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(54) Title: A METHOD FOR THE PRODUCTION OF PAPER

(57) Abstract: A method for the production of paper which is characterized in that it employs an anionic fluorine-based oil-proofing agent and a fixing agent comprising polymer in which at least N-vinylformamide is a polymerization component and/or a derivative of said polymer; together with paper which is characterized in that it contains an anionic fluorine-based oil-proofing agent and a fixing agent comprising polymer in which at least N-vinylformamide is a polymerization component and/or a derivative of said polymer.



WO 2005/014931 A1

A method for the production of paper

Description

5 The present invention relates to a method for the production of paper, and to paper. More particularly, it relates to a paper production method which is ideal for producing paper with outstanding oil resistance, wet strength and water resistance by enhancing the level of fixing of an oil-proofing agent to the paper and, furthermore, where as well as it being possible to improve the operational characteristics such as the drainage at
10 the time of production, it is also possible to achieve a lowering of the environmental burden and greater economic efficiency; and to paper having outstanding oil resistance, wet strength and water resistance.

Oil-proofing agents are used to prevent contamination of food containers, food paper-packaging, paper employed as a construction material and the like, from oil and other oily materials. In particular, in the method of adding an oil-proofing agent to the pulp slurry within the paper manufacturing process (internal addition), fluorine-containing oil-proofing agents which have low surface free energy and can impart high oil resistance are used. When compared to the method of conferring oil resistance on paper by coat-
15 ing with an oil-proofing agent (external addition), paper containing such an internally-added fluorine-containing oil-proofing agent possesses oil resistance right into the paper interior and is characterized by having high oil resistance even in folds and cuts/tears and by having outstanding air permeability.

25 In terms of usability and safety, the aforesaid fluorine-containing oil-proofing agents are generally marketed in the form of aqueous solutions or aqueous dispersions, so treatment is carried out to raise the water solubility of the fluorine-containing oil-proofing compounds by incorporating ionic groups. Again, treatment is also carried out to bring about dispersion of the fluorine-containing oil-proofing agents in water using ionic or
30 nonionic surfactants. As a result, most fluorine-containing oil-proofing agents have ionic character but, in terms of ease of production and safety, the majority of these fluorine-containing oil-proofing agents have anionic character.

When an anionic fluorine-containing oil-proofing agent is added directly to a pulp slurry,
35 the pulp surface similarly has anionic character and so the fluorine-containing oil-proofing agent is insufficiently fixed or secured thereto and it is not possible to achieve a sufficient manifestation of the oil-proofing function. In such circumstances, there can be considered dealing with this problem by increasing the amount of oil-proofing agent used but this brings about the problem of an increased environmental burden in that
40 there is an increase in the waste-water treatment burden due to a build-up of oil-proofing agent within the papermaking system and a fear of release of oil-proofing agent outside the system. Furthermore, an increase in the amount of oil-proofing agent used is undesirable from economic considerations.

Hence, with the objective of enhancing the fixing of the anionic oil-proofing agent to the paper, the necessity arises of mixing a cationic material with the anionic oil-proofing agent or adding a cationic material to the pulp slurry in the paper manufacturing process separately from the anionic oil-proofing agent.

In the case where a cationic material is mixed with the anionic oil-proofing agent, the stability of the mixed liquid is usually impaired due to electrostatic interaction. Furthermore, in order to provide the oil-proofing agent with optimum cationic character in terms of the ion balance in the papermaking system, it is necessary each time to vary the amount of cationic material mixed or the ion strength thereof, or it is necessary to add some other chemical to adjust the ionic character. Consequently, from the point of view of the operational characteristics, this is just an augmentation of extremely inefficient operation.

On the other hand, in the case where the cationic material is added to the pulp slurry separately from the oil-proofing agent, it is sufficient only to adjust the amount of added cationic material so that it is optimal for fixing the oil-proofing agent. Hence, it is preferred that the anionic oil-proofing agent and the cationic material be separately added to the pulp slurry or that the two be mixed together just before the addition.

Most of the cationic materials used as fixing agents for oil-proofing agents are polymers obtained by polymerization of components which include a cationic monomer, or polymers obtained by subjecting polymer obtained by the polymerization of components which include monomer with ionic character or monomer without ionic character to cationic conversion. The majority of these cationic polymers have the purpose only of fixing the oil-proofing agent and they have little role in enhancing the paper strength, sizing properties or drainage properties, etc.

As a known example of a cationic material used as a fixing agent for anionic fluorine-based oil-proofing agents, there is the water-dispersible fluoro copolymer composition containing copolymer of monomer with a polyfluoroalkyl group and monomer which does not have a polyfluoroalkyl group or a carboxypolyfluoroalkyl group, and polyamine copolymer which contains amino groups or ammonium groups in side chains (JP-A-2002-220539).

However, by treatment using this fluoro copolymer composition, it is extremely difficult to produce paper having enhanced oil resistance, wet strength and water resistance, and where the drainage at the time of production is enhanced, all at the same time.

Furthermore, as a cationic material used as a fixing agent for anionic fluorine-based oil-proofing agents, there is also known a water-repellent composition comprising an a-

aqueous emulsion obtained by copolymerization of perfluoroalkyl acrylate monomer, monomer with a carboxyl group and monoethylenic monomer in specified proportions, and a cationic water-soluble polymer material such as a polyallylamine salt (JP-A-6-49319).

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However, by treatment using this water-repellent composition, it is still difficult to produce paper where the oil resistance, wet strength and water resistance, and the drainage at the time of production, are all enhanced at the same time.

- 10 The present invention aims to overcome such difficulties, and it addresses the problem of providing a method of paper production wherein the level of fixing of the oil-proofing agent to the paper is enhanced and which is ideal for the production of paper having outstanding oil resistance, wet strength and water resistance and, in addition, wherein operational characteristics such as the drainage at the time of production are improved,
- 15 while at the same time achieving a reduction in the environmental burden and a raising of economic efficiency; and it also addresses the problem of providing a paper which has outstanding oil resistance, wet strength and water resistance.

The present inventor has carried out considerable research into fixing agents for use along with anionic fluorine-based oil-proofing agents in order to resolve the aforesaid problems, as a result of which he has discovered that by using, as a fixing agent, polymer in which at least N-vinylformamide is a polymerization component and/or a derivative of such polymer, it is possible to resolve the aforesaid problems. The present invention has been perfected based on this discovery.

