strong damage is likely to be visible once the water has evaporated.

N. Image Homogeneity

[0218] This test is used to measure the ability of the media to provide a homogeneous image after printing. 14cm x 2.5cm gradients from 100% color to full black of the colors cyan (C), magenta (M), yellow (Y), red (R), green (G) and blue (B) were printed at 21°C and 55%rH onto a roll of each example with an ink jet printer Roland VS-300 (GPPM: Photo Matte Paper, High Quality, 1440dpi Pre-Press Europe, +5CMYK, Bi-direction), using Eco-Sol Max inks. The temperature of the printing plate and of the drying plate were set at 40°C. At the same time, a continuous 3K black wedge (0% to 100% of black) was printed beside the color patches.

[0219] After drying, image homogeneity was assessed visually. For each of the seven patches, the length along which inhomogeneity due to coalescence of the ink drops was visible with the naked eye was recorded with a ruler. The individual values were summed up and an Image Homogeneity Value was calculated according to the following equation:

$$\text{Image Homogeneity Value} = 5 \cdot \left(1 - \frac{\sum_{i=1-7} individual\ value}{7 \cdot 14} \right)$$

[0220] Samples with high image homogeneity have an Image Homogeneity Value of 7, which means that even demanding pictures will show perfect homogeneity with the naked eye. Samples with very bad image homogeneity have an Image Homogeneity Value of 0, which means that all pictures will show inhomogeneous area observable with the naked eye.

O. Advancing Contact Angle

[0221] The advancing contact angle was measured in DEGMBE (diethylene-glycol mono-n-butylether, Aldrich-Sigma >99%) for each example. We used a MGW Lauda Te2 tensiometer equipped with a HBM (Hottinger Baldwin Messtechnik) inductive force transducer type Q11 (range +/- 5g, sensitivity 0.25mg, accuracy 0.5%). The transducer response was calibrated by suspending a 500mg weight to the transducer hook. The solvent was put in a 20ml-beaker fixed to a vertically moving holder controlled by the computer.

[0222] The surface tension of DEGMBE was measured with a 2cm diameter Pt-Ir du Nouÿ ring that was provided with the tensiometer. Prior to the measurement, the ring was cleaned with ethanol and rinsed with deionised water, then heated to red with a gas flame for 1-2 seconds, placed on the hook connected to the force transducer and left to cool to room temperature. The ring was brought 2-3mm below the solvent surface (just fully immersed) and the transducer response was zeroed before starting the measurement routine provided by the instrument software. The measurement was repeated five times and an average value was calculated. After applying a standard Harkins-Jordan correction (directly in the computer software), the average surface tension of DEGMBE was calculated to be 30.4mN/m. This value was used for the determination of the contact angle in the next step.

[0223] Two 4 x 4 cm pieces of each example were stuck together, backside against backside, with a double-faced adhesive tape. This sample was suspended to the transducer hook and manually placed a few mm above the surface of the solvent. The sample was then lowered at a constant speed of 300μm/sec. At the moment the sample touched the surface of the solvent, both the force and the time were zeroed-in by the software. The software allowed the sample to immerse in the solvent at the same speed until it reached a depth of 25mm. The sample was then lifted out of the solvent at the same speed until it completely emerged. A graph of the force (in mN) against the immersion depth (in mm) was automatically printed.

[0224] The curve of the force as a function of the immersion depth was used to determine the advancing contact angle. From the (0,0) point of the graph, a line was drawn vertically through the graph. The straight obtained by immersing the sample in the solvent till it reached its maximal depth was prolonged until it crossed the vertical zero line. This point corresponds to the maximal force produced by the contact between the sample and the solvent at the beginning of the immersion. The force was then inserted in the following equation to calculate the advancing contact angle:

$$\alpha_{adv} = \cos^{-1}\left(\frac{F}{P \cdot \gamma}\right)$$

with

F = attractive or repulsive force [mN]
P = perimeter of the sample [m]
γ = surface tension of the solvent [in mN/m]
α_{adv} = advancing contact angle

[0225] The perimeter of the sample was measured with a ruler. The measurement process was repeated three times with each sample. An average value was calculated. This is the Advancing Contact Angle indicated in Table 2.

[0226] The process was repeated for all examples with deionised water as the solvent. The surface tension of water was determined with the de Nouÿ ring method (including the Harkins-Jordan correction) to be 71.3mN/m. The water was replaced after each measurement to avoid a decrease of the surface tension due to contamination by the surfactants present in the layers.

