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(54) HIGH PERFORMANCE PAPER AND PROCESS FOR PRODUCING THE SAME

(57) The present invention provides as a first feature thereof a process for producing paper which is characterized in that material paper is passed through a nip provided by a metal roll and another metal roll under a linear pressure of 200 to 2500 kg/cm.

The present invention provides as a second feature thereof a paper which is characterized in that the paper is produced by forming a coating layer containing a moisture-proof resin is formed on both surfaces of material paper before or after the material paper is passed through a nip provided by a metal roll and another metal roll under a linear pressure of 200 to 2500 kg/cm.

The present invention provides as a third feature thereof a paper which is characterized in that the paper is produced by incorporating an interfiber crosslinking agent for cellulose into material paper, and thereafter passing the material paper through a nip provided by a metal roll and another metal roll under a linear pressure of 200 to 2500 kg/cm.

The present invention provides as a fourth feature thereof a process for producing paper comprising at least two laminated sheets of paper, the process being characterized by passing at least two sheets of material paper through a nip provided by a metal roll and another metal roll under a linear pressure of 500 to 2500 kg/cm.

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Description

TECHNICAL FIELD

The present invention relates to paper which is excellent in dimensional stability, elasticity and rigidity and which has a high density (hereinafter referred to as "high performance paper").

The invention relates also to a process for producing paper of desired thickness easily without using an adhesive or the like, i.e., paper comprising at least two superposed sheets of paper.

BACKGROUND ART

Generally paper is produced by preparing stock by beating a pulp, making the stock into a sheet at acidity or neutrality and finishing the sheet as by supercalendering to give surface smoothness and gloss to the sheet. The stock is prepared by admixing with the pulp various additives such as sizing agents, paper strength agents, filter aids, fillers, dyes and other papermaking chemicals. Usually paper of increased density is obtained by using a supercalender having a multiplicity of rolls, i.e., metal rolls and elastic rolls which are arranged alternately, such that the paper to be finished is given a suitable water content and passed through the nip of each pair of adjacent metal roll and elastic roll. The rolls have a temperature of about 80 to about 120 °C.

JP-A-247896/1993 discloses treatment of paper by a machine calender or supercalender. Generally these calenders are not operated at a very high pressure. Especially because the supercalender usually comprises a combination of metal roll and elastic roll which is soft and readily deformable, the nip actually involves face-to-face contact which is less likely to give a high linear pressure.

Paper consists essentially of cellulose fibers. The cellulose of paper has a tough crystal structure and a noncrystal structure. Water penetrates into the noncrystal structure, swelling the fibers, or conversely the structure releases water to contract the fibers. The overall expansion or contraction of paper due to variations in its water content is attributable to the expansion or contraction of the fibers which spreads through the fiber-to-fiber linkage to the entire paper structure.

Conventionally, a polyolefin high-molecular-weight compound such as polyethylene or polypropylene is laminated to paper, or paper is impregnated with a compound such as phenolic resin, followed by curing or crosslinking, so as to diminish the expansion or contraction of the paper.

However, the paper having a laminated film of polyolefin high-molecular-weight compound has the problem that the pulp fibers remain in the form of flocs when the paper is collected as a waste after use since the film is tough, so that the waste paper has only to be disposed of by incineration, hence problems from the viewpoint of protection of the environment and recycling of resources. Furthermore, the paper having the polyolefin high-molecular-weight compound laminated thereto has low heat resistance since the polyolefin resin is a thermoplastic resin and melts when heated.

When paper is impregnated with phenolic resin or like high-molecular-weight compound, followed by curing or crosslinking, the paper becomes embedded in the resin. This entails the problem that the paper can not be recycled after use. The process wherein the phenolic resin is incorporated into paper by impregnation and cured or crosslinked encounters difficulty in handling the phenolic resin because the resin is used as dissolved in a solvent.

Although paper can be prepared with a desired thickness by varying the papermaking condition, paper machines are generally designed to produce large quantities of paper and are therefore inefficient to use in producing small quantities of paper.

There are processes for laminating paper sheets of varying thicknesses for preparing thick paper in small quantities. These processes are divided generally into four types, i.e., the wet lamination process, hot-melt lamination process, dry lamination process and extrusion coating-lamination process. The wet lamination process, dry lamination process and extrusion coating-lamination process are useful for laminating paper sheets.

The wet lamination process usually comprises applying a water-soluble adhesive or water-dispersible adhesive to a sheet, laminating another sheet to the sheet while the adhesive is wet, drying the resulting laminate to cause water to evaporate off from the adhesive and winding up the laminate into a roll after completion of adhesion. This process uses the aqueous adhesive and therefore requires a drying step for the evaporation of water.

With the dry lamination process, a solvent-type adhesive is applied to a sheet and dried, and another sheet is then affixed to the adhesive bearing surface of the sheet. This process also requires the step of drying the solvent.

With the extrusion coating-lamination process, a thermally melted resin is extruded from a slit die in the form of a molten film onto a continuous base sheet such as paper, another sheet of paper to be laminated is placed over the film and bonded to the base sheet under pressure, and the resulting laminate is cooled to solidify the molten film.

The wet lamination process and the dry lamination processes require the drying step, an applicator for the adhesive used, and cumbersome procedures for the maintenance and cleaning of the applicator. The extrusion coating-lamination process necessitates equipment for extruding the molten resin.

An object of the present invention Is to provide paper which is excellent in elasticity and rigidity and has a high density.

Another object of the invention is to provide paper which is excellent in dimensional stability and which can be recycled.

Another object of the invention is provide paper which is easy to handle, outstanding in dimensional stability and excellent in elasticity and rigidity.

Another object of the invention is to provide a process for producing paper having a desired thickness and comprising at least two superposed sheets of paper with ease and without using any adhesive.

DISCLOSURE OF THE INVENTION

The present invention provides as a first feature thereof a process for producing paper which is characterized in that material paper is passed through a nip provided by a metal roll and another metal roll under a linear pressure of 200 to 2500 kg/cm.

The present invention provides as a second feature thereof a paper which is characterized in that the paper is produced by forming a coating layer containing a moisture-proof resin is formed on both surfaces of material paper before or after the material paper is passed through a nip provided by a metal roll and another metal roll under a linear pressure of 200 to 2500 kg/cm.

The present invention provides as a third feature thereof a paper which is characterized in that the paper is produced by incorporating an interfiber crosslinking agent for cellulose into material paper, and thereafter passing the material paper through a nip provided by a metal roll and another metal roll under a linear pressure of 200 to 2500 kg/cm.

The present invention provides as a fourth feature thereof a process for producing paper comprising at least two laminated sheets of paper, the process being characterized by passing at least two sheets of material paper through a nip provided by a metal roll and another metal roll under a linear pressure of 500 to 2500 kg/cm.

We have conducted extensive research on conditions for treating paper in order to obtain filmlike paper of high density which is excellent in elasticity, rigidity and dimensional stability and consequently found that when paper is treated under a high-pressure not available by conventional supercalenders or machine calenders, the treatment readily gives a density of at least 1.2 g/cm^3, or at least 1.3 g/cm^3 without particularly imparting an increased water content to the paper to be treated, consequently affording filmlike paper which is excellent in elasticity, rigidity and dimensional stability. This finding has matured to the invention embodying the first feature thereof. Stated more specifically, when material paper is passed through a nip provided by a metal roll and another metal roll under a pressure of 200 to 2500 kg/cm, preferably 500 to 2500 kg/cm, the treatment greatly diminishes the interstices between the pulp fibers, intimately bonding the pulp fibers to one another as intertwined in the papermaking step and consequently readily giving a high density that is difficult to obtaine by conventional supercalenders. The paper obtained is smooth-surfaced and difficult for air to pass through. When the density of the paper produced is as high as at least 1.2 g/cm^3 or at least 1.3 g/cm^3, the treatment changes the paperlike hand of the material, making the resulting paper feel like a plastic film. The upper limit of the density is about 3 g/cm^3.

The paper of high density thus prepared is usable as substitutes for various film products, while the paper has the remarkable feature of being unlikely to contaminate the natural environment since the paper becomes rapidly decomposed by microorganisms in the natural environment.

Incidentally, if the linear pressure of the nip is less than 200 kg/cm, filmlike paper is unavailable, whereas pressures in excess of 2500 kg/cm produce localized elongation in the paper, failing to give any commercial value to the paper.

When the material paper has an increased water content, paper of high density is obtained easily, while the higher the surface temperature of the metal rolls, the more readily is paper of high density available.

According to the invention, material paper is passed through a nip provided by a metal roll and another metal roll under a pressure of 200 to 2500 kg/cm, while the material can of course be passed through a plurality of nips. Passage through a plurality of nips reduces variations in the thickness of the resulting paper but varies air permeability and other properties of paper.

The papers to be treated according to the invention include wood-free paper, wood-containing paper, etc. made by a Fourdrinier paper machine with cylinder dryers, Fourdrinier Yankee paper machine, cylinder paper machine, etc.

Insofar as the advantage of the invention is not impaired, organic and inorganic fillers and chemicals (auxiliary agents) are usable for the material paper.

Examples of useful fillers are inorganic pigments such as kaolin, talc, clay, calcium carbonate, calcined clay, titanium oxide, kieselguhr, finely divided anhydrous silica, activated clay, zinc oxide, aluminum oxide, aluminum hydroxide, Zinc sulfate, barium sulfate, silicon dioxide and colloidal silica, and organic pigments such as urea-formalin resin filler, nylon powder and polyethylene powder.

When the material paper is impregnated or coated with a resin and subjected to the high-pressure treatment, the paper obtained has barrier properties, water resistance and printability and becomes amenable to the subsequent process.

Impregnating resin can be applied, for example, by a sizing press. The coating resin can be applied by suitable means such as blade coater, air knife coater, gravure coater or roll coater.

