Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2201337 C 2009/05/19

(11)(21) 2 201 337

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 1996/01/25
(87) Date publication PCT/PCT Publication Date: 1996/08/01
(45) Date de délivrance/Issue Date: 2009/05/19
(85) Entrée phase nationale/National Entry: 1997/03/27
(86) N° demande PCT/PCT Application No.: FI 1996/000051
(87) N° publication PCT/PCT Publication No.: 1996/023105
(30) Priorité/Priority: 1995/01/25 (FI950326)

(51) Cl.Int./Int.Cl. *D21H 21/16* (2006.01), *D21H 17/17* (2006.01)

(72) Inventeurs/Inventors:
ZETTER, CLAES, FI;
MALMSTROM, OLOF, FI;
NURMINEN, MARKKU, FI

(73) Propriétaire/Owner:
CIBA SPECIALTY CHEMICALS HOLDING, INC., CH

(74) Agent: MCCARTHY TETRAULT LLP

(54) Titre : PROCEDE D'AMELIORATION DE L'HYDROPHOBICITE DE PAPIERS D'IMPRESSION ET COMPOSITION HYDROPHOBE DU PROCEDE

(54) Title: A METHOD FOR INCREASING THE HYDROPHOBICITY OF PRINTING PAPERS AND A HYDROPHOBE COMPOSITION FOR THE METHOD

(57) Abrégé/Abstract:
The present invention relates to a method of improving the water repellency of paper in papermaking by virtue of adding prior to web formation to the pulp slurry such a sizing dispersion that contains at least a ketene dimer compound as a hydrophobic sizing agent, and further contains water-soluble colloidal polymer in an amount which is at least 100 % by weight of the hydrophobic sizing agent. The invention is particularly applicable for improving the water repellency of paper containing calcium carbonate as the filler.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
D21H 21/16, 17/17

A1

(11) International Publication Number: WO 96/23105

(43) International Publication Date: 1 August 1996 (01.08.96)

(21) International Application Number: PCT/FI96/00051

(22) International Filing Date: 25 January 1996 (25.01.96)

(30) Priority Data:
950326 25 January 1995 (25.01.95) FI

(71) Applicant (*for all designated States except US*): RAISIO CHEMICALS OY [FI/FI]; Raisionkaari 55, FIN-21200 Raisio (FI).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): ZETTER, Claes [FI/FI]; Sirkkalankatu 11 A, FIN-20500 Turku (FI). MALMSTRÖM, Olof [FI/FI]; Stålarminkatu 5 C 30, FIN-20810 Turku (FI). NURMINEN, Markku [FI/FI]; Järviniityntie, FIN-21120 Raisio (FI).

(74) Agent: OY JALO ANT-WUORINEN AB; Iso Roobertinkatu 4-6 A, FIN-00120 Helsinki (FI).

(81) Designated States: CA, CN, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

2201337

Published
With international search report.
With amended claims.
In English translation (filed in Finnish).

(54) Title: A METHOD FOR INCREASING THE HYDROPHOBICITY OF PRINTING PAPERS AND A HYDROPHOBE COMPOSITION FOR THE METHOD

(57) Abstract

The present invention relates to a method of improving the water repellency of paper in papermaking by virtue of adding prior to web formation to the pulp slurry such a sizing dispersion that contains at least a ketene dimer compound as a hydrophobic sizing agent, and further contains water-soluble colloidal polymer in an amount which is at least 100 % by weight of the hydrophobic sizing agent. The invention is particularly applicable for improving the water repellency of paper containing calcium carbonate as the filler.

A method for increasing the hydrophobicity of printing papers and a hydrophobe composition for the method

The present invention relates to a method of improving the hydrophobicity of printing papers by means of internal sizing of the paper. The invention also concerns a hydrophobe composition for performing of the method. A particular object of the invention is to improve the hydrophobicity of paper by means of using a ketene dimer compound as a hydrophobic sizing agent. The purpose of improving the hydrophobicity is to impart the paper web a degree of sizing that makes the paper compatible with ink-jet printing.

The resistance properties of paper to wetting and penetration are conventionally enhanced in papermaking by means of internal sizing, where during the paper making process compounds are added into the paper pulp which increase the hydrophobicity of the paper fibers.

