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(54) THICKENING COMPOSITIONS FOR TEXTILE PRINTING PASTE

VERDICKUNGSZUSAMMENSETZUNG FÜR TEXTILDRUCKPASTE

COMPOSITIONS ÉPAISSISSANTES POUR PÂTE D'IMPRESSION TEXTILE

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Description

TECHNICAL FIELD

[0001] The present invention relates to thickening compositions in solid form comprising a carboxymethyl cellulose (CMC) with high degree of substitution (DS) and a thickener obtained by polymerization of ethylenically unsaturated monomers and their use in textile printing pastes based on reactive dyes.

PRIOR ART

[0002] Textile printing pastes serve to transfer dyes or pigments onto a textile material in a controlled way. The paste composition is critical and largely determines the quality of the final article.

[0003] Printing pastes are usually prepared by solubilizing one or more thickeners (thickening agents) in water and, successively, by adding a dye or a pigment and other possible chemical auxiliaries useful to the process (such as pH regulators, antifoam agents, stabilizers, dispersing agents and others).

[0004] The main function of thickeners is to provide the paste with suitable rheological properties in order to allow a better control in the design pattern reproduction onto the textile material.

[0005] Commonly used thickeners can be natural, semisynthetic or synthetic water soluble polymers of high molecular weight.

[0006] In cases where high ionic environments are encountered, such as in printing pastes containing reactive dyes, polymers with particular characteristic are required. Among the natural polymers, alginate is usually considered as reference in textile printing of reactive dyes, because it shows a suitable ecotoxicological profile and good solubility, it performs well as rheology modifier and it is easily removed by washing at the end of the printing process. In addition, it guarantees a good color yield and a proper definition of printing. However, alternatives to alginate are needed because of its high costs, difficulties of supply and variations in quality.

[0007] In the context of possible alternatives to alginate, carboxymethyl cellulose and its use for textile printing pastes containing reactive dyes have been already described. However, due its cellulosic nature, it is particularly prone to bind to reactive dyes so that it can adversely affect the interaction between the reactive dye and the textile substrate. So, commercially available CMC, usually having a degree of substitution between 0.6 and 1.2, loses rapidly its rheological properties because of the gelification of the polymer induced by the interaction with reactive dyes.

[0008] US 4,426,206 shows that a carboxymethyl cellulose with a high DS is necessary because the etherification cannot be selectively performed on the primary OH of C-6 carbon, which is mostly responsible for the interaction of CMC with the reactive dyes used in textile

printing. In particular, a degree of substitution of at least 2.2 is considered crucial to make the CMC inert to reactive dyes. The high DS is obtained thanks to multiple etherification steps and using isopropanol as solvent. US 4,426,518 similarly describes a two etherification reaction process to produce CMC with high DS. Another similar process is disclosed by US 4,507,474, where the attention is focused on the influence of solvent system on the DS which can be obtained.

[0009] US 5,463,036 teaches how a two-step etherification process with an intermediate step of grinding allows to produce a CMC which is suitable as thickener for textile printing even with a lower degree of substitution (preferably from 1.5 to 2.1).

[0010] Also synthetic polymers, such as polyacrylates, are well-known for their use as thickeners in textile printing of reactive dyes.

[0011] For example, US 4,509,949 discloses polymers comprising from 95.5 to 98.9 % by weight of ethylenically unsaturated carboxylic acids, from 1 to about 3.5 % by weight of an alkyl acrylate ester of acrylic or methacrylic acid wherein the alkyl group contains 10 to 30 carbon atoms and from 0.1 to less than 1 % by weight of a crosslinking monomer, which are useful for printing paste applications wherein there are reactive dyes, direct dyes and disperse dyes.

[0012] Polyacrylates improve the printability of pastes based on reactive dyes, but, they usually have negative effect on the washability of the treated fabric.

[0013] EP 645,429 describes thickening water-in-oil dispersions containing carboxymethyl cellulose with a low/medium DS (about 0.75) and a cross-linked anionic acrylic polymer and their use in textile printing pastes. The anionic acrylic polymer is prepared using acrylic acid, partially salified with sodium or potassium, and, optionally 2-acrylamido 2-methyl propanesulphonate (AMPS), and, as crosslinking agent, a carboxylic compound with at least two ethylenically unsaturated groups.

