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

(11) EP 2 042 656 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
01.04.2009 Bulletin 2009/14

(21) Application number: **07744891.8**

(22) Date of filing: **07.06.2007**

(51) Int Cl.:
D21H 19/36 *(2006.01)* ***D21H 19/38*** *(2006.01)*

(86) International application number:
PCT/JP2007/061563

(87) International publication number:
WO 2007/142302 (13.12.2007 Gazette 2007/50)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK RS

(30) Priority: **07.06.2006 JP 2006159104**
03.08.2006 JP 2006211559
08.09.2006 JP 2006244869
27.03.2007 JP 2007080402
05.06.2007 JP 2007149476

(71) Applicant: **Nippon Paper Industries Co., Ltd.**
Tokyo 114-0002 (JP)

(72) Inventors:
- **KOYAMOYO, Hiroshi**
  Tokyo 114-0002 (JP)
- **KUTSUWA, Koji**
  Tokyo 114-0002 (JP)
- **OKAMOTO, Masashi**
  Tokyo 114-0002 (JP)
- **KAI, Hidehiko**
  Tokyo 114-0002 (JP)
- **OKOMORI, Koji**
  Tokyo 114-0002 (JP)
- **OCHI, Takashi**
  Tokyo 114-0002 (JP)
- **ISHIBASHI, Noriyuki**
  Tokyo 163-1113 (JP)
- **HAYASHI, Nobumasa**
  Tokyo 163-1113 (JP)

(74) Representative: **Hamer, Christopher K. et al**
Mathys & Squire LLP
120 Holborn
London
EC1N 2SQ (GB)

(54) CAST-COATED PAPER

(57) The present invention aims to provide a cast-coated paper having good coated paper quality and printability combined with the property of decomposing hazardous substances upon exposure to light.

A cast-coated paper prepared by applying a cast-coating layer based on a pigment and a binder on a base paper and finished by pressing the cast-coating layer in the wet state against a heated cast drum surface and drying it, wherein the cast-coating layer contains 1 - 30 parts by weight of titanium dioxide having an average secondary particle diameter of 300 - 2000 nm per 100 parts by weight of the pigment and the titanium dioxide is premixed with a silica sol or alumina sol at a ratio of the titanium dioxide to the silica sol or alumina sol of 2: 1 - 1:2.

EP 2 042 656 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to cast-coated paper having excellent coating runnability and good printability by keeping a proper friction coefficient, and also having an excellent air-cleaning effect.

BACKGROUND ART

[0002] Titanium dioxide is gaining the spotlight in line with a growing desire to eliminate hazardous substances in everyday life such as offensive odors as an interest in the living environment rises. Titanium dioxide has been conventionally used as a pigment having excellent opacity and brightness for papermaking, and fine particles of titanium dioxide are known to use light energy to induce redox reactions, thereby decomposing various hazardous substances in the air, so that techniques for supporting them on paper are under development in order to capitalize on this phenomenon. For example, a photocatalytic paper as a filler a water-soluble polymer and a photocatalytic material such as titanium dioxide has been disclosed (see patent document 1), but it cannot be said that the incorporation of a photocatalytic material in paper layers is efficient and sufficiently effective because such a material produces its catalytic effect by exposure to light. Moreover, the resulting color print quality such as ink adhesion, print gloss or print clarity is not sufficient. Printing sheets coated with a coating containing fine powder of titanium dioxide complexed with an inorganic binder such as silica sol and further bound by an organic adhesive have also been disclosed (see patent documents 2 and 3). However, papers coated with a mixed coating of titanium dioxide and silica sol suffered from poor coating runnability because the particle diameters of titanium dioxide and silica sol were so small that the viscosity of the coating color extremely increased. They also had the disadvantage that they could not achieve desired quality such as high sheet gloss and print gloss, print uniformity and surface strength because of the insufficient coverage by the coating. Moreover, even if a photocatalytic effect was conferred on common printing papers such as uncoated paper, lightweight coated paper and woodfree coated paper used for printing texts in insert, magazines, catalogs, etc., it was difficult to sufficiently produce the photocatalytic effect because they were not often used in environments where they were exposed to light. On the other hand, it would be desirable to confer a photocatalytic effect on cast-coated papers characterized by high sheet gloss and print gloss because they are often used in environments where they are exposed to a lot of light, such as in the covers of magazines and posters, i.e., preferred environments where photocatalytic papers should be used. However, it was difficult to prepare a cast-coated paper having an excellent air-cleaning effect by simply using photocatalytic titanium dioxide in conventional formulations or processes because runnability or productivity decreased with changes in the coatings properties or it was difficult to achieve sufficient sheet gloss and good printing quality.

Patent document 1: JPA HEI-10-226983.
Patent document 2: JPA 2000-129595.
Patent document 3: JPA HEI-11-117196.

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0003] In view of these circumstances, an object of the present invention is to provide a cast-coated paper having good coated paper quality and printability combined with the property of decomposing hazardous substances upon exposure to light.

MEANS FOR SOLVING THE PROBLEMS

[0004] As a result of careful studies to achieve the above object, we found that a cast-coated paper having high print gloss and good print uniformity combined with the property of decomposing hazardous substances and odor components upon exposure to light can be obtained by providing a cast-coated paper prepared by applying a cast-coating layer based on a pigment and a binder on a base paper and finished by pressing the cast-coating layer in the wet state against a heated specular drum surface and drying it, wherein the cast-coating layer contains 1 - 30 parts by weight of titanium dioxide having an average secondary particle diameter of 300 - 2000 nm per 100 parts by weight of the pigment. Moreover, a good balance between the printing quality such as good coating runnability, excellent print gloss, print uniformity or surface strength and the photocatalytic effect can be attained by including 5 - 40 parts by weight of an organic binder per 100 parts by weight of the pigment in the cast-coating layer, in which the organic binder includes 50% by weight or more of a copolymer latex. The copolymer latex preferably has a glass transition temperature of -20

to 40˚C. In the present invention, a cast-coated paper in which the deterioration of the paper due to decomposition reaction of the photocatalyst and the deterioration of printing quality due to decomposition of ink components or the like are further reduced and which has good printability can be prepared by premixing titanium dioxide with a silica sol or alumina sol at a ratio of titanium dioxide to silica sol or alumina sol of 2:1 1:2.