Any of apparatus having at least one pair of metal rolls is suitably usable insofar as the nip thereof is adapted to apply a pressure of 200 to 2500 kg/cm. Examples of apparatus fulfilling this pressure requirement are two-roll calenders, multi-roll calenders, etc.

In the case where the paper passing temperature is high, the treated paper also has an elevated temperature and is therefore preferably cooled as by cooling rolls to lower the temperature.

With respect to the second feature of the invention, we have found that the paper treated with a high-pressure has lower dimensional stability than the paper before the treatment. Accordingly, we have made studies on the application of moisture-proof resins to paper to prevent penetration of water into the paper and obtain paper having good dimensional stability, and surprisingly found that when material paper is coated with the moisture-proof resin before or after the high- pressure treatment, the coating produces a remarkable effect. The term dimensional stability as used herein refers to the magnitude of elongation of the paper when the paper is immersed in water, and is expressed in terms of expansion of paper when immersed in water. The paper prepared according to the invention is preferably up to 2%, more preferably in the range of 0 to 1%, in expansion of paper when immersed in water with respect to the cross direction. The expansion of paper when immersed in water was measured by a method based on J. TAPPI No. 27, B Method.

The paper treated under a high-pressure is obtained by passing material paper through a nip provided by a metal roll and another metal roll under a pressure of 200 to 2500 kg/cm. The treatment conducted under this condition greatly diminishes the interstices between the pulp fibers, intimately bonding the pulp fibers to one another as intertwined in the papermaking process and consequently affording paper of high density. Incidentally, if the linear pressure of the nip is less than 200 kg/cm, the desired result is unavailable, whereas pressures in excess of 2500 kg/cm produce localized elongation in the paper, failing to give any commercial value to the paper.

The moisture-proof resin for forming a layer over the material paper before or after the high-pressure treatment is applied by a device, which can be selected optionally from among an air knife coater, bar coater, roll coater, blade coater and gate roll coater although the coating device is not limited particularly. The moisture-proof resin is a resin up to 500 $g/m^2 \cdot 24$ hrs in moisture permeability as measured by JIS Z 0208, the cup method B when the resin is made into a film. The resin layer can be formed from, for example, a wax or shellac, or a coating composition comprising a phillosilicate compound having a mean particle size of 5 to 50 μm and treated with a silane coupling agent, titanate coupling agent or aluminate coupling agent, and a synthetic resin.

The amount of the coating composition to be applied for forming the coating layer over each surface of the material paper is preferably 3 to 50 g/m^2, more preferably 10 to 30 g/m^2. If the amount is less than 3 g/m^2, the resin is ineffective, while amounts in excess of 50 g/m^2 are not desirable economically since the effect of the resin levels off.

The wax to be used in the invention is an ester of a long-chain fatty acid and a long-chain alcohol. Examples of waxes are vegetable waxes, animal waxes, petroleum waxes, mineral waxes and synthetic waxes. Examples of vegetable waxes are carnauba wax, candelilla wax, japan wax, bayberry wax, ouricury wax, raffia wax, palm wax, sugarcane wax, cotton wax, rice-oil wax, cocoa butter wax, etc. Examples of animal waxes are beeswax, insect wax, spermaceti wax, wool wax, etc. Examples of petroleum waxes are paraffin wax and microcrystalline wax, etc. Examples of mineral waxes are montan wax, ozokerite, peat wax, etc. Paraffin wax is desirable among these waxes.

The shellac for use in the present invention is a product obtained by purifying a resinous substance secreted by lac insects measuring about 0.6 to 0.7 mm in body length. Lac insects are grown mainly in India and Thailand in the subtropical zone and also occur in China, Indonesia, Myanmar, Vietnum, etc. Lac insects are raised by tying twigs inhabited by lac insects to plants of the family Leguminosae or Moraceae. The insect sucks the sap and secretes a resinous substance, which is solidified by exposure to air to form a resin layer. The resin layer is crushed, washed with water and purified for use.

The resin is purified, for example, by the thermal melting method, soda method or solvent extraction method. With the thermal melting method, the resin removed from branches is crushed, washed with water, placed into a cotton bag and squeezed, and the resin squeezed out is spread into a thin layer. According to the soda method, the resin is crushed, washed with water, and dissolved with soda ash or a caustic soda solution, extraneous matter is removed from the solution, and the solution is added to a dilute acid solution for separating out, followed by washing with water and drying. The solvent extraction method is such that the resin crushed and washed with water is dissolved in an alcoholic solvent, followed by filtration, collection of the solvent and purification.

The shellac for use in the present invention usually consists essentially of resin acids, i.e., aleuritic acid, jalaric acid and laccijalaric acid, the carboxyl group of each of these resin acids forming an ester linkage with the hydroxyl group of another one of the acids. Also present in the shellac as component waxes are mixed esters of myricyl alcohol, ceryl alcohol, lacceryl alcohol, etc. and lignoceric acid, lacceric acid, stearic acid, palmitic acid, etc. The shellac further contains laccaic acid, erythrolaccin, desoxyerythrolaccin, etc. The method to be used in the invention of purifying the resin is preferably the solvent extraction method from the viewpoint of purity and quality.

The resin is soluble in alkalis and therefore poses no problem in recycling of the paper after use. The resin is tasteless, odorless and nontoxic and produces no adverse effect on the environment. Accordingly, the paper prepared by forming a layer of this resin over the material paper and having good dimensional stability presents no problem in recycling the paper after use.

Various auxiliary agents such as a wetting agent and antiseptic are usable in the shellac coating composition insofar as the agents do not impair the properties of the resulting paper. Pigments such as calcium carbonate and titanium oxide are suitably usable insofar as the properties are not adversely thereby affected.

The silane coupling agent, titanate coupling agent and aluminate coupling agent for use in the invention are used for inorganic-organic composite materials for chemically bonding the two kinds of components or giving them enhanced affinity for each other by a chemical reaction to improve the composite material in transparency, heat resistance, water resistance and mechanical strength. In the present invention, the coupling agent gives the synthetic resin and the phillosilicate compound enhanced affinity for each other to afford improved moisture proofness. Examples of such coupling agents are silane coupling agents having an Si-containing hydrophilic group and including vinyltrimethoxysilane, γ-glycidoxypropyldimethoxysilane, γ-glycidoxypropyltrimethoxysilane, γ-glycidoxypropyltriethoxysilane, γ-methacryloxypropyltrimethoxysilane and N-β (aminoethyl)γ-aminopropyltrimethoxysilane, titanate coupling agents having a Ti-containing hydrophilic group and including isopropyltriisostearoyl titanate, isopropyltrioctanoyl titanate, isopropylisostearoyldiacryl titanate, isopropyltricumylphenyl titanate and isopropyltri(N-aminoethyl • aminoethyl)titanate, and aluminate coupling agents having an Al-containing hydrophilic group and including acetoalkoxyaluminumdiisopropionate.

The phillosilicate compound is treated with the coupling agent, for example, by the integral blending method or pretreatment method. The integral blending method is such that the coupling agent is added directly to a composition containing the phillosilicate compound and synthetic resin. The pretreatment method is such that the phillosilicate compound is treated with the coupling agent first.

The coupling agent is added to the phillosilicate compound in an amount of 0.1 to 5 parts by weight, preferably 0.5 to 2 parts by weight, per 100 parts by weight of the compound. Amounts less than 0.1 part by weight are undesirable since the surface of the phillosilicate compound will not be fully coated with the coupling agent, whereas amounts in excess of 5 parts by weight are uneconomical since the effect of the coupling agent will then level off.

When the phillosilicate compound thus treated with the coupling agent is to be made into an aqueous dispersion, the compound can be dispersed using a surfactant, polyacrylic acid dispersant, or wetting agent such as isopropyl alcohol or sodium dialkylsulfosuccinate.

The phillosilicate compound to be used in the present invention is a substance generally in the form of planar crystals and having a mean particle size of at least several μm, more specifically 3 μm to 100 μm, preferably 5 μm to 50 μm. The phillosilicate compound is preferably 5 to 200 in aspect ratio. According to the invention, the aspect ratio is a value obtained by dividing the mean particle size of the phillosilicate compound by the thickness of the crystals.

The phillosilicate compound to be used in the invention is in the form of sheets or flakes and has a distinct cleavage. The materials included in the category of such compounds are mica group, pyrophyllite, talc, chlorite, septechlorite, serpentine, stilpnomelane and other clay minerals. Mica group and talc are preferable among these.

The mica group includes muscovite, sericite, phlogopite, biotite, fluorphlogopite (artificial mica), lepidolite, paragonite, vanadiummica, illite, tinmica, palagonite and brittle mica. Preferable among these are muscovite and sericite.

Examples of synthetic resins for use in the present invention are styrene-butadiene copolymer (SBR), acryl-styrene copolymer, methacrylate-butadiene copolymer, vinyl acetate-crotonic acid copolymer and styrene-butyl methacrylate-acrylic acid copolymer. SBR is most suitable in view of high water resistance and elongation and reduced susceptibility of the coating layer to cracking due to folding. Other copolymerizable monomers are also usable insofar as the objects of the invention will not be impaired. Examples of coplymerizable monomers are aromatic vinyl monomers such as α-methylstyrene, vinyltoluene and p-tert-butyltoluene, (meth)acrylic acid ester monomers such as methyl (meth)acrylate, ethyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and n-octyl (meth)acrylate, glycidyl esters of ethylenically unsaturated acids such as glycidyl (meth)acrylate, and (meth)acrylamide monomers such as (meth)acrylamide and N-methylol(meth)acrylamide. These monomers are usable singly, or in combination of at least two of them. The term "(meth)acryl-" as used herein refers to acryl- or methacryl-.

