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(54) Titre : BATON DE COLLE A BASE D'ETHERS MIXTES D'AMIDON
(54) Title: GLUE STICK BASED ON STARCH MIXED ETHERS

(57) Abrégé/Abstract:

The subject matter of the present invention is glue stick, containing an aqueous preparation of at least one hydroxyalkylcarboxymethyl starch having a viscosity less than 2,000,000 mPas, determined as a 40-wt% aqueous solution using a Brookfield RVT viscosimeter at 20°C, spindle 7, 20 rpm, and soap, the manufacture thereof, and the use thereof for planar joining of substrates, in particular for joining paper, cardboard, wood, and/or plastic to one another.

ABSTRACT

The subject matter of the present invention is glue stick, containing an aqueous preparation of at least one hydroxyalkylcarboxymethyl starch having a viscosity less than 2,000,000 mPas, determined as a 40-wt% aqueous solution using a Brookfield RVT viscosimeter at 20°C, spindle 7, 20 rpm, and soap, the manufacture thereof, and the use thereof for planar joining of substrates, in particular for joining paper, cardboard, wood, and/or plastic to one another.

GLUE STICK BASED ON STARCH MIXED ETHERS

[0002] The invention is in the field of adhesives, in particular glue sticks, and relates to a glue stick based on special mixed starch ethers, to the manufacture thereof, and to the use thereof.

[0003] Glue sticks (rod-shaped adhesives that are received slidably in a closable casing and leave behind a tacky film when rubbed off onto a substrate surface) are commonly used objects in contemporary everyday life. They contain, for example, water-soluble resp. water-dispersible synthetic polymers of an adhesive nature -- in particular polyvinylpyrrolidone (PVP) -- dissolved in an aqueous-organic liquid phase, together with a shape-imparting structural substance. Alkali resp. ammonium salts of aliphatic carboxylic acids, in particular in the range of number of carbons from 12 to 22, are used in particular as a structural substance. If the aqueous preparations of the polymer substances of an adhesive nature, which are inherently highly tacky, are heated to higher temperatures, in particular above 50°C, together with small quantities of the structural substance based on fatty acid soaps, and if that solution is left to cool undisturbed, the substance mixture solidifies into a more or less rigid soap gel in which the shape-imparting and comparatively rigid micelle structure of such soap gels is at first predominantly apparent. This makes possible the known forming and handling of such substances in stick form in closable casings. Upon rubbing off, the micelle structure becomes destroyed and the rigid mass is thus converted into the pasty state in which the adhesive nature of the substance mixture then becomes paramount.

[0004] Polymers based on natural raw materials are also used as an adhering component instead of the water-soluble resp. water-dispersible synthetic polymers of an adhesive nature.

[0005] WO 93/03109 A1, for example, discloses glue sticks based on reduced-viscosity starch derivatives. Nonionic starch ethers that are obtained by reacting natural starch with ethylene oxide, propylene oxide, butylene oxide, and/or glycidol

are preferably used. Hydroxyalkyl starches are described as being particularly suitable, and mixed etherification products can also be used successfully. Hydroxyethyl starches and hydroxypropyl starches are used predominantly in the Examples, but the use of hydroxyethyl-hydroxypropyl starch can also be gathered from the Examples.

[0006] WO 99/51699 A1 describes glue sticks that are likewise based on reduced-viscosity starch derivatives. These correspond to the derivatives known from WO 93/03109 A1. The glue stick comprises as an adhesive component an aqueous preparation that besides the aforementioned starch ethers also contains sucrose, as well as a soap gel as a structural substance.

[0007] The known glue sticks possess a level of performance that is satisfactory for most applications. From a production-engineering standpoint, however, it is usually necessary to add adjuvants to the glue sticks. Cellulose ethers in particular are thus introduced as adjuvants in order to stabilize the viscosity of the mass. This is significant in particular for the decanting process, since a mass with too low a viscosity would run out of the casings that are made available. At the same time, the cellulose ethers result in shortcomings in terms of the rub-off properties of the stick, in that small particles detach during use and the stick smears. Important utilization properties perceptible to the user, such as the strength and rub-off of these glue sticks, are therefore still capable of improvement.

[0008] A demand therefore exists for glue sticks that do not exhibit the disadvantages set forth above and that possess optimized processing and utilization properties.