ADVANTAGES OF THE INVENTION

[0005] According to the present invention, a cast-coated paper having high sheet gloss typical of cast-coated paper, good printing quality such as print gloss, print uniformity and surface strength, and good printability by keeping a proper friction coefficient, combined with the property of decomposing hazardous substances upon exposure to light and good coating runnability can be obtained.

PREFERRED EMBODIMENTS OF THE INVENTION

[0006] In the present invention, it is important that the pigment included in the cast-coating solution partially contains a specific proportion of fine particles of titanium dioxide having a photocatalytic effect and an average secondary particle diameter of 300 - 2000 nm, preferably 500 - 1500 nm, more preferably 700 - 1300 nm, in order to confer an air-cleaning effect on the cast-coated paper. Titanium dioxide per se has a photocatalytic effect irrespective of the particle diameter. If the average secondary particle diameter is less than 300 nm, the dispersibility of the titanium dioxide slurry decreases and the viscosity of the coating extremely increases to reduce the productivity, and moreover, titanium dioxide falls off to impair the printing quality, printability and photocatalytic function. If the average secondary particle diameter exceeds 2000 nm, however, the smoothness of the coated paper decreases and therefore, printing quality deteriorates. Titanium dioxide preferably has a primary particle diameter of 5 - 100 nm, more preferably 10 - 50 nm, still more preferably 10-35 nm. If the primary particle diameter is less than 5 nm, the dispersibility of the titanium dioxide slurry and the flowability of the coating tend to decrease, thus impairing printing quality and printability. If it exceeds 100 nm, the surface area decreases so that the photocatalytic effect tends to be insufficient.

[0007] Fine particles of titanium dioxide can have the property of decomposing hazardous substances in the air upon exposure to light. The proportion of titanium dioxide is 1 - 30 parts by weight, preferably 5 - 25 parts by weight, more preferably 5 - 20 parts by weight per 100 parts by weight of the pigment. If the proportion of titanium dioxide is less than 1 part by weight, the amount of the photocatalyst is too small to achieve a sufficient air-cleaning effect. In the present invention, it is important to use fine particles of titanium dioxide having a high photocatalytic effect, but fine particles of titanium dioxide have very high viscosity so that they form a slurry with very low solids content when they are used in a coating. Therefore, if the proportion exceeds 30 parts by weight, an air-cleaning effect is obtained, but the solids content of the coating extremely decreases so that it becomes difficult to apply it at a certain coating weight or more and also difficult to obtain high sheet gloss and the resulting paper has poor print uniformity, surface strength and chalking resistance when compared at a coating weight used in conventional cast-coated papers. The chalking resistance refers to the resistance to dusting by photodecomposition and deterioration of the coating layer surface and the base paper layer after exposure to light. The titanium dioxide particles in the present invention can be prepared from not only titanium dioxide but also any titanium oxide or hydroxide called hydrous titanium dioxide, hydrated titanium dioxide, metatitanic acid, orthotitanic acid, and titanium hydroxide. In addition to conventional UV-activatable photocatalysts, visible light-activatable photocatalysts showing a photocatalytic effect in response to visible light can also be used. The titanium dioxide used in the present invention preferably has a specific surface area of 10 - 350 m^2/g. The titanium dioxide of the present invention can also be mixed with a silica sol or alumina sol so that the fine particles of titanium dioxide are covered with the silica sol or alumina sol having an inorganic binder function, thereby reducing the deterioration of the paper due to decomposition reaction of the photocatalyst, and further reducing the deterioration of printing quality due to decomposition of ink components or the like. The ratio between titanium dioxide and an inorganic binder consisting of a silica sol or alumina sol is in the order of 5:1 - 1:5, preferably 2:1 - 1:2, more preferably 2:1 - 1:1.5 expressed in polymerization ratio. If the ratio of titanium dioxide is much higher than 5:1, the paper tends to deteriorate due to decomposition of organic binders or pulp fibers in the coating or the printing quality tends to deteriorate due to decomposition of ink components in printed matters or the like. If the ratio of titanium dioxide is much lower than 1:5, the static friction coefficient of the paper significantly increases to invite a paper jam by multiple sheet feeding during printing, resulting in poor printability. In terms of light transmission, a silica sol is preferably used. In order to efficiently cover fine particles of titanium dioxide during the preparation of the coating color, it is preferable to mix titanium dioxide and a colloidal silica or alumina solution at a predetermined ratio, and stir the mixture for a predetermined period, and then add other pigments and auxiliaries. In the present invention, a mixture of inorganic binders of a silica sol and an alumina sol can also be mixed with titanium dioxide.

[0008] The cast-coated paper can be used to prepare a quality appearance tissue carton having high sheet gloss, but the surface of the cast-coated paper may be damaged by friction during the conversion into the carton. In this case,

damages to the tissue carton are improved by including preferably 5 parts by weight or more, more preferably 5-50 parts by weight or more of the silica sol per 100 parts by weight of the pigment. This is important for improving the appearance of tissue boxes as final products. For use in cartons, the ratio between titanium dioxide and an inorganic binder consisting of a silica sol or alumina sol is also in the order of 5:1 - 1:5, preferably 2:1 - 1:2, more preferably 2:1 - 1:1.5 expressed in polymerization ratio to prevent the deterioration of paper or printing quality or to ensure high printability.