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Specifically, a first means for overcoming the aforesaid problems according to the present invention is

- (1) a method for the production of paper which is characterized in that it employs an anionic fluorine-based oil-proofing agent and a fixing agent comprising polymer in which at least N-vinylformamide is a polymerization component and/or a derivative of said polymer.

Preferred embodiments of this first means are the following paper production methods (a) to (d).

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- (a) A method for the production of paper where the aforesaid polymer derivative is the hydrolysate of the aforesaid polymer in which at least N-vinylformamide is a polymerization component.
- 40 (b) A method for the production of paper where the aforesaid polymer derivative is the hydrolysate of poly(N-vinylformamide).

- (c) A method for the production of paper where the aforesaid hydrolysate is the product obtained by hydrolysis of the formyl groups in the aforesaid polymer at a percentage hydrolysis of 10 to 90% of the total formyl groups.
- 5
- (d) A method for the production of paper where the aforesaid anionic fluorine-based oil-proofing agent is an oil-proofing agent comprising a compound having a phosphoric acid group or phosphate ester group.
- 10 Furthermore, a second means for overcoming the aforesaid problems according to the present invention is
- (2) Paper which is characterized in that it contains an anionic fluorine-based oil-proofing agent and a fixing agent comprising polymer in which at least N-
- 15 vinylformamide is a polymerization component and/or a derivative of said polymer.

As a preferred embodiment of this second means, there is paper where the aforesaid anionic fluorine-based oil-proofing agent is an oil-proofing agent comprising a compound having a phosphoric acid group or phosphate ester group.

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In accordance with the present invention, there is provided a method of paper production in which the level of fixing of the oil-proofing agent to the paper is enhanced and which is ideal for the production of paper having outstanding oil resistance, wet

25 strength and water resistance and, in addition, in which operational characteristics such as the drainage at the time of production are improved, while at the same time achieving a reduction in the environmental burden and a raising of economic efficiency; and there is also provided paper which has outstanding oil resistance, wet strength and water resistance. Hence, the invention makes a very great contribution to the industrial

30 field of papermaking.

- (1) The method of paper production of the present invention is characterized in that it employs an anionic fluorine-based oil-proofing agent and a fixing agent comprising polymer in which at least N-vinylformamide is a polymerization component and/or a derivative of said polymer.
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The anionic fluorine-based oil-proofing agent used in the present invention is not particularly restricted providing that it manifests oil resistance or oil repellency when fixed in the paper interior. Here, anionic refers to the case where the oil-proofing agent itself

40 contains a functional group which exhibits anionic character, or to the case of an aqueous emulsion formed by dispersing in an aqueous medium an oil-proofing agent which does not have anionic character and a material containing a functional group which

shows anionic character. As examples of the functional group which exhibits anionic character, there are the carboxyl group, phosphoric acid group, phosphate ester group, sulphonic acid group, sulphate ester group and the like. Amongst such functional groups, the phosphoric acid group and phosphate ester group are preferred, with the phosphate ester group being particularly preferred. Besides the component which manifests either oil resistance or oil repellency, the oil-proofing agent may also include additives for enhancing the dispersion stability at the time of synthesis or during storage, or for enhancing the sizing properties, etc.

- As preferred examples of the anionic fluorine-based oil-proofing agent used in the present invention, there are oil-proofing agents comprising compounds with a phosphoric acid group or a phosphate ester group. The compound from which the oil-proofing agent is composed may itself have a phosphoric acid group or a phosphate ester group, or the oil-proofing agent may comprise a mixture of a compound which does not have a phosphoric acid group or phosphate ester group and a compound which does have a phosphoric acid group or phosphate ester group. Examples of such anionic fluorine-based oil-proofing agents are the salts of phosphate esters which contain a polyfluoroalkyl group and phosphate esters with a poly(fluoroalkylene oxide).
- Specific examples of the aforesaid salts of phosphate esters containing a polyfluoroalkyl group include the hydrolysates of the reaction products of N-alkylperfluoroalkanesulphonamidoalkylalcohols and phosphorus oxychloride (see JP-B-40-6857) or dichlorophosphoric acid (see JP-B-54-7776), and the hydrolysates of the reaction products of polyfluoroalkanols and phosphorus oxyhalide, phosphorus pentoxide or dialkylphosphite (see JP-B-48-4770) and their ethanolamine salts (see JP-A-53-77015).

Furthermore, in order to improve the dispersion stability in water of the salts of phosphate esters which contain a polyfluoroalkyl group, there may also be compounded a fluoro- or chlorofluoro-aliphatic hydrocarbon (see JP-A-56-138197), an anionic surfactant (see JP-A-64-6196) or a specified nonionic surfactant (see JP-A-2000-144120).

As an example of the aforesaid phosphate esters with a poly(fluoroalkylene oxide), there are the compounds represented by $[XCF_2CF_2O(CFXCF_2O)_xCFXCF_2O]_2PO(OM)$ (where X is an atom or group selected from F and CF_3 , x is an integer in the range 1 to 8, and M is a water-soluble cation selected from alkali metal ions, ammonium ions and substituted ammonium ions) (see US Patent 3492374).

Furthermore, there are also the compounds represented by $A-CF_2O-(CF_2O)_n(C_2F_4O)_m-CF_2-B$ (where n is an integer in the range 1 to 20, m is an integer in the range 1 to 20, A and B are phosphate ester groups represented by $-[CH_2O(RO)_p]_k-P(O)(OH)_{3-k}$ (where

R is an alkylene group, in particular ethylene or propylene, p is an integer in the range 1 to 10, and k is 1 or 2) (see JP-A-2000-219847).

Besides the examples given above, the anionic fluorine-based oil-proofing agent used in the present invention may comprise copolymer of monomer with a fluoroalkyl group and other monomer, fluoroalkylcarboxylic acids, polyperfluoroalkyl-substituted polyamides, organosilicon compounds which contain a fluoroalkyl group and polymer formed from at least one type of monoethylenically unsaturated monomer selected from those with nonionic, anionic and cationic groups, monoethylenically unsaturated monomer containing a fluoroalkyl group and monoethylenically unsaturated monomer containing a silicone group.