[0009] The object of the present invention is therefore to make available a glue stick that on the one hand exhibits good strength in combination with outstanding rub-off properties, as well as good adhesive strength and shelf stability. On the other hand, the mixture on which the stick is based is intended to exhibit, under the

conditions that exist during manufacture (i.e. in particular at temperatures above 50°C), a viscosity that is suitable for problem-free introduction of the adhesive masses into the stick casings, with no need to use cellulose derivatives for viscosity stabilization.

[0010] The manner in which the object is achieved is evident from the fundamental idea of the invention, that of adding special mixed starch ethers to the formulations of the glue sticks.

[0011] The subject matter of the invention is therefore a glue stick that contains an aqueous preparation of at least one hydroxyalkylcarboxymethyl starch having a viscosity less than 2,000,000 mPas, determined as a 40-wt% aqueous solution using a Brookfield RVT viscosimeter at 20°C, spindle 7, 20 rpm, and soap.

[0012] Surprisingly, the use of hydroxyalkylcarboxymethyl starch results both in stabilizing properties during production and in improved rub-off properties, while the adhesive results of the resulting glue sticks remain at least the same. The initial adhesive strength of commercially usual glue sticks based on reduced-viscosity hydroxyalkyl starches can be reached without difficulty, and in fact slightly exceeded. The initial adhesive strength of commercially usual glue sticks based on polyvinylpyrrolidone is appreciably exceeded. The addition of usual substances for viscosity stabilization, in particular cellulose ethers, can be omitted.

[0013] A glue stick according to the present invention is notable for improved strength and a more uniform rub-off as compared with known glue sticks, with outstanding adhesive and storage properties. Even over longer storage times, the adhesive bonds retain their white color and do not become yellow. At temperatures around 80°C the adhesive mixture on which the stick is based moreover exhibits a viscosity such that on the one hand it can easily be introduced into the stick casings, but on the other hand also does not emerge from the casing again through unsealed points in the stick screw seating region.

[0014] Permanent adhesive bonding of substrates can be effected using the glue sticks according to the present invention. They can be used in particular for permanent planar joining of paper, cardboard, wood, and/or plastic to one another.

[0015] The glue sticks according to the present invention contain as an adhesive component an aqueous preparation of at least one hydroxyalkylcarboxymethyl starch having a viscosity less than 2,000,000 mPas, determined as a 40-wt% aqueous solution using a Brookfield RVT viscosimeter at 20°C, spindle 7, 20 rpm.

[0016] Hydroxyalkylcarboxymethyl starches belong the group of the starch ethers, and can also be referred to as "mixed starch ethers." When mixed starch ethers are discussed hereinafter, they are to be understood as hydroxyalkylcarboxymethyl starches.

[0017] According to Ullmann, "Encyklopädie der technischen Chemie" [Encyclopedia of chemical engineering], 4th edition, Verlag Chemie, Weinheim/Bergstraße (1974), starch ethers are formally products of condensation between the hydroxy groups of the anhydroglucose units (AGUs) of starch molecules and alcoholic hydroxy groups of other compounds. Only a few water-soluble ones of these types of starch ethers are manufactured and industrially used on a large scale. These include specific hydroxyalkyl starches, especially hydroxyethyl and hydroxypropyl starches, as well as carboxymethyl starch. A number of different hydroxyalkylcarboxymethyl starches are, however, also commercially available.

[0018] By preference, hydroxy-C₁ to C₁₀ alkylcarboxymethyl starches, particularly preferably hydroxy-C₂ to C₆ alkylcarboxymethyl starches, are used according to the present invention as hydroxyalkylcarboxymethyl starches. Very particularly preferably, the hydroxyalkylcarboxymethyl starch is selected from hydroxyethylcarboxymethyl starches, hydroxypropylcarboxymethyl starches, and/or

hydroxyethylhydroxypropylcarboxymethyl starches, the hydroxypropylcarboxymethyl starches in turn being preferred.

