

(19)



(11)

EP 2 500 464 A2

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:

19.09.2012 Bulletin 2012/38

(51) Int Cl.:

D06P 5/00 (2006.01) D21H 19/10 (2006.01)
D21H 19/12 (2006.01) D21H 19/24 (2006.01)

(21) Application number: **10828375.5**

(86) International application number:

PCT/JP2010/069811

(22) Date of filing: **08.11.2010**

(87) International publication number:

WO 2011/055817 (12.05.2011 Gazette 2011/19)

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

• **TERAO, Hisashige**
Osaka-shi
Osaka 532-0002 (JP)

(30) Priority: **09.11.2009 JP 2009272612**

(74) Representative: **Duckett, Anthony Joseph**
Mathys & Squire LLP
120 Holborn
London
EC1N 2SQ (GB)

(71) Applicant: **Yamamoto, Genshi**
Kyoto 611-0031 (JP)

(72) Inventors:

• **YAMADA, Eiji**
Takatsuki-shi
Osaka 569-1047 (JP)

(54) **PAPER PRINTING METHOD FOR FIBROUS AND LEATHER MATERIALS**

(57) Disclosed is a paper printing method for fibrous and leather materials characterized by having: a step wherein printing paper is obtained by applying a mixed paste comprising a water-soluble synthetic binder, a natural adhesive, and an auxiliary agent to base paper, which is then dried to obtain paper for printing, onto which a dye ink is printed; a step wherein the printing paper is bonded to a fibrous or leather material and fixed using

pressure/heat; and a step wherein the printing paper is removed after a dye fixing process is carried out while the printing paper is fixed to the fibrous or leather material. Further disclosed are the paper for printing and the printing paper used in the paper printing process, and the fibrous and leather materials characterized by being printed on in the paper printing process.

EP 2 500 464 A2

Description

(Technical Field)

[0001] The present invention relates to a printing method of a fiber material or a leather material using a printed paper. More particularly, the present invention relates to a printing method of a fiber material or a leather material, characterized in that a mixed coating composed of a water-soluble synthetic binder, a natural glue and an auxiliary agent is applied on a base paper to obtain a printing paper, a dye ink is printed on the printing paper to obtain a printed paper, and the printed paper is pasted to a fiber material or a leather material and a fixing treatment (steaming and the like) of the dye is performed under this condition.

[0002] This printing method is a novel processing method characterized in that a steaming treatment or the like is carried out under a condition wherein a printed paper is pasted to a fiber material or a leather material. This printing method is named "paper printing method". In the present specification and claims, the "printing base paper" means a base paper used for production of a printing paper, the "printing paper" means a printing base paper to which mixed glue is applied, and the "printed paper" means a printing paper to which a dye ink is applied.

(Background Art)

[0003] As a method of drawing a design fastly and finely on a cloth with a dye, known are transfer printing methods according to a plate printing technique mode such as screen printing, roller printing, rotary screen printing, gravure printing or methods using these printing techniques, and the like, and these are industrially practiced. These plate printing technique methods, however, are limited in color number. Though polychromatic sense can be expressed by a printing technique using a three primary color separation mold form, it has problems that it is difficult to adjust hue and concentration of a three primary color composition, print processing tends to lack in reproducibility due to multi-layer formation, and the like. Additionally, it is pointed out that there are problems of significant wastes and losses in materials such as high cost of sculpture fabrication (plate making) in small lot production and, a necessity of preparation of a color glue in surplus amount more than necessary amount for processing in print processing, and the like.

[0004] As a novel printing method for solving these problems, a plateless printing technique in which an image is processed by a computer and printing is performed by inkjet using an aqueous dye ink (inkjet printing mode) attracts attention. This plateless printing technique is applied to direct printing on a pre-treated cloth, and in addition, applied also to the transfer print field, and the development thereof is remarkable. In the case of small dot printing of an aqueous dye ink on a cloth or a transfer

paper by an inkjet printer, however, problems are pointed out such as a lack in uniform printing due to dot spots, exudation of a dye ink to lose fineness, and the like.

[0005] As a method for solving these problems, a method is proposed in which a paper (release paper) having a mold release agent layer using a water-soluble varnish or a solvent type varnish is used, a water-soluble glue is applied on the mold release agent layer and dried to form a glue layer, a dye ink is inkjet-printed on the glue layer to allow the dye to be kept uniformly in the glue layer to fabricate a transfer paper, and transfer printing is carried out using the transfer paper. Also known is a method of using paper having a special multi-layer structure as the transfer paper.

[0006] These methods are effective for a sublimation transfer method of a polyester fiber using a dispersive dye sublimating by heat (dry transfer printing method) and a wet transfer method in which a cloth composed of a cellulosic fiber or a protein based fiber is moistened with water, held together with a transfer paper and a dye is transfer-printed under strong pressurization (disclosed in Japanese Patent No. 2925562, JP-A No. 06-287870 and the like). However, application of the sublimation transfer method is limited to polyester fibers and fastness thereof is low. Further, the wet transfer method tends to cause a problem of lacking in delicacy and reproducibility of a design.

[0007] Japanese Patent No. 4058470 or JP-A No. 06-270596 discloses a method in which a mixed glue liquid composed of a glue, resin and the like is applied on a mold release agent layer of a release paper and dried to form an ink receiving layer, a dye ink is printed on the ink receiving layer, then, dry-transferred onto a cloth, the release paper is peeled, then, the dye dry-transferred onto the cloth is subjected to a fixing treatment by steaming and the like.

[0008] However, the release paper used in this method needs a costly mold release agent application step in its production, and the production cost thereof is several times (5 to 10 times) higher than the cost of general base papers.

[0009] If the degree of humidity in a transfer industrial factory or the storage conditions or dry transfer conditions of a transfer paper is inappropriate, it is impossible to entirely (100%) transfer an ink receiving layer and to clearly peel only a release paper in some cases. In such cases, defective products are generated and paper recycle is difficult. For small quantity and large variety production, a transfer paper is cut into small pieces, and it is virtually difficult to connect the pieces and recycle them.

[0010] Further, since the melting point of a mold release agent is low in general, it is impossible to raise the drying temperature after coating of a mixed glue liquid. Thus, the drying time becomes longer and the production efficiency crucially deteriorates. For example, since the melting point of a polyethylene laminate mold release agent is about 110°C, the drying temperature cannot be raised to 110°C or higher, and it is difficult to enhance

production capacity (speed).

[0011] That is, this method has problems as shown below.

(A) An expensive release paper is necessary. Therefore, the cost increases.