As examples of commercially-available anionic fluorine-based oil-proofing agents, there are the Asahi Guard AG series (produced by the Asahi Glass Co.), the Fluorolink PT series (produced by Solvay Solexis), the Zonyl series (produced by DuPont) and the Scotchban series (produced by 3M).

The fixing agent used in the present invention is a polymer in which at least N-vinylformamide is a polymerization component and/or a derivative of such polymer.

As examples of the polymer in which at least N-vinylformamide is a polymerization component, there are the homopolymer obtained by the polymerization of N-vinylformamide and the copolymers obtained by the copolymerization of N-vinylformamide and monomers copolymerizable with N-vinylformamide (below said homopolymer and copolymer are merely referred to together as 'polymer'). In the present invention, there can also be used mixtures of homopolymer and copolymer.

Examples of the aforesaid monomers which are copolymerizable with N-vinylformamide include vinyl compounds with a side chain group which contains a nitrogen atom, the vinyl or propenyl esters of saturated carboxylic acids, nonionic (meth)allyl monomers, (meth)allyl monomers having a side chain which contains a nitrogen atom, olefins, ethylenically-unsaturated carboxylic acids, esters or amides of these ethylenically-unsaturated carboxylic acids, monomers with a nitrile group, monomers with a sulphonic acid group, monomers with a phosphoric acid group and styrene-type monomers.

Specific examples of the aforesaid vinyl compounds with a side chain group which contains a nitrogen atom are N-vinyl carboxylic acid amides such as N-vinylacetamide and N-vinylpropionamide, N-substituted-N-vinyl carboxylic acid amides such as N-methyl-N-vinylacetamide and N-ethyl-N-vinylacetamide, N-vinyl lactams such as N-vinylpyrrolidone and N-vinylcaprolactam, N-vinyl-N-alkylamines in which an alkyl group with from 1 to 6 carbon atoms is bonded to the nitrogen atom such as N-vinyl-N-

methyllamine and N-vinyl-N-ethylamine, and also vinyl-heterocyclic compounds such as N-vinylimidazole, 2-vinylimidazole, N-vinyl-2-methyl-imidazole, N-vinyl-4-methyl-imidazole, N-vinyl-5-methylimidazole, N-vinyl-2-ethylimidazole, N-vinylimidazoline, N-vinyl-2-methylimidazoline, N-vinyl-2-ethylimidazoline, N-vinyloxazole and N-vinyloxazoline.

The N-vinylimidazole and N-vinylimidazoline can be employed in their free base form, or they can be employed in the form obtained by neutralization with acid or in the quaternized form. Examples of said acid are mineral acids such as hydrochloric acid, carbonic acid, sulphuric acid and nitric acid, and organic acids such as sulphonic or carboxylic acids like formic acid, acetic acid and propionic acid. The quaternization can be carried out for example using an alkyl halide such as methyl chloride or methyl bromide, an aralkyl halide such as benzyl chloride or benzyl bromide, a dialkyl sulphate such as dimethyl sulphate or diethyl sulphate, or an epihalohydrin such as epichlorohydrin or epibromohydrin.

As examples of the aforesaid vinyl esters of saturated carboxylic acids, there are vinyl formate, vinyl acetate, vinyl propionate and vinyl butyrate, and as examples of the propenyl esters of saturated carboxylic acids, there are propenyl formate, propenyl acetate and propenyl propionate.

Examples of the aforesaid nonionic (meth)allyl monomers include (meth)allyl alcohols such as allyl alcohol and methallyl alcohol, (meth)allyl halides such as allyl chloride, allyl bromide, methallyl chloride and methallyl bromide, (meth)allyl ethers in which an alkyl group with from 1 to 18 carbons is ether-bonded such as allyl methyl ether, allyl ethyl ether, methallyl methyl ether and methallyl ethyl ether, and (meth)allyl esters of saturated carboxylic acids with from 1 to 18 carbons such as allyl formate, allyl acetate, allyl propionate, methallyl formate and methallyl acetate.

Examples of the aforesaid (meth)allyl monomers with a side chain group which contains a nitrogen atom are (meth)allylamines like allylamine and methallylamine, N-alkyl (meth)allylamines which have an alkyl group with from 1 to 18 carbons bonded to the nitrogen atom such as N-methylallylamine, N-ethylallylamine, N-stearylallylamine, N-methylmethallylamine and N-ethylmethallylamine, N,N-dialkyl (meth)allylamines which have alkyl groups with from 1 to 18 carbons bonded to the nitrogen atom such as N,N-dimethylallylamine, N,N-diethylallylamine, N,N-dimethylmethallylamine, N,N-diethylmethallylamine, N-methyl-N-stearylmethallylamine and N,N-distearylmethallylamine, N,N,N-trialkyl (meth)allylammonium halides which have alkyl groups with from 1 to 18 carbons bonded to the nitrogen atom such as N,N,N-trimethylallylammonium chloride, N,N,N-triethylammonium chloride, N,N,N-trimethylmethallylammonium chloride, N,N,N-triethylmethallylammonium chloride, N-methyl-N,N-distearylmethallylammonium chloride and N,N-dimethyl-N-

stearylmethallylammonium chloride, di(meth)allylamines such as diallylamine and dimethallylamine, N-alkyl di(meth)allylamines which have an alkyl group with from 1 to 18 carbons bonded to the nitrogen atom such as N-methyldiallylamine, N-ethyldiallylamine, N-methyldimethallylamine, N-ethyldimethallylamine and N-stearyldimethallylamine, and N,N-dialkyl di(meth)allylammonium halides which have alkyl groups with from 1 to 18 carbons bonded to the nitrogen atom such as N,N-dimethyldiallylammonium chloride, N,N-diethyldiallylammonium chloride, N,N-dimethyldimethallylammonium chloride, N,N-diethyldimethallylammonium chloride and N,N-distearyldimethallylammonium chloride.

The aforesaid (meth)allylamines, N-alkyl(meth)allylamines, N,N-dialkyl(meth)allylamines and N-alkyldi(meth)allylamines can be employed in their free base form, or they can be employed in the form obtained by neutralization with acid or in the quaternized form. Examples of said acid are mineral acids such as hydrochloric acid, carbonic acid, sulphuric acid and nitric acid, and organic acids such as sulphonic or carboxylic acids like formic acid, acetic acid and propionic acid. The quaternization can be carried out for example using an alkyl halide such as methyl chloride or methyl bromide, an aralkyl halide such as benzyl chloride or benzyl bromide, a dialkyl sulphate such as dimethyl sulphate or diethyl sulphate, or an epihalohydrin such as epichlorohydrin or epibromohydrin.