[0019] Hydroxypropylcarboxymethyl starches used with particular preference are obtained by reacting a starch with monochloroacetic acid and/or monochloroacetate and propylene oxide, where monochloroacetic acid and/or monochloroacetate on the one hand and propylene oxide on the other hand are used at a molar ratio from 10 : 1 to 1 : 100, by preference from 5 : 1 to 1 : 50, particularly preferably from 5 : 1 to 1 : 10. As a rule, the reaction occurs in two steps, in a first step the starch being reacted with monochloroacetic acid and/or monochloroacetate, and in a second step the resulting starch derivative then being reacted with propylene oxide. In the first step, carboxymethyl groups are introduced into the starch molecule. By reaction with propylene oxide, hydroxypropyl groups resp. hydroxy-terminated polypropylene oxide chains are linked to these carboxymethyl groups and/or to those free hydroxy groups of the anhydroglucose units (AGUs) of the starch molecules which are still present. The molar ratio of carboxymethyl groups and hydroxypropyl groups in the starch molecule is determined by the corresponding molar ratio of the educts used. If hydroxy-terminated polypropylene oxide chains are constructed, then the molar content of hydroxypropyl groups in the starch molecule is understood as the sum of the molar content of terminal hydroxypropyl groups and of the molar content of propylene oxide units in the polypropylene oxide chain. One mol of a $-\text{CH}_2\text{CH}(\text{CH}_3)-\text{O}-\text{CH}_2\text{CH}(\text{CH}_3)-\text{OH}$ group therefore corresponds, for example, to two mol hydroxypropyl groups in the starch molecule.

[0020] All natural starches can be used in principle to manufacture the mixed starch ethers usable according to the present invention. Suitable starches may be gathered from the aforementioned Ullmann, volume 22, sub-chapters 6.2 to 6.4 of the "Starch" chapter. In addition to cereal starches such as corn, wheat, or rice starch, as well as tuber or root starches such as potato, cassava, or tapioca starch, legume starches such as pea or bean starches are also suitable. The mixed starch

ethers usable according to the present invention are, however, preferably based on tuber or root starches, particularly preferably on potato starch.

[0021] The aqueous preparations of reduced-viscosity mixed starch ethers are preferably manufactured by mixing the mixed starch ethers with water and (very largely irreversibly) breaking down the higher-order structures of the mixed starch ethers by physical, in particular mechanical action, and/or chemically breaking down the mixed starch ethers, for example by oxidation, acid catalysis, or enzymatically resp. thermally. A combination of actions is also possible. Concentrated systems having a starch ether content from approximately 20 to 70 wt% are preferred in this context, since it has been proven that technical handling is easiest in these concentration ranges. The aqueous preparations can then be brought together with the remaining constituents in the manner described. If desired, the starch derivative preparations can be diluted prior to mixing with the other constituents, by preference to a mixed starch ether content from 30 to 60 wt%.

[0022] Mechanical breakdown of the structures of such aqueous systems can be accomplished in mechanical apparatuses known to one skilled in the art. Kneaders, extruders, stator/rotor machines, and/or agitators are suitable, for example, as such apparatuses. The degree of mechanical breakdown of the higher-order structures of the aqueous starch derivative systems depends on concentration, temperature, residence time, and shear. The degree of breakdown of the higher-order starch structures should advantageously be close to the achievable limit value. The degree of breakdown can be ascertained by determining the solution viscosity values. Without disadvantages, the breakdown of the higher-order starch structures can also occur during manufacture of the glue stick substances in batch apparatuses in which a sufficient degree of breakdown of the higher-order starch structures can be achieved.

[0023] The mechanical breakdown of the higher-order starch structures or

higher-order starch ether structures can be supplemented with or replaced by a chemical breakdown of the starch molecules to the viscosity level according to the present invention. The (partial) chemical breakdown of the starch molecules resp. starch ether molecules can be carried out both before and after the mechanical breakdown of the higher-order starch structures. Both processes can also be carried out alone, independently of one another. The reduction in the viscosity of the mixed starch ether solution can also be accomplished exclusively by chemical breakdown to the viscosity level according to the present invention. The breakdown of the starch molecules can occur in accordance with methods known to one skilled in the art, by oxidative, acid-hydrolytic, enzymatic, or thermal breakdown.

[0024] Ullmann's "Encyklopädie der technischen Chemie" [Encyclopedia of chemical engineering], 4th edition, Verlag Chemie, Weinheim (1974) describes in further detail the usual methods for breaking down starches. Preferred oxidizing agents for oxidative breakdown are chromic acid, permanganate, hydrogen peroxide, nitrogen dioxide, hypochlorite, periodate, and peracids such as, for example, peracetic acid. Hydrochloric acid, sulfuric acid, or phosphoric acid are preferably used as acids for acid-hydrolytic breakdown, but the use of other acids such as, for example, acetic acid, oxalic acid, sulfurous acid, perchloric acid, or trichloroacetic acid is also possible. Enzymes that can be used to break down starches are α - and β -amylases, as well as the glucoamylases and debranching enzymes.