Printing papers, which are chiefly used as office paper in various types of copiers, printers and printing machines, are expected to exhibit high brightness among other properties, as well as acceptable permanence in archive document use. The brightness and archiving permanence properties can be affected through the type of filler used for the paper. One filler compatible with the above-described requirements is precipitated calcium carbonate (PCC). However, a problem is involved in the use of this filler, because it requires a neutral or alkaline environment for a proper functioning. Such a process condition excludes the use of conventional hydrophobic sizing of paper by means of the rosin-alum system. As known in the art, this drawback is overcome by the use of hydrophobic sizes based on ketene dimer compounds such as alkyl, alkenyl, aryl and alkaryl ketene dimer sizes.

Such sizes are, however, hampered by other problems particularly in paper grades intended for office printing use that have to be compatible with different printer types. Namely, besides a application in ink-jet printing, the same paper grade should do as copier paper, laser printing paper, etc. When optimized for the above-mentioned ink-jet use, the base paper must be sized with such great amounts of ketene dimer combination sizes that ultimately the size causes problems in the alternative printer types. In practice, the degree of sizing may amount to, e.g., 0.1 - 0.2 % of fiber dry weight in the web.

Over time, ketene dimer compounds have been found problematic as a sizing agent due to their migration tendency in the finished paper. Owing to such migration, the content of the ketene dimer compound is enriched in the outer layers of the sheet. Migration is made possible by the fact that the curing reactions of ketene dimer compounds are so slow that the added agents lose their migration capability not earlier than after a few days from the finishing of the sheet.

A disadvantageous effect of ketene dimer compound enrichment is easier slippage of the sheet surface, i.e., decrease of surface frictional resistance. Reduced friction is harmful particularly in printing and copier paper grades, because the lowered threshold of slippage causes paper handling problems in printing or copying machines whose paper transfer elements fail to provide their intended function on slippery paper grades.

Also the above-mentioned filler, namely, the precipitated calcium carbonate causes indirectly easier slippage of the sheet. This is because this filler has been found to disturb the hydrophobic sizing process, whereby greater amounts of size must be used per unit weight of fiber in comparison to the use of another type of filler.

On the other hand, it has been found that ketene dimer based sizing fails to bond completely on the fiber during sheet formation, whereby a fraction of the sizing agent remains circulating in the system and of this fraction a portion bonds later on the fiber. When circulating in the system, the sizing compound is subjected to the hydrolyzing effect of water resulting in a partial decomposition of the sizing compound into corresponding ketones. Also a fraction of the size retained in the base web will remain unbonded to the fiber, whereby the size may undergo hydrolyzation by the moisture contained in the web. These phenomena are harmful particularly in copier use, where the sheet is subjected to heating in the copying machine, whereby the decomposition of unbonded size and its migration, along with the moisture released from the sheet, to the surface of the sheet are accelerated. Resultingly, the machine parts of the copier may become contaminated and the copying result deteriorated. To eliminate these risks, determination of residual ketone content in paper grades intended for copier use has been instigated.

According to the present invention, an essential improvement has now been achieved to overcome the above-described problem by virtue of performing hydrophobic sizing using a sizing dispersion in which the amount of water-soluble colloidal polymer is at least 100 % of the amount of the hydrophobic sizing compound.

Herein, it has firstly been noted that ketene dimer compound used as the hydrophobic sizing agent is better bonded to the fiber, and, secondly, that the precipitated calcium carbonate used as the filler has no essential disturbing effect on the sizing process. Owing to the latter fact, less is needed, whereby said smaller amount of the hydrophobic sizing agent can be retained close to the fiber in an improved manner until the curing of the hydrophobic sizing agent has proceeded to a level preventing migration. Additionally, it was found that the invention offered improved ink penetration properties with respect to the water penetration. This effect is of extremely high importance to the quality of ink-jet printing that is becoming ever more widely used.

Preferably, the content of hydrophobic sizing agent is approx. 1-15 % by weight, advantageously 6-15 % by weight.

The invention has furthermore been found applicable in cases where the ketene dimer compound employed as a hydrophobic sizing agent in the sizing of paper is complemented with other conventional hydrophobic sizing agents such as alkenyl succinic anhydride (ASA) and/or rosin. In one embodiment, aluminum sulphate is also present at 2-15% by weight of the colloidal polymer.

Preferably, the content of ASA is 20-70 %, advantageously 30-50 %, by weight of the ketene dimer. Preferably, the content of rosin is approx. 20-50 % by weight of the ketene dimer.

The invention is next explained with the help of the following examples elucidating the function of the invention in its different embodiments.