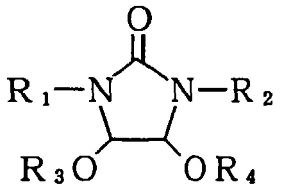
To be suitable, the ratio of the synthetic resin to the phillosilicate compound to be admixed therewith is 70/30 to 30/70 calculated as solids. If the proportion of the phillosilicate compound is less than 30%, the number of layers to be formed by the compound is lesser, increasing the distance between portions of the phillosilicate compound to excess and resulting in insufficient moisture proofness. Consequently, there arises a need to apply an increased amount of coating composition to lead to poor economy. Furthermore, the composition then becomes more susceptible to blocking. Presence of more than 70% of the compound increases the interstices between the synthetic resin and the phillosilicate compound within the coating layer to entail lower moisture proofness.

With respect to the third feature of the invention, we have found that paper having a density of at least 1.2 and excellent in dimensional stability can be obtained by incorporating an interfiber crosslinking agent for cellulose into material paper, thereafter passing the material paper through a nip provided by a metal roll and another metal roll under a linear pressure of 200 to 2500 kg/cm, and curing the resulting sheet by heating.

Further when a glycol is added to the interfiber crosslinking agent, the glycol reacts with the crosslinking agent during the curing to form a crosslinked structure, whereby the expansion or contraction of the pulp fibers can be suppressed. The coating composition, which contains the glycol, rapidly penetrates through the surface of the material paper during coating without remaining on the surface, with the result that the transfer of the composition can be prevented when the material paper is subjected to the subsequent high-pressure treatment.

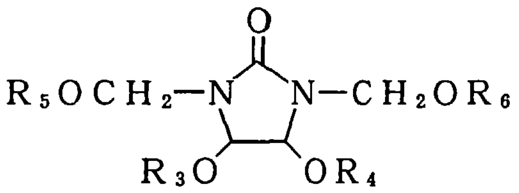
The interfiber crosslinking agent for cellulose as used in the present invention is a compound having in the molecule at least two groups which react, or form a hydrogen bond, with the hydroxyl group of cellulose, thus effecting crosslinking between the cellulose fibers.

Examples of interfiber crosslinking agents for cellulose are a compound having an N-methylol group, compound represented by the formula (1), compound represented by the formula (2), epoxy compound, water-soluble (meth)acrylamide copolymer, mixture of water-soluble (meth)acrylamide copolymer and water-soluble polyvalent aldehyde, etc.



(1)

wherein R_1 and R_2 are each H or alkyl having 1 to 5 carbon atoms, and R_3 and R_4 are each H or CH_3.

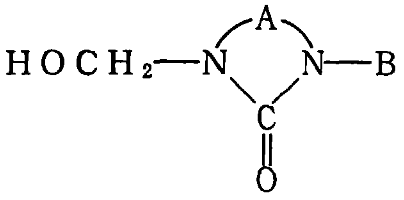


(2)

wherein R_5 and R_6 are each alkyl having 1 to 5 carbon atoms, and R_3 and R_4 are each H or CH_3.

Examples of compounds having an N-methylol group are an initial condensate (reaction product) of urea and formaldehyde, initial condensate (reaction product) of an alkylenediamine, urea and formaldehyde, etc. Also desirable are crosslinking agents having a cyclic structure. Similarly desirable are these agents as partially N-alkoxymethylated for the control of stability or reactivity.

Examples of compounds having an N-methylol group of cyclic structure are those represented by the formula (3)



(3)

wherein $\frown A \frown$ is alkylene which has 2 to 4 carbon atoms and in which the carbon may be substituted with OH, alkyl or alkoxyl, the alkylene having a chain which may contain -O-, -NH- or - NR- (R being alkyl or alkoxyl), and B is H, $-CH_2OH$, $-CH_2OCH_3$ or $-CH_2OC_2H_5$. The examples further include tetramethylolacetylenediurea, trimethylolacetylenediurea, dimethylolacetylenediurea, dimethylolpiperazine, trimethylol isocyanurate, dimethylol isocyanurate, tetramethylolmelamine, trimethylolmelamine, dimethylolmelamine, tetramethylolguanamine, trimethylolguanamine, dimethylolguanamine, etc. Examples of compounds represented by the formula (3) are dimethylolethyleneurea, dimethyloldihydroxyethyleneurea, dimethylolpropyleneurea, 4-methoxy-5,5'-dimethyl-N,N-dimethylolpropyleneurea, dimethylolurone, dimethylolalkyltriazone, 1-methylol-3-methoxymethyl-4,5-dihydroxyethyleneurea, 1-methylol-3-methoxymethyl-4-methoxy-5-hydroxyethyleneurea, 1-methylol-3-methoxymethyl-4-hydroxy-5-methoxyethyleneurea, etc.

Examples of compounds represented by the formula (1) are 1,3-dimethyl-4,5-dihydroxyethyleneurea, 1,3-dimethyl-4,5-dimethoxyethyleneurea, 4-hydroxy-5-methoxyethyleneurea, 4,5-dihydroxyethyleneurea, 4,5-dimethoxyethyleneurea, etc.

Examples of compounds represented by the formula (2) are 1,3-dimethoxymethyl-4,5-dihydroxyethyleneurea, 1,3-

dimethoxymethyl-4-hydroxy-5-methoxyethyleneurea, 1,3-dimethoxymethyl-4,5-dimethoxyethyleneurea, etc.

An enhanced effect is available when the cyclic urea compound is used in combination with a specific ethylene copolymer, such as ethylene-vinyl acetate copolymer, ethylene-vinyl acetate-vinyl chloride copolymer, ethylene-vinyl acetate-acrylate copolymer or styrene-butadiene copolymer, or with a homopolymer of (meth)acrylamide or copolymer thereof with other vinyl monomer. Also effective are reactive polymers such as methylolated product of polyacrylamide.

The epoxy compound to be used in the invention is preferably of the water-soluble type. Examples of such water-soluble epoxy compounds are mono-or di-glycidyl ethers of polyols such as ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, glycerin, sorbitol, polyglycerol, pentaerythritol, tris(2-hydroxyethyl)-isocyanurate, trimethylolpropane, neopentyl glycol, phenol ethylene oxide and lauryl alcohol ethylene oxide. Polyethylene glycol diglycidyl ether is preferred as a straight-chain epoxy compound.

Further when the interfiber crosslinking agent is used in combination with a glycol, the coating composition will not remain on the surface of the material paper but rapidly penetrates through the surface. Examples of such glycols are propylene glycol, polypropylene glycol, dipropylene glycol, diethylene glycol, 1,4-butanediol, 2,3-butanediol, 1,5-pentanediol, triethylene glycol, polyethylene glycol, etc. Especially, dipropylene glycol effectively wets or penetrates into paper having a high degree of surface sizing.

The ratio of the glycol to the interfiber crosslinking agent to be mixed therewith, although dependent on the sizing degree of the material paper to be coated or impregnated with the mixture, is usually preferably 10 to 400%, more preferably 25 to 250%, based on the nonvolatile content of the interfiber crosslinking agent.

Further improved dimensional stability is available by using a catalyst in combination with the interfiber crosslinking agent. Examples of typical catalysts are acids such as hydrochloric acid, sulfuric acid, borofluoric acid, acetic acid, glycollic acid, maleic acid, lactic acid, citric acid, tartaric acid and oxalic acid, metal salts such as magnesium chloride, magnesium nitrate, magnesium borofluoride, zinc borofluoride, zinc chloride, zinc nitrate and sodium bisulfate, ammonium chloride, hydrochlorides of organic amines, hydrochlorides of alkanolamines, etc. These compounds are used singly or in combination. Such compounds are applied to the material paper by being incorporated into the stock, or by impregnation or coating. The effect to give dimensional stability is obtained by a heat treatment.

The crosslinking agent is used in an amount of 2 to 50 wt. %, preferably 5 to 35 wt. %, based on the pulp. If the amount is less than 2 wt. %, the agent is less effective, whereas amounts in excess of 50 wt. % are undesirable, for example, because the fibers become shortened when defiberized.

Water-soluble (meth)acrylamide copolymers are also effective for imparting dimensional stability to paper. The monomers for forming these (meth)acrylamide copolymers include (meth)acrylamide monomers, cationic monomers, hydroxyalkyl (meth)acrylate monomers, hydrophobic unsaturated vinyl monomers and carboxyl-containing monomers. The copolymer comprises at least three kinds of such monomers.

Of these monomers, examples of (meth)acrylamide monomers are (meth)acrylamide, N,N-dimethyl-(meth)acrylamide, N,N-diethyl-(meth)acrylamide, N,N-propyl-(meth)acrylamide, etc.

Examples of cationic monomers are 2-(meth)acryloyloxyethyltrimethylammonium chloride, 2-(meth)acryloyloxyethyltriethylammonium bromide, 3-(meth)acryloyloxypropyldimethylethylammonium chloride, 3-methacryloyloxy-2-hydroxypropyltrimethylammonium chloride, 3-methacryloyloxy-2-hydroxypropylmethyldiethylammonium chloride, 3-acrylamidopropyltrimethylammonium chloride, 2-(meth)acryloylaminoethyltrimethylammonium chloride, 3-(meth)acryloylamino-2-hydroxypropyltrimethylammonium chloride, 3-(meth)acryloylaminoethyltrimethylammonium chloride, (meth)acryloyloxyethyldimethylamine hydrochloride, (meth)acryloyloxyethyldiethylamine hydrochloride, dimethyldiallylammonium chloride, etc.

Examples of hydroxyalkyl (meth)acrylate monomers are hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-chloropropyl (meth)acrylate, ω-hydroxy-poly(ethyleneoxy) (meth)acrylate, ω-hydroxy-poly(propyleneoxy) (meth)acrylate, ω-methoxy-poly(ethyleneoxy) (meth)acrylate, ω-methoxy-poly(propyleneoxy) (meth)acrylate, etc.