[0025] A sufficient degree of breakdown for purposes of the invention is usefully achieved when a 40-wt% aqueous solution of the mixed starch ether being used exhibits at 20°C a viscosity (Brookfield method) of less than 2,000,000 mPas, for example 100 to 1,000,000 mPas, by preference 2,000 to 100,000 mPas, in particular 10,000 to 80,000 mPas.

[0026] The hydroxyalkylcarboxymethyl starches contained in the glue sticks therefore by preference exhibit a viscosity from 100 to 1,000,000 mPas, by

preference from 2,000 to 100,000 mPas, particularly preferably from 10,000 to 80,000 mPas, determined in each case as a 40-wt% aqueous solution using a Brookfield RVT viscosimeter at 20°C, spindle 7, 20 rpm.

[0027] The glue sticks contain the hydroxyalkylcarboxymethyl starch by preference in a total quantity from 5 to 50, particularly preferably from 10 to 40 wt%, based on the total mass of the glue stick. If mixtures of several hydroxyalkylcarboxymethyl starches are used, the total quantity is of course to be understood as the sum of the quantities of each hydroxyalkylcarboxymethyl starch that is used.

[0028] Glue sticks that contain 5 to 10 wt% mixed starch ethers having a viscosity from 1,000,000 mPas to 50,000 mPa, or 10 to 30 wt% having a viscosity from 100,000 to 2,000 mPas, or 30 to 50 wt% having a viscosity from 30,000 to 100 mPas, have proven particularly suitable. The "wt%" refers to the total weight of the glue stick.

[0029] It is preferred to use hydroxyalkylcarboxymethyl starches whose degree of substitution (DS) is 0.1 to 2.0, by preference 0.2 to 1.0.

[0030] The glue stick according to the present invention can contain at least two different hydroxyalkylcarboxymethyl starches. The glue stick according to the present invention by preference contains at least two different hydroxypropylcarboxymethyl starches, particularly preferably at least two different hydroxypropylcarboxymethyl starches that differ from one another in terms of the molar ratio of hydroxypropyl groups to carboxymethyl groups. By preference, what is used as a first hydroxypropylcarboxymethyl starch is a hydroxypropylcarboxymethyl starch that is obtained by a reacting a starch with monochloroacetic acid and/or monochloroacetate and propylene oxide, the monochloroacetic acid and/or monochloroacetate on the one hand and the propylene oxide on the other hand being used at a molar ratio from 1 : 2 to 1 :

100, by preference from 1 : 2 to 1 : 50, particularly preferably from 1 : 2 to 1 : 5. The second hydroxypropylcarboxymethyl starch used is by preference a hydroxypropylcarboxymethyl starch that is obtained by reacting a starch with monochloroacetic acid and/or monochloroacetate and propylene oxide, the monochloroacetic acid and/or monochloroacetate on the one hand and the propylene oxide on the other hand being used at a molar ratio from 10 : 1 to 1 : 1, by preference from 8 : 1 to 2 : 1, particularly preferably from 5 : 1 to 3 : 1. In other words, in the one case the hydroxyalkyl groups, and in the other case the carboxymethyl groups, are present at a molar excess. The first and the second hydroxypropylcarboxymethyl starch are used by preference in quantities such that the weight ratio of the first to the second hydroxypropylcarboxymethyl starch is 100 : 1 to 1 : 1, by preference 50 : 1 to 2 : 1, particularly preferably 25 : 1 to 5 : 1.

[0031] The mixed starch ethers used according to the present invention can be present in uncrosslinked or crosslinked fashion. Crosslinked mixed starch ethers additionally exhibit water-retarding properties, with the result that the viscosity of the stick substance is increased. Surprisingly, however, further positive effects also occur. Better strength values and rub-off properties are achieved. The glue stick applies very uniformly, i.e. shedding only a very few chunks, without losing too much mass.

[0032] A glue stick according to the present invention contains an aqueous preparation of at least one hydroxyalkylcarboxymethyl starch. In addition to the hydroxyalkylcarboxymethyl starch, at least one further macromolecular substance can also be provided. The further macromolecular substance can be selected, for example, from starch derivatives other than hydroxyalkylcarboxymethyl starch, from polyvinyl acetals, polyacrylates, polyurethanes, polyvinylpyrrolidone, alcohols, celluloses, proteins, and/or from mixtures thereof.