(B) Peelability (reproducibility of paper peeling) in a step of transferring an ink receiving layer to a cloth is difficult and entire (100%) transfer of an ink receiving layer to a cloth is impossible (peeling instability) in some cases. If an ink receiving layer partially remains on a transfer paper, the portion is unevenly dyed to generate deficient products.

(C) Since an ink receiving layer is transferred to a cloth (desirably, entirely (100%)), used glue and resin flow into drainage water and also a surplus dye ink flows into drainage water in a step of washing the cloth after the dye fixing treatment, leading to pollution of the drainage water.

(D) Many usual mold release agents have low melting point, and if transfer is carried out at high temperatures, for example at 150°C or higher to improve transferability, a resin constituting the mold release agent melts and adheres to a cloth and the adhered resin cannot be removed in a washing step, thus, the texture of the cloth becomes hard. Additionally, the melted resin allows a part of an ink receiving layer to adhere to and remain on paper, generating deficient products.

(E) There are also problems on production efficiency. For example, when the melting point of a mold release agent is low, the drying temperature after mixed glue liquid coating is limited and it becomes difficult to increase production speed.

(Prior Art Document)

(Patent Document)

[0012]

(Patent document 1) Japanese Patent No. 2925562

(Patent document 2) JP-A No. 06-287870

(Patent document 3) Japanese Patent No. 4058470

(Patent document 4) JP-A No. 06-270596

(Summary of the Invention)

(Problem to be Solved by the Invention)

[0013] An object of the present invention is to provide an ecological and economical printing method of a fiber material or a leather material which gives prominent printing performances excellent in texture, delicacy, fastness, chromogenic property and the like, solves the above-described problems (A) to (E) and the like of the known methods, and can attain reduction of material cost, improvement of processing reproducibility and quality, fur-

ther reduction of drainage load and improvement of production efficiency.

(Means for Solving the Problem)

[0014] The present inventors have intensively studied a method of printing on a cloth or a leather according to an inkjet printing and resultantly found that a printing method giving good dyeing uniformity, fineness and chromogenic property and excellent in economy and ecology can be accomplished by a method in which

a mixed glue composed of

a water-soluble synthetic binder having coat formability, generating strong adhesion force by heating and pressurization, while revealing easy decrease in adhesion force when a dye fixing treatment by steaming or the like is performed,

a natural glue having good compatibility with the water-soluble synthetic binder and excellent in a nature of uniformly absorbing and keeping a dye ink, and an auxiliary agent

is applied on a commercially marketed general paper (base paper) and dried to obtain a printing paper,

a dye ink is printed on this printing paper to obtain a printed paper which is then pasted to a cloth and the like, a dye fixing treatment such as steaming and the like is performed to allow the dye to fix and develop color, and the adhesion force between the printed paper and the cloth or the like is reduced and the printed paper is peeled.

Thus, getting the prospect of practical use and the present invention was completed. Namely, the above-described object of the present invention is solved by a paper printing method shown below.

[0015] That is, the present invention provides a paper printing method of a fiber material or a leather material comprising

a step in which a mixed glue composed of a water-soluble synthetic binder, a natural glue and an auxiliary agent is applied on a base paper and dried to obtain a printing paper and a dye ink is printed on the printing paper to obtain a printed paper,

a step in which the above-described printed paper is closely contacted to a fiber material or a leather material and pasted under pressurization and heating, and

a step in which the above-described printed paper is subjected to a dye fixing treatment under condition pasted to the above-described fiber material or leather material, then, the printed paper is removed (Claim 1).

[0016] The paper printing method of the present invention composed of the above-described constitution is a novel printing method solving problems of known methods, for example, the above-described problems (A) to (E). That is to say, this printing method is characterized in that not an expensive release paper but a commercially marketed cheap paper can be used, that a problem of generating deficient products due to peeling instability in a known transfer printing method can be solved, that drainage load can be further reduced, that pasting at a

high temperature and high concentration dyeing while maintaining good texture can be conducted, that coating efficiency can be improved by raising the drying temperature of a mixed glue liquid without using a mold release agent (of low melting point) (for example, application speed can be increased to 3 times or more by raising the drying temperature after application up to 150 to 180°C), and the like. Further, according to the present invention, a cellulosic fiber, a protein-based fiber, a synthetic fiber or leather can be printed by utilizing roller type or flat plate type pressurization and heating apparatuses widely used in the current dyeing industry.

[0017] The water-soluble synthetic binder constituting the above-described mixed glue is water-soluble, shows development of polymerization by heating to obtain high molecular weight, and has coat formability. Further, the binder generates adhesion force for adhering a fiber or a leather and a base paper by heating and pressurizing the coat formed on a base paper or in a base paper, while has a nature of decreasing the adhesion force by a dye fixing treatment (steaming, humidification, or dry heat treatment at high temperatures). In summary, a binder which is capable of forming a coat having strong adhesion force under dry condition after heating and pressurization, and manifests weakening of adhesion force under wet condition (occasionally, condition after dry heat treatment at high temperature) can be used.

[0018] As this water-soluble synthetic binder, those synthesized in petrochemical are mentioned mainly. Binders showing no dyeing inhibition are desired. Specifically mentioned are water-soluble polyvinyl alcohol binders, water-soluble acrylic binders, water-soluble urethane binders, water-soluble urethane-modified ether binders, water-soluble polyethylene oxide binders, water-soluble polyamide binders, water-soluble phenol binders, water-soluble vinyl acetate binders, water-soluble styrene acrylic acid binders, water-soluble styrene maleic acid binders, water-soluble styrene acrylmaic acid binders, water-soluble polyester binders, water-soluble polyvinylacetal binders, water-soluble polyester-urethane binders, water-soluble polyether urethane binders, water-soluble hot melt adhesives and the like. One or a mixture of two or more selected from the above-exemplified binders can be preferably used.

[0019] Among them, water-soluble polyvinyl alcohol binders, water-soluble acrylic binders, water-soluble polyester binders, water-soluble polyether-urethane binders and water-soluble hot melt adhesives are preferable since they are excellent in water-solubility and temporary adhesiveness (a nature of adhering by heating but decreasing adhesion force under wet condition) and manifest small inhibition of dyeing. The present invention provides, as Claim 2, the paper printing method according to Claim 1 wherein the water-soluble synthetic binder is one or a mixture of two or more selected from the group consisting of water-soluble polyvinyl alcohol binders, water-soluble acrylic binders, water-soluble polyester binders, water-soluble polyether-urethane binders and water-

soluble hot melt adhesives.