[0009] In the present invention, the cast-coating layer can also contain one or more other pigments as appropriate selected from those conventionally used for preparing coated papers, including inorganic pigments such as kaolin, clay, delaminated clay, ground calcium carbonate, precipitated calcium carbonate, talc, titanium dioxide, barium sulfate, calcium sulfate, zinc oxide, silicic acid, silicates, colloidal silica and satin white, as well as organic pigments such as plastic pigments. In the present invention, it is preferable to use kaolin preferably in an amount of 10 parts by weight or more, more preferably 40 parts by weight or more per 100 parts by weight of the pigment, in order to improve the photocatalytic effect, sheet uniformity and sheet gloss.

[0010] In the present invention, the cast-coating layer contains 5-40 parts by weight, preferably 8-40 parts by weight, more preferably 8-30 parts by weight, especially 10-20 parts by weight of an organic binder per 100 parts by weight of the pigment. If the proportion of the organic binder is less than 5 parts by weight, sufficient surface strength cannot be achieved and the suitability for carton processing tends to decrease. However, more than 40 parts by weight are not preferred because the consistency of the coating decreases to invite productivity problems such as difficulty in controlling the coating weight, high drying load and low coating speed or titanium dioxide is covered by the binders, thereby reducing the air-cleaning effect. In terms of the air-cleaning effect, the organic binders are preferably contained at lower proportions. The binder used in the present invention can be selected as appropriate from one or more of organic binders conventionally used for coated papers, e.g., synthetic binders such as various copolymer latexes including styrene-butadiene copolymers, styrene-acrylic copolymers, ethylene-vinyl acetate copolymers, butadiene-methyl methacrylate copolymers and vinyl acetate-butyl acrylate copolymers, or polyvinyl alcohols, maleic anhydride copolymers and acrylic-methyl methacrylate copolymers; proteins such as casein, soybean protein and synthetic proteins; starches such as oxidized starches, cationized starches, urea phosphate-esterified starches and etherified starches such as hydroxyethyl etherified starches; and cellulose derivative binders such as carboxyethyl cellulose, hydroxyethyl cellulose and hydroxymethyl cellulose, provided that a copolymer latex is contained at preferably 50% by weight or more, more preferably 50-90% by weight, still more preferably 60-90% by weight or more of the total organic binder composition. If the proportion of the copolymer latex is less than 50% by weight, it becomes difficult to achieve high sheet gloss typical of cast-coated paper and the photocatalytic effect tends to decrease. If it exceeds 90% by weight, the productivity tends to decrease due to sticking to the casting drum. The copolymer latex used preferably has a glass transition temperature of -20 to 40˚C, more preferably -20 to 30˚C, still more preferably -10 to 30˚C. If the glass transition temperature exceeds 40˚C, sufficient surface strength to usable printing cannot be attained. If the glass transition temperature is less than -20˚C, the photocatalytic effect tends to be insufficient or the runnability tends to decrease due to sticking to rolls such as the casting drum. In the case of copolymer latexes having different glass transition temperatures in particles such as core-shell latexes, the shell layer (surface layer) preferably has a glass transition temperature in the range defined above and the core layer (inside layer) preferably has a glass transition temperature lower than that of the shell layer (surface layer). The copolymer latex preferably has a particle diameter of 50 - 250 nm to ensure printing quality and surface strength. Water-soluble polymer binders such as starches are preferably present at 10 parts by weight or less.

[0011] In addition to the pigments and binders described above, various additives can be used as appropriate in the cast coating layer, including ammonium salts or metal salts of inorganic or organic acids such as sodium chloride, ammonium chloride, zinc chloride, magnesium chloride, sodium sulfate, potassium sulfate, ammonium sulfate, zinc sulfate, magnesium sulfate, ammonium nitrate, monobasic sodium phosphate, ammonium phosphate, calcium phosphate, sodium polyphosphate, sodium hexametaphosphate, sodium formate, ammonium formate, sodium acetate, potassium acetate, sodium monochlorate, sodium malonate, sodium tartrate, potassium tartrate, sodium citrate, potassium citrate, sodium lactate, sodium gluconate, sodium adipate, and sodium dioctylsulfosuccinate; and methyl amine, diethanolamine, diethylene triamine, diisopropyl amine, etc. In addition, various auxiliaries included in typical coating compositions for coated papers such as dispersants, thickeners, water-retention agents, antifoamers, colorants, mold release agents, fluidity modifiers, insolubilizers, preservatives and printability improving agents are used as appropriate.

[0012] The base paper for the cast-coated paper of the present invention contains conventional pulp, fillers, etc. In the present invention, the type or the like of pulp contained in the base paper is not specifically limited. For example, hardwood kraft pulp (hereinafter referred to as LBKP), softwood kraft pulp (hereinafter referred to as NBKP), thermomechanical pulp, groundwood pulp, recycled pulp and the like are used. The pulp preferably contains 60% by weight or less of mechanical pulp in the total pulp composition, most preferably wholly consists of chemical pulp in terms of printing quality because papers excessively containing mechanical pulp or deinking paper pulp derived from mechanical pulp deteriorate and discolor upon exposure to light.

[0013] Fillers that can be used in the base paper include known fillers such as ground calcium carbonate, precipitated calcium carbonate, kaolin, clay, talc, hydrated silica, white carbon, titanium deoxide, synthetic resin fillers, etc. The fillers

are used in an amount of about 1 - 30% by weight, preferably 3 - 20% by weight based on the pulp weight. The base paper can be prepared from the stock optionally containing chemicals conventionally used in papermaking processes, such as paper strength enhancers, sizing agents, antifoamers, colorants, softening agents, bulking agents (density reducing agents) or the like in the range not inhibiting the advantages of the present invention.