As examples of the aforesaid olefins, there are ethylene, propylene and butadiene.

As examples of the aforesaid ethylenically-unsaturated carboxylic acids there are acrylic acid, methacrylic acid, crotonic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, cinnamic acid, vinyl ester acids, 2-(meth)acrylamidoglycolic acid, α,β -unsaturated-tricarboxylic acids and α,β -unsaturated tetracarboxylic acids, together with the alkali metal salts, alkaline earth metal salts and ammonium salts thereof.

Examples of the aforesaid ethylenically unsaturated carboxylic acid esters are (meth)acrylate esters in which an alkyl group with from 1 to 18 carbon atoms is ester-bonded, such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, 2-ethylhexyl acrylate and stearyl acrylate, (meth)acrylate esters where only a single hydroxy group has been esterified such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, 2-methoxybutyl acrylate, 2-methoxybutyl methacrylate and the acrylic acid monoesters of a polyalkylene glycol of molecular weight 500 to 10,000, and the esters of an aminoalcohol and (meth)acrylic acid such as dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, dimethyl-

aminopropyl acrylate, dimethylaminopropyl methacrylate, diethylaminopropyl acrylate, dimethylaminobutyl acrylate and diethylaminobutyl acrylate.

5 These carboxylic acid esters of aminoalcohols can be employed in their free base form, or they may be employed in the form obtained by neutralization with acid or in the quaternized form. Examples of said acid are mineral acids such as hydrochloric acid, carbonic acid, sulphuric acid and nitric acid, and organic acids such as sulphonic or carboxylic acids like formic acid, acetic acid and propionic acid. The quaternization can be carried out for example using an alkyl halide such as methyl chloride or methyl bromide, an aralkyl halide such as benzyl chloride or benzyl bromide, a dialkyl sulphate
10 such as dimethyl sulphate or diethyl sulphate, or an epihalohydrin such as epichlorohydrin or epibromohydrin.

The aforesaid amides of the unsaturated carboxylic acids include the N-alkyl monoamides and N-alkyldiamides of monoethylenically unsaturated carboxylic acids which have an alkyl group with from 1 to 6 carbons, examples of which are acrylamide, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-methylmethacrylamide, N-ethylacrylamide, N-isopropylacrylamide and N-tert-butylacrylamide, and N,N-dialkylaminoalkyl (meth)acrylamides such as dimethylaminoethyl acrylamide, dimethylaminoethyl methacrylamide, diethylaminoethyl acrylamide, diethylaminoethyl methacrylamide, dimethylaminopropyl acrylamide, diethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide and diethylaminopropyl methacrylamide.
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The aforesaid N,N-dialkylaminoalkyl (meth)acrylamides can be employed in their free base form, or they can be employed in the form obtained by neutralization with acid or in the quaternized form. Examples of said acid are mineral acids such as hydrochloric acid, carbonic acid, sulphuric acid and nitric acid, and organic acids such as sulphonic or carboxylic acids like formic acid, acetic acid and propionic acid. The quaternization can be carried out for example using an alkyl halide such as methyl chloride or methyl bromide, an aralkyl halide such as benzyl chloride or benzyl bromide, a dialkyl sulphate
30 such as dimethyl sulphate or diethyl sulphate, or an epihalohydrin such as epichlorohydrin or epibromohydrin.

Examples of the aforesaid monomers with a nitrile group are acrylonitrile, methacrylonitrile and 2-methylene-glutaronitrile.
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Examples of the aforesaid monomers with a sulphonic acid group are vinylsulphonic acid, allylsulphonic acid, methallylsulphonic acid, isoprenesulphonic acid, 3-allyloxy-2-hydroxy-propanesulphonic acid, styrene-sulphonic acid, 3-sulphopropyl acrylate, 2-acrylamido-2-methylpropanesulphonic acid, 2-methacrylamido-2-methylpropanesulphonic acid, sulphoethyl acrylate, the sulphate ester of hydroxyethyl
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acrylate and the sulphate ester of polyoxyalkyleneoxide acrylate, together with the alkali metal salts, alkaline earth metal salts and ammonium salts, etc, of these acids.

As examples of the aforesaid monomers with a phosphoric acid group, there are vinylphosphonic acid and styrene-phosphonic acid, together with the alkali metal salts, alkaline earth metal salts and ammonium salts, etc, of these acids.

As examples of the aforesaid styrene-type monomers, there are styrene *per se*, α -methylstyrene, α -methylstyrene dimer and vinylbenzylamine. The vinylbenzylamine can be employed in its free base form, or it can be employed in the form obtained by neutralization with acid or in the quaternized form. Examples of said acid are mineral acids such as hydrochloric acid, carbonic acid, sulphuric acid and nitric acid, and organic acids such as sulphonic or carboxylic acids like formic acid, acetic acid and propionic acid. The quaternization can be carried out using for example an alkyl halide such as methyl chloride or methyl bromide, an aralkyl halide such as benzyl chloride or benzyl bromide, a dialkyl sulphate such as dimethyl sulphate or diethyl sulphate, or an epihalohydrin such as epichlorohydrin or epibromohydrin.

In the production of the aforesaid N-vinylformamide polymer, there may be used any polymerization method such as an ionic polymerization method like anionic or cationic polymerization, or a radical polymerization method. A radical polymerization method is preferred from the point of view of ready control of the molecular weight, and there can be used for example the method described in JP-A-11-322849.

Furthermore, the production of the aforesaid N-vinylformamide polymer can be carried out by a method such as bulk polymerization, solution polymerization, suspension polymerization or emulsion polymerization. The polymerization reaction is generally conducted under a current of inert gas, normally under temperature conditions of 30 to 100°C.

