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⑤④ **Process and compositions for sizing paper.**

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**GB-A-1 397 933**  
**GB-A-1 482 515**  
**GB-A-1 569 591**  
**GB-A-2 079 768**  
**US-A-1 370 650**  
**US-A-1 958 202**  
**US-A-3 046 186**  
**US-A-4 021 399**  
**US-A-4 214 948**

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## Description

The invention relates to the sizing of cellulosic fibres and to compositions for use in this, and to their manufacture.

During the manufacture of paper it is necessary to render the naturally hydrophilic cellulosic fibres hydrophobic so that penetration of aqueous liquids into the formed sheets is limited thereby making writing and printing on the sheets possible. This process, known as sizing, can be carried out by adding a sizing agent to the pulp slurry (usually termed internal sizing) or the sizing agent can be applied to the formed paper sheet. This invention is concerned with the internal sizing process.

There are two types of sizing agent in general use. One of these is based on rosin which is used in conjunction with alum. The rosin is added as a soap solution or as an emulsion and alum is added afterwards just prior to sheet formation to precipitate the rosin as a fine particulate which is retained by the sheet.

The second type of size is a reactive size, such as a ketene dimer or an anhydride-based size, which reacts chemically with the cellulosic fibres. Preferably it is applied in combination with a polyelectrolyte which will help to retain the size in the sheet.

The reactive size is generally added to the pulp in the form of an aqueous emulsion, generally a cationic emulsion. The emulsion can be prepared at the mill but this necessitates the mill having emulsifying equipment and so it would be more convenient if a concentrated emulsion could be supplied to the mill ready for dilution and use. Unfortunately reactive sizes tend to react with water so that an aqueous emulsion is liable to be rather unstable.

Anhydride based sizes, such as alkenyl succinic anhydride sizes, are so reactive that their emulsions have to be prepared at the mill just prior to use. These sizes are normally supplied to the mill with a cationic starch which generally has to be precooked before emulsification, thus making it even less convenient for the emulsion to be formed at the mill.

Ketene dimer sizes often are supplied to the mill in the form of an emulsion but these emulsions have only limited shelf-life and the maximum concentration of ketene dimer in the emulsion is rather low, generally below 6%, so that very large volumes of emulsion have to be supplied to the paper manufacture.

Emulsification of liquid ketene dimers can be achieved using conventional emulsification equipment but some of the preferred ketene dimers are solids at ambient temperature. As described in U.S. Patent Specification 3,046,186, emulsification of these necessitates initially either melting the solid (so that upon cooling the emulsion is converted to a dispersion) or dissolving the solid in a solvent, generally benzene. A typical important ketene dimer is distearyl ketene dimer and this only has relatively low solubility in organic solvents with the result that the solution of it that is emulsified must be rather dilute. For instance we have found that this dimer precipitates from a 40% by weight solution in benzene (weight ratio benzene:dimer of 1:0.67) and so any solution in benzene must be much more dilute than this. Also this dimer is less soluble in other organic solvents than it is in benzene.

As described in Patent Specification 3,046,186 the emulsions are generally prepared by emulsifying the dimer into an aqueous solution of cationic dispersing agent although that patent does mention that in certain instances the emulsifying agent may be predispersed in the ketene dimer. It is stated that the emulsions may be prepared at any convenient solids content but are used at 1 to 5% solids by weight.

In each of the examples in U.S. Patent Specification 3,046,186 the initial composition that was prepared and that contained both size and polyelectrolyte was very dilute. For instance in Example 1 the initial concentration is about 9% by weight size based on the total composition.

As mentioned above, it is preferred to provide a polyelectrolyte with the reactive size and it might be thought that some of the disadvantages associated with providing emulsions of reactive size and polyelectrolyte could be minimised if the reactive size and the polyelectrolyte were supplied separately. However this incurs other disadvantages.

It would therefore be very desirable if it was possible to supply a stable concentrated composition that contained both reactive size and polyelectrolyte and which was readily dilutable with water at the mill.

A concentrate composition according to the invention comprises a substantially anhydrous dispersion of a polyelectrolyte in an organic liquid comprising a solution of a reactive size in a hydrophobic solvent, and in which the water content is not more than 10% by weight and the ratio size:solvent is at least 0.67:1.