[0014] The process for preparing the base paper is not specifically limited, and the base paper may be prepared by any process for making acidic, neutral or alkaline papers using e.g., a Fourdrinier paper machine including a top wire or the like or a cylinder paper machine and may also be a wood containing base paper containing mechanical pulp as a matter of course. The base paper may be coated with a surface-treating agent based on a water-soluble polymer for the purpose of improving surface strength or sizing performance. Suitable water-soluble polymers include those commonly used as surface-treating agents such as oxidized starches, hydroxyethyl etherified starches, enzyme-modified starches, polyacrylamides and polyvinyl alcohols, and they can be used alone or as mixtures thereof. In addition to the water-soluble polymers, the surface-treating agents can contain paper strength enhancers intended for waterproofing and improving surface strength and external sizing agents intended for conferring sizing effect. The surface-treating agents can be applied by using coater such as film transfer roll coater, e.g., two-roll size press coater, gate roll coater, blade metering size press coater, rod metering size press coater, and Sym-Sizer. In the present invention, base papers coated with not only such a surface-treating agent but also a coating color containing a pigment and a binder used for conventional coated papers using any one of the coaters mentioned above or base papers coated with the coating color using a blade coater, roll coater, air knife coater or the like after the surface-treating agent is applied and dried can also be used as base papers for cast coating. In these cases, the coating weight is desirably about 5-30 g/m^2 in dry weight per side. The base paper can be coated on either one side or both sides depending on the purpose. The wet coating layer is dried by using various types of dryers such as a steam cylinder, hot air dryer, gas heater dryer, electric heater dryer, infrared heater dryer or the like alone or in combination. The coated paper is typically dried to a paper moisture in a range of about 1-10%, desirably in a range of about 2-7%, depending on the type of the base paper, the type of the composition to be applied and other factors. The precoated base paper may be smoothed in advance in a supercalender, soft calender or the like, if desired.

[0015] Suitable base papers to be cast-coated are base papers having a basis weight of about 25 - 600 g/m^2 for use in conventional coated papers and coated paperboards, preferably 50 - 200 g/m^2 for coated papers, and 230 - 500 g/m^2 for coated paperboards.

[0016] A cast coating composition prepared can be applied on a base paper by using known coaters such as film transfer roll coaters, e.g., two-roll size press coaters, gate roll coaters, blade metering size press coaters, rod metering size press coaters, Sym-Sizers, JF sizers; flooded nip/blade coaters, jet fountain/blade coaters, short dwell time applicator type coaters; rod metering coaters using a grooved rod, plain rod or the like in place of a blade; air knife coaters, curtain coaters or die coaters; preferably at a coating weight of 5-30 g/m^2, more preferably 10-25 g/m^2 per side of the base paper. After applying a cast coating layer, it is cast-finished. Cast-finishing methods include the direct method in which a coating layer is cast-finished in the wet state; the gel casting method in which a coating layer in the wet state is gelled and then cast-finished; the rewet cast coating method in which a coating layer in the wet state is once dried and then rewetted with a rewetting liquid and cast-finished, etc., among which the rewet cast coating method is preferred in terms of a photocatalytic effect. Either one side or both sides can be cast-finished depending on the purpose. The surface temperature of the heated specular drum is preferably 100˚C or more during cast-finishing.

[0017] The present invention is remarkably effective in cast-coated papers having a sheet gloss of 80% or more, preferably 85-98% as determined according to JIS-P8142. If the sheet gloss increases, the structure of the coating layer becomes dense, which in turn reduces the probability that the photocatalyst in the coating layer comes into contact with hazardous components in the air, thereby reducing the air-cleaning effect. However, the process of the present invention allows even cast-coated papers having high sheet gloss to show an excellent air-cleaning effect and good printability.

[0018] In the present invention, the cast-coated papers or cast-coated paperboards described above can also be used to prepare tissue cartons and tissue boxes.

[0019] Next, processes for converting the coated papers as described above into tissue cartons and tissue boxes are described below.

[0020] Tissue as used herein refers to sanitary papers such as facial tissue, toilet tissue, paper towels and table napkins as well as paper or nonwoven wipers.

[0021] Tissue cartons are prepared by, but not specifically limited to, the process described below, for example. Printing and conversion of white board are reviewed in "White board and paper containers", 1995, pp. 153-167 published by Shigyo Times Sha Co., Ltd.

[0022] An example of the preparation of a tissue box from a base paper for tissue carton (coated paper) is explained. A picture for enhancing the appearance during the use as a tissue box by consumers, directions for use, the brand name, quality description, the JAN code, an appeal of product characteristics and other information are printed on a base paper for tissue carton having a basis weight of 230 g/m^2 to 640 g/m^2 prepared by the process described above. Printing methods that can be used mainly include offset lithographic printing, intaglio gravure printing, etc., as well as

UV printing, silkscreen stencil printing, flexographic relief printing, and hot stamping by which foil films are transferred under heat and pressure. Hot stamping allows foil films of gold, silver or the like to be applied as printed layers.

[0023] The printed area of the tissue carton is preferably 1-80%, more preferably 1-50% per area exposed to light, because the air-cleaning effect and deodorizing effect of the photocatalytic tissue carton tend to decrease by ink layers and printed film layers. The tissue carton may be glazed or varnished during the preparation, but this step may be omitted because it tends to make the photocatalytic effect insufficient.

[0024] The tissue carton intermediate after printing is die cut. The die cutting process comprises the steps of die cutting the intermediate into the shape of the developed view of a box, forming a perforating line for removal, and drawing ruled lines for folding the box. The die cutting process may further comprise embossing for decorative purpose.

