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(54) **Ink image-receiving element**

(57) An ink image-receiving element comprising a sheetlike or weblike support coated with an ink image-receiving layer containing gelatin as binding agent together with water-insoluble particulate organic material, called matting agent, partially protruding therefrom, characterized in that said layer contains (1) gelatin, (2) a water-soluble alkali metal carboxymethyl cellulose and (3) an organic polymeric particulate matting agent in such an amount that said ingredients (1), (2) and (3) together represent at least 75 % of the total weight of said layer, wherein the coverage of gelatin in said layer is in the range of 0.5 to 10 g/m<sup>2</sup>, the alkali metal carboxymethyl cellulose expressed as ratio by weight with respect to gelatin is present in said layer in the range of 1/20 to 5/1, said particulate polymeric organic matting agent has an average particle size in the range of 1 to 15 µm, and said matting agent is composed of an essentially organic polymeric composition having a glass transition value (T<sub>g</sub>) of at least 25 °C, and wherein the ratio by weight of said matting agent to gelatin is in the range of 1/5 to 15/1.

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## Description

### 1. Field of the Invention

5 This invention relates to an all-round image-receiving element in that it is suited for use in impact as well as in nonimpact type printing and can be written on with pencil.

### 2. Background of the Invention

10 For a long time printing proceeded by pressure-contact of an ink-loaden marker or printing form with an ink-image receiving material, normally plain paper. A very frequently used impact printing technique is known as lithographic printing based on selective acceptance of oleophilic ink on a thereto prepared printing form.

Nowadays a variety of non-impact printing systems has replaced to some extent classical pressure-contact printing. One of the more important non-impact printing techniques is electro(photo)graphic printing in which thermoplastic resin-  
15 containing toner particles are transferred from electrostatic charge patterns to a receiving material and fixed thereon by heat.

According to other non-impact printing techniques ink is applied by means of a pen-plotter or ink jet.

Ink jet printing becoming more and more important is described e.g. in the book "Principles of Non Impact Printing" by Jerome L. Johnson (1986) Palatino Press, 18792 Via Palatino, Irvine CA, 92715 - USA]. In ink jet printing tiny drops  
20 of ink fluid are projected directly onto an ink receptor surface for printing without physical contact between the printing device and the receptor. The placement of each drop on the printing substrate is controlled electronically. Printing is accomplished by moving the print head across the paper or vice versa.

Still another transfer printing technique applies a thermal printer or impact printer (e.g. type writer) to transfer bodily and imagewise coloured waxy strata of a transfer ribbon onto a receiving element (ref. e.g. US-P 5,292,593).

25 High speed printing, whether it be impact or nonimpact printing, requires the fast touch-dryness of each successive print in order to avoid smudging on mutual contact of the fresh prints. So, it is particularly important that the ink-image receiving layer has a high ink absorbing speed (short ink drying time), and that the deposited ink (aqueous or mainly organic) will not feather, not smear and/or not offset immediately after its application on the printing stock in contact with a next superposed sheet. Water-based inks are commonly applied in ink-jet printing and organic inks are applied in  
30 offset printing which is a method derived from lithography in that on a printing machine the printing plate is first moistened with water by means of a roller and then guided towards an inking roller wherefrom greasy or oily ink is imagewise transferred (offset) on the paper printing stock.

Ink receiving materials, especially for use in high quality ink jet printing should have an ink image-receiving layer as thin as possible combined with a high ink absorbance, so that absorbed ink dots will not spread and give rise to sharp  
35 high density images without blotting. On the one hand the ink image-receiving layer must be readily wetted so that there is no "puddling", i.e. coalescence of adjacent ink dots, and on the other hand the ink-absorbing properties of the ink image-receiving layer should be such that the deposited ink image has a good water-fastness, i.e. becomes waterproof.

Furthermore, ink-receiving material in sheet form may not show any curl or may not tend to stick to other sheets when stacked before or after being printed even at high printing speed.

40 According to US-P 3,889,270 ink image-receiving layers suited for use in combination with water-based inks preferably comprise a protein, e.g. gelatin, albumin or casein, polysaccharide, cellulose or cellulose derivative, polyvinyl alcohol or copolymer of vinyl alcohols. The image-receiving layer containing these polymers may contain a hydrophylic silica gel and a white toner.

An improvement in optical density and reduction in drying time can be obtained by using particulate material in the  
45 polymeric binder. For example, according to US-P 3,357,846 pigments such as kaolin, talc, bariet, and TiO<sub>2</sub> applied in starch and polyvinyl alcohol (PVA) as binder are used for said purposes.

A drafting material having good acceptance for ink of ink jet printers and pen-plotters, having also good uptake of drafting pencil, and being suited for strongly fixing thereon toner images obtained by electro(photo)graphy is described in published European patent application (EP-A) 0 565 154. The drafting film more particularly contains (A) gelatin, (B)  
50 one or more silica matting agents, (C) an opacifying agent, (D) an epoxysilane compound, (E) a polyurethane and (F) a hardening agent. The writability by pencil on said drafting film comes mainly from crystalline silica that gives the image-receiving layer a mild abrasive power to ensure good uptake of pencil graphite. The opacity of the drafting film comes preferably from titanium dioxide particles of the anatase crystal modification.

The image-receiving layers of the drafting material according to said EP-A are coated from aqueous medium. The  
55 use of organic solvents in the coating of imaging layers is frequently undesirable from ecological viewpoint and objectionable for reasons of flammability and odour problems.

A recording sheet suitable for use in both ink jet and electrophotographic imaging processes but having no drafting film properties is described e.g. in US-P 5,254,403.

Properties that have to be improved in combination for an all-round image-receiving material are rapid take up of ink, either aqueous or organic, restricted feathering of printed marks and prevention of smearing when stacking fresh printed sheets. Further are required a good water-fastness of the printed images and a controlled mild abrasivity of the recording surface to allow uptake of drawing pencil with the capability of retouching pencil-drafted parts by erasure with pencil or ink gum.

### 3. Objects and Summary of the Invention

It is an object of the present invention to provide an "all-round" ink image-receiving element that comprises a sheetlike or weblike support coated with an ink image-receiving layer suited for use in impact and nonimpact printing with rapid takeup of ink resulting in short ink drying times combined with good water-fastness of printed matter and mild abrasiveness of the recording surface for good proper writing on with pencil.

It is a further object of the present invention to provide such an "all-round" ink receiving element wherein the ink-receiving layer is applied in an ecologically interesting way from aqueous medium.

Other objects and advantages of the present invention will become clear from the following description.