The concentrate composition generally has a reactive size concentration above 20% and preferably at least 28.6%. The concentration of reactive size is often in the range 30 to 60%. The amount may be higher, for instance up to 80% or 85%. All these amounts are by weight of the total composition.

The weight ratio, on a dry basis, of polyelectrolyte:reactive size is generally from 1:1 to 1:10, preferably 1:1.5 or 2 up to 1:4 or 1:5.

In order that the concentrate can conveniently have an appropriately high active content it is necessary for the weight of reactive size to be at least 0.67 parts per part by weight organic solvent (i.e. 40% solution). The weight ratio organic solvent:reactive size is generally from 1:10 to 1:0.67 preferably 1:1 to 1:3.

With the most dilute solution of reactive size in solvent that is generally used in the invention (40 parts size to 60 parts solvent) the amount of polyelectrolyte is generally between 4 parts and 40 parts, giving sizing compositions having a reactive size content of from 38.4 to 28.6%. A composition having 83.3%

reactive size can be formed from, for instance, 100 parts reactive size, 10 parts solvent and 10 parts polyelectrolyte.

Preferred compositions have, per part solvent, about 1 to 3 parts (preferably about 2 parts) reactive size and about 0.5 to 2 parts (preferably about 1 part) polyelectrolyte.

5 The concentrate composition must be substantially anhydrous in order that the composition is stable, and in practice this means that if water is present its amount will be not more than 10% and preferably not more than 5% by weight of the composition. Preferably the water content is not more than 1% or, at the most, 2% by weight of the composition. The amount of water is generally insufficient to form a solution of the polyelectrolyte and preferably is not significantly more than, and most preferably is the same as or less than, the equilibrium moisture content of the polyelectrolyte (i.e. the water content of the electrolyte if it is exposed in the form of dry powder to the ambient atmosphere).

10 The organic liquid in which the polyelectrolyte is dispersed is a solution of the reactive size in a hydrophobic solvent. Suitable solvents are water immiscible organic hydrocarbon liquids such as benzene, xylene, toluene, mineral oils, kerosene, and vegetable oils. In addition to being substantially free of water the composition is preferably also substantially free of any highly polar liquids with which the reactive size might tend to react. Preferably the liquid phase of the composition consists essentially only of hydrophobic solvent and dissolved size.

Any type of reactive size may be used in the invention but the size preferably is a ketene dimer reactive size or an anhydride reactive size.

20 Suitable ketene dimer reactive sizes that may be used include the dimers derived from readily available commercial fatty acids such as palmitic, stearic, oleic or myristic acids or mixtures thereof. Naturally the ketene dimer must be soluble in the organic liquid chosen for the polymer-in-oil dispersion. Suitable materials are well known and are described in, for example, U.S. Patent Specification No. 3,046,186. The ketene dimer may be solid or liquid, but generally the most concentrated products are obtainable when the dimer is liquid.

25 Suitable anhydride reactive sizes that may be used include alkenyl succinic anhydride sizes. Suitable materials are described in U.S. Patent No. 3,102,064.

The polyelectrolyte will generally be water soluble and an advantage of the invention is that it can have any desired molecular weight and in particular can have a molecular weight that is higher than is conveniently possible with existing compositions. For instance the intrinsic viscosity can typically be between 1 and 20, generally 3 to 9.

The polyelectrolytes may be cationic or anionic, the cationic polyelectrolytes generally being preferred.

30 Preferred cationic electrolytes include homopolymers or copolymers of diallyl dialkyl (generally dimethyl) ammonium chloride and homopolymers and copolymers of dialkylaminoalkyl acrylates and methacrylates (preferably dimethylaminoethyl acrylates and methacrylates) present as acid addition salts or quaternary ammonium salts, generally quaternised with methyl chloride or dimethyl sulphate. Copolymers of such monomers may be formed with acrylamide or methacrylamide and will typically contain at least 10%, and usually at least 30%, by weight of the cationic monomer. Other cationic acrylamides and methacrylamides can be used. Other cationic polymers that can be used are polyamines and polyimines such as polyamine-epi-halohydrin polymers and dicyandiamide condensates and polyethylene imines.