[0033] Preferred further macromolecular substances are selected from reduced-viscosity starch ethers, polyvinylpyrrolidone, polyurethanes, polyvinyl alcohols,

and/or from mixtures thereof. Particularly preferred further macromolecular substances are selected from reduced-viscosity starch ethers and polyurethanes. "Reduced-viscosity" starch ethers are understood as starch ethers that not only have been etherified in largely polymer-analogous fashion, but moreover have also been chemically or physically destructured in such a way that their viscosity is less than approx. 2,000,000 mPas (40-percent solution, 20°C, Brookfield).

[0034] Preferred reduced-viscosity starch ethers are nonionic starch ethers that are obtainable by reacting natural starches with ethylene oxide, propylene oxide, butylene oxide, and/or glycidol. The reaction can occur with only one of the substances recited, with mixtures of the substances, or sequentially with several of the substances, for example first with ethylene oxide and then with propylene oxide. The result is to add on an ethylene oxide block to which a propylene oxide block is then attached. Starch derivatives in particular having higher degrees of substitution, by preference nonionogenic starch ethers, can advantageously be adjusted to a relatively low viscosity level by mechanical treatment in aqueous systems by breaking down crystalline structures and/or by oxidative, acid-hydrolytic, enzymatic, and thermal breakdown, and are thus suitable to a particular degree. Hydroxyalkyl starches are particularly preferred in this context. The degree of substitution (DS) should by preference be 0.1 to 2.0, in particular 0.2 to 1.0. The desired viscosity can be established using the methods that have already been described above in the context of manufacture of the hydroxyalkylcarboxymethyl starches used according to the present invention.

[0035] If the glue stick according to the present invention also contains at least one further macromolecular substance in addition to at least one hydroxyalkylcarboxymethyl starch, the total quantity of macromolecular substances, i.e. hydroxyalkylcarboxymethyl starch and further macromolecular substances, is by preference 5 to 50 wt%, particularly preferably 10 to 40 wt%, based in each case on the total mass of the stick.

[0036] The addition of further macromolecular substances is not necessary according to the present invention, however. In particular, the addition of polyvinylpyrrolidones and cellulose derivatives can be omitted. In a special embodiment, the glue stick according to the present invention is free of carboxymethyl celluloses. A glue stick of this kind is notable in particular for more economical application with no change in adhesive performance and with additionally improved long-term stability of the adhesive bond. The glue stick according to the present invention is preferably free of polyvinylpyrrolidones and of any cellulose derivatives. "Free of" is to be understood literally as 0 wt%. Very particularly preferably, the glue stick according to the present invention contains as macromolecular substances exclusively the mixed starch ethers to be used according to the present invention.

[0037] A glue stick according to the present invention furthermore contains soap.

[0038] The soap is preferably the sodium salt of C_{12} to C_{22} fatty acids, in particular of C_{14} to C_{18} fatty acids, of natural or synthetic origin. The soap resp. the soap gel serves chiefly as a shape-imparting structural substance. Sodium salts of fatty acids are harder than, for example, the corresponding potassium salts and are therefore well-suited as structuring agents.

[0039] The soap is contained by preference in quantities from 3 to 20 wt%, particularly preferably from 4 to 10 wt%, based on the total mass of the glue stick. At these proportions the soap gel can optimally form the desired physical structure that constitutes the basis for the outstanding strength of the glue stick according to the present invention. On the other hand, however, the physical structure can also be destroyed sufficiently easy when rubbed off on the surface to be adhesively bonded, so that the adhesive nature of the preparation then, as desired, becomes predominant.

[0040] A glue stick according to the present invention can additionally contain

gelatin. The quantity of gelatin is by preference 0 to 10 wt% and in particular 1.5 to 5 wt%, based on the total mass of the glue stick. Any grades of gelatin can be used in this context.

[0041] A combination of mineral filler, in particular barium sulfate, and gelatin can also be used in a glue stick according to the present invention. The result here can be a synergistic improvement in adhesive properties thanks to the combination of a mineral filler, in particular barium sulfate, and gelatin.

[0042] The glue stick can furthermore contain sucrose. Sucrose, being an economical and moreover entirely harmless substance, is outstandingly suitable as a filler for a glue stick according to the present invention. In a preferred embodiment of the glue stick according to the present invention, the latter therefore contains sucrose, the sucrose content being by preference 15 to 25, particularly preferably 17 to 22 wt%, based on the total mass of the glue stick.