Examples of hydrophobic unsaturated vinyl monomers are methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, styrene, vinyltoluene, α-methylstyrene and other styrene monomers, vinyl acetate and other organic acid vinyl esters, acrylonitrile, methacrylonitrile and other nitriles, vinyl chloride, vinylidene chloride and other olefin halides, etc.

Examples of carboxyl-containing monomers are (meth)acrylic acid, crotonic acid, maleic acid, and sodium salts, ammonium salts and methylamine, dimethylamine, trimethylamine, ethanolamine, diethanolamine and triethanolamine salts of these acids.

The copolymer to be used in the invention has a molecular weight of about 5,000 to about 3,000,000, preferably about 10,000 to about 2,000,000.

Use of the (meth)acrylamide copolymer in combination with a polyvalent aldehyde gives high dimensional stability to paper. Examples of polyvalent aldehydes include glyoxal, malonaldehyde, succinaldehyde and glutaraldehyde.

Use of the interfiber crosslinking agent in combination with a water-soluble high polymer or sizing agent produces an improved effect on dimensional stability. Examples of water-soluble high polymers are PVA, starch, starch oxide and polyacrylamide resin. Also effective are various plant gums, sodium alginate, carboxymethyl cellulose, methyl cellulose, chitosan, glue, casein, polyvinyl acetate and latexes.

Effective sizing agents are synthetic sizing agents of the styrene and olefin types. Alkylketene dimer sizing agents are especially desirable.

Although the apparatus for applying the coating composition of the invention by coating or impregnation is not limited specifically, the coating apparatus can be optionally selected from among an air knife coater, bar coater, roll coater, blade coater and gate roll coater, and the impregnating apparatus from among size press coaters, etc.

The coating composition of the invention is applied by coating or impregnation preferably in an amount of 5 to 60 g/m^2, more preferably 8 to 50 g/m^2. If the amount is less than 5 g/m^2, the composition fails to exhibit its effect, while amounts in excess of 60 g/m^2 are economically undesirable since the effect will then level off.

The crosslinking agent applied by coating or impregnation can be dried by a desired method, whereas the agent must be dried under a condition not permitting curing so as to enable the agent to fully exhibit its effect in the subsequent step of high-pressure treatment. It is generally preferable to dry the agent at a temperature of 50 to 90 °C by exposure to a large amount of air stream.

Various auxiliary agents such as a wetting agent and antiseptic are usable with the crosslinking agent insofar as such agents will not adversely affect the properties of the paper to be obtained. Pigments such as calcium carbonate and titanium oxide are also usable suitably insofar as they produce no undesirable effect on the properties.

The material paper coated or impregnated with the coating composition of the invention is subsequently passed through a nip provided by a metal roll and another metal roll under a pressure of 200 to 2500 kg/cm. The treatment under this condition greatly diminishes the interstices between the pulp fibers, affording paper of high density. If the linear nip pressure is less than 200 kg/cm, the desired effect is unavailable, whereas pressures in excess of 2500 kg/cm result in localized elongation to nullify the commercial value of the paper obtained.

For curing, the treated material paper is heated usually at about 80 to about 200 °C, preferably about 100 to about 160 °C, for about 1 to about 120 minutes, preferably for about 5 to about 60 minutes.

In the fourth feature of the present invention, the sheets of material paper to be laminated are preferably 2 to 15% in water content. The sheets can be laminated more effectively if water is supplied to at least one of the surfaces to be joined to wet the surface. The amount of water to be supplied is preferably 1 to 10 g/m^2. Water can be supplied, for example, by coating at least one of the surfaces to be joined with water or spraying water to the surface in the form of a mist or vapor.

We have made studies on processes for laminating a plurality of sheets of paper by a simple method into a sheet of paper almost without using a drying step, and found that laminated paper can be obtained by passing sheets of material paper through a nip of metal rolls under a high pressure without using any adhesive.

Stated mores specifically, when sheets of paper are passed through a nip provided by a metal roll and another metal roll under a linear pressure of 500 to 2500 kg/cm, the pulp fibers on the opposed surfaces of sheets are intertwined with one another for reasons still remaining to be clarified, laminating the sheets into a sheet of paper presumably because of a hydrogen bond formed between the cellulose molecules in the pulp fibers.

However, if the linear pressure of nip of the metal rolls is lower than 500 kg/cm, the desired effect of the invention is not available, whereas pressures exceeding 2500 kg/cm result in localized elongation in the paper, failing to afford uniform laminated paper.

The sheets of material paper can be laminated more effectively when at least one of the surfaces to be joined is coated with water, or when water is applied by spraying a mist or vapor onto the surface for wetting. The amount of water is preferably 1 to 10 g/m^2, more preferably 2 to 5 g/m^2. The method of applying water by coating or spraying the mist or vapor is not limited specifically. A coating apparatus, such as bar coater, gravure coater or roll coater is usable for the coating method. A spraying device or humidifier is usable for applying the mist or vapor.

In the case where water is applied by coating or in the form of a mist or vapor, the temperature of the metal rolls, although dependent on the speed of passage of the material paper, is preferably up to 150 °C since the pulp fibers are swollen with water.

The expression "paper substantially free from an adhesive over the surface" as used herein refers, for example, to wood-free paper, wood-containing paper, single-faced coated paper, etc. The paper which is surface-sized is also included in the invention.

Laminated paper of desired thickness can be obtained by using an increased number of superposed sheets of material paper or sheets of material paper of selected thickness. Usually, the number of superposed sheets of material paper is preferably 2 to 200. Usually, the sheets of material paper to be laminated are each preferably 20 to 1000 μm in thickness. Usually, the laminated paper to be obtained is preferably 20 to 2500 μm in thickness.

The laminated paper obtained by passing the sheets of material paper between the metal rolls under a high pressure is smooth-surfaced and difficult for air to pass through.

When the rolls used for lamination have a high temperature, the paper as passed therebetween also has an elevated temperature and is therefore cooled as by cooling rolls to lower the temperature of the paper.

The paper embodying the first to third features of the invention can be obtained by passing material paper through a nip provided by a metal roll and another metal roll under a pressure of 200 to 2500 kg/cm. The treatment conducted under this condition greatly diminishes the interstices between the pulp fibers, intimately bonding the pulp fibers to one another as intertwined in the papermaking process and consequently affording paper of high density. Incidentally, if the linear nip pressure is lower than 200 kg/cm, the desired effect is not available, whereas pressures in excess of 2500 kg/cm result in localized elongation of the paper to nullify the commercial value.

The first to fourth features of the invention will be described.

The pulp to be used is not limited specifically. Examples of useful pulps are chemical pulps, such as softwood bleached kraft pulp (hereinafter referred to as "NBKP") and hardwood bleached kraft pulp (hereinafter referred to as "LBKP"), which are usually used, mechanical pulps such as GP, BCTMP, MP and TMP, hemp pulp, pulps prepared from non-wood materials such as kenaf, pulps such as DIP, etc. Also useful are synthetic pulps, for example, of vinylon, nylon, polyethylene terephthalate, polyethylene, polypropylene, poly(meth)acrylic acid ester, polyurethane and polystyrene.

Among the above examples, softwood pulp is excellent in strength but inferior to hardwood pulp in dimensional stability and curl. If the proportion of softwood pulp is not smaller than 50 wt. % of all pulps forming the material paper, the influence of the pulp becomes pronounced, so that the proportion is preferably less than 50 wt. %.

The degree of beating of the pulps for use in the invention is preferably at least 350 ml in Canadian standard freeness (hereinafter referred to as "CSF"). Unbeaten pulps are also usable. If a pulp less than 350 ml in CSF is used, the paper obtained is impaired in curl, dimensional stability and other paper properties. The paper is not desirable also because it can not defibrated readily for recycling. Paper having a high density and excellent in elasticity, rigidity and dimensional stability can be prepared using material paper wherein the proportion of softwood pulp is less than 50 wt. % based on all pulps, and the degree of beating of the pulps is at least 350 ml in CSF.

The stock thus adjusted is made into paper by a Fourdrinier paper machine with cylinder dryers, Fourdrinier Yankee paper machine or cylinder paper machine. The paper thus obtained rapidly restores itself to the state before being subjected to the high-pressure treatment when held immersed in water. This means that the paper of the present invention can be treated in the same manner as usual paper for recycling. The paper is decomposable rapidly with microorganisms in the natural environment and therefore will not lead to environmental destruction.

The internal and surface sizing agents for the paper for use in the present invention are not limited specifically; rosin sizing agents, starches, PVA, etc. are usable suitably. Further use of paper strength agents such as polyamideepichlorohydrin resin tends to result in improved expansion of paper when immersed in water.

The water content of the material paper to be subjected to the high-pressure treatment is preferably 2 to 15%, more preferably 5 to 10%. The treatment then effectively affords paper of high density. If the water content is less than 2%, it is difficult to effectively obtain paper of higher density, whereas when the value is over 15%, the fibers swell to excess, failing to give uniform paper due to localized elongation.

The rolls for use in the high-pressure treatment of paper preferably have a temperature of 20 °C to 300 °C. If the roll temperature is lower than 20 °C, condensation of water vapor generally occurs on the surfaces of the rolls partly because of the influence of the atmospheric temperature, and an operational problem is likely to arise, hence an undesirable result. Since the quantity of heat to be transferred from the rolls to the material paper varies with the speed of passage of the paper, blisters would develop when the speed is low even if the roll temperature is in the preferable temperature range of up to 300 °C. Generally when the temperature is above 300 °C, however, the water in the material paper vaporizes at a time, markedly inflating the paper between the constituent layers thereof, locally permitting the layer to separate off to form blisters on the surface and presenting difficulty in giving uniform paper.