[0014] JP 2008/081855 describes a printing paste comprising a thickening agent which is a mixture of two thickeners: one with a printing viscosity index (PVI) comprised between 0.2 and 0.3 and the other with a PVI between 0.7 and 0.9. Suitable thickeners of the first kind are acrylic polymers and starch or starch derivatives. Suitable thickeners of the second kind are alginate and carboxymethyl cellulose. Examples of printing pastes comprising an alginate and a mineral oil dispersion of an acrylic polymer are provided.

[0015] However printing pastes comprising an oleaginous phase are subjected to serious drawbacks: above all an unsatisfactory stability of the printing paste with separation of the oleaginous phase.

[0016] Moreover the oil can evaporate during the color fixing, which is performed at high temperature, with consequent risks for environment and health, or the oil remaining on the fabrics causes printing defects and must be removed during the washing step, with increased costs.

[0017] It has now been found that oil-free thickening compositions in the form of powder, granules or pellets for textile printing paste, comprising a) a carboxymethyl cellulose (CMC) having degree of substitution (DS) from 1.6 to 3.0 and b) a thickener obtained by polymerization of ethylenically unsaturated monomers, provide improved properties to the printing pastes in comparison with prior art printing pastes.

[0018] As a matter of fact, the textile printing pastes obtained according to the present invention show an improved printability.

[0019] Moreover, the fabrics printed with these textile printing pastes have a higher color strength, as easily verified by visual assessment of the final article and by instrumental color analysis, and can be washed without causing a worsening of the hand of the printed substrate.

[0020] As reported above, JP 2008/081855 discloses mixtures of acrylic polymers and an alginate, which can be optionally substituted by a CMC having a high degree of substitution. However, the acrylic polymers exemplified in the disclosure are added to the printing paste in the form of oil dispersion and no mixture of acrylic polymers and CMC is described or exemplified.

[0021] As far as the Applicant knows, the oil-free thickening compositions in the form of powder of the present disclosure have never been described.

[0022] The expression "degree of substitution" (DS) means the average number of carboxymethyl groups for each anhydroglycosidic unit of the cellulose and can be determined, for example, according to the standard method ASTM D1439 or by ¹H-NMR.

DESCRIPTION OF THE INVENTION

[0023] It is therefore an object of the present invention an oil-free thickening composition in the form of powder, granules or pellets comprising: a) from 25 to 85 % wt, more preferably from 45 to 65 % wt of a carboxymethyl cellulose (CMC) having degree of substitution (DS) of from 1.6 to 3.0 and b) from 15 to 65% wt, more preferably from 20 to 35% wt of a thickener obtained by polymerization of ethylenically unsaturated monomers.

[0024] A further object of this invention is a textile printing paste comprising from 1 to 10 % by weight (% wt), preferably from 2 to 8 % by weight, of said thickening composition and at least one reactive dye.

DETAILED DESCRIPTION OF THE INVENTION

[0025] The carboxymethyl cellulose suitable for the realization of the present invention has a DS comprised between 1.6 and 3.0, preferably between 1.7 and 2.4 and more preferably between 1.9 and 2.2. Moreover it shows a Brookfield LVT® viscosity, at 2 % wt in water, 60 rpm and 20 °C, comprised between 200 and 5000 mPa*s, preferably between 500 and 2000 mPa*s.

[0026] The carboxymethyl cellulose of the present invention can be a technical or purified carboxymethyl cel-

lulose, but it is preferably a technical carboxymethyl cellulose, having a percentage of active substance comprised between 50 and 99.5% by weight on dry matter, preferably between 50 and 80 % by weight, and a moisture content up to 16 % by weight.

[0027] The carboxymethyl cellulose suitable for the realization of the present invention can be prepared by a multiple step reaction of an alkali cellulose with monochloroacetic acid or, for example, with the etherification processes described in US 4,426,206 or US 5,463,036 or any other etherification process known in the art.

[0028] In a preferred embodiment, the carboxymethyl cellulose has more than 90% wt of the particles with a size comprised between 0.05 mm and 2.0 mm.

[0029] According to the present invention, said thickener b) can be obtained by polymerization of at least one ethylenically unsaturated anionic monomer, optionally in the presence of a ethylenically unsaturated nonionic monomer and/or a crosslinking agent.

