(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 704 314 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
03.04.1996 Bulletin 1996/14

(21) Application number: **94202817.6**

(22) Date of filing: **29.09.1994**

(51) Int. Cl.[6]: **B41M 5/00**, C09D 11/00

(84) Designated Contracting States:
BE DE FR GB NL

(71) Applicant: **AGFA-GEVAERT**
naamloze vennootschap
B-2640 Mortsel (BE)

(54) Ink jet printing system

(57) An ink jet printing system is provided consisting of an aqueous ink jet ink and an ink-receiving layer, said ink comprising at least 2 % of a humectant and at least 0.2 % of a viscosity regulator, said receiving layer comprising hydrophilic polymers or copolymers, optionally mixed with hydrophobic polymers or copolymers, and having a dry layer thickness of 3.0 to 20.0 µm and after immersion of said ink-receiving layer in said ink jet composition showing a characteristic of $a \leqq 0.100$ and $b \leqq 0.75$ if fit to the equation $t/\Delta d = at + b$, where t = time in seconds and Δd = thickness change due to swelling in said ink jet ink composition.

EP 0 704 314 A1

Description

1. Field of the invention.

This invention relates to image-recording elements that contain a polymeric substrate on which are coated ink-receptive layers that can be imaged by the application of liquid ink dots (e.g. by ink-jet printers).

2. Background of the invention

Non impact printing technologies are becoming very popular in the arena of hard copy materials. Among different interesting non impact printing technologies, ink jet printing is one of the technologies which is gaining most of the attention. This is primarily due to the availability of very low cost ink jet printers with multi-colour possibilities and very acceptable quality.

In the ink jet printing technique the individual ink droplets can be applied to the receiving substrate in several different ways. The ink solution can be jetted continuously through a small nozzle towards the receiving layer (Hertz method). The ink droplet can also be created "upon demand" by a piezoelectric transducer or a thermal push (Bubble Jet).

Polymeric substrates are becoming more important in the manufacture of high-quality receiving elements for ink-jet printing (e.g. resin coated paper, polyesterfilm, etc). Most methods for ink jet printing do however use an aqueous or polar ink composition that does not absorb well in the polymeric substrate material. For this reason, all ink jet printing processes using aqueous based inks, do require a special treatment of the polymeric substrate material in order to be useful for practical purposes. On the polymeric substrate an additional ink-receiving layer must be applied in order to obtain a material with an acceptable ink absorption speed.

It is known that the ink-receiving layers coated on a polymeric substrate must meet simultaneously a number of different stringent requirements :

- The ink-receiving layer should have a high ink absorbing capacity, so that the dots will not flow out and will not be expanded more than is necessary to obtain a high optical density. Especially in a multi-color ink jet printing system, where ink droplets may be superposed on the same physical spot, the ink absorbing capacity of the ink-receiving layer has to be very high.
- The ink-receiving layer should have a high ink absorbing speed (short ink drying time) so that the ink droplets will not feather if smeared immediately after applying.
- The ink-receiving layer should be excellent in color forming characteristics.
- The ink dots that are applied to the ink-receiving layer should be smooth at their peripheries and have a shape of a true sphere. The dot diameter must be constant and accurately controlled.
- The receiving layer must be readily wetted so that there is no "puddling", i.e. coalescence of adjacent ink dots, and an earlier absorbed ink drop should not show any "bleeding", i.e. overlap with neighbouring or later placed dots.
- The image-recording element must have a low haze and be excellent in transmittance properties if used as e.g. overhead presentation material.
- After being printed the image must have a good resistance regarding waterfastness, lightfastness and indoor-discoloration.
- The image-recording element may not show any curl or sticky behaviour if stacked before or after being printed.

To meet these requirements various types of ink-receiving layers have been disclosed. A dimensionally stable substrate such as polyethyleneterephtalate (PET), cellulosetriacetate, or PE-extruded paper is used most frequently and coated with one or more polymer coatings. These ink-receiving polymer coatings comprise one or more binders and different additives which are necessary to meet the requirements mentioned above.

In the German Patent Application DE 2,234,823 an ink-receiving layer comprising gelatin and different particulates and colour molecules is described. US-P 3,889,270 describes an image receiving layer comprising a molecular or colloidal disperse phase that enables the jetting ink to penetrate a few microns into this layer. The binder (gelatin, albumin, casein, proteins, polysaccharide, cellulose and its derivatives, (copolymers of) polyvinylalcohol is combined with hydrophylic silica and a white toner.

US-P 4,503,111 describes an image receiving layer where a first binder (gelatin or polyvinylalcohol (PVA)) is mixed with a polyvinylpyrrolidone (PVP) having a molecular weight of at least 90000, and for which the ratio PVA/PVP is in the range 3:1 to 1:3. PVP is known for its high water absorbtion capacities. Due to this capacities ink-receiving layers comprising PVP show a short drying time, but show also high susceptibility to fingerprints, low waterfastness and high diffusion of colour images. These drawbacks limit the usefulness of ink-receiving layers comprising a high proportion of PVP.