[0025] A polyethylene film with a slit is then adhered to the tissue carton intermediate with a vinyl acetate, EVA binder or the like using a window patcher after the die cutting process. The present invention may also include tissue boxes without a polyethylene film similar to many such tissue boxes on the market in view of the environmental issue of waste reduction.

[0026] Then, the tissue carton intermediate with or without a polyethylene film is glued and folded by a sack-making machine to prepare a tissue carton. Thus prepared tissue carton is fed to a cartoning step. During the cartoning step, the tissue carton is fed by a processing machine called cartoner and raised to fill tissue paper such as facial tissue from the side face of the tissue carton, then sealed with a binder and pressed to give a tissue box containing tissue paper.

[0027] The contents of the tissue box in the present invention include sanitary papers such as facial tissue, toilet tissue, paper towels and table napkins as well as paper or nonwoven wipers for domestic, business and industrial uses, which may be in the form of V-, C- or Z-folded sheets or rolls.

Figure 1 shows an example of a tissue box prepared in this manner, in which the area of A, B, C, D and E sides of the tissue box shown in Figure 1 (i.e., the sides effectively exposed to sunlight, fluorescent light, incandescent light, etc.) is preferably 400 cm^2 to 2,000 cm^2 from the viewpoint of practical use, air-cleaning effect and deodorizing effect.

[0028] The following examples further illustrate the present invention without, however, limiting the invention thereto as a matter of course. Unless otherwise specified, parts and % in the examples mean parts by weight and % by weight, respectively. Performance during the preparation of base papers for tissue cartons consisting of cast-coated papers and during the conversion from the tissue cartons into tissue boxes was tested by the evaluation methods as shown below.

EXAMPLES

[0029] The following examples further illustrate the present invention without, however, limiting the invention thereto as a matter of course. Unless otherwise specified, parts and % in the examples mean parts by weight and % by weight, respectively. Coating solutions and the resulting cast-coated papers were tested by the evaluation methods as shown below.

(Evaluation methods)

[0030]

(1) Particle size analysis of titanium dioxide: calculated from scanning electron micrographs.

[0031] A thin layer of a slurry of fine particles of titanium dioxide was applied on a sample mount for electron microscopy and dried in a dryer set at 40˚C. Then, microphotographs of the particles were taken at a magnification of 10000x using FE-SEM (Field Emission Scanning Electron Microscope JSM-6700F available from JEOL Ltd.) and observed and analyzed. The average of the measured diameters of agglomerates of 100 particles was reported as average secondary particle diameter.

(2) Cast coating runnability: determined from troubles such as sticking of the cast-coated paper to the cast drum and staining on the cast drum during cast coating.

◎: No trouble such as sticking to the casting drum and staining on the casting drum occurs.
○: Little trouble such as sticking to the casting drum and staining on the casting drum occurs.
▲: Some trouble such as sticking to the casting drum and staining on the casting drum occurs.
×: Troubles such as sticking to the casting drum and staining on the casting drum occur so that cast-coated paper with good quality cannot be produced.

(3) Sheet gloss: determined at an angle of 75˚ according to JIS P 8142: 1998.
(4) Sheet uniformity: visually evaluated from gloss ununiformity or the like on the surface of the cast-coated paper.

◎: very good, ○: good, ▲: slightly poor, ×: poor.

(5) Surface strength: visually evaluated according to the 4-class scale by comparing the dry pick strength in an RI-II print tester using SMX tack grade 20 (black) ink available from Toyo Ink Mfg. Co., Ltd. ◎: very good, ○: good, ▲: slightly poor, ×: poor.

(6) Printing runnability: evaluated according to the 4-class scale by comparing the jamming frequency caused by multiple sheet feeding during printing in a Roland sheetfed press at a printing speed of 8000 sheets/hr. ◎: no jamming with no multiple sheet feeding, ○: multiple sheet feeding slightly appears, but no jamming occurs, ▲: multiple sheet feeding appears and some jamming occurs, ×: multiple sheet feeding appears and jamming frequently occurs.

(7) Photocatalytic effect: evaluated according to the photocatalyst performance evaluation test method II b "gas bag B- method" defined by the Photocatalyst Product Technology Council. The degree of acetaldehyde decomposition (%) was determined after UV irradiation for 20 hours and evaluated according to the 4-class scale. ◎: very good (decomposition degree: 70% or more), o: slightly good (69 - 50%), ▲: slightly poor (49% - 10%), ×: significantly poor (10% or less).

[Example 1]

[0032] In a Cellier mixer, 10 parts (solids) of slurry A of fine particles of titanium dioxide (CSB-M from Sakai Chemical Industry, Co., Ltd.; primary particle diameter 20 - 30 nm, average secondary particle diameter 1000 nm) and 10 parts of colloidal silica (Snowtex 40 from Nissan Chemical Industries, Ltd.) were stirred for 1 hr (titanium dioxide: colloidal silica = 1:1). Into this mixture was added a pigment slurry prepared from a pigment consisting of 60 parts of No.1 grade kaolin (available from Engelhard under trade name UW-90) and 30 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.) dispersed with 0.2 parts of sodium polyacrylate in a Cellier mixer to prepare a pigment slurry having a solids content of 60%. To this were added 0.5 parts of a defoaming agent (San Nopco 1407 from San Nopco Limited), 5 parts of a releasing agent (Nopcote C104 from San Nopco Limited), 15 parts of styrene-butadiene copolymer latex A (glass transition temperature -10˚C, particle diameter 190 nm) and 7 parts of casein as binders (latex proportion: 68%) and water to give a coating color having a solids content of 50%. The coating solution was applied on one side of a base paper having a basis weight of 100 g/m^2 and containing 100 parts of chemical pulp and 12 parts of precipitated calcium carbonate as a filler at a coating weight of 20 g/m^2 using a blade coater and dried. Thus obtained coated paper was rewetted on the surface of the coating layer with a rewetting liquid (0.5% polyethylene emulsion) and then passed through a press nip consisting of a forming roll and a casting drum so that it was pressed against the casting drum at a surface temperature of 115˚C at a speed of 100 m/min and dried, after which it was stripped off the casting drum using a strip-off roll to give a cast-coated paper by rewet cast coating.