[0030] The anionic monomer can be selected among ethylenically unsaturated mono- or dicarboxylic acids or salts thereof or anhydrides thereof, such as acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid; and among sulfonic acids or salts thereof, such as 2-acrylamido-2-methyl propane sulfonic acid (AMPS), vinyl sulfonic acid, 2-sulfoethyl acrylate, 2-sulfoethyl methacrylate, 3-sulfopropyl acrylate, 3-sulfopropyl methacrylate, styrene sulfonic acid, 2-propene-1-sulfonic acid, and mixtures thereof. Preferably, the anionic monomer is selected among acrylic acid, 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and mixtures thereof.

[0031] Preferably, the thickener b) is obtained by polymerization of from 30 to 100% by moles of ethylenically unsaturated anionic monomers.

[0032] Suitable nonionic monomers include ethylenically unsaturated amides, (meth)acrylic C₁-C₆ alkyl esters, substituted or unsubstituted with hydroxy or amino groups, ethylenically unsaturated alcohols and their esters, styrene and substituted styrenes, and vinyl monomers. Specific examples are acrylamide, methacrylamide, N-alkyl acrylamide, N-vinyl pyrrolidone, N-vinyl formamide, N-vinyl acetamide, methyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, n-propyl acrylate, iso-propyl acrylate, butyl acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, vinyl alcohol, allyl alcohol, vinyl acetate, vinyl butyrate, vinyl chloride and the like.

[0033] Preferably, the nonionic monomer is acrylamide.

[0034] Preferably, the thickener b) of the invention comprises from 2 to 30% by moles of ethylenically unsaturated nonionic monomers.

[0035] The thickener b) of the invention can also comprise a crosslinking agent, for example a compound having at least two ethylenically unsaturated groups. The crosslinking agent can be selected in the group comprising N,N'-methylene bisacrylamide (MBA), ethylene glycol diacrylate, polyethylene glycol dimethacrylate, diacr-

ylamide, triallylamine, cyanomethylacrylate, vinyl ox-yethylacrylate or methacrylate, compounds of the glycidyl ether type such as ethyleneglycol diglycidyl ether, or the epoxydes. Preferably, the crosslinking agent is N,N'-methylene bisacrylamide.

[0036] The thickener obtained by polymerization of ethylenically unsaturated monomers of the invention can be prepared following any of the polymerization process known in the art. Examples of these processes are: solution polymerization, direct emulsion polymerization, inverse emulsion polymerization, suspension polymerization, precipitation polymerization, etc., in the presence of catalytic systems and chain-transfer agents, or by a radical mediated system. Preferably, the thickener is obtained using an inverse emulsion polymerization process. At the end of the polymerization, the thickener can be isolated in powder form by filtration, distillation, spray drying or similar techniques.

[0037] In a preferred embodiment, the thickener b) has 100% wt of the particles with a size smaller than 2.0 mm.

[0038] The thickener obtained by polymerization of ethylenically unsaturated monomers of the present invention is characterized by a Brookfield LVT® viscosity, at 0.25 % wt in water, 60 rpm and 20 °C, comprised between 10 and 600 mPa*s, preferably between 200 and 400 mPa*s.

[0039] Optionally, the thickening composition of the invention may comprise another additional thickener chosen among natural gums or their derivatives. Suitable examples include: cellulose derivatives, such as CMC with a DS comprised between 0.8 and 1.2 or a hydroxyethyl cellulose; starch and starch derivatives, such as carboxymethyl starch; guar gum and guar gum derivatives, such as hydroxypropyl guar; xanthan gum, arabic gum, tragacanth gum or mixture thereof. Said additional thickener can be present in amount of from 3 to 30% by weight, based on the total weight of the thickening composition.

[0040] Preferably, the additional thickener is a CMC with a DS comprised between 0.8 and 1.2 and a Brookfield LVT® viscosity at 2% wt in water, 20 rpm and 20 °C, comprised between 2500 and 5000 mPa*s or a carboxymethyl starch, with a DS comprised between 0.1 and 1.0 and a Brookfield LVT® viscosity at 8% wt in water, 20 rpm and 20 °C, comprised between 10,000 and 40,000 mPa*s.

[0041] Preferably, the oil-free thickening composition is provided in the form of powder, granules or pellets.