35 Suitable anionic polymers include polymers formed from monomers including carboxylic or sulphonic acid groups. These groups may be present as free acid or, more usually, as a water soluble ammonium or alkali metal (generally sodium) salt. Suitable acids are acrylic acid, methacrylic acid and 2-acrylamido-2-methyl-propane sulphonic acid. The anionic polymers may be homopolymers of such acids, or mixtures thereof, or copolymers with, for instance, acrylamide. A suitable polymer is polyacrylamide containing up to 25% or more acrylic acid groups.

40 The concentrate composition is best made by adding the reactive size to a substantially anhydrous dispersion of a polyelectrolyte in the hydrophobic liquid and thereby forming a solution of the size in the hydrophobic liquid. The dispersion of the polyelectrolyte in the hydrophobic liquid may be made by dispersing powdered polyelectrolyte mechanically into the liquid or by forming a dispersion in the hydrophobic liquid of aqueous polymer and then dehydrating this dispersion, generally by azeotroping. This dispersion may be made by dispersing aqueous polymer solution into the hydrophobic liquid or by, for instance, reversed phase emulsion or suspension polymerisation. Thus an aqueous solution of the monomer or monomers from which the polyelectrolyte is to be formed may be dispersed in an oil phase and then polymerised by emulsion or suspension polymerisation mechanism to form aqueous polymer droplets dispersed in the oil phase, and the composition is then dried. Any aqueous dispersion is preferably formed initially in the presence of a polymeric dispersion stabiliser (for instance as described in British Patent Specification No. 1,482,515) and possibly also a water-in-oil emulsifying surfactant and the oil that will facilitate subsequent drying of the product by azeotroping.

45 A user composition is made from the concentrate composition, generally by the user, by adding the concentrate composition to water and thereby forming an oil-in-water emulsion of the size solution dispersed in water in which the polyelectrolyte is dissolved. Formation of the oil-in-water emulsion is promoted by application of mechanical high shear and/or by the presence of an oil-in-water emulsifying

agent, such as an ethoxylated nonyl phenyl. The oil-in-water emulsifying agent may be included in the concentrate or in the water in which the emulsion is formed.

The water in which the emulsion is formed may be the water of the cellulosic pulp suspension that is to be treated but preferably the concentrate is first converted into an aqueous emulsion to give a reactive size concentration of from 0.01 to 5%, preferably 0.05 to 1% based on the weight of the aqueous solution.

This emulsion may then be added to the aqueous cellulosic pulp, and paper may be made from it, in the usual way. The amount of reactive size in the aqueous pulp is generally from about 0.01 to about 1% by weight based on the dry weight of the pulp. Upon addition to the pulp slurry, the active size/oil droplets are retained by the polymer on the fibres and the size reacts with the fibres. The size released from an emulsion in this way produces results at least as good as those obtained with the conventional ketene dimer emulsions.

Thus by the invention we obtain sizing results at least as good as those obtained using known compositions and yet for the first time we have the ability of supplying storage stable concentrated compositions that the user can easily convert into aqueous solutions.

The following are examples of the invention.

#### Polyelectrolyte dispersions:

A substantially anhydrous dispersion of a copolymer of methyl chloride quaternised dimethylaminoethyl methacrylate (DMAEMA) and acrylamide was prepared by a reverse phase dispersion polymerisation process. The acrylamide was supplied as a 57% aqueous solution and the quaternised monomer was a 65% aqueous solution. These solutions were dispersed in a blend of Solvent Pale Oil 150 and perchloroethylene in the presence of a polymeric stabiliser and a very small amount of emulsifier. Polymerisation was initiated and allowed to complete in conventional manner and the resultant product was distilled under reduced pressure to remove the water and the perchloroethylene. The intrinsic viscosity of this polymer (and of the polymers in each of Dispersions A to E below) was in the range 4 to 6.

In one process the ratio DMAEMA:acrylamide was 80:20 by weight and the resultant polymer dispersion, labelled Dispersion A, contained 47.5% by weight of active polymer. A 1% solution of the polymer in water had a RVT Brookfield Viscosity of 6,400 mPa · s at room temperature using spindle No. 3 rotating at 10 rpm.