[0043] The glue sticks can furthermore contain superabsorbers. "Superabsorbers" are understood in the context of the present invention as particles of synthetic or at least partly synthetic materials that can absorb at least 4 times, preferably at least 10 times, and particularly preferably at least 100 times their mass of water. A feature common to all superabsorbers, despite differences in chemical structure, is that they are capable of absorbing and retaining the aforementioned multiple of their mass of aqueous liquids even under a moderate pressure load. Superabsorbers such as those that can be used in the context of the present invention have been known hitherto in particular from their utilization in baby diapers and in special hygiene products.

[0044] The superabsorber can be contained, for example, in the form of particles having a particle size from 1 to 1000 μm . The permeability and thus the absorption properties of the superabsorbers are advantageously manifested in this particle-size range. It is preferred to use superabsorbers that have an average particle

diameter of at most 150 μm , preferably 100 μm , and particularly preferably 70 μm . A glue stick containing such superabsorbers is notable in particular for more economical application with no change in adhesive performance and with further improved long-term stability of the adhesive bond.

[0045] The glue stick can contain the superabsorber, for example, in a quantity from 0.2 to 3 wt%, based on the total mass of the glue stick. Within this range a particularly balanced relationship is achieved between outstanding strength of the solidified stick mass and good shelf stability. The superabsorber is contained particularly preferably in a quantity from 0.3 to 2 wt%, based on the total mass of the glue stick. The proportion of superabsorber is in particular 0.4 to 1.2 wt%, based on the total mass of the glue stick. Optimum strength values with consistently good shelf stability are obtained within this range.

[0046] In addition to the components listed so far, further usual adjuvants can concurrently be used, for example substances that promote easy and smooth rub-off. Such substances are, for example, aminocarboxylic acids and/or lactams thereof. Suitable aminocarboxylic acids resp. lactams thereof should contain up to 12 carbon atoms, in particular 4 to 8 carbon atoms. The representative preferred for practical use is caprolactam-epsilon resp. 7-aminocaproic acid deriving therefrom. The quantity of lactams or of corresponding aminocarboxylic acids to be used is usually not more than 15 wt%, for example 0.5 wt% to 5 wt%, based on the total stick mass.

[0047] As further adjuvants the glue sticks according to the present invention can contain (further) pigments, dyes, scents, preservatives, and the like. The quantities of these substances are, as usual, subordinate. Further possible additives are, for example, further fillers, optical brighteners, dextrans, and non-destructured starch derivatives. Mannans, in particular galactomannans, can also be contained in the glue sticks according to the present invention. The galactomannans from the fruits of the locust tree and from guar flour are particularly

suitable. The destructured starch ethers can also be replaced, in a subordinate proportion, by destructured mannans.

[0048] Also to be recited as suitable adjuvants are, for example, plasticizers and/or moisture-regulating substances, for example organic water-soluble solvents that are usually used in glue sticks. The nonvolatile organic solvents should be used at most in quantities of up to 50 wt%, based on the water content of the sticks. Concurrent use of polyvalent (polyfunctional) alcohols such as propylene glycol, glycerol, polyglycerols, trimethylolpropane, polyether glycols, and sorbitol, and/or low-molecular-weight starch hydrolysates that have been converted by hydrogen reduction into corresponding polyols, is also possible. For example, a mixture of glycerol and polyethylene glycol can be concurrently used. The concentration of glycerol and propylene glycol, especially propylene glycol, is by preference 0 to 15 wt%, in particular 5 to 10 wt%, based on the total glue stick.

[0049] The quantities indicated above of the individual ingredients, together with the water that is additionally present, add up in each case to a total of 100 wt%.

[0050] In a preferred embodiment, the glue stick according to the present invention is made up of:

- 5 to 50 wt% macromolecular substance containing at least one hydroxyalkylcarboxymethyl starch,
- 3 to 20 wt% soap,
- 0 to 30 wt% sucrose,
- 0 to 25 wt% further adjuvants, and
- 25 to 92 wt% water,

the total quantity of the ingredients yielding 100 wt%.

[0051] The statements already made above apply analogously regarding preferred ingredients and preferred quantities of the individual constituents.

[0052] A further subject of the present invention is a method for manufacturing a

glue stick according to the present invention, which method is characterized in that the aqueous preparation of at least one hydroxyalkylcarboxymethyl starch is mixed with the soap or with the soap-forming constituents and optionally with the fillers and/or adjuvants, optionally while being heated, until a homogeneous mixture has resulted, and the mixture is allowed to stand or is cooled without mechanical influence. It is preferred to decant the homogeneous mixture, after heating to temperatures of at least 50°C, by preference up to 80°C, directly into stick casings or similar containers, and to allow it to solidify into the desired gels without mechanical influence. This method is advantageous because the mixtures are easy to pour in the aforementioned temperature range. The glue sticks according to the present invention are notable for even further optimized viscosity values at around 80°C as compared with the existing art, and can therefore be processed particularly effectively.