P. Pore Volume and Absorption capacity (AC)

[0227] The pore volume and the absorption of samples of layer structures were measured with the same equipment as used for the determination of the advancing contact angle, with the same measurement parameters (25mm maximal depth, 300μm/sec. immersion speed). The weight difference between the beginning and the end of the measurement, as extrapolated from the graph, indicate the total amount of the liquid absorbed during the process. The measurement was repeated three times and an average value of the total absorbed liquid was calculated.

[0228] In a separate measurement, the absorption of the raw base (substrate layer) was determined in the same way. This measurement was carried out three times and an average value was calculated.

[0229] The average value of liquid absorbed by the layers was determined by subtracting the average amount of liquid absorbed by the base from the average value of the total absorbed liquid.

[0230] The pore volume in ml/m^2 was calculated from the following formula :

$$Pore\,volume = \frac{Absorbed\ liquid\,[mg]}{2 * sample\ width\,[mm] * immersion\,depth\,[mm] * liquid\ density\,[g/ml]} * 10^3$$

[0231] The density of DEGMBE is 0.967g/cm^3.

[0232] The absorption capacity in % of the dry weight of the layers was determined by dividing the average value of liquid adsorbed [g/m^2] by the known dry weight of the layers [g/m^2] (weight of the substrate layer subtracted).

Q. Water Resistance

[0233] An A4 sheet of each example was printed with the same image as in the Volume of Color Space test, with a Roland VS-300 (GPPM: Photo Matte Paper, High Quality, 1440dpi Pre-Press Europe, +5CMYK, Bi-direction), using Eco-Sol Max inks. The temperature of both the printing plate and the drying plate were set at 40°C.

[0234] After 24 hours drying, each A4 sheet was put in a 1L-cylinder full with deionized water for 4 days (96 hours) at 20°C. After 4 days, the sheets were pulled out the water, gently dried with absorbing paper and allowed to dry further for 24 hours.

[0235] The water resistance was quoted as follows:

- no change: the unprinted and the printed surface are unaltered. The front side gloss is within ±10% of the original measurement.
- layer cracking: careful examination with the naked eye shows that small longitudinal cracks appear at the surface. The gloss is lower by more than 10% of the original measurement.
- delamination: the layer is partially or totally separated from the substrate, forming «bubbles» under the layer. Layer cracking usually accompanies delamination.

EXAMPLES

Example 1

Resin-coated base

[0236] A semi-glossy resin-coated base was purchased from Felix Schoeller & Sons (Osnabrück, Germany). It contains 123g/m^2 paper, 20g/m^2 low-density polyethylene on the front side and 33g/m^2 of a blend of low-density polyethylene and high-density polyethylene on the back side. An adhesion promoting layer of 80 mg/m^2 was coated on the front side. According to the technical datasheet of the supplier, the thickness of the base is 172μm and the total weight is 175g/m^2.

Silica dispersion for the drainage layer

[0237] 1.82kg of NaOH 1N were added to 86.18kg of deionized water at room temperature (T=20°C). Then, 12kg fumed silica (Cabot Cab-O-Sil M5, 200m^2/g, Cabot Corp., Billerica, USA) were slowly added under stirring at 3500rpm with an Ystral Conti TDS dispersing device. After adding the silica powder was completed, the temperature was raised at 1°C/min. up to 30°C. After 45 minutes at 30°C, the dispersion was allowed to cool to room temperature at 1°C/min. and was filtrated.

[0238] 100kg of a dispersion containing 12 wt.-% fumed silica were obtained. The pH of this dispersion was 8.9, its zeta-potential was -27mV and its viscosity was 25mPas.

Coating solution 1 for the drainage layer

[0239] 67.21kg of the previously described silica dispersion for the drainage layer, 955g of a 4.0wt.-% solution of borax (Sigma-Aldrich, Buchs, Switzerland) and 996g of a 9 wt.-% solution of the cross-linker adipic acid dihydrazide (Sigma-Aldrich, Buchs, Switzerland) were successively added under gentle stirring to a mixture comprising 7.60kg of deionised water, 13.43kg of an 8.0wt.-% solution of Mowiol 4088 (Clariant AG, Muttenz, Schweiz), 5.38kg of a 10.0wt.-% solution of Poval DF-20 (Kuraray Europe GmbH, Frankfurt am Main, Deutschland), and 3.33kg of a 3 wt.-% solution of the surfactant Triton X100 (octylphenol ethylene oxide condensate with 9-10 ethylene repeating units, purchased from Sigma Corp., St-Louis, USA).