[0042] The thickening composition in powder form can be prepared by simply mixing the carboxymethyl cellulose with the thickener obtained by polymerization of ethylenically unsaturated monomers.

[0043] Granules of the thickening composition can be prepared by means of a fluidized bed, a rolling or a spray drying apparatus, starting from the composition in powder form. Preferably, the granulation is performed by means of a rolling granulating apparatus. The pellets can be prepared, for example, by dry pressing or extrusion

of the composition in powder form, preferably by extrusion.

[0044] The disclosed oil-free thickening composition can be utilized for preparing textile printing pastes with improved printability and higher color yield.

[0045] The textile printing paste of the invention can include at least one reactive dye.

[0046] The reactive dye can be a reactive dye customarily used for printing cellulosic fiber materials, chosen among, for example, those described in the Color Index, 3rd edition (1971) and supplements thereto.

[0047] Preference is given to the use of dyes of the monoazo, diazo, polyazo, metal complex azo, anthraquinone, phthalocyanine, formazan and dioxazine series which contain at least one reactive group.

[0048] These reactive groups are fiber-reactive radicals capable of reacting with the hydroxyl groups of cellulose. They are generally attached directly or via a bridge member to the dye residue. Suitable reactive groups include for example those containing at least one detachable substituent on an aliphatic, aromatic or heterocyclic radical or in which the radicals mentioned contain a radical, for example a halotriazinyl, halopyrimidinyl or vinyl, suitable for reaction with the fiber material. Examples of suitable aliphatic reactive groups are those of formulae -SO₂-Y, -SO₂-NH-Y, -NH-CO-alk-SO₂-Y, -CO-NH-alk-SO₂-Y, or -NH-CO-Y₁, where Y is a leaving group, for example β-sulfatoethyl, β-thiosulfatoethyl, β-phosphatoethyl, β-acyloxyethyl, β-haloethyl or vinyl, Y₁ is for example an α,β-dihaloethyl or α-haloethenyl radical, alk is C₁-C₆ alkylene; halogen is preferably chlorine or bromine. Examples of heterocyclic fibre-reactive radicals are 1,3,5-triazine radicals substituted with fluorine, chlorine or carboxypyridinium.

[0049] Vinylsulfonyl, chlorotriazine and fluorotriazine are the preferred reactive groups. Preferably, the textile printing paste comprises from 0.1 to 15 % by weight, more preferably from 0.2 to 10 % by weight, of at least one reactive dye.

[0050] The textile printing paste of the invention can further comprise a base, which increases the reactivity of the dye toward the hydroxyl group of the cellulose. Suitable bases are sodium carbonate, sodium hydroxide, disodium phosphate, trisodium phosphate, sodium acetate, sodium propionate, sodium bicarbonate, and aqueous ammonia. Also the equivalent potassium salts can be used.

[0051] Sodium bicarbonate and sodium carbonate are the preferred bases. The pH of the textile printing paste is generally in the range from 7.5 to 13.5, preferably from 8.5 to 12.5.

[0052] The textile printing paste according to the invention can further comprise an hydrotrope at a concentration comprised between 0 and 20 % wt. Hydrotropes are those agents capable of converting the dispersion of the dyes or optical brighteners insoluble or low soluble in water into a stable deflocculated form, without any chemical reaction occurring between the dyes or the op-

tical brighteners and the hydrotropic substance. The preferred hydrotrope is urea.

[0053] The textile printing paste of the invention can further comprise textile printing additives, which are well-known to those skilled in the art, such as wetting agents, emulsifiers, dispersing agents, preservatives, sequestrants, water-insoluble solvents, oxidants, reduction inhibitors or defoamers.

[0054] Wetting agents, emulsifiers, dispersing agents can be anionic or nonionic. Examples of these are: reaction products of aliphatic, araliphatic or aromatic hydroxy compounds, carboxylic acids, carboxylic acid amides or amines with ethylene oxide; sulfuric acid half esters or phosphoric acid partial esters thereof; fatty acid esters of mono- or polysaccharides or fatty acid sorbitan esters and ethoxylation products thereof; C₁₀-C₂₀ alkanesulfonates, C₈-C₁₂ alkylbenzene-sulfonates; C₈-C₁₈ alkyl sulfates or phosphates; or condensed aromatic sulfonic acids, such as naphthalene-formaldehyde-sulfonates. Substances of the type mentioned can also serve as leveling agents.