The use of thick coatings of hydrophilic colloids has also been described in e.g. GB 2,050,866, EP-A 175 353, US-P 4,592,954, WO P 88/06532, US-P 5,006,407, US-P 5,208,092 and EP-A 583 141.

An additional improvement in drying time can be obtained using particulates in the binder. Many patent applications have described this effect for many different binder-systems. US-P 3,357,846 describes pigments such as kaolin, talc, barite, TiO_2 used in starch and PVA. US-P 3,889,270 describes silica in gelatin, PVA and cellulose. Pigments and particles have also been described in, e.g. DE OS 2,925,769, GB 2,050,866, US-P 4,474,850, US-P 4,547,405, US-P 4,578,285, WO 88 06532, US-P 4,849,286, EP-A 339 604, EP-A 400 681, EP-A 407 881, EP-A 411 638 and US-P 5,045,864.

The drying time characteristic can also be improved by a better tuning of the pH value of the coating solution, as described in EP-A 594 896.

An improvement in drying time characteristic is also possible by the application of ink-receiving layers having a complex layer structure. In, e.g. US-P 5,027,131 and EP-A 575 644 the use of a special ink transfer layer coated upon an ink receptive layer has been disclosed. A two step fabrication process in which a porous ink-receiving layer is made by coating a polymeric layer, drying it first in a first solvent which is a good solvent for the polymer system, and later on in a second one, which is a poor solvent for the polymer system, is described in EP-A 428 144. The use of a special printing system wherein the print is made upon an intermediate drum which is heated and upon which a silicon coating is applied, so that after transfer to the final substrate a shorter drying time results, is described in US-P 5,099,256.

The image-recording elements with ink-receiving layers that have been described in the prior art do improve the water absorption of the layers but fail more or less to combine a short drying time with a small dry coating thickness of the (mainly hydrophilic) ink-receiving layer. A thick ink-receiving layer does show bad properties regarding humidity dependent curl and so on.

There is thus still a need for thin ink-receiving layers having good ink absorption.

3. Object and summary of the invention:

It is an object of the invention to provide an ink jet printing system for printing on an ink-receiving layer coated on a polymeric film or a resin coated paper in which the ink-receiving layer, when liquid, water based, ink dots are applied to it, gives an image with a short drying time.

It is another object of the invention to provide a ink jet printing system wherein the properties of the water based ink and the ink-receiving layer are optimized with respect to drying time.

By "water based" or "aqueous" ink compositions within the scope of the present invention has to be understood an ink wherein at least 50 % by weight of the total solvent content is water.

Further objects and advantages of the present invention will become clear from the detailed description hereinafter.

According to this invention the above objects are realized by providing an ink jet printing system comprising (i) a water based ink comprising at least 2 % by weight of a humectant comprising hydroxyl moieties and at 0.2 % by weight of a viscosity regulator, and (ii) an ink-receiving element comprising a polymeric film or a resin coated paper support and an ink-receiving layer coated thereon, said ink-receiving layer comprising hydrophilic polymers or copolymers, optionally mixed with hydrophobic polymers or copolymers and having a dry layer thickness of 3.0 to 20.0 µm, characterised in that said ink-receiving layer has, for said ink, solvent absorption characteristics satisfying the equation

$$\frac{t}{\Delta d} = a.t + b \qquad \text{(I)}$$

wherein $a \leq 0.100$ and $b \leq 0.75$, t = immersion time in seconds of said ink-receiving layer in said ink, and Δd = change in ink-receiving layer thickness (expressed in µm).

4. Detailed description of the invention

In the documents, referred to above, the properties of the - receiving layer are described as universal. I.e. once a quality level was reached for printing using a specific water based ink composition, the prior art suggests that the use of any water based ink compositions would give rise to the same quality.

No mention is made that in fact the quality of an ink-jet printing system for making prints on a substrate, comprising a polymeric film or a resin coated paper support, depends on an interaction between the aqueous ink composition and composition of the ink-receiving layer coated on the substrate.

It has surprisingly been found however that minor changes in the composition of the water based ink could make a great difference in the drying properties of the ink-receiving layer.

The present invention is based upon the discovery that a short drying time characteristic for a given ink-receiving layer and a given water based ink composition is obtained if the layer shows a fast ink absorption speed when immersed in said water based ink composition and provided that the ink-receiving layer thickness is situated in a given range.

One of the advantages of ink jet systems according to the present invention is the fact that an ink-receiving layer with low thickness can be provided that shows, for a given water based ink composition, equal to to better drying time characteristics than thicker ink-receiving layers.