In the case of solution polymerization, the polymerization is carried out using water or a polar solvent which can dissolve the N-vinylformamide, and normally it is conducted in an aqueous solution of monomer concentration 5 to 60 mass%. In the case of suspension polymerization, usually the polymerization of an aqueous solution of monomer of concentration 20-80 mass% is carried out in a water-in-oil type dispersion state using a hydrophobic solvent and a dispersion stabilizer. Furthermore, in the case of emulsion polymerization, normally the polymerization of an aqueous solution of monomer of concentration 20-60 mass% is carried out in an oil-in-water type or water-in-oil type emulsion state using a hydrophobic solvent and an emulsifier.

In producing a copolymer of N-vinylformamide and monomer copolymerizable with said N-vinylformamide, there can be produced graft polymer or block polymer by graft po-

lymerization or block copolymerization of the N-vinylformamide and the monomer copolymerizable with said N-vinylformamide.

5 The aforesaid copolymer can be produced by the copolymerization of 90 to 1 mol% of the N-vinylformamide and 10 to 99 mol% of the monomer copolymerizable therewith, preferably 95 to 50 mol% and 5 to 50 mol% respectively.

In producing the aforesaid polymer, it is possible to use a normal polymerization initiator as the radical polymerization catalyst employed in the polymerization reaction, in particular in a radical polymerization reaction. As the polymerization initiator, there can be used for example an azo type polymerization initiator, a persulphate, a peroxide, a bromate, a perborate, a percarbonate or a perphosphate. Specifically, as the azo type polymerization initiator, there can be used azobisisobutyronitrile, 2,2'-azobis-(2,4'-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 2,2'-azobis(2-methylpropionitrile), 2,2'-azobis(2-methylbutyronitrile), 1,1-azobis-(cyclohexane-1-carbonitrile), 2,2'-azobis-[2-methyl-N-(2-hydroxyethyl)propionamide], dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-azobis-(2-amidinopropane), 2,2'-azobis-(2-amidinopropane), 2,2'-azobis-(N,N'-dimethyleneisobutylamine), 2,2'-azobis-(N,N'-dimethyleneisobutylamine), 2,2'-azobis(2-(2-imidazolin-2-yl)propane), 2,2'-azobis(2-(2-imidazolin-2-yl)propane) or 4,4'-azo-bis-(4-cyanovaleric acid) and the salts thereof. As examples of the persulphate, there are sodium persulphate, potassium persulphate and ammonium persulphate. As examples of the peroxide, there are benzoyl peroxide, hydrogen peroxide, tert-butylhydroperoxide and di-tert-butylperoxide. As examples of the bromate, there are sodium bromate and potassium bromate. As examples of the perborate, there are sodium perborate and ammonium perborate. As examples of the percarbonate, there are sodium percarbonate, potassium percarbonate and ammonium percarbonate. As examples of the perphosphate, there are sodium perphosphate, potassium perphosphate and ammonium perphosphate.

30 These polymerization initiators can be used on their own or they can be used in combinations of two or more. Especially preferred initiators are 2,2'-azobis-4-amidinopropane hydrochloride or acetate, the sodium salt of 4,4'-azobis-4-cyanovaleric acid, and azobis-N,N'-dimethyleneisobutylamidine hydrochloride or sulphate.

35 Furthermore, by jointly employing a reducing agent such as a sulphite like sodium sulphite, a bisulphite like sodium bisulphite, a metabisulphite like sodium metabisulphite, an organic amine like N,N,N',N'-tetramethylethylenediamine, or a reducing sugar like an aldose, the peroxide type polymerization initiators can also be used in the form of redox type polymerization initiators. These reducing agents can be used on their own or in combinations of two or more.

40

Polymerization is initiated by the addition of the polymerization initiator to the monomer solution. Moreover, with the objective of reducing the amount of unreacted monomer, a supplementary addition of some polymerization initiator may be made during the course of the polymerization reaction, or continuous addition of the polymerization initiator may be performed by a means such as the dropwise addition method. It is also possible to use the method of irradiating with ionizing radiation, an electron beam or ultraviolet light. These methods may be employed on their own or there can be used a combination of two or more types.

At the time of the polymerization, where required a chain transfer agent can be suitably employed. Examples of the chain transfer agent are compounds having one or more hydroxy groups in the molecule, compounds having one or more mercapto groups in the molecule, compounds having one or more carbon-carbon unsaturated bonds in the molecule, peroxides such as dibutylperoxide, and hypophosphoric acid. The chain transfer agents may be used on their own or in combinations of two or more.

Furthermore, at the time of polymerization, a crosslinking agent may be suitably added where required. Examples of the crosslinking agent are bifunctional polymerizable vinyl monomers such as di(meth)acrylates, bis(meth)acrylamides and divinyl esters which possess two unsaturated bonds, monomers with a crosslinking action due to having functional groups which undergo chain transfer with vinyl groups, monomers which have a crosslinking action due to having groups which react with vinyl groups, trifunctional polymerizable vinyl monomers which have three unsaturated bonds, tetrafunctional polymerizable vinyl monomers which have four unsaturated bonds, water-soluble aziridinyl compounds, water-soluble polyfunctional epoxy compounds and silicon based compounds. These can be used on their own or in combinations of two or more.

Furthermore, insofar as the objectives of the present invention are not impaired, the polymerization of the N-vinylformamide or the copolymerization of the N-vinylformamide and monomer copolymerizable therewith can be carried out in the presence of a water-soluble polymer such as a starch like oxidized starch, cationic starch, amphoteric starch or enzyme-modified starch, a cellulose derivative such as carboxymethylcellulose, polyvinyl alcohol, chitosan or a gum, etc.

As examples of the derivatives of polymer in which at least N-vinylformamide is a polymerization component, and which can be used in the present invention, there are (1) polymer formed by modification of the formamide groups contained in N-vinylformamide homopolymer, (2) polymer formed by modification of the formamide groups contained in copolymer of N-vinylformamide and monomer which can copolymerize with N-vinylformamide, and (3) mixtures of polymer (1) and polymer (2).

Examples of said modification are hydrolysis, amide-exchange, hydrolysis followed by reaction of the amino groups with an alkyl halide such as methyl chloride or methyl bromide, an aralkyl halide such as benzyl chloride or benzyl bromide, a halo-carboxylic acid ester such as a haloformate ester or haloacetate ester, a dialkyl sulphate such as dimethyl sulphate or diethyl sulphate, an epihalohydrin such as epichlorohydrin or epibromohydrin, a saturated aliphatic or aromatic glycidyl ether compound, or urea, amidine modification based on hydrolysis in the presence of ammonia, and cyclic amidine modification conducted by heating a partially hydrolyzed derivative of the aforesaid polymer in which at least N-vinylformamide is a polymerization component. Amongst such materials, the derivatives obtained by hydrolysis of the formyl groups in the aforesaid N-vinylformamide homopolymer and in the copolymers of N-vinylformamide and vinyl monomer polymerizable therewith are preferred.