[Example 2]

[0033] A cast-coated paper was obtained by the same procedure as in Example 1 except that 10 parts (solids) of titanium dioxide slurry A, 10 parts of colloidal silica, 60 parts of first grade kaolin (available from Engelhard under trade name UW-90) and 30 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.) in the coating solution in Example 1 were replaced by 20 parts (solids) of the titanium dioxide slurry, 20 parts of colloidal silica, 50 parts of kaolin (available from J.M.Huber under trade name Japangloss) and 30 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.).

[Example 3]

[0034] A cast-coated paper was obtained by the same procedure as in Example 1 except that 15 parts of styrene-butadiene copolymer latex A (glass transition temperature -10˚C, particle diameter 190 nm) and 7 parts of casein (latex proportion: 70%) in the coating solution in Example 1 were replaced by 19 parts of styrene-butadiene copolymer latex A (latex proportion: 100%).

[Example 4]

[0035] A cast-coated paper was obtained by the same procedure as in Example 1 except that styrene-butadiene copolymer latex A (glass transition temperature -10˚C) in Example 1 was replaced by styrene-butadiene copolymer latex B (glass transition temperature -23˚C).

[Example 5]

[0036] A cast-coated paper was obtained by the same procedure as in Example 1 except that 15 parts of styrene-

butadiene copolymer latex A (glass transition temperature -10˚C, particle diameter 190 nm) and 7 parts of casein (latex proportion: 70%) in the coating solution in Example 1 were replaced by 6 parts of styrene-butadiene copolymer latex A (glass transition temperature -10˚C, particle diameter 190 nm), 12 parts of casein and 12 parts of polyvinyl alcohol (available from Kuraray under trade name PVA117) (latex proportion: 20%).

[Example 6]

[0037] The cast coating in Example 1 was applied at a coating weight of 20 g/m^2 per side using a reverse roll coater provided on a cast coater, and then the wet coating layer was gelled by contact with a gelling solution consisting of an aqueous calcium formate solution (10%), and the coated paper having thus gelled coating layer was passed through a press nip consisting of a forming roll and a casting drum so that it was pressed against the casting drum at a surface temperature of 115˚C at a speed of 70 m/min and dried, after which it was stripped off the casting drum using a strip-off roll to give a cast-coated paper by gel cast coating.

[Example 7]

[0038] A cast-coated paper was obtained by the same procedure as in Example 6 except that a cast coating was used in which 60 parts of first grade kaolin (available from Engelhard under trade name UW-90) and 30 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.) in the coating solution in Example 6 were replaced by 70 parts of engineered kaolin (available from Engelhard under trade name Eclipse 650) and 20 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.).

[Example 8]

[0039] A cast-coated paper was obtained by the same procedure as in Example 1 except that 10 parts of titanium dioxide slurry A, 10 parts of colloidal silica, 60 parts of No.1 grade kaolin (available from Engelhard under trade name UW-90) and 30 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.) in the coating solution in Example 1 were replaced by 10 parts of the titanium dioxide slurry, 16 parts of colloidal silica (titanium dioxide colloidal silica = 1:1.6), 60 parts of kaolin (available from J.M.Huber under trade name Japangloss) and 30 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.).

[Comparative example 1]

[0040] A cast-coated paper was obtained by the same procedure as in Example 1 except that 10 parts of the titanium dioxide slurry, 10 parts of colloidal silica, 60 parts of kaolin (available from Engelhard under trade name UW-90) and 30 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.) in the coating solution in Example 1 were replaced by 70 parts of kaolin (available from Engelhard under trade name UW-90) and 30 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.).

[Comparative example 2]

[0041] A cast-coated paper was obtained by the same procedure as in Example 1 except that 10 parts of the titanium dioxide slurry, 10 parts of colloidal silica, 60 parts of kaolin (available from Engelhard under trade name UW-90) and 30 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.) in the coating solution in Example 1 were replaced by 40 parts of the titanium dioxide slurry, 40 parts of colloidal silica, 40 parts of kaolin (available from Engelhard under trade name UW-90) and 20 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.).

[Comparative example 3]

[0042] A cast-coated paper was obtained by the same procedure as in Example 1 except that 10 parts of titanium dioxide slurry A in the coating solution in Example 1 was replaced by 10 parts of slurry B of fine particles of titanium dioxide (STR-60N from Sakai Chemical Industry, Co., Ltd.; primary particle diameter 40 - 50 nm, average secondary particle diameter 2500 nm).

[0043] The results are shown in Table 1.

[0044]

Table 1

	Pigments			Organic binders					Evaluation					
	Titanium dioxide, parts	Kaolin, parts	Precipitated calcium carbonate, parts	Casein, parts	Latex, parts	PVA, parts	Latex prop%	Type of latex	Sheet gloss	Sheet uniformity	Surface strength	Photocatalytic effect	Coating runnability	Print runnability
Example 1	A10	60	30	7	15	0	68	A	91	◎	◎	◎	◎	◎
Example 2	A20	50	30	7	15	0	68	A	88	○	○	◎	○	○
Example 3	A10	60	30	0	19	0	100	A	92	◎	◎	◎	○	◎
Example 4	A10	60	30	7	15	0	68	B	91	○	◎	○	○	◎
Example 5	A10	60	30	12	6	12	20	A	86	○	◎	○	◎	◎
Example 6	A10	60	30	7	15	0	68	A	93	◎	○	○	○	◎
Example7	A10	Engineered 70	20	7	15	0	68	A	93	◎	○	◎	○	○
Example 8	A10	60	30	7	15	0	68	A	91	◎	◎	◎	◎	○
Comparative example 1	0	70	30	7	15	0	68	A	93	◎	○	×	◎	◎
Comparative Example 2	A40	40	20	7	15	0	68	A	81	×	×	◎	▲	×
Comparative example 3	B10	60	30	7	15	0	68	A	84	○	○	▲	◎	◎

Next, preparation examples of tissue cartons and tissue boxes using cast-coated papers are shown.