Although the speed of passage of the paper according to the invention is closely related with the temperature as mentioned above and can not be strictly determined, the speed is preferably 10 to 500 m/min. If the speed is over 500 m/min, it is difficult to obtain the desired effect since the heat and pressure then will not be sufficiently transmitted to the paper.

The elasticity and rigidity of paper are to be expressed herein in terms of degree of bending recovery. To determine this value, the specimen was bent and the restoring force of the specimen was measured by a Gurley stiffness tester. The greater the elasticity and rigidity of the specimen, the greater is the degree of bending recovery.

BEST MODE OF CARRYING OUT THE INVENTION

The present invention will be described in greater detail with reference to the following examples, whereas the invention is not limited to these examples. The percentages in the examples are by weight unless otherwise specified.

Example 1

A stock was prepared by adjusting a pulp mixture (NBKP/LBKP=3/7) serving as a material pulp to a CSF of 500 ml, adding 0.3% of a rosin size and 1.8% of alum cake to the pulp and further adding talc to the pulp in an amount of 5.5% calculated as an ash content of paper. The stock was made into paper by a Fourdrinier paper machine with cylinder dryers. In the papermaking step, a liquid containing 6.5% of starch (brand name: Ace A, product of Oji Corn Starch Co., Ltd.) was applied by a size press to both surfaces of the paper in a combined amount for the two surfaces of 2 g/m^2 calculated as solids. The paper obtained was 5.5% in water content, 127 g/m^2 in basis weight, 168 μm in thickness and 25 sec/100 cc in air permeability.

The paper was passed through a nip provided by a metal roll and another metal roll under a linear pressure of 500 kg/cm at a roll temperature of 100 °C. The resulting paper was 97 μm in thickness.

Example 2

The same procedure as in Example 1 was repeated except that the material paper obtained was treated under a linear pressure of 500 kg/cm at a temperature of 175 °C. The resulting paper was 94 μm in thickness.

Example 3

The same procedure as in Example 1 was repeated except that the material paper obtained was treated under a linear pressure of 750 kg/cm at a temperature of 175 °C. The resulting paper was 94 μm in thickness.

Example 4

The same procedure as in Example 1 was repeated except that the material paper obtained was treated under a linear pressure of 1000 kg/cm at a temperature of 175 °C. The resulting paper was 94 μm in thickness.

Example 5

The same procedure as in Example 1 was repeated except that the material paper obtained was adjusted to a water content of 13% and treated under a linear pressure of 250 kg/cm at a temperature of 100 °C. The resulting paper was 104 μm in thickness.

Example 6

The same procedure as in Example 1 was repeated except that the material paper obtained was adjusted to a water content of 13% and treated under a linear pressure of 1000 kg/cm at a temperature of 100 °C. The resulting paper was 98 μm in thickness.

Example 7

The paper prepared by the treatment of Example 6 was further treated under a linear pressure of 1000 kg/cm at a temperature of 100 °C. The resulting paper was 93 μm in thickness.

Example 8

An acrylic emulsion (brand name: RX301C, product of Nippon Carbide Industries Co., Inc.) was applied by a size press to both surfaces of the paper prepared in Example 1 in a combined amount for the two surfaces of 7 g/m^2 calculated as solids to obtain paper with a water content of 5.5%. The paper was 135 g/ m^2 in basis weight, 171 μm in thickness and 70 sec/100 cc in air permeability. The paper was treated under a linear pressure of 1000 kg/cm at a temperature of 100 °C. The resulting paper was 104 μm in thickness.

Example 9

An acrylic emulsion (brand name: RX301C, product of Nippon Carbide Industries Co., Inc.) was applied by coating to both surfaces of the paper prepared in Example 1 in an amount of 10 g/m^2 for each surface to obtain paper with a water content of 5.5%. The paper was 147 g/ m^2 in basis weight, 174 μm in thickness and 107580 sec/100 cc in air permeability. The paper was treated under a linear pressure of 1000 kg/cm at a temperature of 100 °C. The resulting paper was 120 μm in thickness. The treated paper was difficult for air to pass through although the value thereof remains to be determined.

Example 10

A stock was made into paper in the same manner as in Example 1 with the exception of using a pulp mixture (NBKP/LBKP=8/2) serving as the material pulp and adjusted to a CSF of 500 ml. The paper made was 127 g/m^2 in basis weight, 168 μm in thickness, 5.5% in water content and 450 sec/100 cc in air permeability. The paper was treated under a linear pressure of 1500 kg/cm at a temperature of 120 °C. The resulting paper was 95 μm in thickness and slightly inferior in paper properties and curl.

Example 11

The same procedure as in Example 1 was repeated except that the material paper obtained was treated under a linear pressure of 2000 kg/cm at a temperature of 150 °C. The resulting paper was 96 μm in thickness.

Comparative Example 1

Paper was made from a stock prepared by adjusting a material pulp, comprising 100% of NBKP, to a CSF of 200 ml and adding 0.5% of a rosin size to the pulp as an internal sizing agent. In the papermaking step, a 7% aqueous solution of PVA 107 (product of Kuraray Co., Ltd.) was applied by a size press to both surfaces of the paper in a combined amount for the two surfaces of 2 g/m^2 calculated as solids. The paper obtained was 70 g/m^2 in basis weight and 500 sec/100 cc in air permeability. The paper was adjusted to a water content of 15% and supercalendered under a linear pressure of 200 kg/cm at a temperature of 100 °C. The resulting paper was 63 μm in thickness.

Comparative Example 2

The same procedure as in Example 1 was repeated except that the material paper obtained was treated under a linear pressure of 150 kg/cm. The resulting paper was 121 μm in thickness.

Comparative Example 3

The same procedure as in Example 1 was repeated except that the material paper obtained was treated under a linear pressure of 2800 kg/cm. The resulting paper was found to be locally stretched and was not uniform.

Comparative Example 4

Commercial wood-free paper with a thickness of 95 μm (brand name: PPC Youshi chuatsuguchi, product of Fuji Xerox Office Supply Co., Ltd.) was not subjected to any high-pressure treatment.

The papers treated as above were checked for degree of bending recovery, air permeability, density and Gurley stiffness. Table 1 shows the results. Samples were tested and evaluated by the following methods.

(1) Degree of bending recovery

The sample, 25.4 mm in width and 63.5 mm in length, was tested by a Gurley stiffness tester. A 5-gram weight was attached to an equilibrium pendulum at a position 50.8 mm away from its pivot. The sample holder of the tester was positioned as set at 38.1 mm, and the sample was attached at its one end to the holder. The other end of the sample was held by hand, raised to the position of the holder and then released, causing the sample to strike against the pendulum when the sample restored itself from the bent state. The position to which the pendulum swung by the resulting reaction was read on the scale to obtain a numerical value. The sample was tested in the machine direction and the cross direction to obtain the average of the values obtained. The average value multiplied by 100 was taken as the degree of bending recovery. Each sample was tested five times.

(2) Air permeability

The time taken for 100 cc of air to pass through the sample was measured as expressed in seconds by a method in accordance with JIS P8117 using a high-pressure Gurley air permeability tester.

Table 1

	pressure (kg/cm)	roll temp (°C)	density (g/cm^3)	air permeability (sec)	Gurley stiffness (mg)	degree of bending recovery
Ex.1	500	100	1.31	1010	238	200
Ex.2	500	175	1.35	7060	271	210
Ex.3	750	175	1.35	12460	289	210
Ex.4	1000	175	1.35	22210	277	210
Ex.5	250	100	1.22	1930	320	200
Ex.6	1000	100	1.30	7980	252	200
Ex.7	1000	100	1.30	7980	252	200
	1000	100	1.37	30680	247	220
Ex.8	1000	100	1.30	25880	315	190
Ex.9	1000	100	1.23	-	577	250
Ex.10	1500	120	1.34	10500	251	210
Ex.11	2000	150	1.36	53582	260	200
Com.Ex.1	200	100	1.11	5000	62	115
Com.Ex.2	150	100	1.05	150	362	135
Com.Ex.3	2800	100	-	-	-	-
Com.Ex.4	-	-	0.73	-	91	125
Air permeability: after high-pressure treatment						

Example 12

A stock was prepared by adjusting a pulp mixture (NBKP/LBKP=2/8) serving as a material pulp to a CSF of 500 ml, adding 0.3% of a rosin size and 1.8% of alum cake to the pulp and further adding talc to the pulp in an amount of 9.7% calculated as an ash content of paper. The stock was made into paper by a Fourdrinier paper machine with cylinder dryers. In the papermaking step, a liquid containing 6.5% of starch (brand name: Ace A, product of Oji Corn Starch Co., Ltd.) was applied by a size press to both surfaces of the paper in a combined amount for the two surfaces of 2 g/m^2 calculated as solids. The paper obtained was 5.5% in water content, 140 g/m^2 in basis weight and 175 μm in thickness. The paper obtained was passed through a nip provided by a metal roll and another metal roll under a linear pressure of 1000 kg/cm, at a roll temperature of 200 °C and at a speed of 50 m/min. The resulting paper was 105 μm in thickness. The paper subjected to the high-pressure treatment was coated over each surface thereof with a shellac (brand name: Shellac BN-W25A, product of Gifu Shellac Seizosho) in an amount of 10 g/m^2 by a bar coater.

Example 13

A stock was prepared by adjusting a material pulp, comprising 100% of LBKP, to a CSF of 500 ml, adding 0.3% of a rosin size and 1.8% of alum cake to the pulp and further adding talc to the pulp in an amount of 16.0% calculated as an ash content of paper. The stock was made into paper by a Fourdrinier paper machine with cylinder dryers. The paper obtained was 5.5% in water content, 90 g/m^2 in basis weight and 124 μm in thickness. The paper was passed through a nip provided by a metal roll and another metal roll under a linear pressure of 500 kg/cm, at a roll temperature of 250 °C and at a speed of 100 m/min. The resulting paper was 64 μm in thickness. The same step as in Example 12 thereafter followed to obtain paper.