Example 1

A pilot-scale test run was carried out, in which internal sizing was performed for a finepaper grade with added precipitated calcium carbonate (PCC) as the filler. The filler (tradename Albacar LO) was used at 22 % level by fiber dry weight. The fiber in the base web was 75 % birch fiber beaten to 23 SR° freeness and the fiber slurry was adjusted to pH 7. The rest, 25 %, of the fiber was pine fiber equally beaten to 23 SR° freeness and fiber slurry also adjusted to pH 7. Internal sizing of the paper web was performed using Raisamyl 135 starch at 5 kg/ton pulp addition rate. The basis weight of the produced paper web was 80 g/m^2. The paper machine was run at 60 m/min resulting in a production rate of 4.08 kg/min. The retention agent used in the process was BMA 590 (colloidal sodium silicate) at an addition rate of 300 g/ton pulp. The paper web was also surface sized using Raisamyl 406 LO starch at 6 % solids addition level. The hydrophobic compound used as a sizing agent was alkyl ketene dimer (AKD).

The test runs were performed using the different formulations of hydrophobic size listed below for internal sizing:

1. Conventional AKD sizing with Raisafob 940, in which the amount of starch protective colloid addition was not more than 20 % by weight of sizing agent.
2. AKD sizing, amount of starch protective colloid addition 50 % by weight of sizing agent.
3. AKD sizing, amount of starch protective colloid addition 100 % by weight of sizing agent.
4. AKD sizing, amount of starch protective colloid addition 150 % by weight of sizing agent.
5. AKD sizing, amount of starch protective colloid addition 200 % by weight of sizing agent.
6. AKD sizing, amount of starch protective colloid addition 250 % by weight of sizing agent.
7. AKD sizing, amount of starch protective colloid addition 300 % by weight of sizing agent.
8. AKD sizing, amount of protective colloid addition using PEI (polyimin KK)* in an amount of 200 % by weight of sizing agent.

Notes: *) polyethylene imine

The tests were run using two levels of sizing agent, namely, adding the sizing agent (AKD) at 0.1 % and 0.2 % levels by fiber dry weight.

The starch used as the protective colloid component was Raisamyl 150 which is a degraded special starch grade.

The degree of sizing in the manufactured papers were tested by measuring the water absorbance of the paper sheets in the $Cobb_{60}$ test from the sheet surface, while the ink penetration of the sheets was measured using the Schröder test. Also the brightness of test sheets was measured.

The test runs gave the following results:

Test no./ Amount of size	$Cobb_{60}$ test [g/m^2] 0.1 %	0.2 %	Schröder test (100-->90%, s) 0.1 %	0.2 %	Brightness [%]
1	78.2	28.3	0	10	92.7
2	76.3	28.1	1	11	92.6
3	41.5	26.6	2	15	92.7
4	29.3	20.2	5	135	92.8
5	25.0	18.4	18	248	93.0
6	24.8	18.3	20	253	92.9
7	24.7	18.2	21	255	93.0
8	28.8	18.1	21	262	91.1

From the above results it can be seen that, at an addition rate of the sizing agent of 0.1 % by fiber dry weight, a sufficient addition rate of the protective colloid component is at approx. 200 % level by hydrophobic sizing agent solids weight, whereby this combination provides such a $Cobb_{60}$ value of less than 25 g/m^2 that conventionally is considered to represent a sufficient level of sizing. For the larger, 0.2 wt.%, addition rate of the sizing agent, the corresponding water repellency value is attained using an addition rate of the protective colloid component as low as 100 % of the hydrophobic sizing agent solids weight. Also polyethylene imine (PEI) was found (test run no. 8) to act as a protective colloid component at the same addition rate (200 %), however, with the penalty that paper brightness is adversely affected particularly in grades manufactured using optical brighteners. The ink penetration property of the paper web is improved significantly up to 200 % addition rate of the protective colloid component, whereafter this property at higher addition rates stays approximately at the same level as when using PEI.

Example 2

A production-scale test run was performed on a finepaper machine by making paper at 78 g/m^2 basis weight. The paper was manufactured using pulp comprised in 60/40 ratio of birch to pine fiber. The amount of filler added to the base web was at 22 % level by fiber dry weight, whereby 70 % of the filler was precipitated calcium carbonate (PCC, Albacar LO) and 30 % of ground $CaCO_3$. The retention system was formed by corn starch and an anionic component (Compozil).

The AKD sizing was applied using two different formulations:

1. Raisafob 940, conventional AKD sizing, amount of protective colloid component not more than 20 % of sizing material dry weight.
2. Raisafob 500, AKD sizing using starch as the protective colloid component with an amount increased to 200 % of size dry weight. The starch added as the protective colloid component was Raisamyl 150 EH.