According to the present invention an ink image-receiving element is provided which element comprises a sheetlike or weblike support coated with an ink image-receiving layer containing gelatin as binding agent together with water-insoluble particulate organic material, called matting agent, partially protruding therefrom, characterized in that said layer contains (1) gelatin, (2) a water-soluble alkali metal carboxymethyl cellulose and (3) an organic polymeric particulate matting agent in such an amount that said ingredients (1), (2) and (3) together represent at least 75 % of the total weight of said layer, wherein the coverage of gelatin in said layer is in the range of 0.5 to 10 g/m<sup>2</sup>, the alkali metal carboxymethyl cellulose expressed as ratio by weight with respect to gelatin is present in said layer in the range of 1/20 to 5/1, said particulate polymeric organic matting agent has an average particle size in the range of 1 to 15 µm, and said matting agent is composed of an essentially organic polymeric composition having a glass transition value (T<sub>g</sub>) of at least 25 °C, and wherein the ratio by weight of said matting agent to gelatin is in the range of 1/5 to 15/1.

The average thickness of the ink image-receiving layer having partially protruding matting agent particles is preferably in the range of 2 to 15 µm. For particularly good acceptance of aqueous ink the coverage of gelatin in said layer is preferably in the range of 1.0 to 5.0 g/m<sup>2</sup>, the ratio by weight of said alkali metal carboxymethyl cellulose to gelatin is preferably in the range of 1/10 to 2/1 and the ratio by weight of said matting agent to gelatin is preferably in the range of 1/2 to 5/1.

### 4. Detailed Description of the Invention

In the ink image-receiving layer of the present image-receiving element any type of commercial gelatin may be used. Commercial gelatin is a mixture of proteins of varying molecular weight from 15,000 to 250,000. Poorly degraded (by hydrolysis) commercial gelatins having an average molecular weight above 55,000 are preferred.

The distribution of the protein-components in gelatin as natural product is dependent on the origin of the raw materials and the treatment they have received. Gelatin can be prepared advantageously starting from a so-called lime-treated collagen-containing pig skin, bone or cattle hide material. As with all types of gelatin, swelling in water is at minimum at the isoelectric point. It is advantageous for improving the take up of aqueous ink in the coated and dry ink image-receiving layer that the pH of the applied ink is substantially different from the pH at the isoelectric point of the gelatin present in the image-receiving layer.

Gelatin gels are distinguished by their gel strength. An ink image receiving layer having good mechanical strength contains preferably gelatin having a gel strength of at least 200 g determined according to British Standard Institution BS 757:1975 "Methods for Sampling and Testing Gelatin".

Gelatins preferred for use in the present ink image-receiving layers are characterized by a viscosity of at least 20 mPa.s when such viscosity is measured at 36 °C at pH 6 for a 10 % by weight aqueous solution at a shear rate of 1000s<sup>-1</sup>.

In the ink image-receiving layer of the present invention the gelatin may be hardened to some degree thereby providing an improved cohesivity and resistance to abrasion together with a reduced bleeding or feathering of aqueous inks and improved water-fastness.

Examples of suitable gelatin hardeners are described in the book "The Theory of the Photographic Process", 4th ed. by T. H. James, Macmillan Publishing Co., Inc. New York (1977), p. 78-84. In that connection are explicitly mentioned aldehyde hardeners such as formaldehyde, glyoxal and glutaraldehyde, s-triazines, e.g. 2,4-dichloro-6-hydroxy-s-triazine in the form of water-soluble sodium salt, active olefins, e.g. bis(vinylsulphonyl) compounds, and carbamoyl pyridinium salts.

Water-soluble carboxymethyl cellulose is normally applied as sodium salt. Types of sodium carboxymethyl cellulose preferred for use according to the present invention have a substitution degree (DS) in the range of 0.5 to 1.3, more preferably in the range of 0.75 to 0.90. The substitution degree (DS) relates to the average number of hydroxyl groups (maximum 3) in pyranose rings of the cellulose that have been transformed into -O-CH<sub>2</sub>-COONa groups.

Such water-soluble sodium carboxymethyl cellulose is mainly responsible for an improved take up of aqueous inks and shortens drying time of aqueous ink images.

Sodium carboxymethyl cellulose is obtained by reaction of alkali-cellulose with  $\text{Cl-CH}_2\text{-COONa}$ , and contains normally from 50 to 600 linked pyranose rings of which the sodium atom of the  $\text{-CH}_2\text{ONa}$  group on part or all of said rings has been substituted by  $\text{-CH}_2\text{-COONa}$ .

The  $\text{-CH}_2\text{-COONa}$  content of the carboxymethyl cellulose may be determined by titration with a strong acid transforming the  $\text{-COONa}$  groups into carboxylic acid groups and may be expressed as mg NaOH per gram of sodium carboxymethyl cellulose polymer corresponding with the equivalent amount of acid used in the transformation of  $\text{-CH}_2\text{-COONa}$  groups into free acid groups. From the measured  $\text{-CH}_2\text{-COONa}$  content compared with the  $\text{-CH}_2\text{-COONa}$  content of a fully substituted cellulose the substitution degree can be easily calculated.

The water-insoluble polymeric matting agent particles protruding partially from the recording layer provide a rapid touch-dryness of the aqueous and non-aqueous inks and prevents sticking of stacked printed sheets immediately after their ink reception, preventing thereby smearing of printed parts. Further said matting agent provides for a strong adherence of oleophilic inks used in impact printing and provides for a strong heat-fixing of toner images obtained by electro(photo)graphic imaging with triboelectrically charged toner particles containing heat-softenable thermoplastic resin.

As been mentioned before the organic matting agent is present in the ink-receiving layer in the form of single particles having an average particle size of 1-15  $\mu\text{m}$ , but preferably of 3-10  $\mu\text{m}$ . The use of said particles in the indicated percentage by weight of said matting agent to gelatin gives a certain surface roughness to the ink-receiving layer and capillarity enhancing its ink absorption capacity.

For obtaining a sufficient pencil-uptake and rapid touch dryness after ink image reception the surface roughness of the present ink image-receiving layers is preferably in the range of 0.5 to 3.0  $\mu\text{m}$  being Ra-values determined by means of a PERTH-O-METER (tradename) according to ANSI norm ASME B 46.1-1985.

Preferred particulate organic polymeric matting agent material for use in the image-receiving layer of the ink image-receiving material according to the present invention is in the form of polymer beads the glass transition temperature of which is at least 25 °C and more preferably above 40 °C. The preparation of said matting agents may proceed by addition polymerization of  $\alpha,\beta$ -ethylenically unsaturated monomers applying common polymerization initiator substances in a liquid medium serving as dispersion medium for the formed polymer that is obtained as a latex. The polymer beads may consist of a homopolymer or copolymer and may be a graft polymer comprising a core and envelope of different polymers. The latter type of graft polymer is preferred for the structure of the polymer beads has at its surface micro-cavities formed by grafted dangling polymer chains which cavities provide a good ink retention.