Although the swelling characteristics of a coated ink-receiving layer under influence of a solvent is a very complicated theoretical matter, it has been found that, for the scope of the present invention, the solvent absorption characteristics of ink-receiving layers can be described by a simple equation :

$$\frac{t}{\Delta d} = a.t + b \qquad (I)$$

wherein t = immersion time in seconds; Δd = change in ink-receiving layer thickness (expressend in μm).
I.e. a plot of time divided by the vertical swelling value versus time gives a straight line with slope a and intersect b.
b is related to the extrapolated initial velocity of swelling, while a is related to the swelling characteristic at equilibrium.

It is surprising to note that the design of a combination of an water based ink and an ink-receiving layer with a certain thickness yielding appropriate values for a and b according to the above stated equation leads to a high quality printout with short drying time, regardless of the surface roughness of the ink-receiving layer or dry layer thickness.

It has been found that those combinations of a water based ink and an ink-receiving layer that according to equation I give a value of a $\leqq$ 0.100 and of b $\leqq$ 0.75 gave very good drying times. Preferred are those combination of a water based ink and an ink-receiving layer for which a $\leqq$ 0.060 and b $\leqq$ 0.55.

The ink-receiving layers in the novel image-recording elements according to this invention contain at least a binder which may be selected from the group consisting of:
(1) hydroxyethyl cellulose; (2) hydroxypropyl cellulose; (3) hydroxyethylmethyl cellulose; (4) hydroxypropyl methyl cellulose; (5) hydroxybutylmethyl cellulose; (6) methyl cellulose; (7) sodium carboxymethyl cellulose; (8) sodium carboxymethylhydroxethyl cellulose; (9) water soluble ethylhydroxyethyl cellulose; (10) cellulose sulfate; (11) polyvinyl alcohol; (12) polyvinyl acetate; (13) polyvinylacetal; (14) polyvinyl pyrrolidone; (15) polyacrylamide; (16) acrylamide/acrylic acid copolymer; (17) styrene/acrylic acid copolymer; (18) ethylene-vinylacetate copolymer; (19) vinylmethyl ether/maleic acid copolymer; (20) poly(2-acrylamido- 2-methyl propane sulfonic acid); (21) poly(diethylene triamine- co-adipic acid); (22) polyvinyl pyridine; (23) polyvinyl imidazole; (24) polyimidazoline quaternized; (25) polyethylene imine epichlorohydrin-modified; (26) polyethylene imine ethoxylated; (27) poly(N,N-dimethyl-3,5-dimethylene piperidinium chloride; (28) polyethylene oxide; (29) polyurethane; (30) melamin resins; (31) epoxy resins; (32) urea resins; (33) styrene-butadiene rubbers; (34) chloroprene rubbers; (35) nitrile rubbers; (36) gelatin; (37) carrageenan; (38) dextran; (39) gum arabic; (40) casein; (41) pectin; (42) albumin; (43) starch; (44) collagen derivatives; (45) collodion and (46) agar-agar.

The ink-receiving layer coatings according to the present invention may also comprise as binder :

i. binary blends consisting of from about 10 to about 90 percent by weight of polyethylene oxide or gelatine and from about 90 to about 10 percent by weight of an other component selected from the group mentioned above.
ii. ternary blends consisting of from about 10 to about 50 percent by weight of polyethylene oxide from about 85 to about 5 percent by weight of sodium carboxymethyl cellulose and from about 5 to about 45 percent by weight of an other component selected from the group mentioned above.
iii. ternary blends consisting of from about 10 to about 50 percent by weight of gelatin, from about 85 to about 5 percent by weight of sodium carboxymethyl cellulose and from about 5 to about 45 percent by weight of a component selected from the group mentioned above.
iv. ternary blends consisting of from about 10 to about 50 percent by weight of gelatin, from about 85 to about 5 percent by weight of polyvinyl pyrrolidone and from about 5 to about 45 percent by weight of an other component selected from the group mentioned above.

Preferred binary blends of binders for the ink-receiving layers according to this invention are :

- hydroxyethylmethyl cellulose, 75 percent by weight, and polyethylene oxide, 25 percent by weight;
- gelatin, 80 percent by weight and polyethylene oxide, 20 percent by weight;
- gelatin, 70 percent by weight, and polyvinyl pyrrolidone, 30 percent by weight;
- gelatin, 80 percent by weight, and polyvinylalcohol, 20 percent by weight;
- sodium carboxymethyl cellulose, 80 percent by weight, and gelatin, 20 percent by weight.

Preferred ternary blends of binder materials for coating the ink-receiving layers according to this invention are :

- gelatin, 50 percent by weight, sodium carboxymethyl cellulose, 25 percent by weight, and polyethylene oxide, 25 percent by weight;
- gelatin, 60 percent by weight, polyvinyl pyrrolidone, 20 percent by weight, and polyvinyl alcohol, 20 percent by weight;
- gelatin, 50 percent by weight, polyvinyl pyrrolidone, 25 percent by weight, and sodium carboxymethyl cellulose, 25 percent by weight.