Example 14

Paper was prepared in the same manner as in Example 12 except that the paper delivered from the machine in Example 13 was passed through a nip provided by a metal roll and another metal roll at a roll temperature of 300 °C.

Example 15

Paper was prepared in the same manner as in Example 12 except that the paper delivered from the machine in Example 12 was passed through a nip provided by a metal roll and another metal roll under a linear pressure of 1000 kg/cm, at a roll temperature of 100 °C and at a speed of 50 m/min, and coated over each surface thereof with a shellac (brand name: Shellac BN- W25A, product of Gifu Shellac Seizosho) in an amount of 5 g/m^2.

Example 16

Paper was prepared in the same manner as in Example 15 except that the amount of resin applied in Example 15 was changed to 20 g/m^2.

Example 17

The paper delivered from the machine in Example 12 was subjected to the same high-pressure treatment as in Example 12 and then coated over each surface thereof with paraffin wax (brand name: Hidorin P-7, product of Chukyo Yushi Co., Ltd.) in an amount of 10 g/m^2 by a bar coater.

Example 18

A 10 wt. % toluene solution of an aminosilane coupling agent (brand name: KBM603, product of Shin- Etsu Chemical Co., Ltd.) was prepared, and 10 parts of the solution was added dropwise to 100 parts of muscovite having a mean particle size of 20 μm and an aspect ratio of 20 to 30 (brand name: Mica A21, product of Yamaguchi Ummo Kogyo Co., Ltd.) which was dried at 120 °C for 1 hour, followed by agitation in a mixer at 1000 rpm for 10 minutes and then by drying at 80 °C for 2 hours. The philiosilicate compound thus surface-treated (100 parts), 0.2 part of a dispersant (brand name: CARRYBON L400, product of Sanyo Chemical Industry Co., Ltd.), 20 parts of 5 wt. % aqueous ammonia and 80 parts of water were mixed together and treated in a Cowles dissolver at 2000 rpm for 30 minutes to obtain a dispersion. A synthetic resin latex (brand name: LK407S1X1, product of Nippon Zeon Co., Ltd.) was admixed with the dispersion in a phillosilicate compound/synthetic resin latex ratio of 50/50 calculated as solids to obtain a coating composition, which was applied by a bar coater to the paper made in Example 12 and subjected to the same high-pressure treatment as in Example 12 over each surface thereof in an amount of 15 g/m^2.

Example 19

The paper delivered from the machine in Example 12 was coated with a shellac (brand name: Shellac GN-W25A, product of Gigu Shellac Seizosho) over each surface thereof in an amount of 9 g/m^2 using a bar coater, and thereafter passed through a nip provided by a metal roll and another metal roll under a linear pressure of 1000 kg/cm, at a roll temperature of 50 °C and at a speed of 10 m/min.

Comparative Example 5

The paper delivered from the machine in Example 12 was used.

Comparative Example 6

The paper delivered from the machine in Example 13 was coated with a shellac (brand name: Shellac BN-W25A, product of Gigu Shellac Seizosho) over each surface thereof in an amount of 10 g/m^2 using a bar coater to obtain paper.

Comparative Example 7

The paper delivered from the machine in Example 12 was thereafter passed through a nip provided by a metal roll and another metal roll under a linear pressure of 1000 kg/cm, at a roll temperature of 350 °C and at a speed of 20 m/min. This treatment produced blisters on the surface, failing to give uniform paper.

Comparative Example 8

The paper delivered from the machine in Example 12 was thereafter passed through a nip provided by a metal roll and another metal roll under a linear pressure of 1000 kg/cm, at a roll temperature of 100 °C and at a speed of 50 m/min. The resulting paper was coated with a shellac (brand name: Shellac BN-W25A, product of Gigu Shellac Seizosho) over each surface thereof in an amount of 2 g/m^2 using a bar coater to obtain paper.

[Method of Measuring Expansion of Paper when immersed in Water]

Measured by a method in accordance with J. TAPPI No. 27, B Method. More specifically, the sample was immersed in water for 5 minutes and thereafter checked for elongation by a Fenchel dimensional stability tester. The expansion of paper when immersed in water was calculated from the following equation.

$$\text{Expansion of paper (\%)} = [(L'-L)/L\} \times 100$$

wherein L is the initial length (mm), and L' is the length after immersion (mm).

Table 2 shows the property values of the papers obtained in Examples 12 to 19 and Comparative Examples 5 to 8.

Table 2

	basis weight (g/m^2)	high-pressure condition			resin coating amount (g/m^2)	expansion of paper (%)
		temp (°C)	linear pressure (kg/cm)	velocity (m/min)		
Ex.12	140	200	1000	50	20	0.35
Ex.13	90	250	500	100	20	1.58
Ex.14	90	300	1000	50	20	0.31
Ex.15	140	100	1000	50	10	0.37
Ex.16	140	100	1000	50	40	0.12
Ex.17	140	200	1000	50	20	0.32
Ex.18	140	200	1000	50	30	0.20
Ex.19	140	50	1000	10	18	0.40
Com.Ex.5	140	-	-	-	-	2.19
Com.Ex.6	90	-	-	-	20	2.42
Com.Ex.7	140	350	1000	20	*	*
Com.Ex.8	140	100	1000	50	4	2.24
* Not coatable or measurable owing to blisters.						

Example 20

To an initial condensate of urea, glyoxal and formaldehyde (brand name: BECKAMINE LK-S, product of Dainippon Ink & Chemicals Inc., urea:glyoxal:formaldehyde molar ratio = about 1:1:2.5) was added a catalyst consisting primarily of magnesium chloride (brand name: CATALYST G, product of Dainippon Ink & Chemicals Inc.) in an amount of 6.4% based on the nonvolatile content of the condensate, and the mixture was adjusted to a concentration of 35% to prepare a coating composition. The composition was applied by a bar coater to the paper delivered from the machine in Example 12 in an amount of 10 g/m^2. The coated paper was 6.0% in water content, 150 g/m^2 in basis weight and 194 μm in thickness. The paper was passed through a nip provided by a metal roll and another metal roll under a linear pressure of 1000 kg/cm, at a roll temperature of 150 °C and at a speed of 20 m/min. The paper was thereafter heated for curing in a hot air dryer at 120 °C for 30 minutes. The resulting paper was 107 μm in thickness.

Example 21

To an initial condensate of urea, glyoxal and formaldehyde (brand name: BECKAMINE DC-W, product of Dainippon Ink & Chemicals Inc., urea:glyoxal:formaldehyde molar ratio = about 1:1:2.1) was added a catalyst consisting primarily of magnesium chloride (brand name: CATALYST G, product of Dainippon Ink & Chemicals Inc.) in an amount of 6.4% based on the nonvolatile content of the condensate, and the mixture was adjusted to a concentration of 35% to prepare a coating composition. The composition was applied by a bar coater to the paper delivered from the machine in Example 12 in an amount of 9.6 g/m^2. The paper was passed through a nip provided by a metal roll and another metal roll under a linear pressure of 1000 kg/cm, at a roll temperature of 150 °C and at a speed of 10 m/min. The paper was thereafter heated for curing in a hot air dryer at 120 °C for 30 minutes. The resulting paper was 110 μm in thickness.

Example 22

Paper was prepared in the same manner as in Example 20 except that the coated paper was treated under a linear pressure of 500 kg/cm, at a roll temperature of 250 °C and at a speed of 50 m/sec. The paper obtained was 106 μm in thickness.

Example 23

Paper was prepared in the same manner as in Example 20 except that the coated paper was treated under pressure at a roll temperature of 30 °C. The paper obtained was 129 μm in thickness.

Example 24

Paper was prepared in the same manner as in Example 20 with the exception of using the resin of Example 21, applying the coating composition in an amount of 21.2 g/m^2 and using the metal rolls at a temperature of 100 °C. The paper obtained was 121 μm in thickness.

Example 25

A stock was prepared by adjusting a material pulp, comprising 100% of LBKP, to a CSF of 510 ml, adding 0.05% of an alkenylsuccinic anhydride (brand name: Fibran 81, product of National Starch and Chemical Co., Ltd.) and 0.7% of a cationic starch (brand name: Cato F, product of Oji Corn Starch Co., Ltd.) to the pulp and further adding talc to the pulp in an amount of 14% calculated as an ash content of paper. The stock was made into paper by a Fourdrinier paper machine with cylinder dryers. In the papermaking step, a liquid containing 6.5% of a starch (brand name: Ace A, product of Oji Corn Starch Co., Ltd.) was applied by a size press to both surfaces of the paper in a combined amount for the two surfaces of 2 g/m^2 calculated as solids. The paper obtained was 5.5% in water content, 262 g/m^2 in basis weight, 296 μm in thickness and at least 100 sec in sizing degree. To an initial condensate of urea, glyoxal and formaldehyde (brand name: BECKAMINE DC-W, product of Dainippon Ink & Chemicals Inc., urea:glyoxal:formaldehyde molar ratio = about 1:1:2.1) was added dipropylene glycol in an amount of 100% based on the nonvolatile content of the condensate to prepare a solution. To the solution was added a catalyst consisting primarily of magnesium chloride (brand name: CATALYST G, product of Dainippon Ink & Chemicals Inc.) in an amount of 6.4% based on the nonvolatile content of the condensate to prepare a coating composition. The composition was applied by a bar coater to the paper in an amount of 25 g/m^2. The coated paper was 6.0% in water content, 287 g/m^2 in basis weight and 317 μm in thickness. The paper was passed through a nip provided by a metal roll and another metal roll under a linear pressure of 1000 kg/cm, at a roll temperature of 100 °C and at a speed of 20 m/min. The paper was thereafter heated for curing in a hot air dryer at 120 °C for 60 minutes. The resulting paper was 197 μm in thickness.