[0053] A glue stick according to the present invention exhibits outstanding compressive strength. At the same time it possesses optimized rub-off properties. This is to be understood to mean that the stick on the one hand applies uniformly and on the hand applies sufficient mass that good adhesive bonding of the substrates is achieved, but almost no excess adhesive is delivered, i.e. the stick loses almost no clumps and the formation of local adhesive excesses and irregularities on the substrate surface is minimized. In addition, the optimized rub-off is expressed as more pleasant utilization for the user, and the stick slides better over the surface to be bonded. The adhesive properties of a glue stick according to the present invention are likewise outstanding. Shelf stability is moreover enhanced, and even over longer storage times the adhesive bonds retain their white color and do not become yellow.

[0054] A further subject of the present invention is the use of a glue stick according to the present invention for planar joining, in particular for adhesive bonding, of substrates, in particular for joining paper, cardboard, wood, and/or plastic to one another.

[0055] The invention will be explained in further detail below with reference to exemplifying embodiments. Unless otherwise indicated, percentages and quantitative ratios refer to weight.

EXAMPLES

I. Starting materials

[0056] - Mixed starch ether A: Hydroxypropylcarboxymethyl starch based on potato starch; molar ratio of hydroxypropyl to carboxymethyl > 1 ; viscosity, determined as a 40-wt% aqueous solution using a Brookfield RVT viscosimeter at 20°C, spindle 7, 20 rpm: approx. 70,000 mPas;

[0057] - Mixed starch ether B: Hydroxypropylcarboxymethyl starch based on a mixture of potato starch and tapioca starch; molar ratio of hydroxypropyl to carboxymethyl > 1 ; viscosity, determined as a 40-wt% aqueous solution using a Brookfield RVT viscosimeter at 20°C, spindle 7, 20 rpm: approx. 80,000 mPas;

[0058] - Mixed starch ether C: Hydroxypropylcarboxymethyl starch based on potato starch; molar ratio of hydroxypropyl to carboxymethyl < 1 ; viscosity, determined as a 10-wt% aqueous solution using a Brookfield RVT viscosimeter at 20°C, spindle 4 or 5, 20 rpm: approx. 5,000 mPas.

[0059] - Fatty acids: commercially obtainable fatty acids having 14 to 18 carbon atoms.

II. Manufacturing the glue sticks

[0060] The components according to Table I were mixed at 80°C and processed into glue sticks in accordance with the description. The respective compositions are indicated in parts by weight.

III. Properties of the glue sticks

a) Compressive strength

[0061] The term "compressive strength" is to be understood as the maximum load measured upon collapse of the stick shape under compressive stress parallel to the longitudinal axis.

[0062] An Erichsen model 464L tester, measurement head 709, is used to measure compressive strength.

[0063] The adhesive, cut off directly above the piston and having a minimum length of 30 mm, is inserted between two holding pieces; these are disks of hard PVC whose thickness is approx. 10 mm and which exhibit a circular depression of about 3 mm adapted to the respective stick diameter. The stick, fitted with the holding pieces, is placed centeredly onto the test stage of the compressive strength tester. The height of the force measurement instrument above the test stage is adapted to the height of the test article. The measurement head is then advanced onto the stick to be tested at a feed rate of approx. 70 mm per minute. Once the maximum compressive force is reached, the value (in newtons) is read from the digital display.

b) Application characteristics (lumps)

[0064] The so-called "lump test" describes the (undesirable) shedding of smaller and larger lumps, deviating from a continuous adhesive film, upon application of the glue stick onto paper,. Here the sticks are moved over a DIN A4 sheet in several tracks under the load of a defined test weight. The sliding characteristics are assessed qualitatively. The uniformity of the adhesive film and the formation of lumps are assessed visually.

IV. Results

[0065] The results are summarized in Table II.