The test runs were carried out using AKD sizing at 0.12 % level by fiber dry weight. Tests were performed in multiple series using both of the above sizing formulations in identical conditions to eliminate random error from the results. The test data is listed in the table below:

Test run	AKD type	$Cobb_{60}$		Schröder test (100-->91%, s)	Coefficient of friction		Ink-jet, black-and-white			Ink-jet, color			
no.		felt side	wire side	felt side	static	kinetic	black density (100%)	ink drying time [s]	wicking mean	ink drying time [s]	wicking mean	color-to-color bleeding	black density (100%)
77	RF940	21.7	22.2	59	0.79	0.54	1.60	9	4	19	10	8	1.08
79	RF940	20.7	21.5	49	0.67	0.50	1.64	11	4	20	10	8	0.98
81	RF940	21.2	20.7	54	0.77	0.54	1.64	9	6	18	10	8	0.97
84	RF940	20.4	20.6	78	0.75	0.58	1.76	12	4	15	10	8	1.03
87	RF500	19.9	19.8	205	0.76	0.53	1.91	22	2	109	10	8	1.38
89	RF500	19.3	19.0	181	0.75	0.53	1.93	14	2	144	10	8	1.38
91	RF500	19.4	19.2	209	0.82	0.57	1.94	21	2	154	10	8	1.42
93	RF500	19.4	19.4	203	0.81	0.57	1.90	19	2	157	10	8	1.46
95	RF500	19.5	18.9	277	0.78	0.60	1.96	24	2	172	10	8	1.51

As is evident from the above results, sizing properties are clearly improved by the use of RF 500 and the coefficient of friction is simultaneously retained at the same level or even improved. The ink-jet printing tests indicate that the use of RF 500 gives positively improved black-and-white printing results over conventional sizing, and simultaneously, the ink-jet color printing test remains unchanged, which indicates that the level of sizing herein is overproportioned for ink-jet color printing.

Example 3

A production-scale test run was carried out in which the following sizing formulations were compared:

1.	Raisafob 940	AKD sizing, amount of starch protective colloid addition not more than 20 % by weight of sizing agent.
2.	Raisafob 500	AKD sizing, amount of starch protective colloid addition 200 % by weight of sizing agent.

The paper made herein was a office paper grade intended for multipurpose use. The production target values for the paper grade were set as follows: residual ketone content less than 0.4 mg/g (for copier use), black density greater than 1.2 in B/W printing on ink-jet printers and combination black density greater than 0.75 in multicolor printing.

Test run conditions:

Paper grade:	Office paper (multipurpose)
Basis weight:	80 g/m^2
Base web composition:	70% birch fiber at 23 °SR freeness 70% pine fiber at 23 °SR freeness
Filler:	Precipitated calcium carbonate (PCC)
Retentionsystem:	Two-component formulation (polymer + bentonite)
Surface sizing:	Raisamyl 408 starch + 1.5 kg styrene acrylate polymer/ton pulp solids
Paper machine speed:	980 m/min
AKD addition rate:	1 kg AKD/ton pulp solids, or alternatively, 1.4 kg AKD/ton pulp solids

Test results:

Sizing agent	Addition rate [kg/ton]	$Cobb_{60}$ [g/m²]	Ink penetration HST 80 [%, s]	Residual ketone [mg/g]	Black density, B/W printing, felt side	Black density, comp. color printing, felt side
RF940	1	25	80	0.41	1.02	0.64
RF940	1.4	23	153	0.68	1.22	0.82
RF500	1.4	21	238	0.27	1.38	0.90

As is evident from the above results, the sizing properties are clearly improved by the use of RF 500. Additionally, the residual ketone content remains below the set target value. Also the density target values set for ink-jet printing are exceeded. By contrast, using the RF 940 sizing formulation with a low protective colloid content it is not possible to meet the upper limit set for the residual ketone content. Hence, the paper made in this process is not suited for the intended copier use. If the size addition rate is reduced to a level of 1 kg/ton pulp solids, the RF 940 sizing formulation may marginally meet the level set for the maximum allowable residual ketone content, however, with the penalty of not meeting required ink penetration criteria.