[0240] 100kg of a coating solution for the drainage layer containing 8.07 wt.-% fumed silica were obtained.

Coating solution 2 for the permeation layer

[0241] 1.53kg of Dispercoll U53 (40% polyurethane dispersion in water, Bayer Material Science AG, Leverkusen, Germany) and 1.46kg Joncryl 544 (42% acrylic resin dispersion in water, BASF Performance Chemicals, Ludwigshafen, Germany) were added under gentle stirring to a mixture of 1.96kg of deionised water and 50g of a 3 wt.-% solution of the surfactant Triton X100 (Sigma Corp., St-Louis, USA).

[0242] 5kg of a coating solution 2 for the permeation layer containing 12.25wt.-% Dispercoll U53 and 12.25w.-% Joncryl 544 were obtained.

Coating

[0243] On the resin-coated base described above, 223.2g/m^2 of the coating solution 1 for the drainage layer and 8.16g/m^2 of the coating solution 2 for the permeation layer were coated simultaneously with a slide-bead coating device at a temperature of 40°C and a constant speed of 20m/min.

Drying

[0244] After cooling at 2°C for 20 seconds, the coated material was dried at 35°C and 10%rH for 30 seconds then at 45°C and 15%rH for 70 seconds, and finally at 52°C and 15%rH during 30 seconds.

Properties

[0245] The final coated material contained 18g/m^2 fumed silica in the drainage layer and 2g/m^2 of a 1:1 blend of Dispercoll U53 (polyurethane dispersion) and Joncryl 544 (polyacrylic resin emulsion) in the permeation layer.

Example 2

Resin-coated base

[0246] The resin-coated base used in Example 2 was the same as described in Example 1.

Silica dispersion for the drainage layer

[0247] The silica dispersion for the drainage layer of Example 2 was the same as described in Example 1.

Coating solution 1 for the drainage layer

[0248] The coating solution for the drainage layer of Example 2 was the same as described in Example 1.

Coating solution 2 for the permeation layer

[0249] 2.75kg of Printrite DP262 (thermoplastic polymer with Tg = -11.6°C, 44.5% dispersion in water, purchased from Lubrizol Corp., Brecksville Road, Cleveland, USA) were added under gentle stirring to a mixture of 2.20kg of deionised water and 50g of a 3 wt.-% solution of the surfactant Triton X100 (Sigma Corp., St-Louis, USA).

[0250] 5kg of a coating solution 2 for the permeation layer containing 24.5w.-% of Printrite DP262 were obtained.

Coating

[0251] On the resin-coated base described above, 223.2g/m^2 of the coating solution 1 for the drainage layer and 8.16g/m^2 of the coating solution 2 for the permeation layer were coated with the same coating parameters as Example 1.

Drying

[0252] The drying step was performed identically to Example 1.

Properties

[0253] The final coated material contained 18g/m^2 fumed silica in the drainage layer and 2g/m^2 of the Printrite DP262 polymer in the permeation layer.

Comparative Example 1

Coated vinyl substrate

[0254] As first comparative example, a standard matte uncoated vinyl substrate (MPI2020, matte white, Avery-Dennison, Kreuzlingen, Switzerland) was submitted to the same testing procedure as Examples 1 and 2.

Example 3

Barrier-paper base

[0255] For this example, a barrier-type paper base was purchased at OJI Paper (purchased from Oji Paper Co. Ltd, Tokyo, Japan). It comprises a paper core of 159g/m^2, and two symmetrical barrier layers of 25g/m^2 on both sides, giving a (theoretical) total weight of 209g/m^2. The barrier layer consists of a mixture of calcium carbonate, kaolin, starch and latex binder. Its thickness is 196μm.

Silica dispersion for the drainage layer

[0256] 0.70kg aluminium chlorohydrate (Locron P, available from Clariant AG, Muttenz, Switzerland), 0.56kg boric acid and 1.82kg *n*-butylaminopropyltrimethoxysilane (Dynasilan 1189, 98%, available from Degussa AG, Düsseldorf, Germany) were sequentially added to 72.92kg of deionised water under gentle mechanical stirring at room temperature. Stirring was continued during 15 minutes. To this solution, 24kg of fumed silicone dioxide with a specific surface of 200m^2/g (Cab-O-Sil M5, available from Cabot Corp., Billerica, USA) were slowly added under stirring at 3500rpm with an Ystral Conti TDS dispersing device. After all the silica powder was added, the temperature was raised at 1°C/min. up to 50°C. After 45 minutes at 50°C, the dispersion was allowed to cool to room temperature at 1°C/min. and was filtrated.