Preferred binders are gelatin, vinylpyrrolidone and polyvinylalcohol or binary or ternary blends of these. Gelatin is thus a particularly preferred material for use in forming the ink-receiving layer of materials according to this invention. Among the reasons is the fact that it forms a clear coating, is readily cross-linked in an easily controllable manner, and is highly absorptive of water-based liquid inks to thereby provide rapid-drying characteristics.

Dry ink-receiving layers according to the present invention therefor comprise most preferably at least 30 % by weight of gelatin with respect to the weight of all ingedients in said ink-receiving layer.

The ink-receiving layer according to this invention is preferably cross-linked to provide such desired features as waterfastness and non-blocking characteristics. The cross-linking is also useful in providing abrasion resistance and resistance to the formation of fingerprints on the element as a result of handling. There are a vast number of known cross-linking agents - also known as hardening agents - that will function to cross-link film forming materials, and they are commonly used in the photographic industry to harden gelatin emulsion layers and other layers of photographic silver-halide elements.

Hardening agents can be used individually or in combination and in free or in blocked form. A great many hardeners, useful for the present invention, are known, including formaldehyde and free dialdehydes, such as succinaldehyde and glutaraldehyde, blocked dialdehydes, active esters, sulfonate esters, active halogen compounds, s-triazines and diazines, epoxides, active olefins having two or more active bonds, active olefins, carbodiimides, isoxazolium salts unsubsituted in the 3-position, esters of 2-alkoxy-N-carboxy-dihydroquinoline, N-carbamoyl and N-carbamoylpyridinium salts, hardeners of mixed function, such as halogen-substituted aldehyde acids (e.g. mucochloric and mucobromic acids), onium substituted acroleins and vinyl sulfones and polymeric hardeners, such as dialdehyde starches and copoly(acroleinmethacrylic acid).

The ink-receiving layers comprising at least 30 % by weight of gelatin with respect to the weight of all ingedients in said ink-receiving layer according to the present invention are most preferably hardened by formaldehyd that is applied in an amount of 0.001 to 0.05 parts pro part of gelatine present.

The ink-receptive layer in the novel image-recording elements according to this invention may also comprise particulate material, both porous and non-porous, which may consist either of primary particles comprising single particles or of porous particles comprising secondary particles formed from aggregation of the primary particles. Among these particulate materials, particularly preferrable are porous particles. Most preferably said porous particles have an average particle size from 1 to 30 µm, preferably from 3 to 10 µm which can be formed by aggregation of smaller particles, having a size of 0.01 to 2 µm, preferably 0.1 to 0.5 µm. These porous particles formed by secondary or tertiary aggregation will not easily desintegrate. The porous material is preferably made of at least one of the organic materials such as polystyrene, polymethacrylate, polymethylmethacrylate, elastomers, ethylene-vinyl acetate copolymers, polyesters, polyester-copolymers, polyacrylates polyvinylethers, polyamides, polyolefines, polysilicones, guanamine resins, polytetrafluoroethylenes, elastomeric styrene-butadiene rubber (SBR), elastomeric butadiene-acrylonitrile rubber (NBR), urea resins, urea-formalin resins, etc., or inorganic materials such as synthetic silica, talc, clay, koalin, diatomaceous earth, calcium carbonate, magnesium carbonate, aluminium hydroxide, aluminium oxide, titanium oxide, zinc oxide, barium sulfate, calcium sulfate, zinc sulfide, satin white, aluminium silicate, calcium silicate, lithopone, etc. The specific surface area of the particulate material may vary from 10 to 200 m^2/g (BET specific surface), and the oil absorption index may range from $5\ 10^{-6}$ to $3.5\ 10^{-5}\ ms^{-1/2}$.

Polymethylmethacrylate beads may be added as matting agents. They are usually added to the receptive layer in a range of 0.4 to 1.2 g/m^2 and preferably in a range of 0.40 to 0.90 g/m^2 with 0.50 g/m^2 being most preferred.

When the element is intended for viewing in reflection, the ink-receiving layer of the invention may contain a whitening agent. TiO_2 (rutile or anatase) is preferably used as whitening agent in an amount sufficient to produce in the film element a transmission density to white light of at least 0.05, and preferably 0.3 or higher. Amounts of whitener present in the film element can range from 0.1 to 5.0 g/m^2, and preferably from 0.2 to 2.0 g/m^2, and most preferably 0.3 g/m^2. A slurry of the whitener may be added by batchwise addition or by in-line injection just prior to coating the receptor layer(s) on the support.

The ink-receiving layer of the present invention can also comprise a plasticizer such as ethylene glycol, diethylene glycol, propylene glycol, polyethylene glycol, glycerol monomethylether, glycerol monochlorohydrin, ethylene carbonate, propylene carbonate, tetrachlorophthalic anhydride, tetrabromophthalicanhydride, urea phosphate, triphenylphosphate, glycerolmonostearate, propylene glycol monostearate, tetramethylene sulfone, n-methyl-2-pyrrolidone, n-vinyl-2-pyrrolidone, and polymer latices with low Tg-value such as polyethylacrylate, polymethylacrylate, etc.