[0020] As the natural glue constituting the above-described mixed glue, naturally produced glue raw materials are used as they are or after being physically or chemically processed. Though the natural glue shows adhesion force, a phenomenon of developing polymerization to increase adhesion force like in the case of a water-soluble synthetic binder is not observed even if the natural glue is heated. The natural glue can be removed by steaming or a dry heating treatment. Therefore, preferably the natural glue is hydrophilic. The natural glue is required to have high compatibility with a dye ink and to have a nature of uniformly absorbing and keeping a dye ink.

[0021] This natural glue is classified into animal glues, plant glues and mineral glues. As the animal glue, gelatin extracted from collagen contained in skins and bones of animals, and the like can be mentioned. As the plant glue, carboxymethylcellulose processed from starch and cellulose, a starting raw material, and the like can be mentioned. As the mineral glue, clays extracted from clay minerals, and the like can be mentioned. More specifically mentioned are natural gum glues (etherized tamarind gum, etherized locust bean gum, etherized guar gum, acacia arabica gum and the like), cellulose derivative glues (carboxymethyl cellulose, etherized carboxymethyl cellulose, hydroxyethyl cellulose and the like), polysaccharides (starch, glycogen, dextrin, amylose, hyaluronic acid, Arrow root, Amorphophallus konjac, potato starch, etherified starch, esterified starch and the like), seaweed glues (sodium alginate, agar and the like), mineral glues (bentonite, porcelain clay, aluminum silicate and derivatives thereof, silica, diatomaceous earth, clay, kaolin, acid clay and the like) and animal glues (casein, gelatin, egg protein and the like). One or a mixture of two or more selected from the exemplified glues can be preferably used.

[0022] Among them, cellulose derivative glues such as a natural gum glue, carboxymethyl cellulose and the like, starch derivative glues such as an etherized starch and the like, seaweed glues such as sodium alginate and the like, mineral glues such as aluminum silicate, clay and the like, animal glue and the like are preferable natural glues. The present invention provides, as Claim 3, the paper printing method according to Claim 1 or 2 wherein the natural glue is one or a mixture of two or more selected from the group consisting of natural gum glues, cellulose derivatives, starch derivatives, seaweed glues, mineral glues and animal glues.

[0023] The present invention provides, as Claim 4, the paper printing method according to any one of Claims 1 to 3 wherein the compounding proportion of the water-soluble synthetic binder to the natural glue is in the range of water-soluble synthetic binder:natural glue = 95:5 to 20:80 (weight ratio) in terms of solid component.

[0024] The compounding proportion of the water-soluble synthetic binder to the natural glue is preferably in the range of water-soluble synthetic binder:natural glue

= 95:5 to 20:80 (weight ratio) in terms of solid component. When the compounding proportion of the water-soluble synthetic binder is less than 20 % by weight with respect to the total weight of the water-soluble synthetic binder and the natural glue or when the compounding proportion of the water-soluble synthetic binder is over 95 % by weight, namely, the compounding proportion of the natural glue is less than 5 % by weight, there is a tendency of generation of problems such as deterioration of paper desquamation after dye fixation (easiness of peeling of printed paper) and of dyeing property · dyeing uniformity, lowering of paper-cloth adhesion force, lowering of fineness, and the like.

[0025] The auxiliary agent constituting the above-described mixed glue is added in order to improve the various physical properties of the mixed glue liquid, to promote the dyeing property of a dye, and the like. Examples of the auxiliary agent include surfactants, thickeners, moisturizing agents, pH regulators, alkaline agents, deep coloring agents, preservatives, fungicides, degassing agents, antifoaming agents, reduction inhibitors and the like. The present invention provides, as Claim 5, the paper printing method according to any one of Claims 1 to 4 wherein the above-described auxiliary agent is one or a mixture of two or more selected from auxiliary agents above exemplified.

[0026] The above-described mixed glue used in the paper printing method of the present invention is a hydrophilic mixture containing a water-soluble synthetic binder, natural glue and an auxiliary agent. This mixed glue (hydrophilic mixture) or its solution (mixed glue liquid) is applied on a base paper and dried, to obtain a printing paper to be used in the present invention.

[0027] The mixed glue liquid is applied on a base paper, then, dried, to form a layer composed of the mixed glue on a base paper (when the application is effected by coating and the like. However, even in the case of coating, the glue is partially absorbed in the paper) or in a base paper (when the application is effected by absorption and the like). This layer is a multicomponent glue layer containing a mixture of a water-soluble synthetic binder and natural glue and further containing various auxiliary agents. This layer has a function as an ink receiving layer for keeping a dye ink to be printed on a printing paper. Simultaneously, this layer is also an adhesive layer for temporarily adhering to a printed paper (composed of a printing paper and a multicomponent glue layer) strongly to a fiber of a cloth or the like when the printed paper is closely contacted to the cloth or the like and heated and pressurized.

[0028] A dye ink is printed based on a printing design on the printing paper produced as described above, then, dried to fabricate a printed paper. When the above-described mixed glue is applied on one surface of the printing paper, a dye ink is printed on the surface.

[0029] Specific examples of the dye ink herein used include inks using a reactive dye, an acidic dye, a metal complex salt type dye, a direct dye, a disperse dye, a

cationic dye and the like as a dye. The dye ink is prepared by dissolving or dispersing one or more dyes selected from the above-exemplified dyes in a dye dissolving medium such as water and the like.

[0030] The present invention provides, as Claim 6, the paper printing method according to any one of Claims 1 to 5 wherein the dye contained in the above-described dye ink is selected from the group consisting of a reactive dye, an acidic dye, a metal complex salt type dye, a direct dye, a disperse dye and a cationic dye.

[0031] As the method of printing a dye ink on a transfer paper, methods of inkjet printing using an aqueous dye ink are preferable. The aqueous dye ink is an ink composed of water or a solvent which is dissolved in water as the main component and a dye dissolved or dispersed therein. The present invention provides, as Claim 7, the paper printing method according to any one of Claims 1 to 6 wherein the above-described dye ink is an aqueous dye ink and the above-described printing is carried out by inkjet printing.

[0032] The transfer paper fabricated as described above is closely contacted to a fiber material or a leather material and heated and pressurized, and a dye fixing treatment is carried out under the closely contacted condition. As the conditions of heating and pressurization, the same conditions as in the case of usual transfer printing can be applied, and it is preferable that pressure is set at relatively higher level. By this heating and pressurization, the transfer paper is adhered to a fiber material or a leather material.