Examples of suitable matting agents are in the form of polymethylmethacrylate or polystyrene beads, e.g. prepared by suspension polymerisation. These particles are known matting agents or spacer beads in photographic silver halide emulsion materials (ref. e.g. US-P 5,057,407). The glass transition temperature ( $T_g$ ) of polymethylmethacrylate and polystyrene is 105 °C and 100 °C respectively whereby these polymers have at room temperature a hardness sufficient to act as mild abrasive material for pencil.

Other suitable organic polymeric matting agents that by proper selection of their monomer components and polymerization degree have a glass transition temperature ( $T_g$ ) above 60 °C may be prepared as described in US-P 3,941,727 and FR-P 1 545 262.

Still other suitable organic polymeric matting agents can be prepared according to techniques described in published European patent applications (EP-A) 0 466 982 and 0 584 407. The matting agents prepared according to the last mentioned EP-A are alkali-soluble.

Preferred organic matting agents providing rapid touch dryness of ink images and making the ink image-receiving layer writable on with pencil are prepared according to US-P 4,287,299 and 4,614,708. According to the method described therein finely divided solid spherical polymer beads having an average particle size between about 0.5 and about 15  $\mu\text{m}$  can be produced, said beads having a glass transition temperature of at least 40°C. Said method disclosed in said US-P documents comprises the steps of :

A) dissolving in an aqueous solvent mixture of water and at least one water-miscible polar organic solvent

- 1) at least one  $\alpha,\beta$ -ethylenically unsaturated monomer capable of forming a polymer that is soluble in its own monomer(s) present in said aqueous solvent mixture but which is insoluble in said aqueous solvent mixture,
- 2) a free radical-forming polymerization initiator (e.g. potassium, sodium, or ammonium persulphate) that is soluble in the aqueous solvent mixture, and
- 3) a graft-polymerizable polymer containing hydrophilic groups (e.g. sodium or potassium carboxylate or sulphate groups, hydroxide groups, ethylene oxide groups, and amide or cyclic amide groups), said graft-polymerizable polymer being soluble in said aqueous solvent mixture,

the weight ratio of said graft-polymerizable polymer to said monomer(s) being in the range from 1.5 : 100 to 8 : 100 and the weight ratio of polymerization initiator to monomer(s) being from 0.1 : 100 to 5 : 100, and

B) heating the solution obtained to a temperature from 50°C to the reflux temperature thereof, with continuous stirring to initiate by polymerization the simultaneous massive formation of homopolymer or copolymer from said monomer(s) and precipitation thereof, and the formation of a small proportion of grafted polymer.

5 In the production of an aqueous homogeneous dispersion of polymer beads for use in an image-receiving element in accordance with the invention the size of the beads is determined by the nature of the graft-polymerizable polymer, but can also be controlled by reaction temperature, and adjustment of other reaction parameters e.g. the concentration of the  $\alpha,\beta$ -ethylenically unsaturated monomer(s) and especially the proportion between the volumes of water and of the water-miscible solvent, e.g. alcohol, in the aqueous solvent mixture. Polymer beads with an average size in the range  
10 of 0.5 to 15  $\mu\text{m}$  can be prepared in this way.

Before the beginning of the polymerization the reaction medium mainly consists of a homogeneous solution at room temperature, in the solvent mixture, of the graft-polymerizable polymer, the water-soluble free radical-forming polymerization initiator, and at least one  $\alpha,\beta$ -ethylenically unsaturated monomer.

15 By heating this reaction medium the dissolved initiator decomposes and forms free radicals, which then enter into reaction with the dissolved graft-polymerizable polymer either via a labile hydrogen atom or via a reactive position and thus form living molecules, which while remaining dissolved in the aqueous solvent mixture, encounter either reactive monomers or already growing polymer chains of such monomers, thus forming a graft polymer. Polymer beads are thus formed, which are composed of a nucleus and an envelope.

20 The nucleus of the beads consists of a bundle of intertwined polymer chains obtained by polymerization of the monomer(s) which is (are) insoluble in the aqueous solvent mixture, and of a small proportion of some polymer chains obtained by copolymerization of the monomer(s) and the initial dissolved polymer, said polymer chains being intertwined with polymer chains grafted by one end to the core of the polymer beads and thus forming an envelope for the polymer beads.

25 The enveloping polymer acts by sterical hindering as dispersion stabilizer in aqueous medium. The enveloping polymer contains preferably hydrophilic groups, e.g. carboxylic acid or carboxylic anhydride groups that provide good adherence to the gelatin matrix of the ink image-receiving layer.

30 Suitable  $\alpha,\beta$ -ethylenically unsaturated monomers for use in the preparation of the nucleus of said polymer beads are e.g. styrene, vinyltoluene and substituted vinyltoluene e.g. vinyl benzyl chloride and the homologues thereof, chlorostyrene, alkyl methacrylates e.g. methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate and the higher methacrylates, e.g. stearyl methacrylate; substituted alkyl methacrylates e.g. hydroxyethyl methacrylate; butadiene, isobutylene, chlorobutadiene, 2-methylbutadiene; vinyl pyridines e.g. 2- and 4-vinylpyridine, etc. A combination of these monomers as well as one of them alone may be chosen depending on the particular needs in particular the Tg. Other monomers than those listed above can be used if only they fulfil the solubility and Tg requirements set. It is possible to combine one or more of the monomers described above with other monomers that themselves do not comply  
35 with the requirements described herein for the  $\alpha,\beta$ -ethylenically unsaturated monomers. For instance vinylidene chloride, vinyl chloride, acrylonitrile, and methacrylonitrile are not solvents for their own polymers and can thus not be used for the formation of homopolymers. Nevertheless they can be combined with one or more suitable monomers complying with the requirements set forth to form copolymers that are soluble in the latter monomers.

40 Particularly suitable graft-polymerizable polymers for use in the preparation of the envelope of the polymeric matting agents in the form of enveloped-core micro-beads are e.g. polyethylene oxide, low molecular weight polyvinyl alcohol, polyvinyl pyrrolidone, co(vinyl alcohol/vinyl acetate) containing 12 mol % of vinyl acetate units and the same copolymer containing 40 mol % of vinyl acetate units, sodium or potassium salts of co(acrylic acid/styrene) containing 40 to 60 mol % of acrylic acid, co(vinyl acetate/crotonic acid), the reaction products of copoly (styrene/maleic anhydride), of copoly(vinyl acetate/maleic anhydride), of copoly (ethylene/maleic anhydride), or of copoly (N-vinyl pyrrolidone/maleic  
45 anhydride) with hydroxyalkyl or aminoalkyl(meth)acrylates, co(styrene/maleic acid monosodium salt), and preferably the latter copolymer containing 50 mol% of styrene and 50 mol% of maleic acid monosodium salt. Other graft-polymerizable polymers can be used, but hydrophilic ones are preferred.