As examples of the derivatives obtained by hydrolysis of the aforesaid polymers, there are the hydrolysates obtained by hydrolysis of the formyl groups in these polymers. Such derivatives can be obtained by performing hydrolysis in the solution state or after dehydrating or drying to produce a powder state, using known hydrolysis methods such as for example an acidic hydrolysis method, a basic hydrolysis method, a method of acidic hydrolysis in a hydrophilic solvent such as alcohol containing water, or an alcoholysis method under acidic conditions. Amongst these methods of hydrolysis, the acidic and basic hydrolysis methods are preferred.

The modifying agent used in acidic hydrolysis can be any compound which acts as a strong acid such as hydrochloric acid, hydrobromic acid, hydrofluoric acid, sulphuric acid, nitric acid, phosphoric acid, sulfamic acid or methanesulphonic acid, but a monobasic acid is preferred in terms of facilitating the dissolution of the hydrolysate in water.

The modifying agent used in basic hydrolysis may be any compound which acts as a strong base such as sodium hydroxide, potassium hydroxide, lithium hydroxide or a quaternary ammonium hydroxide.

As examples of the alcohol used in the case of alcoholysis, there are alcohols with from 1 to 4 carbons such as methanol, ethanol, propanol and butanol, but methanol is preferred.

The amount of modifying agent used for the hydrolysis will be suitably selected in accordance with the desired percentage modification, normally from within the range 0.05 to 5 mol per mol of formyl groups in the aforesaid polymer. The reaction temperature at the time of the hydrolysis is normally in the range 30 to 110°C, and the reaction time is normally from 0.1 to 24 hours.

The percentage hydrolysis of the formyl groups in the polymer in which at least N-vinylformamide is a polymerization component is preferably from 10% to 90% of the total formyl groups in the polymer, with from 30% to 70% being still further preferred. If the percentage hydrolysis is too low, there may be insufficient oil-proofing agent fixing effect, while conversely if the percentage hydrolysis is too great then the ion balance in the papermaking system may be damaged, and the yield, paper quality such as texture, and operational properties may be impaired.

When carrying out the hydrolysis, for the purposes of preventing the gelling brought about by impurities, the modification may be conducted with the optional addition of a gelling inhibitor such as hydroxylamine hydrochloride or hydroxylamine sulphate. Furthermore, hydrolysis can also be carried out after performing treatment with the gelling inhibitor prior to modification. The hydrolysis can be conducted in a homogeneous solution using water or a mixture of water and a polar solvent such as methanol, or in a heterogeneous solution comprising a non-polar solvent such as hexane or toluene and a polar solvent containing at least water.

By means of the aforesaid polymerization process or process of derivative preparation, the solids concentration of the solution of polymer in which at least N-vinylformamide is a polymerization component and/or of derivative thereof obtained is normally from 3 to 40 mass%. Furthermore, when the viscosity of this polymer solution and/or derivative solution is measured with a Brookfield rotary viscometer at 25°C, normally it is no more than 100,000 mPa.s and preferably no more than 20,000 mPa.s. In the present invention, this polymer solution and/or derivative solution can be employed as it is for use as the fixing agent.

As examples of the paper raw material pulp used in the paper production method of the present invention, there are kraft pulp, sulphite pulp and other such bleached and unbleached chemical pulps, groundwood pulp, mechanical pulp, thermomechanical pulp, chemithermomechanical pulp and other such bleached or unbleached high-yield pulps, and also pulps containing pulps of waste paper such as newspaper, magazine paper, cardboard and the like. As well as wood pulp, there may also be used non wood-based pulps such as those based on straw or kenaf. Furthermore, there may be used a mixture of an aforesaid pulp and a synthetic fibre such as polyamide, polyester, polyolefin or polyvinyl alcohol, etc.

The anionic fluorine-based oil-proofing agent and fixing agent of the present invention can be added prior to the dryer part of the papermaking process and the method of addition is not particularly restricted, but it is preferred that they be added to the paper materials prior to the wet web formation. There are no particular restrictions on the order of addition of the anionic fluorine-based oil-proofing agent and the fixing agent,

and again both may be added at the same location or they may be mixed together just before the addition. Furthermore, one may be added prior to the other.

5 In the case where the anionic fluorine-based oil-proofing agent and the fixing agent are added to the paper materials prior to the wet web formation, they may be added at the same time as, or before or after, other chemical agents. There are no particular restrictions on these chemical agents, examples of which include coagulants, dry paper
10 strengtheners, wet paper strengtheners, sizing agents, fillers, yield enhancers and drainage enhancers, and these are added where required so that there may be manifested the properties required in accordance with the paper type, or so that the operational characteristics are enhanced. One such chemical agent may be incorporated or there may be used two or more types in combination.

15 Examples of the aforesaid coagulants are poly(diallyldimethylammonium chloride) and the reaction product of amines and epihalohydrins. Examples of the dry paper strengtheners are anionic polyacrylamide, cationic polyacrylamide, amphoteric polyacrylamide, cationic starch and amphoteric starch. Examples of the wet paper strengtheners are polyamide epichlorohydrin resins, polyamine epichlorohydrin resins, melamine formaldehyde resin and urea formaldehyde resin, etc.

20 Furthermore, examples of the sizing agents are fatty acid soaps, solution rosin, acidic rosin emulsion, neutral rosin emulsion, alkenylsuccinic anhydride emulsion or its hydrolylate salts, 2-oxetanone emulsion, paraffin wax emulsion, cationic sizes obtained by the reaction of a carboxylic acid and a polyfunctional amine, emulsions of the reaction
25 products of aliphatic oxyacids and aliphatic amines or aliphatic alcohols, and cationic styrene type emulsion sizes.