[0033] The dye fixing treatment includes heating by steam usually carried out in printing using a reactive dye or the like and heating under condition of humidification and application of water, and the like. In the case of printing of a polyester fiber and a synthetic fiber, methods of dry heating can also be adopted. By this heating by steam and heating under condition of humidification and application of water, peeling of a transfer paper is made possible. In the case of printing of a polyester fiber and a synthetic fiber, though peeling of a transfer paper is made possible by dry heating methods in some cases, if water is applied after dry heating (fixation), peeling can be performed more easily.

[0034] The dye fixing treatment may be carried out after heating and pressurization or may be carried out simultaneously with the above-described heating and pressurization. By heating and pressurization and dye fixing treatment, a great part of a dye in a dye ink printed on a printing paper is absorbed and dyed in a fiber material or a leather material. By the dye fixing treatment, a dye dyed in a fiber material or a leather material is fixed and the adhesion force between a printed paper and a fiber material or a leather material lowers.

[0035] The layer of a mixed glue formed on a base paper or in a base paper as described above shows a function as an adhesion layer by the above-described heating and pressurization, while shows lowering of its adhesion force by a dye fixing treatment step by steaming

and the like so that peeling of a transfer paper from a cloth or the like can be carried out easily. That is, the layer of mixed glue is desired to have a nature of easily lowering adhesion force by a dye fixing treatment step by steaming and the like or by moisture application in a step of peeling a printer paper.

[0036] By a treatment step by steaming and the like, fixation of a dye to a fiber material or a leather material and color development thereof are carried out. After peeling of a transfer paper, a washing step such as water-washing, soaping and the like is usually carried out. It is preferable that the mixed glue has a nature which can be easily washed and removed by this washing step.

[0037] As described above, the mixed glue is required to have a function as an ink receiving layer, a function as a temporary adhesive layer, and a nature which shows lowering of adhesion force in the final stage of a dye fixing treatment step by steaming and the like and can be removed easily. Specifically, it is required that the following conditions are satisfied.

1. Compatibility with a dye ink is excellent, and dyeing of a dye on a fiber is not inhibited. That is, it is mixed glue which gives excellent reproducibility of concentration and hue after dyeing of a dye.
2. A fiber (fiber material, leather material) and paper can be temporarily strongly adhered by heating and pressurization treatment. That is, it has adhesion force for temporarily (until the final stage of a fixing treatment step) strongly adhering the fiber and the paper under dry condition after pressurization and heating.
3. It has good ink absorbability, has an apparent ink drying property, and is excellent also in colored design fineness. That is, ink receptivity is large.
4. It has a nature of easy lowering of adhesion force by a dye fixing treatment step by steaming and the like. That is, it is mixed glue which easily loses adhesion force when water or moisture is applied and gives easy peeling of a transfer paper from a fiber material or leather.
5. It can be removed from a color developed material in water-washing, soaping and the like after dye fixing. That is, it is mixed glue showing large water-solubility even after heating.

Using mixed glue composed of a water-soluble synthetic binder and a natural glue satisfying these conditions, the object of the present invention can be attained.

[0038] In addition to the above-described paper printing method, the present invention provides a printing paper and a printed paper used in this method. That is, the present invention provides

a printing paper used in the paper printing method according to any one of Claims 1 to 7, obtained by applying a mixed glue composed of a water-soluble synthetic binder, a natural glue and an auxiliary agent to a base paper and then drying the paper(Claim 8), and

a printed paper used in the paper printing method according to any one of Claims 1 to 7, obtained by applying a mixed glue composed of a water-soluble synthetic binder, a natural glue and an auxiliary agent to a base paper and then drying the paper to obtain a printing paper, and printing a dye ink on the printing paper thus obtained and then drying the printing paper (Claim 9).

[0039] Further, the present invention provides a fiber material or a leather material which is printed by the above-described paper printing method. That is, this invention is a fiber material or a leather material which is printed by the paper printing method according to any one of Claims 1 to 7 (Claim 10).

[0040] As described above, the feature of the paper printing method of the present invention is use of a printing paper having a layer acting as an ink receiving layer and an adhesive layer simultaneously which is constituted of a mixed glue obtained by compounding various auxiliary agents into a multicomponent mixed system composed of a water-soluble synthetic binder and a natural glue causing no dyeing inhibition and shows lowering of adhesion force by a dye fixing treatment by steaming and the like (application of moisture, and occasionally, heating). This is a completely novel printing method in which a dye is printed on a printing paper to fabricate a printed paper, the printed paper is pasted to a cloth or leather, a dye fixing treatment by steaming and the like is carried out under this pasted condition, and then the printed paper is peeled. By these features, a printed article having excellent quality can be obtained.

(Effect of the Invention)

[0041] According to the paper printing method of the present invention, excellent effects can be obtained, that is,

a generally commercially available cheap paper can be used, instead of expensive peeling paper,
 a problem of deficient products generated due to peeling instability in known transfer printing methods can be solved,
 drainage load can be further reduced,
 pasting at a high temperature and high concentration dyeing become possible while maintaining good smooth texture,
 the drying temperature of a mixed glue liquid can be raised to improve the coating efficiency since a mold release agent is not used,
 and the like. As a result, expression of a fine printing design can be provided with good reproducibility under excellent economy and ecology.

(Modes for Carrying Out the Invention)

[0042] The present invention will be illustrated below based on embodiments thereof. The present invention is not limited to the following embodiments. The following embodiments can be variously modified in a range which

is the same as and equivalent to the present invention.

[0043] The base paper used in the paper printing method of the present invention is not particularly restricted providing that the above-described mixed glue can be applied on the paper and the paper has enough strength, flexibility and the like which can be used as a printed paper. Therefore, generally used paper and commercially available usual paper can be used as they are as the base paper. Therefore, the cost is low. Although processed paper such as coat paper and the like may be used, there is no need to use an expensive release paper having a release layer. Thus, the production cost can be reduced significantly.

[0044] For example, use is made of cheap papers generally used, such as recycled papers and pulp papers made by using, as a raw material, recycled paper and pulp such as kraft pulp or grind pulp and the like. Preferably, basis weight of base paper is in a range of 10 to 100 g/m², more preferably in a range of 20 to 80 g/m². From the standpoint of workability, the paper thickness is preferably about 0.01 to 0.5 mm. Specific examples thereof include white paper, bleached or unbleached kraft paper and wood-free paper manufactured by Nippon Paper Industries Co., Ltd., papers manufactured by Nippon Daishowa Paperboard Co., Ltd. and having brand name of Gintake, Ginmine, Shirogane and the like, machine glazed kraft paper, glassine paper, bleached kraft paper and unbleached kraft paper manufactured by Daishowa Paper Manufacturing Co., Ltd., various coated papers manufactured by Mishima Paper Co., Ltd., and the like, although these are only examples.