50 In building the polymeric bead envelope with grafted co(styrene/maleic acid monosodium salt), which is composed of equimolar amounts of its monomer components, highly homodisperse beads having an average particle size from 0.5 to 15  $\mu\text{m}$  can be obtained.

The weight ratio of the graft-polymerizable core polymer to said monomer(s) is generally comprised between 1.5 : 100 and 8 : 100. Optimum proportions for obtaining a given average particle size can be easily determined by making some simple tests.

55 Polymer beads obtained with the above co(styrene/maleic acid monosodium salt) through graft-polymerization on polymerized methyl methacrylate (core-polymer) are particularly suited for use in a coating composition for preparing an aqueous ink image-receiving layer of an image-receiving material according to the present invention.

It has been observed that in the preparation of polymer beads with co(styrene/maleic acid monosodium salt) as graft-polymerizable polymer the stability of the dispersion is related to the pH-value. With methyl methacrylate as the  $\alpha,\beta$ -ethylenically unsaturated monomer and co(styrene/maleic acid monosodium salt) as the graft-polymerizable polymer

the beads obtained are converted into conglomerates when the pH of the dispersion is lowered to 4.0 by means of hydrochloric acid as a result of the conversion of the carboxylate groups of the polymer into insolubilizing free carboxylic acid groups. If, however, the pH-value is increased again by means of sodium hydroxide, a stable dispersion without conglomerates is restored.

5 A characteristic of polymer bead dispersions prepared according to said US-P 4,614,708 is that it contains discrete solid polymer which are stabilized sterically as a result of the stable arrangement in space of the grafted polymer chains (envelope) around the nuclei of the beads. The presence of ionic groups in the grafted polymer provides for a certain solvation in aqueous medium. This solvation has a stabilizing effect supplemental to the steric stabilization of the grafted polymer chains of the bead-envelope.

10 As a result of the strong anchoring of the polymers grafted to the polymeric nucleus and the absence of enclosed solvent in the beads, the formation of conglomerates of beads upon dilution of the dispersion e.g. by mixing the dispersion with hydrophilic colloid binder such as gelatin is prevented. Moreover, by the presence of ionic groups or polar groups in the grafted polymer of the envelope a strong bonding of the beads to gelatin is obtained which is in favour of the mechanical strength of the image-receiving layer.

15 In addition to the above mentioned ingredients (1), (2) and (3) of the image-receiving layer, viz. gelatin, alkali metal carboxymethyl cellulose (CMC) and organic particulate polymeric matting agent, the ink image-receiving layer may contain other kinds of ingredients that improve one or more of the properties aimed at such as good ink reception (wetting), good ink absorption, rapid touch-dryness and good writing on capability with pencil.

Ingredients that improve one or more of said properties are e.g. other hydrophilic binding agents than gelatin and  
 20 CMC such as (1) hydroxyethyl cellulose; (2) hydroxypropyl cellulose; (3) hydroxyethylmethyl cellulose; (4) hydroxypropyl methyl cellulose; (5) hydroxybutylmethyl cellulose; (6) methyl cellulose; (7) sodium carboxymethylhydroxyethyl cellulose; (8) water soluble ethylhydroxyethyl cellulose; (9) cellulose sulfate; (10) polyvinyl alcohol; (11) polyvinyl acetate; (12) polyvinylacetate; (13) polyvinyl pyrrolidone; (14) polyacrylamide; (15) acrylamide/acrylic acid copolymer; (16) styrene/acrylic acid copolymer; (17) ethylene-vinylacetate copolymer; (18) vinylmethyl ether/maleic acid copolymer; (19)  
 25 poly(2-acrylamido-2-methyl propane sulfonic acid); (20) poly (diethylene triamine- co-adipic acid); (21) polyvinyl pyridine; (22) polyvinyl imidazole; (23) polyimidazoline quaternized; (24) polyethylene imine epichlorohydrin modified; (25) polyethylene imine ethoxylated; (26) poly(N,N-dimethyl-3,5-dimethylene piperidinium chloride); (27) polyethylene oxide; (28) polyurethane; (29) melamine resins; (30) epoxy resins; (31) urea resins; (32) carrageenin; (33) dextran; (34) gum arabic; (35) casein; (36) pectin; (37) albumin; (38) starch; (39) collagen derivatives; (40) collodion, (41) agar-agar, and (42)  
 30 alginic acid and alginates.

Wetting power for aqueous inks is improved in particular with surfactants that may be any of the cationic, anionic, amphoteric, and nonionic type.

Examples of useful surfactants are alkali metal salts of fatty acids (soaps), N-alkylamino acid salts, alkylether carboxylic acid salts, acylated peptides, alkylsulfonic acid salts, alkylbenzene and alkyl-naphthalene sulfonic acid salts,  
 35 sulfosuccinic acid salts, olefin sulfonic acid salts, N-acylsulfonic acid salts, sulfonated oils, alkylsulfonic acid salts, alkylether sulfonic acid salts, alkylallylethersulfonic acid salts, alkylamidesulfonic acid salts, alkylphosphoric acid salts, alkyletherphosphoric acid salts, alkylallyletherphosphoric acid salts, alkyl and alkylallylpolyoxyethylene ethers, alkylallylformaldehyde condensed acid salts, alkylallylethersulfonic acid salts, alkylamidesulfonic acid salts, alkylphosphoric acid salts, alkyletherphosphoric acid salts, alkylallyletherphosphoric acid salts, alkyl and alkylallylpolyoxyethylene ethers,  
 40 alkylallylformaldehyde condensed polyoxyethylene ethers, blocked polymers having polyoxypropylene, polyoxyethylene polyoxypropylalkylethers, polyoxyethyleneether of glycolesters, polyoxyethyleneether of sorbitanesters, polyoxyethyleneether of sorbitolesters, polyethyleneglycol aliphatic acid esters, glycerol esters, sorbitane esters, propyleneglycol esters, sugar esters, fluorinated surfactants, e.g. fluoro C2-C10 alkylcarboxylic acids, disodium N-perfluorooctanesulfonyl glutamate, sodium 3-(fluoro-C6-C11alkylxy)-1-C3-C4 alkyl sulfonates, sodium 3-( $\omega$ -fluoro-C6-C8 alkanoyl-N-ethyl-  
 45 amino)-1-propane sulfonates, N-[3-(perfluorooctanesulfonamide)-propyl]-N,N-dimethyl-N-carboxymethylene ammonium betaine, fluoro-C11-C20 alkylcarboxylic acids, perfluoro C7-C13 alkyl carboxylic acids, perfluorooctane sulfonic acid diethanolamide, Li K and Na perfluoro C4-C12 alkyl sulfonates, N-propyl-N-(2-hydroxyethyl)perfluorooctane sulfonamide, perfluoro C6-C10 alkylsulfonamide propyl sulfonyl glycinates, bis-(N-perfluorooctylsulfonyl-N-ethanolaminoethyl)phosphonate, mono-perfluoro C6-C16 alkyl-ethyl phosphonates, and perfluoroalkylbetaine.