[0066] Table I: Compositions (indications in wt%)

Component	Example	
	1	2
Mixed starch ether A (44% aqueous preparation)	-	54.0
Mixed starch ether B (44% aqueous preparation)	53.0	-
Mixed starch ether C (solid)	-	2.4
Sodium hydroxide (10%)	1.4	-
Fatty acids	5.7	5.7
Sucrose	20.0	20.3
Caprolactam	1.0	1.0
Adjuvants	2.7	0.3
Demineralized water	to 100	to 100

[0067] Table II: Test results with sticks manufactured from compositions according to Table I

Property	Example	
	1	2
Compressive strength (20 g) [N]	86	92
Application (lumps, visual)	minimal clumping; minimal smearing; good sliding characteristics	minimal clumping; minimal smearing; very good sliding characteristics

[0068] The results presented in Table II shows that the glue sticks according to the present invention have outstanding compressive strength and application characteristics. Thanks to the use of a mixture of two mixed starch ethers based entirely on potato starch, the hydroxyalkyl groups in one case and the carboxymethyl groups in the other case being present at a molar excess, the compressive strength and sliding characteristics can be further optimized. The initial adhesive strength that is achieved corresponds to, resp. slightly exceeds, the initial

adhesive strength that can be achieved when using commercially usual glue sticks based on reduced-viscosity hydroxyalkyl starches. The initial adhesive strength of commercially usual glue sticks based on polyvinylpyrrolidone is appreciably exceeded.

CLAIMS

1. A glue stick, containing an aqueous preparation of at least one hydroxyalkylcarboxymethyl starch having a viscosity less than 2,000,000 mPas, determined as a 40-wt% aqueous solution using a Brookfield RVT viscosimeter at 20°C, spindle 7, 20 rpm, and soap.
2. The glue stick according to claim 1, wherein the hydroxyalkylcarboxymethyl starch is selected from hydroxyethylcarboxymethyl starches, hydroxypropylcarboxymethyl starches, and/or hydroxyethylhydroxypropylcarboxymethyl starches.
3. The glue stick according to claim 1 or 2, wherein the hydroxyalkylcarboxymethyl starch is selected from hydroxypropylcarboxymethyl starches.
4. The glue stick according to claim 3, wherein the hydroxypropylcarboxymethyl starches are obtained by reacting a starch with monochloroacetic acid and/or monochloroacetate and propylene oxide, where monochloroacetic acid and/or monochloroacetate on the one hand and propylene oxide on the other hand are used at a molar ratio from 10 : 1 to 1 : 100.
5. The glue stick according to any one of claims 1 to 4, wherein the degree of substitution (DS) of the hydroxyalkylcarboxymethyl starch is 0.1 to 2.0.
6. The glue stick according to any one of claims 1 to 4, wherein the degree of substitution (DS) of the hydroxyalkylcarboxymethyl starch is 0.2 to 1.0.
7. The glue stick according to any one of claims 1 to 6, wherein hydroxyalkylcarboxymethyl starch is contained in a total quantity from 5 to 50 wt%, based on the total mass of the glue stick.

8. The glue stick according to any one of claims 1 to 6, wherein hydroxyalkylcarboxymethyl starch is contained in a total quantity from 10 to 40 wt%, based on the total mass of the glue stick.
9. The glue stick according to any one of claims 1 to 8, wherein the hydroxyalkylcarboxymethyl starch has a viscosity from 100 to 1,000,000 mPas, determined as a 40-wt% aqueous solution using a Brookfield RVT viscosimeter at 20°C, spindle 7, 20 rpm.
10. The glue stick according to any one of claims 1 to 8, wherein the hydroxyalkylcarboxymethyl starch has a viscosity from 2000 to 100,000 mPas, determined as a 40-wt% aqueous solution using a Brookfield RVT viscosimeter at 20°C, spindle 7, 20 rpm.
11. The glue stick according to any one of claims 1 to 8, wherein the hydroxyalkylcarboxymethyl starch has a viscosity from 10,000 to 80,000 mPas, determined as a 40-wt% aqueous solution using a Brookfield RVT viscosimeter at 20°C, spindle 7, 20 rpm.
12. The glue stick according to any one of claims 1 to 11, wherein the hydroxyalkylcarboxymethyl starch is a corresponding derivative of potato starch.
13. The glue stick according to any one of claims 1 to 12, wherein it is made up of:
 - 5 to 50 wt% macromolecular substance containing at least one hydroxyalkylcarboxymethyl starch,
 - 3 to 20 wt% soap,
 - 0 to 25 wt% further adjuvants, and
 - 25 to 92 wt% water,
 - and further comprising 0 to 30 wt% sucrose,the total quantity of the ingredients yielding 100 wt%.

14. Use of a glue stick according to any one of claims 1 to 13 for planar joining of substrates.
15. Use of a glue stick according to claim 14 for joining paper, cardboard, wood, and/or plastic to one another.