[0257] 100kg of a dispersion containing 24wt.-% positively charged fumed silica were obtained. The pH of this dispersion was 5.5, its zeta-potential was 41mV and its viscosity was 95mPas.

Coating solution 1 for the drainage layer

[0258] To 56.25kg of the previously described silica dispersion for the drainage layer were sequentially added 6.21kg of deionised water, 0.41kg of boric acid (Sigma-Aldrich, Buchs, Switzerland), 33.8kg of an 8.0wt.-% solution of Mowiol 4088 (Clariant AG, Muttenz, Schweiz) and 3.33kg of a 3 wt.-% solution of the surfactant Triton X100 (Sigma Corp., St-Louis, USA).

[0259] 100kg of a coating solution for the drainage layer containing 13.5wt.-% positively charged fumed silica were obtained.

Coating solution 2 for the permeation layer

[0260] 2.66kg of Printrite DP275 (thermoplastic polymer with T_g = -48.8°C, 46% dispersion in water, purchased from Lubrizol Corp., Brecksville Road, Cleveland, USA) were added under gentle stirring to a mixture of 2.29kg of deionised water and 50g of a 3 wt.-% solution of the surfactant Triton X100 (Sigma Corp., St-Louis, USA).

[0261] 5kg of a coating solution 2 for the permeation layer containing 24.5w.-% of Printrite DP275 were obtained.

Coating of the drainage layer

[0262] On the barrier-type paper base described above, 133.3g/m^2 of the coating solution 1 for the drainage layer were coated with a slide-bead coating device at a temperature of 40°C and a constant speed of 20m/min.

Drying of the drainage layer

[0263] The drying of the coated drainage layer was performed identically to Example 1.

Coating of the permeation layer

[0264] On the previously coated and dried drainage layer, 8.16g/m^2 of the coating solution 2 for the permeation layer were coated with a slide-bead coating device at a temperature of 40°C and a constant speed of 20m/min.

Drying of the permeation layer

[0265] The drying of the coated permeation layer was performed identically to the drying of the drainage layer.

Properties

[0266] The final coated material contained 18g/m^2 positively charged fumed silica in the drainage layer and 2g/m^2 of the Printrite DP275 polymer in the permeation layer.

Example 4

Resin-coated base

[0267] A glossy resin-coated base was purchased from Felix Schoeller & Sons (Osnabrück, Germany). It contains 176g/m^2 paper, 20g/m^2 low-density polyethylene on the front side and 33g/m^2 of a blend of low-density polyethylene and high-density polyethylene on the back side. An adhesion promoting layer of 80 mg/m^2 was coated on the front side. According to the technical datasheet of the supplier, the thickness of the base is 217μm and the total weight is 230g/m^2.

Silica dispersion for the drainage layer

[0268] The silica dispersion for the drainage layer was the same as described in Example 3.

Coating solution 1 for the drainage layer

[0269] The coating solution 1 for the drainage layer was the same as described in Example 3.

Coating solution 2 for the intermediate layer

[0270] 1.25kg of an 8wt.-% solution of Mowiol 4088 (PVA, Clariant AG, Muttenz, Schweiz), 0.45g of boric acid (Sigma-Aldrich, Buchs, Switzerland) and 25g of a 3 wt.-% solution of the surfactant Triton X100 (Sigma Corp., St-Louis, USA) were successively added to 3.72kg of deionised water.

[0271] 5kg of a coating solution 3 for the intermediate layer containing 2w.-% of Mowiol 4088 were obtained.

Coating solution 3 for the permeation layer

[0272] The coating solution 3 for the permeation layer is identical to the coating solution 2 for the permeation layer of Example 1.

Coating

[0273] On the resin-coated paper base described above, 133.3g/m^2 of the coating solution 1 for the drainage layer, 5g/m^2 of the coating solution 2 for the intermediate layer and 8.16g/m^2 of the coating solution 3 for the permeation layer were coated simultaneously with a slide-bead coating device at a temperature of 40°C and a constant speed of 20m/min.

Drying of the drainage layer

[0274] The drying step was performed identically to Example 1.

Properties

[0275] The final coated material contained 18g/m^2 positively charged fumed silica in the drainage layer, 0.1g/m^2 PVA in the intermediate layer and respectively 1g/m^2 Dispercoll U53 and 1g/m^2 Joncryl 544 in the permeation layer.