Example 26

To an initial condensate of urea, glyoxal and formaldehyde (brand name: BECKAMINE DC-W, product of Dainippon Ink & Chemicals Inc., urea:glyoxal:formaldehyde molar ratio = about 1:1:2.1) was added polyethylene glycol (about 600 in average molecular weight) in an amount of 100% based on the nonvolatile content of the condensate to prepare a solution. To the solution was added a catalyst consisting primarily of magnesium chloride (brand name: CATALYST G, product of Dainippon Ink & Chemicals Inc.) in an amount of 12.8% based on the nonvolatile content of the condensate to prepare a coating composition. The composition was applied by a bar coater to the paper delivered from the machine in Example 25 in an amount of 35 g/m^2. The coated paper was 6.0% in water content, 297 g/m^2 in basis weight and 324 μm in thickness. The paper was passed through a nip provided by a metal roll and another metal roll under a linear pressure of 1000 kg/cm, at a roll temperature of 150 °C and at a speed of 10 m/min. The paper was thereafter heated for curing in a hot air dryer at 120 °C for 30 minutes. The resulting paper was 204 μm in thickness.

Example 27

To an initial condensate of urea, glyoxal and formaldehyde (brand name: BECKAMINE DC-W, product of Dainippon Ink & Chemicals Inc., urea:glyoxal:formaldehyde molar ratio = about 1:1:2.1) was added dipropylene glycol in an amount of 54% based on the nonvolatile content of the condensate to prepare a solution for use as a coating composition. The composition was applied by a bar coater to the paper delivered from the machine in Example 25 in an amount of 26 g/m^2. The coated paper was 6.0% in water content, 288 g/m^2 in basis weight and 313 μm in thickness. The paper was passed through a nip provided by a metal roll and another metal roll under a linear pressure of 1000 kg/cm, at a roll temperature of 100 °C and at a speed of 10 m/min. The paper was thereafter heated for curing in a hot air dryer at 190 °C for 2.5 hours. The resulting paper was 200 μm in thickness.

Example 28

A stock was prepared by adjusting a pulp mixture (NBKP/LBKP=3/7) serving as a material pulp to a CSF of 500 ml, adding 0.3% of a rosin size and 1.8% of alum cake to the pulp and further adding talc to the pulp in an amount of 5.5% calculated as an ash content of paper. The stock was made into paper by a Fourdrinier paper machine with cylinder dryers. In the papermaking step, an initial condensate of melamine (brand name: Cymel 350, product of Mitsui Cytec Ltd.) adjusted to a concentration of 50% was applied by a size press to the paper in an amount of 30 g/m^2. The paper was passed through a nip provided by a metal roll and another metal roll under a linear pressure of 1000 kg/cm, at a roll temperature of 150 °C and at a speed of 10 m/min. The paper was thereafter heated for curing in a hot air dryer at 120 °C for 30 minutes. The resulting paper was 157 g/m^2 in basis weight and 107 μm in thickness.

Example 29

In 1,3-dimethyl-4,5-dihydroxyethyleneurea (brand name: Sumitex NF-500K, product of Sumitomo Chemical Co., Ltd.) was dissolved dipropylene glycol in an amount of 33% based on the nonvolatile content of the urea, and a catalyst consisting primarily of zinc borofluoride (brand name: Sumitex Accelerator X-60, product of Sumitomo Chemical Co., Ltd.) was subsequently added to the solution in an amount of 5.6% based on the nonvolatile content of the urea to prepare a composition. The paper delivered from the machine in Example 25 was coated with the composition over each surface thereof in an amount of 20 g/m^2 by a bar coater. The coated paper was thereafter treated in the same manner as in Example 25. The resulting paper was 190 μm in thickness.

Example 30

To polyethylene glycol diglycidyl ether (brand name: DENACOL 821, product of Nagase Kaseikogyo Co., Ltd.) was added zinc borofluoride serving as a catalyst in an amount of 5% based on the ether to prepare a composition, which was then applied by a bar coater to the paper delivered from the machine in Example 25 over each surface thereof in an amount of 15 g/m^2. The coated paper was thereafter treated in the same manner as in Example 25. The resulting paper was 185 μm in thickness.

Example 31

Into a reactor were placed 70 parts of acrylamide, 5 parts of methacrylamide, 10 parts of polyoxypropylene glycol monomethacrylate having a number average molecular weight of 370 (brand name: BLEMMER PP1000, product of Nippon Oils & Fats Co., Ltd.), 10 parts of methylolacrylamide, 5 parts of acrylonitrile and 400 parts of water subjected to ion exchange. Nitrogen gas was bubbled through the mixture for 30 minutes to remove oxygen from the system. With the mixture adjusted to a temperature of 20 °C, a mixture of 10 parts of a 50% aqueous solution of diethanolamine and 10 parts of a 20% aqueous solution of ammonium persulfate serving as a redox initiator was added to the mixture for the start of polymerization. The reaction was continued for 1 hour after the temperature of the mixture reached 63 °C, affording a copolymer in the form of a 20% aqueous solution.

To the copolymer was added glyoxal in an amount of 3% based on the nonvolatile content thereof, and an aqueous solution of polyacrylic acid (35% in concentration) was further added in an amount of 10% based on the combined nonvolatile content of the copolymer and glyoxal. The concentration of the copolymer was then adjusted to 10% with ion-exchanged water. A stock was prepared by adjusting a material pulp, comprising 100% of LBKP, to a CSF of 500 ml, adding 0.3% of a rosin size and 1.8% of alum cake to the pulp and further adding talc in an amount of 16.0% calculated as an ash content of paper, and made into paper by a Fourdrinier paper machine with cylinder dryers.

The paper was 5.5% in water content, 127 g/m^2 in basis weight and 165 μm in thickness. The copolymer having its concentration adjsuted was applied by a bar coater to the paper over each surface thereof in an amount of 15 g/m^2.

The coated paper was 6.0% in water content, 157 g/m^2 in basis weight and 190 μm in thickness. The paper was passed through a nip provided by a metal roll and another metal roll under a linear pressure of 1000 kg/cm, at a roll temperature of 150 °C and at a speed of 10 m/min.

Comparative Example 9

The paper delivered from the machine in Example 20 was used.

Comparative Example 10

The paper passed through the nip of the metal rolls in Example 20 was used without being heat-treated. The paper was 111 μm in thickness.

Comparative Example 11

Paper was prepared in the same manner as in Example 20 except that the resin coating composition was applied in an amount of 2.4 g/m^2. The resulting paper was 109 μm in thickness.

Comparative Example 12

Paper was prepared in the same manner as in Example 20 except that the linear pressure was 100 kg/cm. The resulting paper was 148 μm in thickness.

Comparative Example 13

When the coated paper was passed through the nip at a roll temperature of 350 °C in the procedure of Example 20, the paper developed blisters.

Comparative Example 14

Paper was prepared in the same manner as in Example 23 except that the coated paper was heated for curing in a hot air dryer at 120 °C for 30 minutes and thereafter treated under a linear pressure of 1000 kg/cm at a roll temperature of 30 °C. The resulting paper was 155 μm in thickness.

Comparative Example 15

The paper delivered from the machine in Example 25 was merely passed through a nip of metal rolls under a linear pressure of 1000 kg/cm, at a roll temperature of 100 °C and at a speed of 20 m/min for use in this example.

Tables 3 and 4 show the treatment conditions for the papers obtained in Examples 20 to 31 and Comparative Examples 9 to 15, and the property values thereof.

Table 3

	glycol	basis weight (g/m^2)	resin coating amount (g/m^2)	treatment condition			
				temp (°C)	linear pressure (kg/cm)	velocity (m/min)	density (g/cm^3)
Ex.20	-	140	10.0	150	1000	20	1.40
Ex.21	-	140	9.6	150	1000	10	1.36
Ex.22	-	140	10.0	250	500	50	1.42
Ex.23	-	140	10.0	30	1000	20	1.36
Ex.24	-	140	21.2	100	1000	20	1.33
Ex.25	DPG	262	25.0	100	1000	20	1.46
Ex.26	PEG	262	35.0	150	1000	10	1.46
Ex.27	DPG	262	26.0	100	1000	20	1.44
Ex.28	-	-	30.0	150	1000	10	1.47
Ex.29	DPG	262	40.0	100	1000	20	1.59
Ex.30	-	262	30.0	100	1000	20	1.58
Ex.31	-	127	30.0	100	1000	20	1.32
Com.Ex.9	-	140	-	-	-	-	0.80
Com.Ex.10	-	140	10.0	150	1000	20	1.35
Cpm.Ex.11	-	140	2.4	150	1000	20	1.31
Com.Ex.12	-	140	10.0	150	100	20	0.96
Com.Ex.13	-	140	10.0	350	1000	20	*
Com.Ex.14	-	140	10.0	30	1000	10	0.96
Com.Ex.15	-	262	-	100	1000	20	1.40

The material papers used in Examples 25 to 27, 29 and 30 were at least 100 sec in sizing degree.
DPG: dipropylene glycol
PEG: polyethylene glycol (about 600 in molecular weight)
* Not measurable owing to blistering.