In another experiment the monomer proportions were the same and the molecular weight of the resultant polymer was above  $10^6$ . The resultant dispersion was labelled Dispersion B.

In another process, a dispersion, labelled Dispersion C, was obtained broadly as described for Dispersion A and was a 50% active polymer dispersion in mineral oil.

In another process the ratio DMAEMA:acrylamide was 30:70 by weight and the resultant dispersion, labelled Dispersion D, contained 50% by weight active polymer. The polymer in the dispersion was of low molecular weight, having an intrinsic viscosity of 3.16.

In another process a substantially anhydrous dispersion of a polyamine-epichlorhydrin condensate was prepared by emulsifying the polymer produced in an aqueous phase polymerisation process into a mixture of solvent pale oil 60 and SBP 11 with a very small amount of emulsifiers prior to distilling off the water under reduced pressure. The resultant polymer dispersion, labelled Dispersion E, contained 37.6% by weight of active polymer.

#### Examples 1 to 5

A series of concentrate compositions according to the invention were made by dissolving a reactive size in each of Dispersions A to E.

In Example 1 the size was hexadecenyl dimer and the concentrate contained 1.05 g Dispersion A and 4 g of hexadecenyl ketene dimer, and 1 g of an oil-in-water emulsifier to give a 64.5% active sizing composition. The water content of the concentrate was less than 1%. The product is concentrate A.

In Example 2 the concentrate was made by mixing 2 ml of Dispersion B with 2 ml octadecenyl ketene dimer, to make concentrate B.

In Example 3 one part by weight Dispersion C was mixed with one part by weight alkenyl succinic anhydride reactive size to form concentrate C.

In Example 4 alkenyl succinic anhydride was dissolved into a mixture of Dispersion D and a mineral oil such that concentrate D contained 2 g Dispersion D, 5 g alkenyl succinic anhydride, 2.25 g mineral oil and 0.75 g of an oil-in-water emulsifier to give a 50% active sizing concentrate D, having a water content of less than 1%.

In Example 5 alkenyl succinic anhydride was dissolved into Dispersion E in the presence of emulsifiers to form concentrate E containing 5 g alkenyl succinic anhydride, 5.31 g Dispersion E and 1.28 g of the oil-in-water emulsifiers to give a 43.1% active size concentrate.

Each of concentrates A to E was used to prepare a corresponding aqueous emulsion, having a 1% by weight active size content, by stirring the appropriate amount of dispersion into water. Each of these 1% active emulsions was further diluted to 0.1% by weight active size content and these 0.1% emulsions were labelled Emulsions A to E (having been prepared from, respectively, concentrates A to E).

The effectiveness of each of the emulsions for sizing cellulosic fibres was determined by the 1 minute Cobb Test. In each of these tests hand sheets were prepared on a standard laboratory sheet making

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machine from a stock containing calcium carbonate and the sheets were then dried and the 1 minute Cobb value determined. For Emulsions A to D the stock was a bleached sulphate/bleached bird stock but for Emulsion E it was a bleached sulphate (kraft).

In Test A the hand sheets were 100 g/m<sup>2</sup> and the stock contained 20% calcium carbonate and was a 0.5% constituted stock. The emulsion was either Emulsion A or, as a comparison, with Emulsion F which was a conventional emulsion prepared from a commercially available 6% emulsion of ketene dimer in water stabilised with cationic starch.

In Test B hand sheets were prepared from a furnish of 50% bleached sulphate, 40% bleached birch and 10% calcium carbonate, beaten to a freeness of 52° S.R. The stock was sized with Emulsion B or, as a comparison, with Emulsion G obtained by mixing 2 ml of the 50% dispersion of polymer in oil used in the preparation of Dispersion B into 196 mls deionised water followed by rapid stirring with a Silverson mixer at maximum speed and injection into the resultant solution of 2 mls octadecenyl ketene, Silverson mixing being continued for a further 25 seconds. The resultant 1% emulsion was diluted to 0.1% to form Emulsion G.