Comparative Example 2 (pure polymer layer, glossy resin-coated base)

Resin-coated base

[0276] The resin-coated base used in Comparative Example 2 was the same as described in Example 4.

Coating solution 1 for the permeation layer

[0277] The coating solution 1 for the permeation layer is identical to the coating solution 2 for the permeation layer of Example 3.

[0278] 60kg of a coating solution 1 for the permeation layer containing 24.5w.-% of Printrite DP275 were obtained.

Coating

[0279] On the resin-coated base described above, 102g/m^2 of the coating solution 1 for the permeation layer were coated with a slide-bead coating device at a temperature of 40°C and a constant speed of 20m/min.

Drying of the drainage layer

[0280] The drying step was performed identically to Example 1.

Properties

[0281] The final coated material contained 25g/m^2 of the polymer Printrite 275.

Comparative Example 3

Resin-coated base

[0282] The resin-coated base used in Comparative Example 3 was the same as described in Example 4.

Silica dispersion for the drainage layer

[0283] The silica dispersion used in Comparative Example 3 is the same as described in Example 1 above.

Coating solution 1 for the drainage layer

[0284] The coating solution 1 for the drainage layer used in Comparative Example 3 is the same as described in Example 1 above.

Coating

[0285] On the resin-coated base described above, 223.2g/m^2 of the coating solution 1 for the drainage were coated with a slide-bead coating device at a temperature of 40°C and a constant speed of 20m/min.

Drying

[0286] After cooling at 2°C for 20 seconds, the coated material was dried at 35°C and 10%rH for 30 seconds then at 45°C and 15%rH for 70 seconds, and finally at 52°C and 15%rH during 30 seconds.

Properties

[0287] The final coated material contained 18g/m^2 of negatively charged fumed silica.

Table 1

		Example 1	Example 2	Comp. Ex. 1	Example 3	Example e 4	Comp. Ex. 2	Comp. Ex. 3
Type		Hybrid	Hybrid	Vinyl	Hybrid	Hybrid	Polymer	Nanoporous
Charge of permeation layer		Anionic	Anionic		Anionic	Anionic	Anionic	
Charge of drainage layer		Anionic	Anionic		Cationic	Cationic		Anionic
Intermediate layer		no	no		no	yes	no	no
Coating		1-pass	1-pass		2-pass	1-pass	1-pass	1-pass
Base		Semi-glossy RC	Semi-glossy RC		Barrier paper	Glossy RC	Glossy RC	Glossy RC
Gloss Value	20°	9,7°	3,6°	1,8°	22,7°	63,7°	42,3°	3,9°
	60°	42,9°	31,0°	8,4°	66,6°	88,1°	64,6°	10,7°
	85°	70,5°	53,1°	16,8°	84,0°	98,6°	82,5°	67,6°
Volume of Color Space		306 k	363 k	285 k	349 k	325 k	342 k	294 k
Pigment Adhesion Value	Dry	4,5	5,0	5,0	1,0	5,0	1,0	0,0
	Wet	7,0	7,0	7,0	7,0	7,0	4,0	0,0
Minimum Drying Time after Printing	Transfer on backside	33min.	29min.	11min.	33min.	33min.	53min.	0min.
	Damage on front side	25min.	23min.	9min.	19min.	15min.	49min.	0min.
	Extent of damage	weak	weak	weak	weak	weak	strong	none
Water resistance	4d 20°C	no change	no change	no change	layer cracking	layer cracking	delamination	delamination
Image Homogeneity Value		5,8	6,3	2,5	5,5	6,1	3,6	4,9

Table 2

Example	Type	Base	Advancing contact angle in DEGMBE	Advancing contact angle in water	Pore volume [ml/m^2]	Absorption capacity [g/g % of layer weight]	Swell ratio
Example 1	Anionic/anionic 1-pass	Semi-glossy RC	19,0°	97,0°	27,0ml/m^2	109%	A
Example 2	Anionic/anionic 1-pass	Semi-glossy RC	18,9°	99,0°	29,3ml/m^2	117%	A
Comp. Ex. 1	Vinyl reference	Vinyl	26,9°	102,0°	22,2ml/m^2		A
Example 3	Anionic/cationic 2-pass	Barrier paper	19,8°	99,0°	26,8ml/m^2	104%	A
Example 4	Anionic/cationic 1-pass	Glossy RC	11,0°	101,0°	25,8ml/m^2	99%	A
Comp. Ex. 2	Polymer layer	Glossy RC	18,4°	57,0°	37,4ml/m^2	145%	E
Comp Ex. 3	Porous layer	Glossy RC	19,3°	51,0°	29,1ml/m^2	129%	A