Table 4

	expansion of paper (%)	degree of bending recovery	heating	note
Ex.20	0.45	215	yes	catalysed
Ex.21	0.49	255	yes	catalysed
Ex.22	0.51	200	yes	catalysed
Ex.23	0.54	180	yes	catalysed
Ex.24	0.40	240	yes	catalysed
Ex.25	0.96	435	yes	catalysed
Ex.26	0.88	415	yes	catalysed
Ex.27	0.76	420	yes	no catalyst
Ex.28	0.68	210	yes	no catalyst
Ex.29	0.82	342	yes	catalysed
Ex.30	1.13	334	yes	catalysed
Ex.31	1.20	235	yes	glyoxal polyacrylic acid
Com.Ex.9	2.19	175	-	-
Com.Ex.10	2.03	170	no	catalysed
Com.Ex.11	1.15	155	yes	catalysed
Com.Ex.12	0.42	150	yes	catalysed
Com.Ex.13	*	*	-	catalysed
Com.Ex.14	0.67	190	yes+	catalysed
Com.Ex.15	3.08	325	-	-
Yes+: heat-treated before pressure treatment				

Example 32

A stock was prepared by adjusting a pulp mixture (NBKP/LBKP=2/8) serving as a material pulp to a CSF of 500 ml, adding 0.3% of a rosin size and 1.8% of alum cake to the pulp and further adding talc to the pulp in an amount of 9.7% calculated as an ash content of paper. The stock was made into paper by a Fourdrinier paper machine with cylinder dryers. In the papermaking step, a liquid containing 6.5% of starch (brand name: Ace A, product of Oji Corn Starch Co., Ltd.) was applied by a size press to both surfaces of the paper in a combined amount for the two surfaces of 2 g/m^2 calculated as solids. The paper obtained was 6% in water content, 140 g/m^2 in basis weight and 175 μm in thickness. Two sheets of this paper were passed as superposed through a nip provided by a metal roll and another metal roll under a linear pressure of 2000 kg/cm, at a roll temperature of 200 °C and at a speed of 80 m/min to obtain laminated paper. The laminated paper was 205 μm in thickness, and the component sheets were held bonded to each other without separation.

Example 33

A stock was prepared by adjusting a material pulp, comprising 100% of LBKP, to a CSF of 500 ml, adding 0.3% of a rosin size and 1.8% of alum cake to the pulp and further adding talc to the pulp in an amount of 16.0% calculated as an ash content of paper. The stock was made into paper by a Fourdrinier paper machine with cylinder dryers. The paper obtained was 90 g/m^2 in basis weight, 5% in water content and 124 μm in thickness. Water was applied by a bar coater to one surface of a sheet of this paper in an amount of 3 g/m^2, another sheet of the same paper was superposed on the wet surface of the first sheet, and the two sheets were passed through a nip provided by a metal roll and another metal roll under a linear pressure of 1000 kg/cm, at a roll temperature of 100 °C and at a speed of 100 m/min to obtain laminated paper. The resulting paper was 125 μm in thickness, and the component sheets were found to have been completely laminated.

Comparative Example 16

Laminated paper was prepared in the same manner as in Example 32 except that the linear pressure was 200 kg/cm. The component sheets were found to have not been perfectly laminated and easily separated by hand from each other.

INDUSTRIAL APPLICABILITY

Table 1 reveals that the present invention provides paper which is difficult for air to pass through and has great elasticity when at least 1.2 g/cm^3 in density.

The paper of the invention is excellent also in dimensional stability. While the papers of Examples 13 and 14 are not treated by a size press, Table 2 shows that the paper treated at the higher linear pressure at the higher temperature exhibits more excellent dimensional stability. The values achieved by Examples 12, 15 and 16 indicate that the greater the amount of resin coating composition applied, the higher is the dimensional stability. The alkali-soluble resin coating is formed on paper which has been treated under high pressure and therefore poses no problem in recycling the paper.

The paper of the invention is excellent in dimensional stability as will be apparent from Table 3. If no heat treatment is conducted, the effect to give dimensional stability is unavailable. Example 20 and Comparative Example 10 show that the effect to afford dimensional stability is not obtained unless the pressure treatment is followed by the heat treatment. Example 23 and Comparative Example 14 indicate that the heat treatment preceding the pressure treatment is effective to dimensional stability but fails to impart a high density or excellent elasticity and rigidity. If the linear pressure is low, a high density can not be obtained as will be apparent from Comparative Example 12. Further the addition of glycols causes the coating composition to penetrate into the paper effectively without allowing the composition to remain on the surface of paper even if the paper has a high sizing degree.

The process of the invention for producing paper comprising at least two laminated sheets of paper affords laminated paper by merely passing the component sheets through a nip provided by a metal roll and another metal roll under a specified pressure without necessitating a drying step and without using any adhesive.

Claims

1. A process for producing paper which process is characterized in that material paper is passed through a nip provided by a metal roll and another metal roll under a pressure of 200 to 2500 kg/cm.

2. A process as defined in claim 1 wherein the pressure is 500 to 2500 kg/cm.

3. A process as defined in claim 1 or 2 wherein the material paper is made from pulps including a softwood pulp in a proportion of less than 50 wt. % based on all the pulps.

4. A process as defined in any one of claims 1 to 3 wherein the material paper is made from pulps having a degree of beating which is at least 350 ml in terms of Canadian standard freeness.

5. A process as defined in any one of claims 1 to 4 wherein the paper treated under the pressure is at least 1.2 g/cm^3 in density.

6. A process as defined in any one of claims 1 to 5 wherein the paper treated under the pressure is at least 150 in degree of bending recovery.

7. A paper characterized in that the paper is produced by forming a moisture-proof resin layer on each of both surfaces of material paper before or after the material paper is passed through a nip provided by a metal roll and another metal roll under a linear pressure of 200 to 2500 kg/cm.

8. A paper as defined in claim 7 wherein the moisture-proof resin layer consists primarily of a wax.

9. A paper as defined in claim 7 wherein the moisture-proof resin layer consists primarily of a shellac.

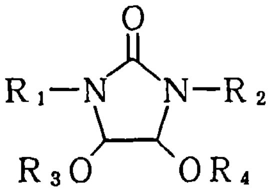
10. A paper as defined in claim 7 wherein the moisture-proof resin layer consists primarily of a phillosilicate compound having a mean particle size of 5 to 50 μm and an aspect ratio of at least 5 and treated with one of a silane coupling

agent, titanate coupling agent and aluminate coupling agent, and a synthetic resin.

11. A paper characterized in that the paper is produced by incorporating an interfiber crosslinking agent for cellulose into material paper, and thereafter passing the material paper through a nip provided by a metal roll and another metal roll under a linear pressure of 200 to 2500 kg/cm.

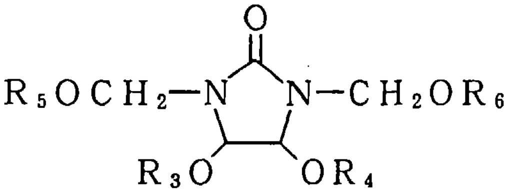
12. A paper as defined in claim 11 wherein the interfiber crosslinking agent has in the molecule thereof at least two groups which react with or form a hydrogen bond with the hydroxyl group of cellulose.

13. A paper as defined in claim 11 wherein the interfiber crosslinking agent is at least one of a compound having an N-methylol group, a compound represented by the formula (1)



(1)

wherein R_1 and R_2 are each H or alkyl having 1 to 5 carbon atoms, and R_3 and R_4 are each H or CH_3, a compound represented by the formula (2)



(2)

wherein R_5 and R_6 are each alkyl having 1 to 5 carbon atoms, and R_3 and R_4 are each H or CH_3, and an epoxy compound.

14. A paper as defined in claim 11 wherein the interfiber crosslinking agent is a water-soluble (meth)acrylamide copolymer.

15. A paper as defined in claim 11 wherein the interfiber crosslinking agent is a mixture of a water- soluble (meth)acrylamide copolymer and a water-soluble polyvalent aldehyde.

16. A paper as defined in claim 15 wherein a polyacrylic acid is added to the interfiber crosslinking agent.

17. A paper as defined in any one of claims 11 to 13 wherein a glycol is added to the interfiber crosslinking agent.

18. A paper as defined in any one of claims 11 to 13 wherein a catalyst is added to the interfiber crosslinking agent.

19. A paper as defined in any one of claims 7 to 18 which is up to 2% in expansion of paper when immersed in water in the cross direction.

20. A process for producing paper comprising at least two laminated sheets of paper, the process being characterized by passing at least two sheets of material paper through a nip provided by a metal roll and another metal roll under a pressure of 500 to 2500 kg/cm.

21. A process as defined in claim 20 wherein the material paper is 2 to 15% in water content.

22. A process as defined in claim 20 wherein water is applied at a position immediately upstream from the nip in an amount of 1 to 10 g/m^2 to at least one surface of the sheets to be laminated.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/03838

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^6 D21G1/00, D21H17/07, D21H17/47, D21H17/68

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)

Int. Cl^6 D21G1/00, D21H17/03-D21H17/70

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922 - 1997
Kokai Jitsuyo Shinan Koho	1971 - 1996
Toroku Jitsuyo Shinan Koho	1994 - 1997

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 01-260094, A (Kanzaki Paper Mfg. Co., Ltd.) October 17, 1989 (17. 10. 89), Claim; page 9, lower right column, lines 9, 10 (Family: none)	1, 3-22
Y	JP, 03-213598, A (Oji Paper Co., Ltd.), September 18, 1991 (18. 09. 91), Page 6, right column, lines 9 to 13 (Family: none)	1 - 22
Y	JP, 06-81299, A (New Oji Paper Co., Ltd.), March 22, 1994 (22. 03. 94), Column 5, line 4 (Family: none)	4 - 6
Y	JP, 49-50209, A (Seiko Kagaku Kogyo K.K.), May 15, 1974 (15. 05. 74), Claim (Family: none)	8, 9
Y	JP, 01-190483, A (Canon Inc.), July 31, 1989 (31. 07. 89), Claim (Family: none)	12, 13

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

* Special categories of cited documents:

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Date of the actual completion of the international search April 17, 1997 (17. 04. 97)	Date of mailing of the international search report April 30, 1997 (30. 04. 97)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/03838

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, 05-263393, A (Arakawa Chemical Industries, Ltd.), October 12, 1993 (12. 10. 93), Claim (Family: none)	14

Form PCT/ISA/210 (continuation of second sheet) (July 1992)