In Test C 70 g/m<sup>2</sup> hand sheets were prepared from a stock of 50 parts bleached sulphate, 40 parts bleached birch and 10 parts calcium carbonate and these were sized either with Emulsion C or with comparison Emulsion H. This was prepared as follows. A 12% aqueous dispersion of a cationic starch was cooked at 95°C for 20 minutes with constant stirring. The cooked starch was cooled and diluted to 9% activity. 2 parts by weight of alkenyl succinic anhydride was added to 3 parts by weight of cationic starch with agitation. High shear mixing using a Silverson mixer was continued to achieve a fine particle size emulsion. This emulsion was diluted with water to 0.75% active size, which was further diluted to 0.1%.

In Test D 70 g/m<sup>2</sup> hand sheets were prepared from a stock of 50 parts bleached sulphate, 40 parts bleached birch and 10 parts calcium carbonate beaten to 50° S.R. and after manufacture the sheets were placed on glazing plates and pressed at 3.43 mPa (3.5 kg/cm<sup>2</sup>) for 5 minutes prior to drying on rings at 110°C for 2 hours. Emulsion D was used for sizing each of these sheets.

In Test E 70 gms hand sheets were prepared from a bleached sulphate stock in conventional manner and dried and pressed as in Test D, the sheets being sized using Emulsion E.

The dosage and the Cobb value are shown in the following Table. The dosage is recorded as percent active size based on dry weight of paper. The Cobb figure is the 1 minute Cobb value.

Test	Emulsion	Dose	Cobb
A	A	0.15	27.4
	A	0.2	25.8
	F	0.15	33.2
B	B	0.2	26
	G	0.2	65
C	C	0.3	21.2
	C	0.4	19.4
	H	0.3	21.6
	H	0.4	19.8
D	D	0.2	25.6
	D	0.3	17.0
	D	0.5	14.3
E	E	0.5	36.2

These results show that the methods and emulsions of the invention, A to E, are all capable of giving satisfactory sizing. Test C shows that the results can be similar to those obtainable with a conventional commercially available 2-pack system H while Test B shows that the results can be surprisingly better than the results obtained by sequential formation of a single emulsion G. Test A shows that the results can be better than obtainable with a conventional emulsion system. Similarly satisfactory results are obtained when the polymer is polyacrylamide containing 10% molar acrylic acid groups (as sodium salt) and the stock contains alum and has a pH of 5.5.

Additional to these results is the remarkable convenience of the invention to the mill operator in that instead of having to purchase or prepare large volumes of a dilute emulsion, which then have to be stored at the mill, it is possible for the mill operator to purchase or prepare small volumes of a very concentrated emulsion and merely dilute this at the point of use when required.

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## Claims

1. A concentrate composition suitable, upon dilution with water, for sizing cellulosic fibres and comprising a substantially anhydrous dispersion of a polyelectrolyte in an organic liquid comprising a solution of a reactive size in a hydrophobic solvent, and in which the weight ratio reactive size:organic solvent is at least 0.67:1 and the water content of the composition is not more than 10% by weight.
2. A composition according to claim 1 in which the concentration of reactive size is above 20% by weight of the total composition and above 40% by weight of the combined weight of size and solvent.
3. A composition according to claim 1 in which the concentration of the reactive size is 30 to 85% by weight of the total composition and the weight ratio organic solvent:reactive size is from 1:10 to 1:0.67 and the water content is not more than 2% by weight.
4. A composition according to any preceding claim in which the weight ratio polyelectrolyte:reactive size is from 1:1 to 1:10.
5. A composition according to any preceding claim containing, by weight, 1 part solvent, 1 to 3 parts reactive size and 0.5 to 2 parts polyelectrolyte.
6. A composition according to any preceding claim in which the reactive size is selected from ketene dimer and anhydride reactive sizes.
7. A composition according to any preceding claim in which the polyelectrolyte is selected from water soluble cationic and anionic polymers.
8. A composition according to any preceding claim in which the polyelectrolyte is selected from polymers formed from at least one monomer selected from dialkylaminoalkyl acrylates and methacrylates and their acid addition salts and their quaternary ammonium salts, diallyl dialkyl ammonium chlorides, acrylamide, acrylic acid, methacrylic acid and 2-acrylamido-2-methyl propane sulphonic acid and from polyamine and polyimine polymers.
9. A composition according to any preceding claim additionally including an oil-in-water emulsifier.
10. A method of making a composition according to any preceding claim comprising adding the reactive size to a substantially anhydrous dispersion of the polyelectrolyte in the hydrophobic liquid.
11. A method of making a composition according to any of claims 1 to 9 comprising forming an aqueous dispersion of the polyelectrolyte in hydrophobic liquid by reverse phase polymerisation, dehydrating the dispersion by azeotroping and then adding the reactive size.
12. A method of making an aqueous sizing composition comprising dispersing into water a concentrate according to any of claims 1 to 9 in an amount sufficient to give a reactive size concentration in the water of from 0.01 to 5% by weight.
13. A method in which cellulosic fibres are sized by treating aqueous cellulosic pulp or cellulosic paper made from such pulp with an aqueous composition made by a method according to claim 12.