Surfactants may be incorporated in the ink-receptive layer of the present invention. They can be any of the cationic, anionic, amphoteric, and nonionic ones as described in JP-62-280068 (1987). Examples of the surfactants are soap, N-alkylamino acid salts, alkylether carboxylic acid salts, acylated peptides, alkylsulfonic acid salts, alkylbenzene and alkylnaphthalene sulfonic acid salts, sulfosuccinic acid salts, a-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, 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, sugaresters, fluoro C2-C10 alkylcarboxylic acids, disodium N-perfluorooctanesulfonyl glutamate, sodium 3-(fluoro-C6-C11alkyloxy)-1-C3-C4 alkyl sulfonates, sodium 3-(ω-fluoro-C6-C8 alkanoyl-N-ethylamino)-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.

Especially useful are the fluorocarbon surfactants as described in e.g. US-P 4,781,985, having a structure of : $F(CF_2)_{4-9}CH_2CH_2SCH_2CH_2N^+R_3X^-$ 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. The concentration of the surfactant component in the ink-receptive layer is typically in the range of 0.1 to 2 percent, preferably in the range of 0.4 to 1.5 percent and is most preferably 0.75 percent by weight based on the total dry weight of the layer.

The image-receiving layers of the present invention may additionally comprise mordanting polymers such as ammonium and/or phosphonium moiety containing polymers. Very appropriate polymers containing phosphonium moieties are described in EP-A 609 930. When using polymers containing phosphonium moieties in the ink-receiving layers, it is preferred that said ink-receiving layer comprises two distinct layers wherein at least one layer comprises a polymer containing a phosphonium moiety.

The image-receiving layers of the present invention may additionally comprise different additives which are well known in the art, and include UV-filters and antistatic agents.

The coating composition for ink-receiving layers according to the present invention comprise at most 7 % by weight of an hydrophilic polymer or polymer blend.

The image-recording elements of this invention comprise a polymeric support or a PE-coated paper support for the ink-receptive layer. A wide variety of polymeric supports are known and are commonly employed in the art. They include, for example, transparent supports as those used in the manufacture of photographic films including cellulose acetate propionate or cellulose acetate butyrate, polyesters such as poly(ethyleneterephthalate), poly(ethylenenaphthalate) and polyesters comprising recurring units containg hydrophilic groups e.g. sulfoisophthalic acid, sulfonated diols, etc., polyamides, polycarbonates, polyimides, polyolefins, poly(vinylacetals), polyethers and polysulfonamides. Other examples of useful high-quality polymeric supports for the present invention include opaque white polyesters and extrusion blends of poly(ethylenenterephthalate) and polypropyleen. Polyester film supports and especially poly(ethyleneterephthalate) are preferred because of their excellent properties of dimensional stability. When such a polyester is used as the support material, for an ink-receiving layer comprising at least 30 % by weight of gelatin with respect to the weight of all ingedients in said ink-receiving layer, a subbing layer must be employed to improve the bonding of the ink-receptive layer to the support. Useful subbing layers for this purpose are well known in the photographic art and include, for example, polymers of vinylidene chloride such as vinylidene chloride/acrylonitrile/acylic acid terpolymers or vinylidene chloride/methyl acrylate/itaconic acid terpolymers. The subbing layer can also be a chlorine free subbing layer as described in e.g. EP-A 078 559 and EP-A 559 244. The subbing layer can also be a antistatic subbing layer comprising a polythiophene derivative as described in e.g. EP-A 602 713.

The image-recording elements of this invention are employed in printing processes where liquid ink dots are applied to the ink-receiving layer of the element. A typical process is a ink-jet printing process which involves a method of forming the image on a paper or transparency by ejecting ink droplets from a print head from one or more nozzles. Several schemes can be used to control the deposition of the ink droplets on the image-recording element to form the desired ink dot pattern used to build the image. For example, one method comprises deflecting electrically charged ink droplets by electrostatic means. Another method comprises the ejection of single droplets "upon demand" under the control of a piezoelectric device which can operate by volume change or "wall" motion, or under the control of a thermal excitation.

The inks used to image the image-recording elements of this invention comprise at least 2 % by weight of humectants containing hydroxyl moieties and also at least 0.2 % by weight of viscosity regulators wherein the main solvent is water. The composition of the inks for the image-recording elements of the present invention are specifically tuned for obtaining a good value regarding a and b parameters if tested for the behaviour according to the equation described above. The inks in the present invention can also contain additional ingredients, which are well known to those skilled in the art, including surface tension regulators, preservatives, organic solvents, etc...

The dyes used in these ink-jet ink compositions are typically water-soluble direct dyes or acid type dyes, although also pigmented inks fall within the scope of the present invention.

The following examples are presented to illustrate this invention, but not to limit the present invention thereto.