[0045] As the water-soluble synthetic binder constituting the mixed glue which is applied on this base paper, those exemplified above (those mentioned in Claim 2) can be preferably used. Among them, examples of water-soluble hot melt adhesives include alkali water-soluble hot melt adhesives which are maleic acid alternating copolymers, water-sensitive hot melt adhesives, polyvinyl alcohol hot melt adhesives and the like.

[0046] Regarding the auxiliary agent constituting the mixed glue, the contents thereof in the mixed glue liquid are:

0.2 to 5 % by weight in the case of an anionic surfactant or the like to be added as a surface tension depressant and a penetrating agent,

1 to 15 % by weight in the case of a moisturizing agent (wetting agent) to be added for improving adhesion force of a transfer paper to a cloth or the like and improving dyeing power thereof, including polyhydric alcohols such as polyethylene glycol, glycerin, thiodiglycol, diethyleneglycol and the like, urea, thiourea, dicyandiamide and the like,

0 to 3 % by weight in the case of acrylic synthetic glue which is a thickener for increasing the viscosity of the mixed glue liquid to render application to a base paper easy,

0.1 to 5 % by weight in the case of a preservative, a

fungicide, an antifoaming agent, a degassing agent and a reduction inhibitor, 1 to 15 % by weight in the case of an alkaline agent such as soda ash (coarse anhydrous sodium carbonate), sodium bicarbonate, sodium silicate, sodium acetate and the like to be added when a reactive dye is used, and 0.1 to 3 % by weight in the case of a pH regulator such as ammonium sulfate, sodium dihydrogen phosphate and the like to be added when a dispersive dye and an acidic dye are used, and preferable results are obtained under these compounding amounts.

[0047] Mixed glue (hydrophilic mixture) composed of a water-soluble synthetic binder, natural glue and an auxiliary agent or a solution of the mixed glue (mixed glue liquid) is applied on a base paper and dried, to obtain a printing paper to be used in the present invention. The method of applying on a base paper is not particularly restricted, and includes a method in which the above-described components constituting a mixed glue are dissolved in a solvent such as water and the like to obtain a mixed glue liquid which is applied on a base paper, a method of spraying a mixed glue liquid, a method of immersing a base paper in a mixed glue liquid to cause absorption thereof, and the like. A mixed glue liquid is applied on a base paper, then, dried, to form a layer (a layer acting as an ink receiving layer and an adhesive layer simultaneously) composed of the mixed glue on a base paper (when application is effected by coating and the like) or in a base paper (when application is effected by absorption and the like), obtaining a printing paper,

[0048] The coating mass of mixed glue to a base paper is preferably 10 to 100 g/m² in terms of dry weight. The coating mass of mixed glue is correlated with the cost of a printing paper and strength when binders adhere to a cloth and chromogenic property thereof. When this application is effected by coating using a coater, management of adhesion amount such as the clearance of a coater, regulation of winding speed, and the like is important.

[0049] Depending on the kind of mixed glue liquid and a base paper, shrinkage of paper occurs in application and uniform application on a base paper is difficult, in some cases. These phenomena can be improved by adjusting the kind of mixed glue, solid content of the glue, the kind of a surface tension depressant (anionic, nonionic surfactant, alcohols and the like) and the addition amount thereof, and the like according to the kind of paper, formulation conditions and the like. Specific examples of the apparatus for applying a mixed glue liquid include a comma coater, a gravure coater, a reverse coater, an air knife coater, a jet coater, an impregnating apparatus and the like, although these are only examples.

[0050] A dye ink is printed on thus obtained printing paper and dried, to fabricate a printed paper. As the printing method, inkjet printing is preferable, though other methods such as gravure printing, screen printing and

the like can also be mentioned. The printing can be performed according to the same methods and conditions as in known transfer printing.

[0051] As the dye ink used in inkjet printing in the present invention, those prepared by dissolving or dispersing a dye in a dye dissolving agent or a dispersing agent can be used. Examples of the dye dissolving agent include water, thiodiglycol, polyethylene glycol, glycerin, ethylene glycol and ϵ -caprolactam. To the dye ink, a drying inhibitor, a surface tension regulator, a viscosity regulator, a pH regulator, a preservative, a fungicide, a sequestering agent, an antifoaming agent, a degassing agent and the like can be added further, if necessary. These components are mixed, a trace amount of insoluble components are filtrated through a membrane filter of 1 μm or less and degassed to give a dye ink to be used in the present invention.

[0052] The kind of the dye is selected from a reactive dye, a direct dye, an acidic dye, a metal complex salt type dye, a disperse dye, a cationic dye and the like depending on the kind of a fiber constituting the cloth, and when a disperse dye is processed into an ink, it is desirable that the average particle size of the dye is atomized to about 0.1 μm using zirconium beads of 0.1 to 0.3 mm.

[0053] The printed paper fabricated as described above is closely contacted to a cloth or the like, and then pressurized and heated. Then, a dye fixing treatment by steaming or the like is carried out, under condition of adhesion of the printed paper to a cloth or the like. By this treatment, dyeing of a dye on a cloth or leather (color development or dye fixation) is carried out and simultaneously, the adhesion force of a layer acting as an ink receiving layer and an adhesive layer simultaneously lowers and peeling and removal of the printed paper become easy.

[0054] After peeling and removal of the printed paper, the cloth or the like is washed (water-washing, soaping, water-washing) to remove a small amount of water-soluble synthetic binder and a natural glue adhered to the cloth or the like, thereby a fine printed material or a fine printed article having good fiber texture is obtained. In the case of a synthetic fiber such as polyester and the like, the washing step can be omitted.

[0055] In the case of transfer printing using a release paper, there is a problem of serious drainage pollution caused by a surplus dye not fixed and a glue since an ink receiving layer and a dye ink migrate totally to a cloth. In the method of the present invention, however, a great part of a dye not fixed (surplus dye) and mixed glue adhere to the printed paper which is peeled from a cloth or the like, while a surplus dye and mixed glue scarcely adhere to the cloth or the like. Thus, drainage load in washing the cloth or the like is reduced remarkably as compared with known methods. Also in this context, the present invention is an ecological processing method.

[0056] The paper printing method of the present invention is applied to printing of a cloth composed of a fiber material or a leather material. The fiber material to which

the present invention applied includes any of natural fiber materials and synthetic fiber materials. The natural fiber materials include cellulose fiber materials such as cotton, hemp, lyocell, rayon, acetate and the like, and protein fiber materials such as silk, wool, animal hair and the like. The synthetic fiber materials include polyamide fibers (nylon) and fibers called vinylon, polyester, polyacryl and the like.