[0055] Suitable reduction inhibitors (anti-reduction agent) include for example aromatic nitrocompounds, especially salts of aromatic mono- or dinitrocarboxylic acids or sulfonic acids, which are optionally present as alkylene oxides, especially alkali metal salts of a nitrobenzenesulfonic acid, e.g. sodium 3-nitrobenzenesulfonate. Defoamers are, for example, compositions comprising vegetable oils or silicone oils or, in particular, propylene oxide/ethylene oxide block polymers.

[0056] According to the invention, the textile printing additives mentioned in the preceding paragraphs can be present in an amount of 0 to 10% by weight, based on the total weight of the pastes.

[0057] The textile printing pastes of the invention can be prepared according to the usual procedures, by slowly adding the thickener composition to water, under mechanical stirring, until complete dissolution is achieved, and subsequently by adding other additives (wetting agent, dispersing agent, defoamer, and so on) and the reactive dye to the thickened solution.

[0058] The textile printing pastes prepared according to the invention have a Brookfield® RTV viscosity of from 3000 to 15000 mPa*s, measured at 20 rpm and 20 °C.

[0059] The textile printing pastes of the invention can be used in any printing process of textile materials and with any textile printing techniques known in the art, for example intaglio, rotary and flat screen printing, hand printing, airbrush printing, etc. Textile materials which can be printed using the pastes according to the invention are fiber materials of loose fibers, woven or knitted goods or those in the form of nonwovens, based on cellulosic materials or silk. Examples of cellulosic materials are cotton, linen or hemp, or regenerated cellulosic materials such as, for example, viscose, polynosic or cupro, or cellulosic blend materials such as, for example, cotton/polyester materials.

[0060] To demonstrate the advantages and uses of the

thickening composition of the present invention, printing pastes were made with exemplary thickening agents, evaluating the rheologic behaviour of the paste and, when printed on a substrate, the printability and color yield.

EXAMPLES

[0061] The oil-free thickening composition of the present invention (Example 1) was prepared by carefully mixing 70 g of carboxymethyl cellulose (DS 2.01; Brookfield LVT® viscosity, at 2 % wt in water solution, 20 °C and 60 rpm, of 700 mPa*s; 60 % by dry weight of active substance) and 30 g of acrylic thickener (acrylic acid/acrylamide copolymer (75/25 by moles); Brookfield LVT® viscosity, at 0.25 % wt in water solution, 20 °C and 60 rpm, of 360 mPa*s).

[0062] The performances of the thickening composition of the invention was compared with the performances of the single thickeners (Example 2 for the CMC and Example 3 for the acrylic thickener) and with the performances of a thickening composition comprising 70 g of the same acrylic thickener and 30 g of a low DS carboxymethyl cellulose (DS 0.9; Brookfield LVT® viscosity, at 2 % wt in water solution, 20 °C and 60 rpm, of 2350 mPa*s; >98 % by dry weight of active substance) (Example 4). A commercially available sodium alginate (Printex CR7, a medium viscosity alginate commercialized by Lamberti S.p.A.), was used as further comparative thickener. The amount of thickening agents required to reach a viscosity of about 10,000 mPa*s, measured at 20 rpm and 20 °C, was added, under mechanical stirring, to 800 g of water and mixed until complete dissolution. 120 g of urea, 30 g of sodium carbonate and 10 g of anti-reduction agent were then added to the viscosified solution to obtain a base paste. Subsequently, 40 g of C.I. Reactive Blue 72 (BLUE) or C.I. Reactive Red 218 (RED), were mixed with 960 g of said base paste.

[0063] A white cotton fabric was printed with the printing pastes using a 55 threads/cm polyester screen (30x40 cm rectangle design, printed surface 0.12 m²) and a Zimmer magnetic laboratory printing machine set at speed 40 and pressure 2. A 6 mm steel rod was used.