[Example 9]

[0045] In a Cellier mixer, 10 parts (solids) of slurry A of fine particles of titanium dioxide (CSB-M from Sakai Chemical Industry, Co., Ltd.; primary particle diameter 20 - 30 nm, average secondary particle diameter 1000 nm) and 16 parts of colloidal silica (Snowtex 40 from Nissan Chemical Industries, Ltd.) were stirred for 1 hr. Into this mixture was added a pigment slurry prepared from a pigment consisting of 60 parts of No.1 grade kaolin (available from Engelhard under trade name UW-90) and 30 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.) dispersed with 0.2 parts of sodium polyacrylate in a Cellier mixer to prepare a pigment slurry having a solids content of 60%.

[0046] To this were added 0.5 parts of a defoaming agent (San Nopco 1407 from San Nopco Limited), 5 parts of a releasing agent (Nopcote C104 from San Nopco Limited), 15 parts of styrene-butadiene copolymer latex A (glass transition temperature -10˚C, particle diameter 190 nm) and 7 parts of casein as binders (latex proportion: 68%) and water to give a coating color having a solids content of 50%. The coating color was applied on one side of a patent coated board having a basis weight of 430 g/m^2 at a coating weight of 29 g/m^2 using a blade coater and dried. Thus obtained coated paper was rewetted on the surface of the coating layer with a rewetting liquid (0.5% polyethylene emulsion) and then passed through a press nip consisting of a forming roll and a casting drum so that it was pressed against the casting drum at a surface temperature of 115˚C at a speed of 100 m/min and dried, after which it was stripped off the casting drum using a strip-off roll to give a cast-coated paper having a basis weight of 460 g/m^2 by rewet cast coating. This cast-coated paper was used as a base paper for tissue carton.

[0047] The base paper for tissue carton was printed in a printing step (offset printing) to include characters or pictures on sides A, B, C, D and E of a finished tissue box shown in Figure 1. The printed area was 20% of the total area of sides A + B + C + D + E. Then, the base paper was die cut into the shape of the developed view of the box by a die cutter and processed to form a perforating line for removal and ruled lines for folding in E on the face of Figure 1, thereby giving a tissue carton.

[0048] A film was adhered to side E on the reverse side of Figure 1 showing a top view by a window patcher, after which the carton was die cut by a sack-making machine and then folded and pressed with a vinyl acetate binder applied on overlaps in the developed view of the finished box.

[0049] Then, the carton was filled with 200 sheets of facial tissue in a tissue cartoning step (cartoner) to give a tissue-containing box.

[Example 10]

[0050] A tissue-containing box was obtained by the same procedure as in Example 9 except that the cast coating in Example 9 was applied at a coating weight of 30 g/m^2 per side using a reverse roll coater provided on a cast coater, and then the wet coating layer was gelled by contact with a gelling solution consisting of an aqueous calcium formate solution (10%), and the coated paper having thus gelled coating layer was passed through a press nip consisting of a forming roll and a cast drum so that it was pressed against the casting drum at a surface temperature of 115˚C at a speed of 70 m/min and dried, after which it was stripped off the cast drum using a strip-off roll to give a cast-coated paper for use as a base paper for tissue carton by gel cast coating.

[Example 11]

[0051] A cast-coated paper for use as a base paper for tissue carton having a basis weight of 360 g/m^2 was obtained by using a patent coated board having a basis weight of 330 g/m^2 in place of the patent coated board having a basis weight of 430 g/m^2 in Example 9.

[0052] Then, the base paper was printed by offset printing so that the printed area (on sides A, B, C, D and E) represented 40%. Then, the base paper was processed through the steps similar to those subsequent to the printing step in the preparation process of a tissue carton described in Example 9, and filled with toilet tissue in a tissue cartoning step to give a box containing toilet tissue.

[Example 12]

[0053] A tissue-containing box was obtained by the same procedure as in Example 9 except that 10 parts (solids) of slurry A of fine particles of titanium dioxide (CSB-M from Sakai Chemical Industry, Co., Ltd.; primary particle diameter 20 - 30 nm, average secondary particle diameter 1000 nm) and 16 parts of colloidal silica (Snowtex 40 from Nissan Chemical Industries, Ltd.) in Example 9 were replaced by 10 parts (solids) of slurry A of fine particles of titanium dioxide (CSB-M from Sakai Chemical Industry, Co., Ltd.; primary particle diameter 20 - 30 nm, average secondary particle

diameter 1000 nm) and 10 parts of colloidal silica (Snowtex 40 from Nissan Chemical Industries, Ltd.).

[Comparative example 4]

[0054] A cast-coated paper was obtained by the same procedure as in Example 9 except that 10 parts of the titanium dioxide slurry, 16 parts of colloidal silica, 60 parts of kaolin (available from Engelhard under trade name UW-90) and 30 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.) in the coating solution in Example 9 were replaced by 70 parts of kaolin (available from Engelhard under trade name UW-90) and 30 parts of precipitated calcium carbonate (TP121 from Okutama Kogyo Co., Ltd.). This cast-coated paper was used as a base paper for tissue carton to give a tissue-containing box in the same manner as in Example 9.

[0055] The results are shown in Table 2.