[0057] The leather material to which the present invention is applied includes materials made from animal leathers obtained through known tannery and tanning processes and drying process. As the animal leathers, natural leathers of cow, water buffalo, pig, horse, sheep, goat, kangaroo, deer, panther, rabbit, fox, camel and the like can be mentioned. The paper printing method of the present invention is applied to woven fabric, knitted fabric and non-woven fabric of the fiber materials, a single leather, and single fabric, blended fabric, mix-woven fabric or intermingled fabric thereof. Further, it may be applied to composite fibers also.

[0058] If necessary, the cloth or the like may be pre-treated with a chemical exerting an influence on dyeing of a dye or a chemical having an effect on promotion of dyeing, and the like before used in paper printing. For example, in the case of dyeing of a reactive dye, a mixed liquid containing 3 to 15 % by weight of sodium carbonate, potassium carbonate, sodium bicarbonate, sodium silicate, sodium acetate, sesquisodium carbonate, trichloro sodium acetate and the like as an alkaline agent, 3 to 25 % by weight of urea for the purpose of prevention of yellowing in transferring, improvement of transferability, improvement of dyeing and the like, and 0.05 to 1 % by weight of a hydrophilic thickening substance such as sodium alginate, as a migration inhibitor, may be pad-dried on a cloth. In the case of printing of an acidic dye, a mixed liquid containing 0.5 to 5 % by weight of an acid ammonium salt as a dyeing promotion agent, such as ammonium sulfate, ammonium tartrate and the like and 0.05 to 0.5 % by weight of acid-resistant natural gums as a migration inhibitor may be pad-dried. However, the present invention is characteristic in that these material pre-treatments are not required usually.

[0059] As the conditions of a dye fixing treatment by steaming and the like effected under condition of close contact of a printed paper to a cloth or the like, the same conditions for a dye fixing treatment by steaming and the like adopted in usual direct printing methods can be adopted as they are. For example, when the dye is a reactive dye, the same conditions as for steaming at 100 to 105°C for 5 to 20 minutes according to a single-phase steam fixing method can be adopted and in the case of an ink receiving layer containing no alkali, the same conditions as for steaming according to a two-phase method (for example, cold fix method and the like) can be adopted. When the dye is an acidic dye, a steaming treatment can be carried out at 100 to 105°C for 10 to 30 minutes. When a paper is peeled from a material, paper stripping (peeling of paper) becomes easy if water or moisture is

added after steaming. When the dye is a disperse dye, a HT steaming or dry heat treatment is carried out at 160 to 220°C for 1 to 15 minutes. Though paper peeling is made possible by a dry heat treatment in some cases, peeling becomes easier by adding a small amount of moisture or water after the dry heat treatment.

[0060] After a dye fixing treatment by steaming or the like, a washing treatment, for example, water-washing, soaping, water-washing, or, in the case of a disperse dye, water-washing, reduction cleaning, water-washing, is effected under the same conditions as for conventional transfer printing methods, thereby a fine and dense printed article showing soft texture can be obtained. In the case of a disperse dye, a fine and dense printed article showing excellent texture can be obtained even if washing is omitted.

(EXAMPLES)

[0061] The present invention will be illustrated further in detail by examples below, but the present invention is not limited to these examples. In the example, % means % by weight.

Example 1

[0062] A mixture of 134 g of Poval AP-17 (water-soluble polyvinyl alcohol binder 15% aqueous solution: manufactured by JAPAN VAM & POVAL CO., LTD.), 100 g of HYDRAN AP-20 (aqueous polyester · urethane binder 45% liquid: manufactured by DIC), 20 g of urea, 10 g of dicyandiamide, 30 g of soda ash, 10 g of FD ALGIN BL (manufactured by Furukawa Chemical Industry Co., Ltd.: sodium alginate low viscosity article powder), 86 g of water and 10 g of thickener F (acrylic synthetic glue: manufactured by SANO K.K.) (400 g in total) was stirred thoroughly by a high speed disperser type stirring machine (about 5000 r.p.m.) to obtain a glue (mixed glue liquid) having high viscosity. This mixed glue liquid for making a layer acting as an ink receiving layer and an adhesive layer simultaneously was applied on a paper (manufactured by Nippon Paper Industries Co., Ltd., unbleached kraft paper, 70 g/m², thickness 0.15 mm) by using a coater (manufactured by YOKOYAMA Corporation) and dried. The coated amount (dry weight) of the mixed glue liquid was 38 g/m². As described above, a printing paper for a reactive dye was obtained.

[0063] Next, a reactive dye ink liquid (C. I. Reactive Red 226 10%, polyethylene glycol 5%, glycerin 5%, ε-caprolactam 5%, ion exchanged water 75%) was printed on the above-described printing paper by an ink jet printer (HYPERECO: manufactured by Mutoh Industries Ltd.: on-demand type piezo inkjet printer) and dried, to obtain a printed paper.

[0064] Then, this reactive dye-printed paper and a cotton broad cloth were allowed to contact closely, and heated and pressurized (155°C, 0.4 Mpa, 3 m/min, roller type) to paste the printed paper to the cotton broad cloth. Then,

the cotton broad cloth was subjected to a HT steaming treatment at 105°C for 10 minutes while keeping the printed paper pasted to the cloth. Thereafter, the printed paper was peeled and the peeling was conducted easily. After removal of the printed paper, water-washing, soaping, water-washing and drying were carried out according to ordinary methods. Thus obtained printed cloth was a printed cloth showing soft texture in which a delicate design is dyed finely, fast and densely.

Example 2

[0065] Same procedures as in Example 1 were repeated except that 65g of FD ALGIN BL was used instead of 10 g of FD ALGIN BL, thickener F was not used, the amount of water was increased to 300 to adjust viscosity, and the temperature of pasting the printed paper changed to 140°C. As the result, a printed cloth showing soft texture in which a delicate design is dyed finely, fast and densely same as the printed cloth obtained in Example 1 was obtained.