[0064] The printed fabric so obtained was then dried at a temperature of 90°C in oven and treated for 10 minutes, for color fixing, in an Arioli steamer machine set at 102 °C. The printed fabric was washed with a 2 % wt solution of Lamegal DSP (commercialized by Lamberti S.p.A.) in tap water, at room temperature, then at 60 °C and, finally, at 100 °C. After the washing, the fabric was rinsed, dried and ironed. The printability was determined by weighing the cotton fabric before and soon after the printing (on the wet fabric) and applying the following formula:

$$\text{Printability (g/m}^2\text{)} = \frac{(B - A)}{S}$$

wherein A and B are the weight in grams of the fabric before and after the printing respectively, and S is the area of the printed surface in square meters. The results are reported in Table 1.

[0065] The appearance of the finished printed fabrics were evaluated both visually and instrumentally using a DataColor Int. reflectance spectrophotometer (Spectral Test SE600 PLUS-CT) under a DL65/10° illuminant. The color yield values were calculated according to AATCC Evaluation Procedure 6.

[0066] The area printed with the paste prepared according to the invention clearly showed, under the visual inspection, a more homogeneous dye distribution than the area printed with the alginate-based paste. In addition, the paste of the present invention showed good washability, similarly to the alginate-based paste.

[0067] Table 1 shows the color yield (% yield) of the cotton fabrics printed using the paste of Example 1 compared to that of the fabric printed using the comparative paste with the alginate, considered 100%.

Table 1

Thickener	BLUE		RED
	Printability	% Yield	% Yield
Example 1	50	121	115
Example 2*	30	102	105
Example 3*	30	100	103
Example 4*	20	97	95
Printex CR7*	20	100	100
* Comparative			

[0068] The results of Table 1 demonstrate the superior performances of the oil-free thickening composition of the invention, surprisingly better than those obtained using the single raw materials (Examples 2 and 3) or using the composition of Example 4, comprising an acrylic thickener and a low DS CMC.

[0069] The composition of the invention also showed better performances than a commonly used commercial thickener.

Claims

1. Oil-free thickening composition in the form of powder, granules or pellets for textile printing paste comprising a) from 25 to 85 % by weight (% wt) of a carboxymethyl cellulose (CMC) having degree of substitution (DS) from 1.6 to 3.0 and b) from 15 to

65% by weight of a thickener obtained by polymerization of ethylenically unsaturated monomers.

2. The oil-free thickening composition according to Claim 1 comprising: a) from 45 to 65 % by weight (% wt) of said CMC and b) from 20 to 35% by weight of said thickener obtained by polymerization of ethylenically unsaturated monomers.
3. The oil-free thickening composition according to Claim 1, in which the carboxymethyl cellulose a) has degree of substitution (DS) from 1.7 to 2.4.
4. The oil-free thickening composition according to Claim 1, in which the thickener b) is obtained by polymerizing at least one ethylenically unsaturated anionic monomer, optionally in the presence of a ethylenically unsaturated nonionic monomer and/or a crosslinking agent.
5. The oil-free thickening composition according to Claim 4, in which said ethylenically unsaturated anionic monomer is selected among acrylic acid, 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and mixtures thereof.
6. The oil-free thickening composition according to Claim 4, wherein the thickener b) is obtained by polymerization of from 30 to 100% by moles of ethylenically unsaturated anionic monomers.
7. The oil-free thickening composition according to Claim 4, wherein the thickener b) comprises a ethylenically unsaturated nonionic monomer.
8. The oil-free thickening composition according to Claim 7, wherein said ethylenically unsaturated nonionic monomer is acrylamide.
9. The oil-free thickening composition according to Claim 1 comprising from 3 to 30 % wt of an additional thickener chosen among natural gums and their derivatives.
10. Textile printing paste comprising from 1 to 10 % wt of the thickening composition of Claim 1 and at least one reactive dye.

Patentansprüche

1. Ölfreie Verdickungszusammensetzung in Form von Pulver, Granulaten oder Pellets für eine Textildruckpaste, umfassend a) von 25 bis 85 Gewichts-% (Gew.-%) einer Carboxymethylcellulose (CMC) mit einem Substitutionsgrad (SG) von 1,6 bis 3,0 und b) von 15 bis 65 Gewichts-% eines durch Polymerisation von ethylenisch ungesättigten Monomeren er-

haltenen Verdickungsmittels.