## Patentansprüche

1. Nach Verdünnung mit Wasser zur Leimung von Zellulosefasern geeignete Konzentrat-Zusammensetzung, enthaltend eine im wesentlichen wasserfreie Dispersion eines Polyelektrolyten in einer organischen Flüssigkeit, die eine Lösung eines reaktionsfähigen Leims in einem hydrophoben Lösungsmittel umfasst, und worin das Gewichtsverhältnis von reaktionsfähigem Leim: organischem Lösungsmittel wenigstens 0,67:1 beträgt und der Wassergehalt der Zusammensetzung nicht mehr als 10 Gew.-% ausmacht.
2. Zusammensetzung nach Anspruch 1, worin die Konzentration des reaktionsfähigen Leims über 20 Gew.-% der Gesamtzusammensetzung beträgt und über 40 Gew.-% der Gewichtssumme aus Leim und Lösungsmittel ausmacht.
3. Zusammensetzung nach Anspruch 1, worin die Konzentration des reaktionsfähigen Leims 30—85 Gew.-% der Gesamtzusammensetzung beträgt und das Gewichtsverhältnis von organischem Lösungsmittel:reaktionsfähigem Leim von 1:10 bis 1:0,67 ausmacht und der Wassergehalt nicht über 2 Gew.-% liegt.
4. Zusammensetzung nach einem der vorstehenden Ansprüche, worin das Gewichtsverhältnis von Polyelektrolyt:reaktionsfähigem Leim von 1:1 bis 1:10 beträgt.
5. Zusammensetzung nach einem der vorstehenden Ansprüche, mit einem Gehalt an 1 Gewichtsteil Lösungsmittel, 1—3 Gewichtsteilen reaktionsfähigem Leim und 0,5—2 Gewichtsteilen Polyelektrolyt.
6. Zusammensetzung nach einem der vorstehenden Ansprüche, worin der reaktionsfähige Leim unter reaktionsfähigen Ketendimerleimen und Anhydridleimen ausgewählt ist.
7. Zusammensetzung nach einem der vorstehenden Ansprüche, worin der Polyelektrolyt unter wasserlöslichen und anionischen Polymeren ausgewählt ist.
8. Zusammensetzung nach einem der vorstehenden Ansprüche, worin der Polyelektrolyt unter

Polymeren ausgewählt ist, die aus wenigstens einem Monomer, ausgewählt unter Dialkylaminoalkylacrylaten und -methacrylaten und ihren Säureadditionssalzen und ihren quaternären Ammoniumsalzen, Diallyldialkylammoniumchloriden, Acrylamid, Acrylsäure, Methacrylsäure und 2-Acrylamido-2-methylpropansulfonsäure und unter Polyamin- und Polyiminpolymeren, gebildet sind.

5 9. Zusammensetzung nach einem der vorstehenden Ansprüche mit einem zusätzlichen Gehalt an einem Öl-in-Wasser-Emulgator.

10. Verfahren zur Herstellung einer Zusammensetzung nach einem der vorstehenden Ansprüche, umfassend eine Zugabe des reaktionsfähigen Leims zu einer im wesentlichen wasserfreien Dispersion des Polyelektrolyten in der hydrophoben Flüssigkeit.

10 11. Verfahren zur Herstellung einer Zusammensetzung nach einem der Ansprüche 1—9, umfassend die Ausbildung einer wäßrigen Dispersion des Polyelektrolyten in einer hydrophoben Flüssigkeit durch Umkehrphasenpolymerisation, Entwässern der Dispersion durch Azeotropbildung und anschließendes Zugaben des reaktionsfähigen Leims.