The invention has further been found suitable for use in such paper sizing applications in which a fraction of the hydrophobic sizing agent is composed, besides of AKD, additionally of another sizing agent suited for improvement of water repellency such as alkenyl succinic anhydride (ASA). However, as ASA sizing formulations do not offer hydrophobic properties as effective as those of AKD sizing formulations, they must be used in larger amounts to achieve comparable ink-jet printability qualities. Due to the staining problems caused by the required large addition rates of ASA sizing in papermaking, this sizing approach appears less favored. However, because the use of an ASA sizing formulation in the present application would give a low residual ketone content in the finished sized paper, which is a definite benefit when using the paper in copiers. The well-known problematic properties of this sizing agent require that the sizing furnish be prepared in the immediate vicinity of the papermaking process. In the following example, the behavior of this sizing formulation type is described.

Example 4

A production-scale test run was carried out to compare the behavior of the following sizing formulations:

1.	Raisafob 500	AKD sizing, amount of starch protective colloid addition 200 % by weight of the ketene dimer.
2.	Raisafob MF	ASA sizing, dispersed in bulk sizing starch Raisamyl 135 in an ASA/starch ratio of 1:2.
3.	Raisafob 500 + Raisafob MF	AKD sizing plus Raisafob MF, added separately.
4.	New sizing	AKD/Raisafob 500 type sizing formulation dispersion + ASA dispersed therein in AKD/ASA ratio of 50/50.

The paper made herein was a office paper grade intended for multipurpose use. The production target values for the paper grade were set as follows: ketene content less than 0.4 mg/g (for copier use), black density greater than 1.2 in B/W printing on ink-jet printers and combination black density greater than 0.75 in multicolor printing.

Test run conditions:

Paper grade:	Office paper (multipurpose)
Basis weight:	80 g/m^2
Base web composition:	70 % birch fiber at 23 SR° freeness 30 % pine fiber at 23 SR° freeness
Filler:	Precipitated calcium carbonate (PCC) at 20 % level by fiber dry weight
Retention system:	Two-component formulation (polymer + bentonite)
Surface sizing:	Raisamyl 408 starch + 1.5 kg styrene acrylate polymer/ton pulp solids
Paper machine speed:	980 m/min
AKD addition rate:	1.4 kg/ton pulp solids (as AKD, combined with Raisafob RF500)
ASA addition rate:	1.4 kg/ton pulp solids (combined with Raisafob MF)
AKD/ASA addition rate:	0.7 kg + 0.7 kg/ton pulp solids (combined with Raisafob RF500 and Raisafob MF, respectively, using separate additions)
New sizing formulation:	0.7 kg + 0.7 kg/ton pulp solids (ASA dispersed in Raisafob RF500)

Test results:

Sizing agent	Addition rate [kg/ton]	$Cobb_{60}$ [g/m²]	Ink penetration HST 80 [%,s]	Residual ketone [mg/g]	Black density, B/W printing, felt side	Black density, comp. color printing, felt side
RF500	1.4	22	24	0.29	1.32	1.06
RF MF	1.4	23	122	0	1.14	0.58
RF500 +RF MF	0.7+0.7	22	173	0.15	1.18	0.78
New formulation	0.7+07	21	208	0.15	1.21	0.86

As is evident from the above results, the requirements set for the compatibility of the manufactured paper with ink-jet printability are not met using ASA sizing alone. Admittedly, the paper exhibits zero residual ketone content. The novel type of combination sizing formulation is capable of meeting the requirements set for both copier and ink-jet printing use. The results also show the effect of the hydrolysis of ASA on the sizing efficiency when the ASA is dispersed in warm starch used as the internal size and then added separately. With regard to ink-jet printing, also herein the novel sizing formulation gives better density values than those achieved using ASA alone.

In a similar fashion as combining with ASA sizing, the AKD dispersion based on Raisafob 500 may be combined with rosin sizing. In general, rosin imparts good friction properties and does not make the paper slippery as typically is the case using AKD sizing alone. This improvement is described in the example below.

Example 5

In this example a pilot-scale paper machine was employed to compare the water repellency of a paper web achievable by three different sizing formulations: first, using conventional AKD sizing (Raisafob 940), second, using AKD combined a protective colloid component formed by Raisamyl 150 EH in an amount of 200 % of sizing agent dry weight, and third, testing the effect according to the present invention of the protective colloid component (Raisamyl 150 EH, 200 % by sizing agent dry weight) combined with AKD plus rosin used as a hydrophobic sizing agent. The dry weight ratio of AKD to rosin was 50/50.