50 Especially useful are the fluorocarbon surfactants described e.g. in US P 4,781,985, and having the following structure :

$F(CF_2)_{4-9}CH_2CH_2SCH_2CH_2N^+R_3X^-$  wherein R is an hydrogen or an alkyl group; and in US P 5,084,340, having a structure of:  $CF_3(CF_2)_mCH_2CH_2O(CH_2CH_2O)_nR$  wherein  $m = 2$  to  $10$ ;  $n = 1$  to  $18$ ; R is hydrogen or an alkyl group of 1 to 10 carbon atoms. These surfactants are commercially available from DuPont and 3M.

55 The concentration of surfactant(s) in an ink image-receiving layer for aqueous ink reception is typically in the range of 0.1 to 2 percent by weight, preferably in the range of 0.4 to 1.5 percent by weight on the total dry weight of that layer.

Other ingredients are applied for improving water-fastness of the ink image and for preventing bleeding of the obtained images. These ingredients may be a reactive component that form a substance improving water-fastness with

a reactive component contained in the ink as described e.g. in US-P 4,694,302, wherein the formation in situ of a water-insoluble salt, e.g. aluminium salt, of carboxymethylcellulose has been mentioned.

Other water-fastness improving compositions are described e.g. in US-P 5,206,071 according to which a hydrogel complex is combined with a high molecular weight quaternary ammonium salt.

5 Water-fastness of dye images is obtained with so-called mordants that are nonwandering in the ink image-receiving layer. If acid or anionic type dyes have to be mordanted, which is usually the case, the ink image-receiving layer contains basic or onium type mordants such as polymers containing ammonium groups. Examples of such polymers are described in US P 4,371,582, US P 4,575,465, US P 4,649,064, GB-P 1,221,131, GB-P 1,221,195, GB-P 2,210,071 and EP 423 829.

10 In US P 4,371,582 a basic polymer latex comprising tertiary amino- or quaternary ammonium groups is described as dye fixing agent, and in US P 4,575,465 an ink image-receiving layer comprising a hydrophilic polymer with up to 50% by weight of vinylpyridine/vinylbenzylquaternary ammonium salt copolymers is claimed. Other types of basic or onium type polymeric mordants are described in Research Disclosure November 1976, item 15162, and in unpublished European patent application No. 94200124.9 relating to polymeric mordants containing a phosphonium moiety.

15 When the ink receiving element is intended for viewing in reflection and the ink-receiving layer is applied on a transparent base the ink receiving layer itself may be opacified with a whitening agent. For that purpose TiO<sub>2</sub> (rutile or anatase) pigment is used preferably in an amount sufficient to produce a transmission density to white light of at least 0.05, and preferably 0.3 or higher. The coverage of the whitener can range from 0.1 to 10 g/m<sup>2</sup>, and is preferably from 1 to 3 g/m<sup>2</sup>. A slurry of the whitener may be added by batchwise addition or by in-line injection just prior to coating the  
20 image-receiving layer on its support.

Other useful opacifying pigments being inorganic particulate materials that may have a porous character or form porous conglomerates are e.g. colloidal particles of silica, talc, clay, koalin, diatomaceous earth, calcium carbonate, magnesium carbonate, aluminium hydroxide, aluminium oxide, zinc oxide, barium sulfate, calcium sulfate, zinc sulfide, aluminium silicate, calcium silicate and lithopone.

25 The specific surface area of these inorganic particulate materials may vary from 10 to 200 m<sup>2</sup>/g (BET specific surface), and oil absorption may be 150 ml/100 g or more as described for silica particles in US-P 5,213,873.

The ink acceptance of inks containing polar solvents may be improved by compounds acting as plasticizers for gelatin such as ethylene glycol, diethylene glycol, propylene glycol, polyethylene glycol, glycerol monomethylether, glycerol monochlorohydrin, ethylene carbonate, propylene carbonate, tetrachlorophthalic anhydride, tetrabromophthalic  
30 anhydride, urea phosphate, triphenylphosphate, glycerolmonostearate, propylene glycol monostearate, tetramethylene sulfone, N-methyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, and polymer latices with low T<sub>g</sub>-value such as polyethylacrylate, polymethylacrylate, etc.

The ink image-receiving layer of the material of the present invention may comprise still other additives e.g. compounds absorbing ultra-violet radiation, e.g. optical brightening agents and antistatic agents.

35 When the ink-receiving layer is intended for forming therein a silver image by the silver complex diffusion transfer reversal (DTR) process said layer or an adjacent layer in water-permeable relationship therewith may contain physical development nuclei.

The silver complex diffusion transfer reversal (DTR) process in which transferred silver complex compounds stemming from an image-wise exposed and developed silver halide emulsion material are reduced to silver metal by a reducing  
40 agent and catalytic action of physical development nuclei is described e.g. in the book "Photographic Silver Halide Diffusion Processes" by André Rott and Edith Weyde - The Focal Press London and New York (1972).

Preferred physical development nuclei are colloidal noble metal particles, e.g. silver particles, colloidal heavy metal sulfide particles such as colloidal palladium sulfide, nickel sulfide and mixed silver-nickel sulfide.

45 According to a particular embodiment said nuclei are formed in situ with reactants contained in the ink-receiving material.

The ink-receiving layer may contain the physical development nuclei in operative contact with physical development accelerators, examples of which are thioether compounds described e.g. in published German patent application (DE-OS) 1,124,354, US-P 4,013,471; 4,072,526 and published European patent application (EP-A) 0,026,520.

50 According to a special embodiment described in unpublished European patent application (EP-A) No. 94 201 994.4 filed July 11, 1994 an ink image receiving layer for ink jet printing contains physical development nuclei and a reducing agent for a reducible metal contained in the ink. The present ink receiving material may be adapted to serve as receiving material for reactive inks, e.g. contains physical development nuclei and a reducing agent whereby in the receiving layer a metal image, e.g. silver image, is formed by catalyzed reduction of a reducible metal salt deposited by ink jet.

55 In the image-receiving elements according to the present invention the ink image-receiving layers may be single or double-side coated on all kinds of support materials being transparent, translucent or opaque, e.g. metal, glass, resin and paper supports.

Particularly useful transparent supports are the resin supports applied in the manufacture of photographic films, e.g. made of cellulose ester such as cellulose acetate, polyesters such as polyethylene terephthalate, polyethylene naphthalate, and polyesters containing in their structure hydrophilic moieties derived e.g. from sulfo-isophthalic acid and

polyoxyalkylene diols, further polyamides, polycarbonates, polyimides, polyolefins, e.g. polypropylene, polyalkylmethacrylates, polyvinylchloride, poly(vinylacetals), polyethers and polysulfonamides.