Example 3

[0066] A mixture of 85 g of NK binder-M-302HN (water-soluble acryl type binder 46% aqueous solution: manufactured by Shin-Nakamura Chemical Co., Ltd.), 134 g of Poval AP-17 (water-soluble polyvinyl alcohol binder 15% aqueous solution: manufactured by JAPAN VAM & POVAL CO., LTD.), 30 g of urea, 10 g of dicyandiamide, 35 g of soda ash, 10 g of FD ALGIN BL (manufactured by Furukawa Chemical Industry Co., Ltd.: sodium alginate low viscosity article powder) and 96 g of water was stirred thoroughly by a high speed disperser type stirring machine (about 5000 r.p.m.) to obtain a glue (a mixed glue liquid) having high viscosity. This mixed glue liquid for making a layer acting as an ink receiving layer and an adhesive layer simultaneously was applied on an inorganic coated paper (manufactured by Mishima Paper Co., Ltd., 50 g/m²) by using a coater and dried. The coated amount (dry weight) of the mixed glue liquid was 40 g/m². As described above, a printing paper for a reactive dye was obtained.

[0067] Next, a reactive dye ink liquid (C. I. Reactive Yellow 95 15%, polyethylene glycol 5%, glycerin 5%, ε-caprolactam 5%, ion exchanged water 70%) was printed to make a pattern on the above-described printing paper by an ink jet printer (HYPERECO: manufactured by Mutoh Industries Ltd.: on-demand type piezo inkjet printer) and then dried, to obtain a printed paper.

[0068] Then, this reactive dye-printed paper and Satin fabric of a lyocell fiber (Courtaulds Co. Ltd., Registered Trade Mark "Tencel") were allowed to contact closely, and heated and pressurized (150°C, 0.4 Mpa, 2.5 m/min, roller type) to paste the printed paper to the lyocell fabric. Then, the fabric was subjected to a HT steaming treatment at 105°C for 8 minutes while keeping the printed

paper pasted to the fabric. Thereafter, the printed paper was peeled and the peeling was conducted easily. After removal of the printed paper, water-washing, soaping, water-washing and drying were carried out according to ordinary methods. Thus obtained printed cloth of lyocell fabric shows soft texture and a delicate design, and various fastness thereof such as light fastness, washing fastness and perspiration fastness are grade 4 or better.

Example 4

[0069] A mixture of 200g of Poval AP-17 (water-soluble polyvinyl alcohol binder 15% aqueous solution: manufactured by JAPAN VAM & POVAL CO., LTD.), 100 g of HYDRAN AP-20 (aqueous polyester · urethane binder 45% liquid: manufactured by DIC), 20 g of urea, 10 g of dicyandiamide, 2 g of ammonium sulfate, 15g of FD ALGIN BL (manufactured by Furukawa Chemical Industry Co., Ltd.: sodium alginate) and 53 g of water was stirred thoroughly by a high speed disperser type stirring machine (about 5000 r.p.m.) to obtain a glue (a mixed glue liquid) having high viscosity. This mixed glue liquid for making a layer acting as an ink receiving layer and an adhesive layer simultaneously was applied on a paper (Gintake, manufactured by Nippon Daishowa Paperboard Co., Ltd., 50 g/m²) by using a coater and dried. The coated amount (dry weight) of the mixed glue liquid was 35 g/m². As described above, a printing paper for a disperse dye was obtained.

[0070] Next, a disperse dye ink liquid (C. I. Disperse Blue 60 6%, ethylene glycol 5%, glycerin 15%, nonionic type dispersant 5%, anion type dispersant 5%, ion exchanged water 64%) was printed to make a pattern on the above-described printing paper by an ink jet printer (HYPERECO: manufactured by Mutoh Industries Ltd.: on-demand type piezo inkjet printer) and then dried, to obtain a printed paper.

[0071] Then, this disperse dye-printed paper and Polyester Satin fabric were allowed to contact closely, and heated and pressurized (150°C, 0.4 Mpa, 3 m/min, roller type) to paste the printed paper to the Polyester fabric. Then, the fabric was subjected to a HT steaming treatment at 180°C for 8 minutes while keeping the printed paper pasted to the fabric. Thereafter, the printed paper was peeled and the peeling was conducted easily. After removal of the printed paper, water-washing, reduction cleaning, water-washing and drying were carried out according to ordinary methods. Thus obtained printed cloth of Polyester fabric shows soft texture and a delicate design, and various fastness thereof are grade 4 or better.

Example 5

[0072] Same procedures as in Example 4 were repeated except that Nylon taffeta was used instead of Polyester fabric, an acidic dye ink was used instead of dye ink, and the steaming treatment was conducted at 180°C for 8

minutes to 140 °C. As the result, the printed cloth of Nylon taffeta thus obtained shows soft texture and a delicate design, and is excellent in various fastness such as light fastness, washing fastness and perspiration fastness are.

Example 6

[0073] A mixture of 700g of PLAS COAT RZ-142(water-soluble polyester type binder 25% aqueous solution: manufactured by GOO CHEMICAL CO., LTD.), 10 g of SORBITOZE C-5 (etherified starch: manufactured by AVEBE B.A.), 198g of FD ALGIN BL (manufactured by Furukawa Chemical Industry Co., Ltd.: low viscosity sodium alginate powder), 190g of ENBATEX D-23 (Aluminum silicate derivative: manufactured by Kyoei Kagaku Kogyo Co., Ltd.), 5 g of MICROID ML389 (Silicon Oxide: manufactured by Toyo Chemical), 70 g of dicyandiamide, 85 g of soda ash and 1000 g of water was stirred thoroughly by a high speed disperser type stirring machine (about 5000 r.p.m.) to obtain a glue (a mixed glue liquid) having high viscosity. This mixed glue liquid was applied on a paper (manufactured by Nippon Paper Industries Co., Ltd., bleached kraft paper, 70 g/m², thickness 125 μ m) by using a coater (manufactured by YOKOYAMA Corporation) and dried. The coated amount of the mixed glue liquid was 38 g/m². As described above, a printing paper for a reactive dye was obtained.

[0074] Next, a reactive dye ink liquid (C. I. Reactive Blue 19 15%, polyethylene glycol 5%, glycerin 15%, ε-caprolactam 5%, ion exchanged water 70%) was printed to make a pattern on the above-described printing paper by an ink jet printer (HYPERECO: manufactured by Mutoh Industries Ltd.: on-demand type piezo inkjet printer) and then dried, to obtain a printed paper.

[0075] Then, this reactive dye-printed paper and a Cotton lawn cloth were allowed to contact closely, and heated and pressurized (150°C, 0.4 Mpa, 3 m/min, roller type) to paste the printed paper to the Cotton broad cloth. Then, the Cotton lawn cloth was subjected to a HT steaming treatment at 100°C for 10 minutes while keeping the printed paper pasted to the cloth. Thereafter, the printed paper was peeled and the peeling was conducted easily. After removal of the printed paper, water-washing, soaping, water-washing and drying were carried out according to ordinary methods. Thus obtained printed cloth shows soft texture and a delicate design is dyed finely, fast and densely.