EXAMPLES

1. MEASUREMENTS

MEASUREMENT A : Determination of the value a and b of equation (I)

A small film sample of ink-receiving element was placed upon a vacuum table made of porous metal and fixed to it by switching on the vacuum to provide a flat surface. On top of the ink-receiving layer an open ended metal cylinder was placed. The whole apparatus was conditioned at 25°C and the thickness of the dry film sample was measured using a quartz tube with an ending radius of 10.73 mm and a load of 6.0 g upon the dry layer, said tube connected to an inductive measuring probe giving, after amplification, an electrical signal corresponding with the actual position of the surface of the layer. This device was operated on a time-base scale wherein every second the actual measurement was done during 25 ms and the measurement lasted for 30 sec to give 30 measurements of the thickness of the dry layer. The thickness of the dry layer was determined by averaging the tickness values obtained by the 30 measurements. The quartz tube was removed from the film and the ink composition under study was poored into the open ended cylinder to be able to penetrate the layer. After pooring said ink composition into the cylinder the quartz tube was replaced and the tickness was again measured on a time-base scale wherein every second the actual measurement was done during 25 ms and the measurement lasted for 120 sec. Every second the thickness (expressed in μm) of the ink-receiving layer absorbing the ink composition was captured with a datalogging system. From these 120 measurements the thickness of the dry layer was subtracted, giving 120 values of Δd. These values were fitted to equation (I) and the values of a and b for the combination ink-receiving layer/ink composition under study determined.

MEASUREMENT B : determination of the roughness of the surface

The roughness of the surface of the receiving layers was measured with a Perthometer S6p with measuring probe RTK50 according to ANSI, ASME B 46.1-1985 and referred to as Roughness Average, Ra.

2. PREPARATION OF THE INK-RECEIVING ELEMENTS

INK-RECEIVING ELEMENT 1

A polyethylene terephthalate film (PET-100 μm thick with typical photographic subbing layers, used for a better bonding between the PET and the gelatinous layers) was used as the substrate. The composition A was applied to this substrate with a pilot coating machine at a temperature of 40°C, so as to give a dry film-coating thickness of 5 μm; chilled at 5°C for 20 s; and dried at 25°C for 220 s (RH (Relative Humidity) = 30%).

<u>Coating composition A</u>

50 parts of a gelatin with a gel strength higher than 220 g, the viscosity of a 10% solution of it at 40° C being higher than 50 mPas and containing 25 to 30 % microgels were mixed with 0.25 parts of diisooctylsulfosuccinate commercially available through American Cyanamid Co under tradename AEROSOL OT 75. Water was added to give 1000 parts. The pH of the coating composition was adjusted to pH 5.5 by the addition of a sodium hydroxyde solution.

INK-RECEIVING ELEMENT 2

An ink-receiving element with an ink-receiving layer was prepared as described for element 1, except for the fact that in coating composition A 70 parts of gelatin were used in stead of only 50 parts. The ink-receiving layer was coated directly, without any dilution, from this more concentrated solution.

INK-RECEIVING ELEMENTS 3-5

A recording medium with an ink-receiving layer was prepared as described for element 1, except for the fact that coating composition B was used instead of coating composition A.

<u>Coating composition B</u>

38 parts of a gelatin with a gel strength higher than 220 g, the viscosity of a 10% solution of it at 40° C being higher than 50 mPas and containing 25 to 30 % microgels were mixed with 5 parts of Carboxymethylcellulose commercially available under the tradename WALOCEL CRT 30 PA/GA sold by Wolf-Walsrode, Germany, with 34 parts of polymethylmethacr-

ylate beads, prepared as described for element 1 of US-P 4,614,708, having an average particle diameter of 3.3 micron, with 0.17 parts of formaldehyde and with 0.25 parts of diisooctylsulfosuccinate commercially available through American Cyanamid Co under tradename AEROSOL OT 75. Water was added to give 1000 parts.
For receiving element 3 the final dry layer thickness was set to 4.6 micron, for receiving elements 4 and 5, it was set to 6.0 and 10.6 micron, respectively.

INK-RECEIVING ELEMENT 6

On a polyethylene terephthalate film (PET-100 µm thick with typical photographic subbing layers, used for a better bonding between the PET and the gelatinous layers) as substrate an ink-receiving layer consisting of 2 layers (A and B) was coated by simultaneously applying to one side of the substrate a layer with coating composition B and a layer with coating composition C on a pilot coating machine with layer B being the outermost layer. Coating composition C differed from coating composition B in that only 19 parts of gelatin were used and combined with 18 parts of polyvinylpyrrolidone (LUVISKOL K90, a tradename for polyvinylpyrrolidone with a MW of 630000, commercially available from BASF AG, Germany), and 0.5 parts of detergent. The coatings were chilled at 5°C for 20 seconds, dried at 35°C for 280 seconds at 30% relative humidity, so as to give a dry film coating thickness of 5.3 micron for each layer.