Polyester film supports and especially supports made of poly (ethyleneterephthalate) are preferred because of their excellent dimensional stability. When such a polyester is used as the support material, a subbing layer is normally present to improve the bonding of the gelatin-containing image-receiving layer to the support. Useful subbing layers for this purpose are well known from the production of photographic silver halide emulsion materials as described e.g. in Research Disclosure November 1989, item 307105 and include, for example, polymers of vinylidene chloride such as vinylidene chloride/acrylonitrile/acrylic acid terpolymers or vinylidene chloride/methyl acrylate/itaconic acid terpolymers.

Common opaque supports are paper supports in which the paper may be coated with a resin layer, e.g. polyolefin resin layer, preferably polyethylene-coated paper.

In a particular embodiment high-quality opacified resin supports are used, e.g. whitener-loaded polyesters or resin supports having internal light-scattering voids, e.g. obtained by extrusion of blends of poly (ethyleneterephthalate) and polypropylene, so-called synthetic paper or paper-like film [ref. e.g. (PCT) WO 94/06849].

The inks used to image the image-recording elements of the present invention may be of various types and are not necessarily restricted to water-based inks since rapid touch dryness on the present ink image-receiving materials can be obtained likewise with common offset inks which are oil-based.

The ink compositions used in ink-jet printing are typically liquid compositions comprising a solvent or carrier liquid, dyes or pigments, humectants, organic solvents, detergents, thickeners, preservatives, etc. The solvent or carrier liquid is predominantly water, although ink in which organic materials such as polyhydric alcohols are used as carrier liquid, can be used. The dyes used in such ink-jet ink compositions are typically water-soluble direct dyes or acid type dyes (anionic dyes). Such liquid ink compositions have been extensively described in e.g. US P 4,381,946, US P 4,781,758, and US P 4,994,110.

The image-receiving material according to the present invention is suited for the production of identification documents, so-called I.D. cards in the form of laminar articles in which image information is protected against mechanical damage and counterfeiting or forgery.

In view of the widespread use of I.D. cards as security document, e.g. to establish a person's authorization to conduct certain activities (e.g. driver's licence) or to have access to certain areas or to engage in particular commercial actions, it is important that forgery of the I.D. card by alteration of certain of its data and/or photograph is made impossible.

A laminar article according to the present invention comprises the above defined image-receiving layer incorporating an image, e.g. a black-and-white and/or dye image obtained by a diffusion transfer technique, enveloped between a resin support, e.g. vinyl chloride polymer support and a resin cover sheet fixed to the image-receiving layer by lamination using pressure and heat.

The cover sheet may be any hydrophobic thermoplastic resin sheet, e.g. made of polyester resin such as polyethylene terephthalate, a polycarbonate of a bis-phenol, a polyolefin e.g. polyethylene or polypropylene, or a vinyl chloride polymer as defined herein. According to a particular embodiment the cover sheet is a polyethylene terephthalate sheet being coated with a resinous melt-adhesive layer, e.g. a polyethylene or polypropylene layer.

The lamination of the imaged image-receiving material with said resin cover sheet proceeds preferably by heat-sealing between flat steel plates or roller laminator under a pressure of e.g. 10 to 15 kg/cm<sup>2</sup> at a temperature in the range of 120 to 150°C, e.g. at 135°C. Cooling of the just laminated article proceeds under pressure to avoid distortion.

The laminate may contain the image-receiving layer over the whole area of the support or in a part thereof, e.g. leaving free the edge area as described in US-P 4,425,421.

According to an embodiment the image-receiving layer is coated onto an opaque polyvinyl chloride having a thickness of only 0.050 to 0.300 mm. A sheet of that thickness can receive printed data by means of a mechanical printing process, e.g. offset or intaglio printing.

The image receiving layer can be coated on a support containing itself and/or an associated coating security marks. When using a paper support the security mark may be in the form of a watermark. Security marks that can be printed on the support or subbing layer are finger prints, printed patterns known from bank notes, e.g. guilloches, coded information, e.g. magnetic binary code information, signature or other printed personal data that may be applied with nacreous pigment inks, or ultra-violet legible printing inks as described e.g. in GB-P 1,518,946 and US-P 4,105,333, or by applying marks containing liquid crystals as described e.g. in European patent (EP) 0 400 220.

Other possibilities to increase security against counterfeiting are the inclusion in the image-receiving layer itself and/or in or on a covering layer for forming a laminate of pigments, e.g. nacreous pigments by which is meant light-interference pigments changing colour by viewing in transmission or reflection, infra-red absorbing markings, magnetic dots or stripes and electronic microcircuits either or not combined with ultra-violet radiation absorbing markings hidden from visibility and/or holograms as described e.g. in DE-OS 2,639,952, GB-P 1,502,460 and 1,572,442 and US-P 3,668,795. The holographic patterns may be obtained in silver halide emulsion layers, normally Lippmann emulsions, especially designed for that purpose and can either or not be combined with a photograph in the laminate.

According to an embodiment wherein the resin sheet used as support of the laminate has to possess a thickness required for an identification card to be inserted in a slot of an electronic identification apparatus several sheets of matted polyvinyl chloride are stacked and laminated so as to reach a final thickness of e.g. 0.68 mm to 0.84 mm.

5 The following examples are presented to illustrate the present invention, but are not intended to limit it thereto. All parts, ratios and percentages are by weight unless otherwise stated.

#### INVENTION EXAMPLES 1 to 8 AND NON-INVENTION EXAMPLES 9-12

10 A polyethylene terephthalate film having a thickness of 100  $\mu\text{m}$  was double-side subbed for improving adherence to a gelatin-containing layer and double-side coated with one of the following aqueous coating compositions 1 to 12 (see TABLE 1 hereinafter). The coating proceeded at 36 °C. The coated layer was chilled at 5 °C for 20 s and finally dried at 35 °C for 120 s at relative humidity (RH) conditions of 30 %.

15 The basic ingredients of these coating compositions were water, dissolved gelatin and sodium carboxymethyl cellulose (CMC) and dispersed polymer beads (PB) prepared according to Example 1 of US-P 4,614,708, wherein the reaction conditions were adapted in such a way that polymethyl methacrylate beads grafted with co(styrene/maleic acid monosodium salt chains were obtained having an average size by volume of 3.3  $\mu\text{m}$  for the beads used in EXAMPLES 1, 2, 3, 4, 6, 8 and 10, and of 4.5  $\mu\text{m}$  in EXAMPLE 7. The beads of EXAMPLE 5 and of EXAMPLES 9 and 11 had an average particle size by volume of 6.2  $\mu\text{m}$ . Particle size measurements were carried out by means of the COULTER (registered trade mark) NANO-SIZER.