Annotations: 1) DEGMBE: diethyleneglycol-mono-n-butylether; 2.) Surface tension of DEGMBE: 30.4mN/m; 3.) Surface tension of deionised water: 71. 7mN/m

Results Table 1

[0288] Examples 1 and 2 on a semi-gloss base show improved results over Comparative Example 1 for all parameters related to image quality. Especially the image homogeneity is much better. Examples 1 and 2 are water fast, which make them well suited for outdoor use.

[0289] Examples 3 and 4 on a glossy base exhibit very high gloss values compared to Comparative Example 1. Water resistance is inferior to Example 1, 2 and Comparative Example 1. Example 3 and 4 are well suited for indoor use where very high photographic quality is required.

[0290] Comparative Example 2, which comprises only a permeation layer, exhibits high gloss and large color space. However, pigment adhesion, drying times and image homogeneity are not satisfactory.

[0291] In Comparative Example 3, which comprises only a drainage layer, drying times are short. However, gloss, color space and pigment adhesion are not satisfactory.

[0292] It is noteworthy that the good results of examples 1 to 4 are not the combination of properties of the layers of comparative examples 2 and 3, e. g. pigment adhesion, color space and image homogeneity are much increased compared to both comparative examples 2 and 3.

Results Table 2

[0293] Examples 1, 2, 3 and 4 show low contact angles in diethylene glycol mono-*n*-butylether. This indicates good wetting with organic solvents usually present in solvent inks, exemplified for diethylene glycol mono-*n*-butylether. Further, contact angles higher than 90° with water were observed. This indicates that the layer structures of examples 1, 2, 3 and 4 are very well suited for printing with solvent inks, but not with aqueous inks. This is further a good indication of water resistance. For this reason, examples 1 - 4 appear to be better suited for outdoor use than comparative examples 1 and 3.Comparative Example 2 exhibits a low contact angle with diethylene glycol mono-*n*-butylether, but high swell ratio and long drying times.

[0294] Comparative Example 3 shows a low contact angle with diethylene glycol mono-*n*-butylether and a low swell ratio, and also low contact angle with water. However, gloss and pigment adhesion are not satisfactory.

[0295] Comparative Example 1 exhibits a low contact angle with diethylene glycol mono-*n*-butylether, a high contact angle with water and a low swell ratio. However, its absorption capacity is insufficient, which results in poor image homogeneity.

REFERENCE NUMBERS

[0296]

(1)	layer structure
(2)	substrate layer
(3)	drainage layer
(4)	silicon oxide particles
(5)	further, intermediate layer (optional)
(6)	permeation layer
(7)	reservoir
(8)	liquid phase
(9)	printed article
(10)	pigment

Claims

1. A layer structure (1) comprising:

(a) a substrate layer (2);
(b) a drainage layer (3) at least partially superimposed to the substrate layer (2), wherein the drainage layer (3) comprises a plurality of silicon oxide particles, and
(c) a permeation layer (6)
which is at least partially superimposed to the drainage layer (3),
wherein the contact angle is 30° or less between the permeation layer (6) and diethylene glycol mono-n-butyl ether.

2. The layer structure (1) according to claim 1, wherein the combined absorption capacity of the drainage layer (3) and the permeation layer (6) together is at least 50 % of the total dry weight of those two layers.

3. The layer structure (1) according to any one of the preceding claims, wherein the ratio of the thickness of the drainage layer (3) and the thickness of the permeation layer (6) is at least 5:1, each determined in g/m^3.

4. The layer structure (1) according to any one of the preceding claims, wherein the permeation layer (6) comprises less than 5 wt.-% of a hydrophilic or water soluble polymer.

5. The layer structure (1) according to any one of the preceding claims, wherein the drainage layer (6) comprises at least one binder which at least one binder is selected from the group of reactive polymers.

6. The layer structure (1) according to any one of the preceding claims, wherein the contact angle between the permeation layer (6) and deionized water is 65° or more.

7. The layer structure (1) according to any one of the preceding claims, wherein the swell ratio of the swollen layer structure and the layer structure before swelling is less than 1.2.