Furthermore, as examples of fillers, there are calcium carbonate, talc, clay and white carbon, and as examples of yield enhancers there are anionic high molecular weight
30 polyacrylamides, cationic high molecular weight polyacrylamides, amphoteric high molecular weight polyacrylamides, silica sol and bentonite, etc.

35 Examples of drainage enhancers are polyethyleneimine, anionic polyacrylamide, cationic polyacrylamide and amphoteric polyacrylamide, while examples of other types of chemical agent include alum, polyaluminium chloride and other types of aluminium compounds, dyes, defoaming agents and pH regulators.

40 In the case where the anionic fluorine-based oil-proofing agent and the fixing agent are applied to the paper after the wet web formation by spraying or the like, or again in the case of the coating of the surface of the paper using a coating machine or printing machine, etc, other chemical agents may also be jointly employed. There are no particular restrictions on the jointly employed chemicals, and examples are surface strength-

eners, interlayer paper strengtheners, surface sizes, slippage preventives and viscosity regulators, etc, and these may be suitably selected and used to manifest the properties required in accordance with paper type, or to enhance operational characteristics. They can be used on their own or two or more types can be jointly used.

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The amount of anionic fluorine-based oil-proofing agent added or applied to the paper in the present invention can be suitably adjusted according to the degree of oil resistance required of the paper. In the case where the anionic fluorine-based oil-proofing agent is added to the paper materials prior to the wet web formation, the percentage added is normally 0.01 to 10 mass% and preferably 0.1 to 2 mass% in terms of the dry mass of raw material pulp. If the percentage anionic fluorine-based oil-proofing agent added is too low, then even where said anionic fluorine-based oil-proofing agent is fully fixed within the paper, there may not be shown the oil resisting effect required. Conversely, if the percentage anionic fluorine-based oil-proofing agent added is too great, then the oil-proofing agent which is not fixed within the paper builds up in the white water, leading to an increased burden on the waste water treatment facility and also to a higher than necessary cost of chemical agent.

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In the case where the anionic fluorine-based oil-proofing agent is applied to the paper by spraying or the like following the formation of the wet web, or in the case where the surface of the paper is coated using a coating machine or printing machine, the amount applied is normally from 0.1 to 50 g/m² and preferably 1 to 20 g/m² in terms of the dry mass of paper, and it can be suitably adjusted in accordance with the degree of oil resistance of the paper required.

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With regard to the amount of fixing agent added or applied to the paper in the present invention, the optimum value thereof needs to be selected in accordance with the degree of oil resistance and other properties required of the paper, the added or applied amount of the anionic fluorine-based oil-proofing agent, the ion balance within the papermaking system and the operational characteristics, etc. The amount of fixing agent added is normally from 0.01 to 10 times, and preferably from 0.1 to 2 times, the added amount by solids concentration of the anionic fluorine-based oil-proofing agent. If too little fixing agent is added, then there will be inadequate fixing of the anionic fluorine-based oil-proofing agent within the paper, and not only is it not possible to show the oil resistance effect demanded but also, in the case of the internal addition of anionic fluorine-based oil-proofing agent, the anionic fluorine-based oil-proofing agent which is not fixed within the paper builds up in the white water and may increase the burden on the waste water treatment facility. Conversely, if the amount added is too great, then the ion balance within the papermaking system is destroyed, and the yield, paper properties such as texture and operational properties may be impaired.

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- (2) Furthermore, the paper of the present invention contains anionic fluorine-based oil-proofing agent and a fixing agent comprising polymer in which at least N-vinylformamide is a polymerization component and/or a derivative of said polymer.

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The anionic fluorine-based oil-proofing agent, and the fixing agent comprising polymer in which at least N-vinylformamide is a polymerization component and/or derivative of said polymer, are the same as those used in the aforesaid method of paper production (1). The paper of the present invention can be produced by the method of paper production in (1) above.

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Examples of the paper produced by the method of paper production described in (1) above, and of aforesaid paper (2), are any type of paper where it is required to confer oil resistance by means of an anionic fluorine-based oil-proofing agent or where some other additional effect is required and is obtained by including this anionic fluorine-based oil-proofing agent. Paper in the present invention also includes sheet/board. Examples of the paper types are food packaging paper, food containers, packaging paper for metals and other types of oil-resistant paper, PPC paper, inkjet printing paper, laser printer paper, paper business forms, thermal transfer paper, heat-sensitive recording paper, pressure-sensitive recording paper, groundwood paper and other types of paper employed for information purposes, photographic printing paper and its base paper, art paper, cast-coat paper, lightweight coated paper and other types of coated paper and the base paper therefor, kraft paper, pure white roll paper and other types of packaging paper, and also writing paper, paper for books, various types of paper for printing, newspaper roll paper, manila board, white board, chipboard and other types of board for paperware articles/boxes, liners, water-resistant liners, packing, water-resistant packing, gypsum board base paper and other types of board/sheet, etc.

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Examples

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Below, the present invention is explained in more specific terms by means of examples and comparative examples but the invention is not to be restricted in any way by the examples given. Unless otherwise stated, reference to '%' means 'mass%' in every case.

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Fixing Agent Production Example 1

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80 g (1125 mmol) of N-vinylformamide was dissolved in 385 g of water in a 2L capacity flask equipped with a stirrer, thermometer and a means for operating under a nitrogen atmosphere. 0.65 g (2.4 mmol) of 2,2'-azobis-(2-amidinopropane) hydrochloride was mixed therewith and, by introducing nitrogen, oxygen was eliminated. The reaction mixture was then heated to 55°C within 1 hour. After maintaining for 5 hours at this

temperature, in order to enhance the conversion the temperature was raised to 60°C for 30 minutes and the percentage conversion made 100%. Next, 68.5 g (676 mmol) of 36% aqueous hydrochloric acid was mixed with the viscous polymer solution thus obtained, then heating carried out for 2 hours at 90°C and hydrolysis performed. The aqueous polymer solution obtained totalled 534.5 g and its viscosity was 1500 mPa.s (Brookfield viscosity, 25°C). It was confirmed by ¹H-NMR that 60% of the formyl groups had been hydrolysed.

Fixing Agent Production Example 2

Reaction was carried out in the same way as in Example 1 except that, instead of 68.5 g (676 mmol) of the 36% aqueous hydrochloric acid used in Fixing Agent Production Example 1, there was mixed 40.5 g (400 mmol) of 36% aqueous hydrochloric acid solution. An aqueous polymer solution was obtained of viscosity 1400 mPa.s (Brookfield viscosity, 25°C) where 40% of the formyl groups had been hydrolysed (as confirmed by ¹H-NMR).