20 In Example 4 the coating composition contained polyvinylpyrrolidone [LUVISKOL K90 (tradename of BASF, Germany)], having an average molecular weight of 630,000 and applied at a coverage of 1.30 g/m<sup>2</sup>.

The gelatin used in each coating compositions had a gel strength of 250. The sodium carboxymethyl cellulose (CMC) used had a DS value in the range of 6.5 - 8.5 and a 2 % aqueous solution thereof had a viscosity at 25 °C of 25 - 40 mPa.s. Such type of CMC is commercially available under the tradename WALOCEL CRT 30 PA/GA sold by Wolf-  
25 Walsrode, Germany.

Further each coating composition contained 0.25 parts of di-isooctylsulfosuccinate (wetting agent), and 0.17 parts of formaldehyde on a totality of 1000 parts by volume of coating composition ready for coating.

30 The coating compositions of EXAMPLES 1 to 8 of TABLE 1 were applied to manufacture INVENTION MATERIALS 1 to 8 representing drafting films particularly suited for use as ink receptive material in ink jet printing and as toner receptive material in electrophotographic printing and being writable on with pencil.

The coating compositions of EXAMPLES 9 to 12 of TABLE 1 were applied to manufacture comparative NON-INVENTION MATERIALS 9 to 12.

In TABLE 1 the coverages of gelatin, CMC and the defined polymer beads are expressed in g/m<sup>2</sup>.

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In TABLE 1 data obtained with an ink-absorbency test (ABS-test) as described furtheron and surface roughness (Ra-values expressed in  $\mu\text{m}$ ) of the dried image-receiving layers are presented.

TABLE 1

EXAMPLE	Gelatin	CMC	PB	ABS-test	Ra
1	2.51	0.33	2.22	15	0.76
2	10.1	1.33	8.89	5	0.71
3	2.18	0.67	2.22	9	3.21
4	1.60	0.40	2.67	9	3.17
5	2.51	0.33	0.95	14	1.14
6	2.51	0.33	1.11	15	0.54
7	2.51	0.33	1.11	16	0.82
8	3.02	0.40	4.00	7	1.09
9	5.00	0.00	0.06	>25	0.79
10	2.51	0.00	2.22	20	0.75

11	5.00	0.00	0.01	>25	0.43
12	2.51	0.33	0.00	>25	0.45

Ink absorbency test (ABS-test)

The image-receiving elements containing said coating compositions 1 to 12 before use in ink jet printing were first conditioned for at least 2 hours at 25°C and 30% relative humidity (RH), and then a test image was applied thereon by ink jet. The application of the ink proceeded with a Hewlett-Packard DeskJet 500C (tradename) multicolour printer operating with aqueous coloured inks cyan, magenta and yellow.

The ink absorbency was evaluated as follows : an ink jet print in the form of several solid area (blocks) applied with colored inks (yellow, magenta and cyan) and black ink was made on the image receiving materials, but so that there was a large lapse of time between succesively numbered blocks of the applied inks. Immediately after finishing a print, the inked side was put into contact with a conventional paper for use in dry toner electrophotography. The thus obtained sandwich was conducted through the nip of a roller pair with constant pressure. After peeling off the image receiving material the optical density of the blocks on the paper substrate was measured with a Macbeth TR-1224 (tradename) optical densitometer.

The block number corresponding with a reflection density smaller than a given comparison density was determined for each color. A mean value for yellow, magenta, cyan and black is given in Table 1, wherein a smaller value corresponds with a faster drying of the ink whereby risk of image smearing and ink-offset on a next stacked-on printing sheet becomes less.

The smaller that value the faster the ink absorption proceeds and consequently the more rapid touch dryness is obtained avoiding image smearing.

The ink-receiving layers of the image receiving materials according to the present invention, (INVENTION EXAMPLES 1 to 8) show much smaller drying times than the ink-receiving layers of the image-receiving materials of comparative NON-INVENTION EXAMPLES 9 to 12) especially with respect to the ink absorbency and rapid touch dryness.

The ink-receiving layers of the image receiving materials 1 to 12 were also used in an electrophotographic laser printing machine HEWLETT PACKARD LaserJet III (tradename) to form thereon a toner image using a commercial thermoplastic resinous toner containing carbon black.

The adherence of said toner after heat-fixing was assessed by means of a "tape test" proceeding as follows :

#### TAPE TEST AND RESULTS

A transparent pressure-adhesive tape (SCOTCH BRAND TAPE) commercially available from 3M Co. U.S.A was stuck to a conditioned (2 hours storage at 22 °C and 30 % relative humidity) image-receiving material being used for transferring thereon an electrophotographically produced "dry" toner image representing different line patterns and solid area of transferred and heat-fixed toner. The tape was pressed by finger nail onto the toner-imaged material for a few seconds and then teared off abruptly in the direction of the image plane, i.e. horizontally. The optical density of toner transferred to the tape was measured and compared with toner transfer onto a commercially available transparent toner receptor film material [TRANSPAREX T787 (tradename of Agfa-Gevaert N.V. Belgium)] having a rating "good" corresponding with practically no torn-off toner. The image-receiving materials of Invention Examples 1 to 8 had the same rating, whereas the image-receiving materials of Non-invention Examples 9, 11 and 12 were rated "bad".

#### WRITABILITY TEST AND RESULTS

In the present writability test a commercial propelling pencil containing a pencil lead MARS MICROGRAPH Super 15 HB 2 (tradename of Staedler, Germany) of having hardness degree 2 was used to write a solid area by fixed number of crossing lines.

The take up of pencil was determined by measuring optical density which for the Invention materials 1 to 8 was above 1.0 measured with MACBETH TR-1224 (tradename) densitometer and was assessed to be good.

The take up of pencil by the Non-invention materials 9, 11 and 12 could not reach optical density 1.0 and was assessed to be poor.

#### OFFSET-PRINTING TEST AND RESULTS

An aluminium offset printing plate prepared by the silver complex diffusion reversal (DTR) process as described in Example 1 of US-P 3,989,522 was mounted on a commercial offset printing apparatus A. B. Dick 350 CD (tradename) in which the plate was wet with a lithographic graphic preparation as described in said Example and used in offset printing with a fatty printing ink as described in Example 1 of US-P 3,989,522. Said fatty printing ink is a conventional offset printing ink described in the book "Printing Ink Technology" by E. A. Apps, Leonard Hill [Books] Limited, Edenstreet, London, N.W. 1 (1961) on page 348, on the basis of an oxidatively drying styrenated linseed-tung oil alkyd resin in aliphatic petroleum having a boiling range of 260-290 °C containing a red azopigment LAKE RED (C.I. 15,585) and as oxidative drying catalyst a mixture of lead and cobalt naphthenate.

Offset printing with said fatty ink did not result in ink-offsetting on succesively printed sheets of double-side coated printing stock having the composition as defined in present Invention Examples 1 to 8, whereas stain formed by ink-offsetting was found on the rear sides of the Non-invention materials 9, 11 and 12.