8. The layer structure (1) according to any one of the preceding claims, wherein the average particle diameter of at least 75 % by weight of the silicon oxide particles (4) of the drainage player is 300 nm or less, the weight being based on the total weight of the silicon oxide particles (4) in the drainage layer (3).

9. The layer structure (1) according to any one of the preceding claims wherein the BET specific surface area of the silicon oxide particles (4) of the drainage layer (3) is in the range of from 100 - 300 m^2/g.

10. The layer structure (1) according any one of the preceding claims wherein the permeation layer (6) comprises at least one polymer, wherein one or more, or all polymers of the permeation layer (6) have a glass transition temperature T_g in the range of from +20 to - 50 °C.

11. The layer structure (1) according to any of the preceding claims wherein the permeation layer (6) has a thickness in the range of from 0.1 to 10 μm.

12. The layer structure (1) according to any one of the preceding claims, wherein the permeation layer (6) comprises at least one thermoplastic polymer selected from the group consisting of a polyurethane, a polyacrylate, a polyamide, a polyester, a polyvinylacetate, and a polycarbonate.

13. The layer structure (1) according to any one of the preceding claims wherein the ratio of the rate of diffusion of the drainage layer rD^1 to the rate of diffusion of the permeation layer rD^2 is more than 1, each determined with diethylene glycol mono-n-butyl-ether.

14. The layer structure (1) according to any one of the preceding claims wherein the absorption capacity of the drainage layer (3) is higher than the absorption capacity of the permeation layer (6), each determined with diethylene glycol mono-n-butyl-ether.

15. The layer structure (1) according to any of the preceding claims which further comprises an intermediate layer (5) which intermediate layer (5) is arranged between to the drainage layer (3) and the permeation layer (6).

16. A process for preparing a layer structure (1) having a substrate layer (2), an drainage layer (3) and a permeation layer (6) comprising at least the process steps:

(I) providing a substrate layer (2);
(II) superimposing to the substrate layer (2) an drainage layer (3), wherein the drainage layer (3) comprises a plurality of silicon oxide particles (4),
(III) superimposing at least one permeation layer (6) onto the drainage layer (3), which is at least partially superimposed to the drainage layer (3),
wherein the contact angle between the permeation layer (6) and diethylene glycol mono-n-butyl ether is 30° or less.

17. The process according to claim 16, wherein step (II) is performed by at least the following steps:

i. preparing a liquid phase comprising a plurality of silicon oxide particles (4) and at least a liquid A;
ii. coating the liquid phase with amount in the range of from 5 to 300 g/m^2 onto the substrate layer (2); and then
iii. drying the coating formed in step ii. resulting in the drainage layer (3).

18. The process according to claim 16 or 17, wherein step (III) is performed by at least the following steps:

i) preparing a liquid phase comprising a polymer which can be used in a permeation layer (6) and at least a liquid B;
ii) coating the liquid phase with amount in the range of from 1 to 50 g/m^2 onto the drainage layer (3); and then
iii) drying the coating formed in step ii) resulting in the permeation layer (6).

19. The process according to claim 16, wherein process steps (II) and (III) are performed by at least the following steps:

1) preparing a liquid phase comprising a plurality of silicon oxide particles (4) and at least a liquid A;
2) preparing a liquid phase comprising a polymer which can be used in a permeation layer (6) and at least a liquid B;
3) coating the liquid phase of 1) with amount in the range of from 5 to 300 g/m^2 onto the substrate layer (2);
4) coating the liquid phase of 2) with amount in the range of from 1 to 50 g/m^2 onto the drainage layer (3); and then
5) drying the coatings formed in step 3) and step 4), whereby the drainage layer (3), and the permeation layer (6) are formed.

20. The process according to any of claims 16 to 19, wherein at least one of steps (II) and (III) is performed as a curtain coating process or a cascade coating process.

21. A layer structure (1) obtainable by a process according to any of claims 16 to 20.

22. The layer structure (1) according to any of claims 1 to 15 or 21, wherein the drainage layer (3) is a transparent layer.

23. A method for applying a liquid phase onto a layer structure (1) comprising at least the following steps

α) Providing a layer structure (1) as defined any of claims 1 to 15 or 21 to 22, and
β Providing a reservoir (7) comprising a liquid phase (8),
wherein the liquid phase comprises

  1) at least 75 % by weight of an organic solvent; and
  2) from 0.1 to 10 % by weight of a pigment,
  3) from 0.1 to 10 % by weight of a at least a binder,
  4) less than 1 % by weight of water;

γ) Transferring of at least a part of the liquid phase (8) from the reservoir (7) to the permeation layer (6) of the layer structure (1),
δ) Removing of at least a part of the liquid phase (8) from the permeation layer (6).