Fixing Agent Production Example 3

Reaction was carried out in the same way as in Example 1 except that, instead of the 68.5 g (676 mmol) of 36% aqueous hydrochloric acid used in Fixing Agent Production Example 1, there was mixed 81.0 g (800 mmol) of 36% aqueous hydrochloric acid solution. An aqueous polymer solution was obtained of viscosity 1600 mPa.s (Brookfield viscosity, 25°C) where 80% of the formyl groups had been hydrolysed (as confirmed by ¹H-NMR).

Paper Production Examples

Examples 1 to 3

0.5% alum, 0.1% of commercial copolymerized polyacrylamide type dry paper strengthener (commercial name "DS437", produced by the Seiko PMC Corporation), 0.15% of the fixing agent shown in Table 1 and 0.5% of the commercial perfluoroalkyl-phosphate ester salt type anionic oil-proofing agent ("Asahi Guard AG-530", produced by the Asahi Glass Co.) were added in turn to a 2.4% pulp slurry (LBKP/NBKP = 9/1, Canadian Standard Freeness 400). After stirring, the pulp slurry was diluted with pure water to 0.5% and part removed for measurement of the drainage property.

The drainage property was determined using equipment identical to the "Dynamic Drainage Jar" described on page 46 of the Tappi Journal Vol.56, No.10 (1973), with 500 ml of the pulp slurry being poured into a jar of diameter 7.5 cm and, while stirring at 600 rpm, the lower cock was opened and fluid allowed to pass through a 100 mesh

strainer. The time taken to obtain 250 g of filtrate was measured and used for the evaluation.

5 Then, using the remaining pulp slurry, wet paper of weight per unit area 80 g/m^2 was obtained by means of a Noble and Wood handsheet machine. The papermaking pH at this time was 6.8. The wet paper obtained was pressed and then dried for 80 seconds at 100°C with a drum dryer. The handsheet paper obtained was conditioned for 24 hours at 23°C and 50%RH, after which measurement of the oil resistance was carried out by means of the "Paper and Board - Oil Repellency Test Method - Kit Method" in 10 Japan Tappi No.41. Furthermore, the water resistance was measured based on JIS P8122 "Paper Stockigt Sizing Test Method" and the wet breaking length was measured based on JIS P8113 "Method for Testing the Tensile Properties of Paper and Paper Board". The amounts of aforesaid chemical agents added are expressed as the solids concentration mass ratio in terms of the absolute dry mass of pulp. The results are 15 shown in Table 1.

Comparative Example 1

20 Handsheet paper was produced in the same way as in Example 1 except that no fixing agent was added. The evaluations were conducted in the same way as in Example 1 and the results are shown in Table 1.

Comparative Example 2

25 Handsheet paper was produced in the same way as in Example 1 except that there was added 0.3% of a commercial fixing agent (produced by Meisei Chemical Works Co., commercial name "AG Fix M-15") which is a cationic (methacrylate ester/acrylamide) type polymer. The evaluations were conducted in the same way as in Example 1 and the results are shown in Table 1.

30

Comparative Example 3

35 Handsheet paper was produced in the same way as in Example 1 except that there was added 0.3% of a commercial fixing agent (produced by the Seiko PMC Corporation, commercial name "Fikstar X-15") which is a cationic (diallylamine/acrylamide) type polymer. The evaluations were conducted in the same way as in Example 1 and the results are shown in Table 1.

Table 1

	Fixing A- gent	250 g Drai- nage (secs)	Oil Resis- tance (-)	Stockigt Sizing (secs)	Wet Paper Breaking Length (km)
Example 1	Production Example 1	8.1	9.5	66	0.47
Example 2	Production Example 2	14.1	9.0	61	0.39
Example 3	Production Example 3	8.7	8.5	48	0.46
Comp.Ex.1	none	55.7	1.0	28	0.10
Comp.Ex.2	as stated	18.2	7.0	45	0.15
Comp.Ex.3	as stated	27.5	4.0	39	0.25

5 Table 1 confirms that by using the fixing agents produced in Production Examples 1 to 3, it is possible to confer on paper outstanding oil resistance, together with outstanding wet strength and water resistance. In addition, it is possible to realize an enhancement in the drainage property.

Claims

1. A method for the production of paper which is characterized in that it employs an anionic fluorine-based oil-proofing agent and a fixing agent comprising polymer in which at least N-vinylformamide is a polymerization component and/or a derivative of said polymer.
5
2. A method for the production of paper according to Claim 1 where the aforesaid polymer derivative is the hydrolysate of the aforesaid polymer in which at least N-vinylformamide is a polymerization component.
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3. A method for the production of paper according to Claim 1 or Claim 2 where the aforesaid polymer derivative is the hydrolysate of poly(N-vinylformamide).
- 15 4. A method for the production of paper according to Claim 2 or Claim 3 where the aforesaid hydrolysate is the product obtained by hydrolysis of the formyl groups in the aforesaid polymer at a percentage hydrolysis of 10 to 90% of the total formyl groups.
- 20 5. A method for the production of paper according to any of Claims 1 to 4 where the aforesaid anionic fluorine-based oil-proofing agent is an oil-proofing agent comprising a compound having a phosphoric acid group or phosphate ester group.
- 25 6. Paper which is characterized in that it contains an anionic fluorine-based oil-proofing agent and a fixing agent comprising polymer in which at least N-vinylformamide is a polymerization component and/or a derivative of said polymer.
- 30 7. Paper according to Claim 6 where the anionic fluorine-based oil-proofing agent is an oil-proofing agent comprising a compound having a phosphoric acid group or phosphate ester group.

INTERNATIONAL SEARCH REPORT

International Application No

/EP2004/008088

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D21H21/14

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)

IPC 7 D21H

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

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

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 597 314 A (ULMSCHNEIDER DIETER ET AL) 3 August 1971 (1971-08-03) the whole document	1-7
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A	US 3 492 374 A (BLEU RONALD E LE ET AL) 27 January 1970 (1970-01-27) the whole document	1-7
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

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- *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
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- * & * document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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