Example 7

[0076] A mixture of 75 g of Poval JP-18 (water-soluble polyvinyl alcohol binder powder: manufactured by JAPAN VAM & POVAL CO., LTD.), 56 g of SORBITOZE C-5 (etherified starch: manufactured by AVEBE B.A.), 30 g of EX-100S (Tamarind gum: manufactured by TOMOE Paste Industry Co. Ltd.), 5 g of Antifoaming agent 104 (manufactured by SANO K.K.), 2 g of NEOSINTOURU

LB (a preservative: manufactured by Sumika Enviro-Science Co. Ltd.) and 2 g of NEOSINTOURU TF-1 (a fungicide: manufactured by Sumika Enviro-Science Co. Ltd.) was stirred thoroughly by a high speed disperser type stirring machine (about 5000 r.p.m.) to obtain a glue (a mixed glue liquid) having high viscosity. This mixed glue liquid was applied on a paper (Gintake, manufactured by Nippon Daishowa Paperboard Co., Ltd., 50 g/m²) by using a coater and dried. The coated amount (dry weight) of the mixed glue liquid was 40 g/m². As described above, a printing paper for a disperse dye was obtained.

[0077] Next, a disperse dye ink liquid (C. I. Disperse Red 86 press cale 4%, ethylene glycol 5%, glycerin 15%, nonionic type dispersant 5%, anion type dispersant 5%, ion exchanged water 66%) was printed to make a pattern on the above-described printing paper by an ink jet printer (HYPERECO: manufactured by Mutoh Industries Ltd.: on-demand type piezo inkjet printer) and then dried, to obtain a printed paper.

[0078] Then, this disperse dye-printed paper and Polyester Satin fabric were allowed to contact closely, and heated and pressurized at 210°C, 0.5 Mpa for 2 minutes with a flat plate press machine to paste the printed paper to the Polyester fabric. Then, the printed paper was peeled with blowing steam to the paper and the peeling was conducted easily. Thus obtained printed cloth of Polyester fabric shows soft texture and a delicate design, and various fastness thereof are grade 4 or better. The printed cloth was then subjected to a reduction cleaning according to an ordinary method, and the washing wastewater was colorless and transparent and no change of the texture was observed. Thus, it is demonstrated that a reduction cleaning can be omitted.

Example 8

[0079] The printed paper obtained in Example 6 was allowed to contact bull leather obtained by a usual single bath chrome tanning method, set on a flat plate press machine HSP-2210 manufactured by HASHIMA Co., Ltd. On the leather, a cotton material which was got wet with water and then strongly squeezed was applied, and pressurized and heated at 120°C, 0.9MPa for 2 minutes, to effect pasting and fixation simultaneously. Then, the printed paper was peeled, and the peeling was conducted easily. Thereafter, it was washed with water and dried. As a result, bull leather dyed finely at high concentration and excellent in texture was obtained. The light resistant fastness was grade 4 to 5, and the moist friction fastness was grade 3 to 4.

(Industrial Applicability)

[0080] The paper printing method of the present invention is applied to all fiber materials and leather materials, and is a transfer printing method which is capable of providing, with good reproducibility, the expression of a fine

printed design which had been conventionally regarded as difficult, under excellent economy and ecology. According to the method of the present invention, a production system which is capable of quickly and efficiently responding to needs of small quantity and large variety production and multiplicity can be constructed. Therefore, the paper printing method of the present invention is a method excellent in environmental compatibility and also in economy and a quality effect, and is a novel printing method contributing significantly to improvement of added value and enlargement of applications of printed fiber products and leather products.

Claims

1. A paper printing method of a fiber material or a leather material comprising a step in which a mixed glue composed of a water-soluble synthetic binder, a natural glue and an auxiliary agent is applied on a base paper and dried to obtain a printing paper and a dye ink is printed on the printing paper to obtain a printed paper, a step in which the above-described printed paper is closely contacted to a fiber material or a leather material and pasted under pressurization and heating, and a step in which the above-described printed paper is subjected to a dye fixing treatment under condition pasted to the above-described fiber material or leather material, then, the printed paper is removed.
2. The paper printing method according to Claim 1 wherein the water-soluble synthetic binder is one or a mixture of two or more selected from the group consisting of water-soluble polyvinyl alcohol binders, water-soluble acrylic binders, water-soluble polyester binders, water-soluble polyether · urethane binders and water-soluble hot melt adhesives.
3. The paper printing method according to Claim 1 or 2 wherein the natural glue is one or a mixture of two or more selected from the group consisting of natural gum glues, cellulose derivatives, starch derivatives, seaweed glues, mineral glues and animal glues.
4. The paper printing method according to any one of Claims 1 to 3 wherein the compounding proportion of the water-soluble synthetic binder to the natural glue is in the range of water-soluble synthetic binder: natural glue = 95:5 to 20:80 (weight ratio) in terms of solid component.
5. The paper printing method according to any one of Claims 1 to 4 wherein the above-described auxiliary agent is one or a mixture of two or more selected from the group consisting of surfactants, thickeners, moisturizing agents, pH regulators, alkaline agents,

deep coloring agents, preservatives, fungicides, de-gassing agents, antifoaming agents and reduction inhibitors.

6. The paper printing method according to any one of Claims 1 to 5 wherein the dye contained in the above-described dye ink is selected from the group consisting of a reactive dye, an acidic dye, a metal complex salt type dye, a direct dye, a disperse dye and a cationic dye. 5
10
7. The paper printing method according to any one of Claims 1 to 6 wherein the above-described dye ink is an aqueous dye ink and the above-described printing is carried out by inkjet printing. 15
8. A printing paper used in the paper printing method according to any one of Claims 1 to 7, obtained by applying a mixed glue composed of a water-soluble synthetic binder, a natural glue and an auxiliary agent to a base paper and then drying the paper. 20
9. A printed paper used in the paper printing method according to any one of Claims 1 to 7, obtained by applying a mixed glue composed of a water-soluble synthetic binder, a natural glue and an auxiliary agent to a base paper and then drying the paper to obtain a printing paper, and printing a dye ink on the printing paper thus obtained and then drying the printing paper. 25
30
10. A fiber material or a leather material which is printed by the above-described paper printing method. 35

35

40

45

50

55

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2925562 B [0006] [0012]
- JP 6287870 A [0006] [0012]
- JP 4058470 B [0007] [0012]
- JP 6270596 A [0007] [0012]