24. A printed article (9) which comprises a layer structure (1) according to any one of claims 1 to 15, wherein the pigment (10) is positioned on the side of the permeation layer (6) which faces away from the drainage layer (3).

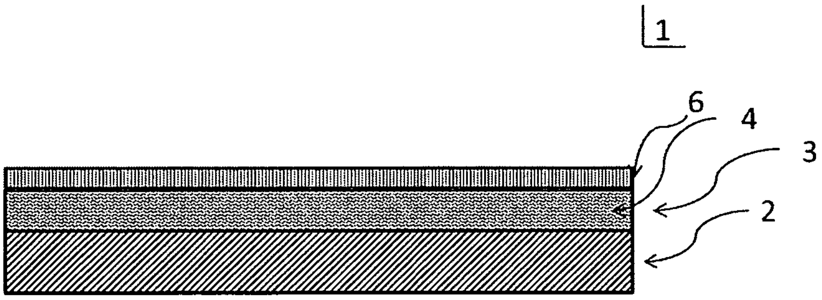


Figure 1

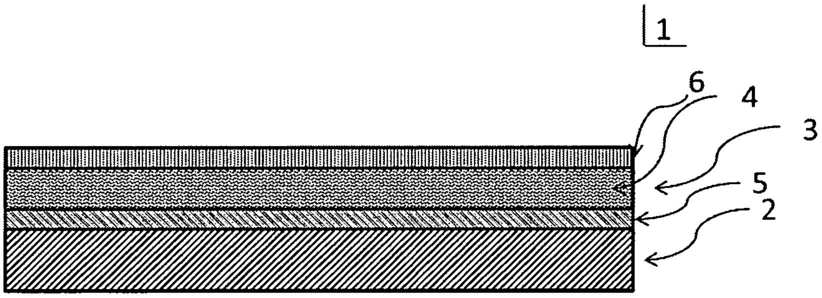


Figure 2

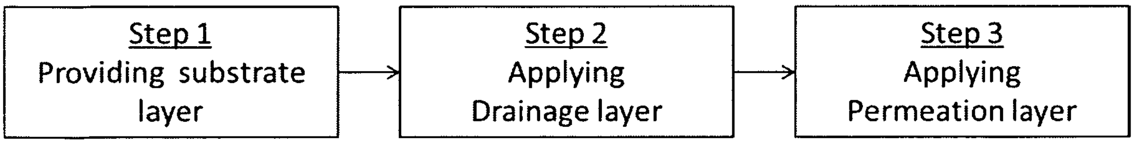


Figure 3

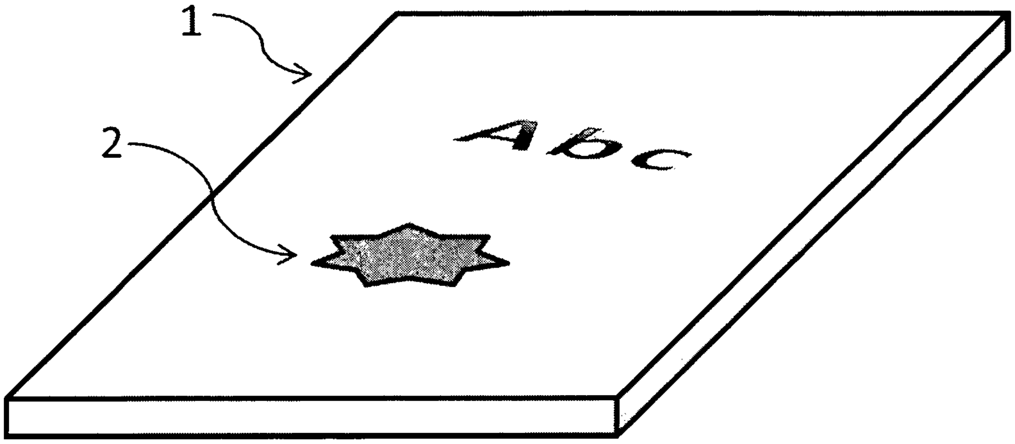


Figure 4

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EUROPEAN SEARCH REPORT

Application Number
EP 13 00 0383

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TECHNICAL FIELDS SEARCHED (IPC)

B41M

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	5 June 2013	Vogel, Thomas

CATEGORY OF CITED DOCUMENTS

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