15 12. Verfahren zur Herstellung einer wäßrigen Leimungszusammensetzung, umfassend ein Dispergieren eines Konzentrats nach einem der Ansprüche 1—9 in einer ausreichenden Menge in Wasser, um eine Konzentration des reaktionsfähigen Leims in dem Wasser von 0,01 bis 5 Gew.-% zu ergeben.

13. Verfahren, worin Zellulosefasern durch Behandeln einer wäßrigen Zellulosepulpe oder eines aus einer solchen Pulpe bereiteten Zellulosepapiers mit einer nach einem Verfahren gemäß Anspruch 12 bereiteten wäßrigen Zusammensetzung geleimt werden.

## 20 Revendications

1. Une composition concentrée utile, après dilution par de l'eau, pour l'encollage des fibres cellulosiques, et comprenant une dispersion sensiblement anhydre d'un polyélectrolyte dans un liquide  
25 organique comprenant une solution d'une colle réactive dans un solvant hydrophobe et dans laquelle le rapport pondéral colle réactive:solvant organique est d'au moins 0,67:1 et la teneur en eau de la composition ne dépasse pas 10% en poids.

2. Une composition selon la revendication 1, dans laquelle la concentration en colle réactive est supérieure à 20% en poids de la composition totale et supérieure à 40% en poids du poids combiné de la  
30 colle et du solvant.

3. Une composition selon la revendication 1, dans laquelle la concentration de la colle réactive est de 30 à 85% en poids de la composition totale et le rapport pondéral solvant organique:colle réactive est de 1:10 à 1:0,67 et la teneur en eau ne dépasse pas 2% en poids.

4. Une composition selon l'une quelconque des revendications précédentes, dans laquelle le rapport  
35 pondéral polyélectrolyte:colle réactive est de 1:1 à 1:10.

5. Une composition selon l'une quelconque des revendications précédentes, contenant, en poids, 1 partie de solvant, 1 à 3 parties de colle réactive et 0,5 à 2 parties de polyélectrolyte.

6. Une composition selon l'une quelconque des revendications précédentes, dans laquelle la colle réactive est choisie parmi les colles de dimère de cétène et les colles réactives d'anhydride.

40 7. Une composition selon l'une quelconque des revendications précédentes, dans laquelle le polyélectrolyte est choisi parmi les polymères anioniques et cationiques solubles dans l'eau.

8. Une composition selon l'une quelconque des revendications précédentes, dans laquelle le polyélectrolyte est choisi parmi les polymères formés à partir d'au moins un monomère choisi parmi les acrylates et méthacrylates de dialkylaminoalkyle et leurs sels d'addition d'acides et leurs sels d'ammonium  
45 quaternaire, les chlorures de diallyldialkylammonium, l'acrylamide, l'acide acrylique, l'acide méthacrylique et l'acide 2-acrylamido-2-méthylpropane sulfonique et parmi les polymères de polyamine et de polyimine.

9. Une composition selon l'une quelconque des revendications précédentes incluant en outre un émulsifiant du type huile-dans-eau.

10. Un procédé pour préparer une composition selon l'une quelconque des revendications  
50 précédentes, comprenant l'addition de la colle réactive à une dispersion sensiblement anhydre du polyélectrolyte dans un liquide hydrophobe.

11. Un procédé de fabrication d'une composition selon l'une quelconque des revendications précédentes 1 à 9, comprenant la formation d'une dispersion aqueuse du polyélectrolyte dans le liquide hydrophobe par polymérisation en phase inverse, déshydratation de la dispersion par entraînement  
55 azéotropique et ensuite addition de la colle réactive.

12. Un procédé de fabrication d'une composition aqueuse d'encollage, comprenant la dispersion dans l'eau d'un concentré selon l'une quelconque des revendications 1 à 9 en quantité suffisante pour donner une concentration de colle réactive dans l'eau de 0,01 à 5% en poids.

13. Un procédé, selon lequel des fibres cellulosiques sont encollées par traitement de la pâte  
60 cellulosique aqueuse ou du papier cellulosique préparé à partir d'une telle pâte avec une composition aqueuse préparée par un procédé selon la revendication 12.