(Evaluation methods)

[0056]

(8) Fade test: evaluated from the loss of ISO brightness determined before and 24 hours after UV irradiation (samples were irradiated with a UV black light at an intensity of 2.5 mW/cm^2) .

[0057]

Loss of brightness (%) = (brightness before UV irradiation - brightness after UV irradiation) / brightness before UV irradiation x 100.

(9) Resistance to carton damage: visually evaluated for the resistance to damages to the surface of the coating layer during the conversion from a base paper for carton into a box according to the 4-class scale below: ◎: very good, o: slightly good, A: slightly poor, x: significantly poor.

(10) Transportability of carton: evaluated by comparison for the transportability during the preparation of a tissue carton and during the conversion into a tissue box according to the 4-class scale below: ◎: very good, o: slightly good, ▲: slightly poor, ×: poor.

[0058]

Table 2

	Sheet gloss	Surface strength	Photocatalytic effect	Fade test: brightness loss (%)	Resistance to carton damage	Transportability of carton
Example 9	93	◎	◎	2.7	◎	○
Example 10	95	◎	○	2.8	○	○
Example 11	93	◎	◎	2.7	◎	○
Example 12	94	◎	◎	2.9	◎	◎
Comparative examples 4	96	○	×	6.1	▲	◎

As shown in Table 2, Examples 9 - 12 exhibit high sheet gloss, photocatalytic effect and fade resistance as well as excellent suitability for carton processing such as resistance to carton damage and transportability of carton. In contrast, Comparative example 4 is poor in photocatalytic effect, fade resistance and resistance to carton damage.

Claims

1. A cast-coated paper prepared by applying a cast-coating layer based on a pigment and a binder on a base paper and finished by pressing the cast-coating layer in the wet state against a heated cast drum surface and drying it, wherein the cast-coating layer contains 1 - 30 parts by weight of titanium dioxide having an average secondary particle diameter of 300 - 2000 nm per 100 parts by weight of the pigment.

2. The cast-coated paper of claim 1, **characterized in that** the cast-coating layer contains 5 - 40 parts by weight of an organic binder per 100 parts by weight of the pigment and that the organic binder includes 50% by weight or more of a copolymer latex.

3. The cast-coated paper of claim 1 or 2, **characterized in that** a copolymer latex having a glass transition temperature of -20 to 40˚C is used as a binder in the cast-coating layer.

4. A cast-coated paper prepared by applying a cast-coating layer based on a pigment and a binder on a base paper and finished by pressing the cast-coating layer in the wet state against a heated cast drum surface and drying it, wherein the cast-coating layer contains 1 - 30 parts by weight of titanium dioxide having an average secondary particle diameter of 300 - 2000 nm per 100 parts by weight of the pigment and the titanium dioxide is premixed with a silica sol or alumina sol.

5. The cast-coated paper of claim 4, **characterized in that** the premixing is performed at a ratio of the titanium dioxide to the silica sol or alumina sol of 2:1 - 1:2.

6. The cast-coated paper of any one of claims 1 to 5, which has a sheet gloss of 80% or more on the cast-coated surface as determined according to JIS-P8142.

7. The cast-coated paper of any one of claims 1 to 6, **characterized in that** the titanium dioxide has a primary particle diameter of 5 - 100 nm.

8. The cast-coated paper of any one of claims 1 to 7, **characterized in that** it is cast-finished by the rewet cast coating method in which the coating layer in the wet state is once dried and then rewetted with a rewetting liquid.

9. A tissue carton or a tissue box prepared from the cast-coated paper of any one of claims 1 to 8.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/061563

A. CLASSIFICATION OF SUBJECT MATTER
D21H19/36(2006.01)i, *D21H19/38*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D21H11/00-27/42(2006.01)i, *D21J1/00-7/00*(2006.01)i

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2007
Kokai Jitsuyo Shinan Koho 1971-2007 Toroku Jitsuyo Shinan Koho 1994-2007

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2005-536656 A (International Paper Co.), 02 December, 2005 (02.12.05), Claims; Par. Nos. [0001], [0002], [0011]; examples & WO 2004/018769 A1 & US 2004/197496 A1 & EP 1546457 A1 & US 7018708 B2 & US 2006/159910 A1	1-9
Y	JP 2000-073297 A (Nippon Paper Industries Co., Ltd.), 07 March, 2000 (07.03.00), Claims; Par. Nos. [0015], [0016], [0023] (Family: none)	1-9

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 September, 2007 (10.09.07)	25 September, 2007 (25.09.07)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/061563

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2000-129595 A (Nippon Paper Industries Co., Ltd.), 09 May, 2000 (09.05.00), Claims; Par. Nos. [0011], [0012], [0020] & DE 69917980 T2	1-9
Y	JP 04-352898 A (Kanzaki Paper Mfg. Co., Ltd.), 07 December, 1992 (07.12.92), Claims; Par. No. [0002] (Family: none)	8,9
Y	JP 2006-015510 A (Oji Paper Co., Ltd.), 19 January, 2006 (19.01.06), Claims; Par. No. [0059] (Family: none)	8,9
A	JP 2001-010220 A (Oji Paper Co., Ltd.), 16 January, 2001 (16.01.01), Claims & EP 1048479 A2 & US 6511736 B1 & EP 1048479 B1	1-9
A	JP 2006-021421 A (Oji Paper Co., Ltd.), 26 January, 2006 (26.01.06), Claims (Family: none)	1-9
A	JP 08-173805 A (Mitsubishi Paper Mills Ltd.), 09 July, 1996 (09.07.96), Claims (Family: none)	1-9

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

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 HEI10226983 A **[0002]**
- JP 2000129595 A **[0002]**
- JP HEI11117196 A **[0002]**

Non-patent literature cited in the description

- White board and paper containers. Shigyo Times Sha Co., Ltd, 1995, 153-167 **[0021]**