The base web was formed from a pulp comprising 75 % of birch fiber at 23 SR° freeness and 25 % of pine fiber at 23 SR° freeness. Bulk sizing of the paper web was performed using Raisamyl 125 at 0.5 % addition level by fiber dry weight. The retention system was formed by a two-component system in which Percol 162 was added at 0.02 % level and bentonite at 0.2 % level by fiber dry weight. The paper web was surface sized using Raisamyl 408 SP, which was added at 5 % level by fiber dry weight. The amount of filler added to the base web was kaolin at 20 % level by fiber dry weight. The pulp slurry pH was in the range 6.9 - 7.0. The sheets produced were measured for water absorbance in the $Cobb_{60}$ test on both the felt and wire sides of the sheet. Similarly, the static and kinetic coefficients of friction were determined. Also the addition rate of surface sizing was monitored. The test results are given in the table below.

Sizing formulation	Raisafob 940	AKD+ Raisamyl 150 EH	AKD+rosin+ Raisamyl 150 EH
Addition rate	0.12	0.12	0.20
$Cobb_{60}$, felt side	18.6	18.3	28.1
$Cobb_{60}$, wire side	20.1	20.2	31.9
Static coeff. of friction	0.395	0.428	0.465

Kinetic coeff. of friction	0.222	0.229	0.355
Surface size addition rate	1.9 l/min	1.8 l/min	1.4 l/min

As is evident from the above results, the best sizing properties are achieved using the AKD sizing dispersion containing Raisamyl 150 EH starch as the protective colloid component. Also the friction properties of the sheet are improved over a sheet sized using a conventional AKD sizing formulation (Raisafob 940). The results also indicate that a sizing dispersion having the AKD/rosin combination as the sizing agent in the protective colloid also performs excellently particularly in terms of its friction values, which refer to minimal migration tendency of the sizing agent in spite of the slightly increased size addition rate over that used in the comparative test runs. Admittedly, the sizing efficiency in terms of water repellency herein remains lower than that achieved in the comparative test runs.

CLAIMS

1. A method of improving ink-jet printability of printing paper manufactured using precipitated calcium carbonate as filler, comprising adding a ketene dimer compound to a pulp slurry, prior to web formation, wherein a sizing dispersion is used that contains at least the ketene dimer compound as a hydrophobic sizing agent in an amount of 0.1-0.2 % of fiber dry weight and further contains a water-soluble colloidal polymer, and wherein the amount of the water-soluble colloidal polymer is at least 100 % by weight of the hydrophobic sizing agent.

2. A method as defined in claim 1, wherein a sizing dispersion is used in which the amount of the colloidal polymer is in the range of 150-250 % by weight of the hydrophobic sizing agent.

3. A method as defined in claim 1, wherein a sizing dispersion is used containing at least one further sizing agent selected from the group consisting of alkenyl succinic anhydride and rosin.

4. A method as defined in any one of claims 1-3, wherein the water-soluble colloidal polymer is selected from the group consisting of starches, carboxy methyl cellulose, ethyl cellulose, polyacryl amides, polyethylene imines, polyesters, polyethers, polyamides, polyvinyl alcohols, gelatine, tristearate, gum arabic, sugars, and mixtures thereof.

5. A method as defined in claim 4, wherein the water-soluble colloidal polymer is an amphoteric low-viscosity starch.

6. A method as defined in claim 3, wherein the further sizing agent is an alkenyl succinic anhydride in an amount of 20-70 % by weight of the ketene dimer.

7. A method as defined in claim 6, wherein the further sizing agent is an alkenyl succinic anhydride in an amount of 30-50 % by weight of the ketene dimer

8. A method as defined in claim 3, wherein the further sizing agent is fortified rosin.

9. A method as defined in claim 3 or 8, wherein the further sizing agent is rosin in an amount of 20-50 % by weight of the ketene dimer compound.

10. A method as defined in any one of claims 1-9, wherein the sizing dispersion further contains at least one of a surface-active compound, a biocidal agent, and a pH-controlling agent.

11. A method as defined in claim 8 or 9, wherein the sizing dispersion contains aluminium sulphate at 2-15 % by weight of the colloidal polymer.

12. A method as defined in any one of claims 1-11, wherein the ketene dimer compound is selected from the group consisting of alkyl, alkenyl, aryl, and alkaryl ketene dimers.

13. A method as defined in any one of claims 1-12, wherein the content of the hydrophobic sizing agent in the sizing dispersion is 1-15 wt.%.

14. A method as defined in claim 13, wherein the content of the hydrophobic sizing agent in the sizing dispersion is 6-15 wt.%