2. Die ölfreie Verdickungszusammensetzung nach Anspruch 1, umfassend: a) von 45 bis 65 Gewichts-% (Gew.-%) der CMC und b) von 20 bis 35 Gewichts-% des durch Polymerisation von ethylenisch ungesättigten Monomeren erhaltenen Verdickungsmittels. 5
3. Die ölfreie Verdickungszusammensetzung nach Anspruch 1, wobei die Carboxymethylcellulose a) einen Substitutionsgrad (SG) von 1,7 bis 2,4 aufweist. 10
4. Die ölfreie Verdickungszusammensetzung nach Anspruch 1, wobei das Verdickungsmittel b) durch Polymerisation wenigstens eines ethylenisch ungesättigten anionischen Monomers erhalten wird, gegebenenfalls in Gegenwart eines ethylenisch ungesättigten nichtionischen Monomers und/oder eines Vernetzungsmittels. 15 20
5. Die ölfreie Verdickungszusammensetzung nach Anspruch 4, wobei das ethylenisch ungesättigte anionische Monomer ausgewählt ist aus Acrylsäure, 2-Acrylamido-2-methylpropane-sulfonsäure (AMPS) und Mischungen davon. 25
6. Die ölfreie Verdickungszusammensetzung nach Anspruch 4, wobei das Verdickungsmittel b) durch Polymerisation von 30 bis 100 Mol-% ethylenisch ungesättigter anionischer Monomere erhalten wird. 30
7. Die ölfreie Verdickungszusammensetzung nach Anspruch 4, wobei das Verdickungsmittel b) ein ethylenisch ungesättigtes nichtionisches Monomer umfasst. 35
8. Die ölfreie Verdickungszusammensetzung nach Anspruch 7, wobei das ethylenisch ungesättigte nichtionische Monomer Acrylamid ist. 40
9. Die ölfreie Verdickungszusammensetzung nach Anspruch 1, umfassend von 3 bis 30 Gew.-% eines zusätzlichen Verdickungsmittels, ausgewählt aus natürlichen Gummiharzen und deren Derivaten. 45
10. Textildruckpaste umfassend von 1 bis 10 Gew.-% der Verdickungszusammensetzung nach Anspruch 1 und wenigstens einen Reaktivfarbstoff. 50

Revendications

1. Composition épaississante sans huile sous forme de poudre, de granulés ou de pellets pour pâte d'impression textile comprenant a) de 25 à 85 % en poids d'une carboxyméthylcellulose (CMC) ayant un degré de substitution (DS) de 1,6 à 3,0 et b) de 15 à 65 % 55

en poids d'un épaississant obtenu par polymérisation de monomères éthyléniquement insaturés.

2. Composition épaississante sans huile selon la revendication 1 comprenant : a) de 45 à 65 % en poids dudit CMC et b) de 20 à 35 % en poids dudit épaississant obtenu par polymérisation de monomères éthyléniquement insaturés.
3. Composition épaississante sans huile selon la revendication 1, dans laquelle la carboxyméthylcellulose a) présente un degré de substitution (DS) de 1,7 à 2,4.
4. Composition épaississante sans huile selon la revendication 1, dans laquelle l'épaississant b) est obtenu par polymérisation d'au moins un monomère anionique éthyléniquement insaturé, éventuellement en présence d'un monomère non ionique éthyléniquement insaturé et/ou d'un agent de réticulation.
5. Composition épaississante sans huile selon la revendication 4, dans laquelle ledit monomère anionique éthyléniquement insaturé est choisi parmi l'acide acrylique, l'acide 2-acrylamido-2-méthylpropane sulfonique (AMPS) et leurs mélanges.
6. Composition épaississante sans huile selon la revendication 4, dans laquelle l'épaississant b) est obtenu par polymérisation de 30 à 100 % en moles de monomères anioniques éthyléniquement insaturés.
7. Composition épaississante sans huile selon la revendication 4, dans laquelle l'épaississant b) comprend un monomère non ionique éthyléniquement insaturé.
8. Composition épaississante sans huile selon la revendication 7, dans laquelle ledit monomère non ionique éthyléniquement insaturé est l'acrylamide.
9. Composition épaississante sans huile selon la revendication 1 comprenant de 3 à 30 % en poids d'un épaississant supplémentaire choisi parmi les gommes naturelles et leurs dérivés.
10. Pâte d'impression textile comprenant de 1 à 10 % en poids de la composition épaississante de la revendication 1 et au moins un colorant réactif.

REFERENCES CITED IN THE DESCRIPTION

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