INK-RECEIVING ELEMENT 7

A recording medium with an ink-receiving layer was prepared as described in example 2, except for the fact that in coating composition A gelatin was replaced by hydroxyethylcellulose (CELLOSIZE WP09H, a tradename for a low molecular weight hydroxyethylcellulose, commercialy available from Union Carbide, USA). The coating was chilled at 5°C for 20 seconds, dried at 35°C for 400 seconds at 30% relative humidity, so as to give a dry film coating thickness of 21.4 micron.

INK-RECEIVING ELEMENTS 8-9

A recording medium with an ink-receiving layer was prepared as described for element 1, except for the fact that coating composition D was used to obtain a dry coating thickness of 2.4 micron (element 8) and 12.0 micron (element 9), element 9 being dried for 400 seconds and element 8 for 220 sec.

<u>Coating composition D</u>

25 parts of a Polyvinylalcohol (MOWIOL 8-88, a tradename for polyvinylalcohol with a degree of hydrolysis of 88 mol. % and a molecular weight of 49000 (Mw), commercialy available through the Hoechst Company, Germany) were mixed with 25 parts of Polyvinylpyrrolidone (LUVISKOL K90, a tradename for polyvinylpyrrolidone with MW 630,000 of BASF, AG , Germany), 2.0 parts of SiO_2 particles with a mean particle diameter of 3.7 micron, and with 0.25 parts of diisooctylsulfosuccinate commercially available through American Cyanamid Co under tradename AEROSOL OT 75. Water was added to give 1000 parts.

INK-RECEIVING ELEMENT 10

A recording medium with an ink-receiving layer was prepared as described for element 1, except for the fact that coating composition E was used instead of coating composition A, and the total dry coating thickness was set to 5.7 micron.

<u>Coating composition E</u>

25 parts of polyvinylpyrrolidone (LUVISKOL K90, a tradename for polyvinylpyrrolidone with MW 630,000 of BASF, AG, Germany), 25 parts of a copolymer of methylmethacrylate and acrylic acid (90/10), 0.4 parts of starch particles with a mean diameter of 16.7 micron, and 0.25 parts of diisooctylsulfosuccinate commercially available through American Cyanamid Co under tradename AEROSOL OT 75 were used and adjusted by a 50/50 mixture of tetrahydrofurane and ethylacetate to give 1000 parts.

3. THE INK COMPOSITIONS

The inks used for ink jet printing in the present invention were all from the aqueous type comprising the ingredients, as illustrated in table 1. Before putting the ink in the DeskJet cassettes (these are the cassettes of a commercial Hewlett-Packard DESKJET 500C (tradename) printer. it was filtered through a MILLIPORE type GS filter having pores with average diameter of 0.22 micron, placed under an inert N2 atmosphere in an ultrasonic vibrator and degassed for 5 minutes. After being filled the cassettes were left in the N2 atmosphere for 1 hour and then sealed before further use.

TABLE 1

	INK 1	INK 2	INK 3
Water	929	914	723
Methylethylketone	0	0	190
1,5-pentane-diol	20	50	50
carboxymethylcellulose	2	5	6
Poly(ethylene)oxide-surfactant	5	5	5
Food Black 2 (commercial product of Bayer AG)	25	25	25
Sodium borate	1	1	1

4. PRINTING EXAMPLES

Before using the ink-receiving elements they were first acclimatised for at least 2 hours at 25°C and 30%RH, and then a test image was jetted upon it, using one of the 3 ink jet compositions described above via the black cassette of a commercial Hewlett-Packard DeskJet 500C printer. The different combinations of ink-receiving layers and inks, together with the thickness of the ink-receiving layer and the values of a and b of formula (I) are given in table 2.

The values of a and b were determined via measurement A

The roughness of the surface of the ink-receiving layers was determined via measurement B

Every combination of ink-receiving layers and inks, enumerated in table 2, was used for making an ink jet print, where 4 rows of 25 blocks of black were printed simultaneously. The total printing time was 5 minutes. This means that the 25th block of each row was printed 288 seconds after the first. The blocks in each row were numbered from 25 (the block printed first) to 1 (the block printed last). 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, used in reflection mode.

The block number corresponding with a reflection density that was barely distinguishable from the paper background was noted for each of the 4 rows, and the numbers added.

When in each row block 25 is visible on the conventional paper for use in dry toner electrophotography, which is the worst case, the combination gets a drying time (D.T.) value of 100. When in each row block 1 is visible on the conventional paper for use in dry toner electrophotography, the combination gets a drying time value of 4. When no blocks are visible, the combination gets drying time value 0. The values from this analysis is given in table 2. The smaller the value the better.

The results of these evaluations are given in table 2.