#### EXAMPLE 13

To the coating composition of the image-receiving layer material according to INVENTION EXAMPLE 1 physical development nuclei in the form of colloidal nanometer size  $Ag_2S.NiS$  particles were added at a coverage of 5 mg/m<sup>2</sup>.

Onto the dried image-receiving layer by the common silver complex diffusion transfer reversal (DTR) process a black-and-white silver image serving for identification purposes was produced therein.

Onto the the imaged and dried image-receiving layer a polyethylene terephthalate sheet having a thickness of 100 μm previously being coated at one side with a polyethylene sheet of 75 μm was laid and laminated with the polyethylene in contact with the imaged image-receiving layer. A hot roll laminator was used for pressing the layers together at a temperature of 110 °C.

The image contained in the thus obtained laminate was protected against forgery and could not be peeled apart without destroying the DTR-image contained therein.

## Claims

1. An ink image-receiving element comprising a sheetlike or weblike support coated with an ink image-receiving layer containing gelatin as binding agent together with water-insoluble particulate organic material, called matting agent, partially protruding therefrom, characterized in that said layer contains (1) gelatin, (2) a water-soluble alkali metal carboxymethyl cellulose and (3) an organic polymeric particulate matting agent in such an amount that said ingredients (1), (2) and (3) together represent at least 75 % of the total weight of said layer, wherein the coverage of gelatin in said layer is in the range of 0.5 to 10 g/m<sup>2</sup>, the alkali metal carboxymethyl cellulose expressed as ratio by weight with respect to gelatin is present in said layer in the range of 1/20 to 5/1, said particulate polymeric organic matting agent has an average particle size in the range of 1 to 15 μm, and said matting agent is composed of an essentially organic polymeric composition having a glass transition value (T<sub>g</sub>) of at least 25 °C, and wherein the ratio by weight of said matting agent to gelatin is in the range of 1/5 to 15/1.
2. Ink image-receiving element according to claim 1, wherein the average thickness of said ink image-receiving layer having partially protruding matting agent particles is in the range of 2 to 15 μm.
3. Ink image-receiving element according to claim 1 or 2, wherein the coverage of gelatin in said image-receiving layer is in the range of 1.0 to 5.0 g/m<sup>2</sup>, the ratio by weight of said alkali metal carboxymethyl cellulose to gelatin is in the range of 1/10 to 2/1 and the ratio by weight of said matting agent to gelatin is in the range of 1/2 to 5/1.
4. Ink image-receiving element according to any of claims 1 to 3, wherein said gelatin has a gel strength of at least 200 g.
5. Ink image-receiving element according to any of claims 1 to 4, wherein the alkali metal carboxymethyl cellulose is sodium carboxymethyl cellulose having a substitution degree in the range of 0.75 to 0.9.
6. Ink image-receiving element according to any of claims 1 to 5, wherein the organic matting agent particles have an average particle size of 3 to 10 μm.
7. Ink image-receiving element according to any of claims 1 to 6, wherein the surface roughness of said image-receiving layers is in the range of 0.5 to 3.0 μm being Ra-values determined according to ANSI norm ASME B 46.1-1985.
8. Ink image-receiving element according to any of claims 1 to 7, wherein said particulate organic polymeric matting agent material is in the form of polymer beads the glass transition temperature of which is at least 25 °C.
9. Ink image-receiving element according to claim 8, wherein said beads have been prepared by addition polymerization of α,β-ethylenically unsaturated monomers and are graft polymers comprising a core and envelope of different polymers, wherein the polymers forming said envelope contain hydrophilic groups.
10. Ink image-receiving element according to claim 8, wherein said beads are in the form of finely divided solid spherical polymer beads having an average particle size between 1 and 15 μm and a glass transition temperature of at least 40°C being prepared by a method comprising the following steps :
- A) dissolving in an aqueous solvent mixture of water and at least one water-miscible polar organic solvent
- 1) at least one α,β-ethylenically unsaturated monomer capable of forming a polymer that is soluble in its own monomer(s) present in said aqueous solvent mixture but which is insoluble in said aqueous solvent mixture,
  - 2) a free radical-forming polymerization initiator (e.g. potassium, sodium, or ammonium persulphate) that is soluble in the aqueous solvent mixture, and
  - 3) a graft-polymerizable polymer containing hydrophilic groups (e.g. sodium or potassium carboxylate or sulphonate groups, hydroxide groups, ethylene oxide groups, and amide or cyclic amide groups), said graft-polymerizable polymer being soluble in said aqueous solvent mixture,
- the weight ratio of said graft-polymerizable polymer to said monomer(s) being in the range from 1.5 : 100 to 8 : 100 and the weight ratio of polymerization initiator to monomer(s) being from 0.1 : 100 to 5 : 100, and
- B) heating the solution obtained to a temperature from 50°C to the reflux temperature thereof, with continuous stirring to initiate by polymerization the simultaneous massive formation of homopolymer or copolymer from said monomer(s) and precipitation thereof, and the formation of a small proportion of grafted polymer.

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11. Ink image-receiving element according to any of claims 9 to 10, wherein said beads having a core of polymerized methyl methacrylate have a polymeric envelope with grafted co(styrene/maleic acid monosodium salt).

5 12. Ink image-receiving element according to any of the preceding claims, wherein said image-receiving layer contains polyvinylpyrrolidone and/or polyvinyl alcohol.

13. Ink image-receiving element according to any of the preceding claims, wherein said image-receiving layer contains a surfactant that improves wetting power of the ink image-receiving layer for aqueous inks.

10 14. Ink image-receiving element according to any of the preceding claims, wherein the gelatin in the image-receiving layer has been hardened to some extent.

15 15. Ink image-receiving element according to any of the preceding claims, wherein the image-receiving layer contains physical development nuclei whereby in said layer a silver image can be formed by the silver complex diffusion transfer reversal (DTR) process.

16. Ink image-receiving element according to claim 15, wherein said image-receiving layer contains a reducing agent.

20 17. Ink image-receiving element according to any of the preceding claims, wherein said image-receiving layer after forming therein an image makes part of a laminate wherein said layer is enveloped between a resin support and a resin cover sheet fixed to the image-receiving layer by lamination wherein pressure and heat have been used.

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European Patent  
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EUROPEAN SEARCH REPORT

Application Number  
EP 94 20 2686

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	WO-A-94 20303 (MITSUBISHI PAPER MILLS LIMITED) * page 5, line 1 - line 27 * * page 9, line 20 - line 25 * * page 21, line 27 - page 22, line 17 * * claim 1 * -----	1-17	B41M5/00
			TECHNICAL FIELDS SEARCHED (Int.Cl.6) B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 February 1995	Examiner Bacon, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			

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