TABLE 2

Example number	I.R.L.* of element	Thickness	Ink	a	b	D.T.**	Ra+
1	1	5.0	1	0.091	0.33	38	0.22
2	3	4.6	2	0.092	0.72	37	3.21
3	4	6.0	1	0.082	0.21	37	0.76
4	4	6.0	2	0.071	0.75	30	0.76
5	5	10.6	1	0.049	0.15	23	0.73
6	5	10.6	3	0.041	0.33	20	0.73
7	6	10.6	1	0.051	0.09	16	4.04
8	6	10.6	3	0.059	0.52	21	4.04
9	9	12.0	2	0.047	0.18	26	0.32
10	9	12.0	3	0.028	0.09	23	0.32
C1++	2	5.0	1	0.140	0.22	70	0.16
C2	3	4.6	1	0.124	0.47	62	3.21
C3	7	21.4	2	0.112	0.27	60	0.14
C4	8	2.4	2	0.080	0.003	80	0.48
C5	10	5.7	2	0.294	3.00	45	0.90

* I.R.L. = Receiving Layer
** D.T. = Drying Time characteristic
+ Ra = surface roughness
++ C1 = comparative example 1

It is evident from the data in table 2 that good ink jet receiving layers applied upon a plastic substrate, only show a short drying time characteristic for the ink type applied, if a ≦ 0.100 and b ≦ 0.75 for a dry layer thickness in the range 3 to 20 µm. The drying time is especially short when a ≦ 0.060 and b ≦ 0.55. It is also evident that surface roughness of the ink-receiving layer is at best a secundary element for producing ink-receiving layer showing short drying times : e.g. examples 6 and 8 show no significant difference in drying time characteristic. Furtheron, it is no guarantee of using a high surface roughness to obtain a fast drying time as indicated in comparative example 2 (C2) which shows a high degree of surface roughness but nevertheless a slow drying time characteristic.
From the comparison of the thickness of the ink-receiving layers used in examples 1 and 2, having a good drying time characteristic, with the thickness of the ink-receiving layer used in comparative example 3 (C3), it is clear that simply having a thicker ink-receiving layer is not a warrant to have an ink-receiving layer with good drying time characteristic.

Claims

1. An ink jet printing system comprising (i) a water based ink comprising at least 2 % by weight of a humectant comprising hydroxyl moieties and at least 0.2 % by weight of a viscosity regulator, and (ii) an ink-receiving element comprising a polymeric film or a resin coated paper support and an ink-receiving layer coated thereon, said ink-receiving layer comprising hydrophilic polymers or copolymers, optionally mixed with hydrophobic polymers or copolymers and having a dry layer thickness of 3.0 to 20.0 µm, characterised in that said ink-receiving layer has, for said ink, solvent absorption characteristics satifying the equation

$$\frac{t}{\Delta d} = a.t + b \qquad (I)$$

wherein a ≦ 0.100 and b ≦ 0.75, t = immersion time in seconds of said ink-receiving layer in said ink, and Δd = change in ink-receiving layer thickness (expressed in µm).

2. An ink jet printing system according to claim 1, wherein in equation (I) a ≦ 0.060 and b ≦ 0.55.

3. An ink jet printing system according to claims 1 and 2, wherein said ink-receiving layer has a dry layer thickness between 5.0 to 15.0 µm.

4. An ink jet printing system according to any of the preceding claims wherein said ink-receiving layer comprises at least 30 % by weight of gelatin with respect to the weight of all ingedients in said ink-receiving layer.

5. An ink jet printing system according to claim 4, wherein said ink-receiving layer comprises further at least one binder selected form the group consisting of polyvinyl pyrrolidone and polyvinyl alcohol.

6. An ink jet printing system according to any of the preceding claims wherein said ink-receiving layer comprises two distinct layers wherein at least one layer comprises a polymer containing a phosphonium moiety.

7. An ink jet printing system according to any of the preceding claims wherein said ink-receiving layer comprises a porous particulate material.

8. An ink jet printing system according to any of the preceding claims wherein said ink-receiving layer is hardened by formaldehyd that is applied in an amount of 0.001 to 0.05 parts pro part of gelatine present.

9. An ink jet printing system according to any of the preceding claims wherein the coating composition for said ink-receiving layer comprises at most 7 % by weight of an hydrophilic polymer or polymer blend.

10. An ink jet printing system according to any of the preceding claims wherein said ink-receiving layer comprises a surfactant and a UV-filter and/or an antistatic agent and/or a matting agent.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 20 2817

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)
X,D	EP-A-0 594 896 (AGFA-GEVAERT N.V.) * page 3, line 9 - line 34 * * page 6, line 5 - line 50 * * claims 1-3; example 1 *	1-10	B41M5/00 C09D11/00
X,D	EP-A-0 125 113 (TEKTRONIX, INC.) * page 1, line 25 - page 2, line 10 * * page 3, line 23 - page 4, line 34; claims 1-3; example 1 *	1-10	
X	GB-A-2 134 129 (RICOH COMPANY LIMITED) * page 2, line 6 - line 31 * * page 6, line 23 - page 7, line 34 * * page 9, line 13 - line 34; claims 1-7,15; example 1 *	1-10	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

B41M
C09D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 February 1995	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

EPO FORM 1503 03.82 (P04C01)