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(54) **GREASEPROOF PAPER**

(57) The invention pertains to the application of degraded amylopectin root or tuber starch in the production of making paper-pulp based solid substrates, such as paper and cardboard, by applying such starches in combination with fluorochemicals to paper. The invention per-

tains to paper obtained by this process, to compositions used in this process, as well as to a method to obtain such paper and use of the compositions to improve oil- and grease resistance.

EP 3 301 220 A1

Description

[0001] The invention is in the field of paper-pulp based solid substrates with grease resistance, most notably grease-resistant paper and cardboard.

Background

[0002] The treatment of paper and board with fluorinated compounds to achieve oil and grease resistance is well known in the art. The grease resistance is based on a reduction of the surface energy of the substrate by fluorochemical agents.

[0003] Fluorochemical agents are generally applied via surface treatment to a cellulosic substrate. The use of starches as carrier in the surface treatment is well known in the prior art. In US 2005/0252628 a highly acid thinned hydroxyethylated starch is used. US2007/0020462 mentions the use of many starch types including but not limited to oxidized, ethylated, cationic or pearl starch. However, the prior art is silent on the use of amylopectin-starches as carrier for fluorochemicals. Generally, the ratio between starch and fluorochemical in known papers and compositions for improving oil- and grease resistance is between 10 and 20.

[0004] Oil and grease resistance is generally required at the surface of paper or board. Penetration of the fluorochemical into the paper or board leads to a reduced performance and/or increased consumption of the fluorochemical. As fluorochemicals contribute significantly to the cost of the final paper, it is important to optimize or minimize the quantity used. Moreover, from an environmental point of view it also important to minimize the overall fluorochemical consumption. Several attempts have been made to improve the efficacy of the fluorochemical treatment to improve oil- and grease resistance of paper.

[0005] US2011/0189395 describes a process that comprises a printing process to apply a (per)fluoropolyether to at least part of a substrate with the objective to reduce the total amount of fluoro-containing additives. Disadvantage of this invention is that it requires the installation of expensive specialized equipment.

[0006] EP2 492 395 B1 describes a composition for improving the performance of fluorochemical compounds such as (per)fluoropolyethers comprising a fluorocarbon resin, a guar gum and an inorganic phosphate salt, which composition may comprise starch. Disadvantage of this composition is the price and availability of guar gum, and the applied ratio between starch and fluorochemical is not higher than 6.3, and the starch used is not amylopectin-rich starch.

[0007] There is still a need for compositions and methods to improve the efficiency of fluorochemical compounds to improve oil- and grease resistance of paper and cardboard. It is furthermore preferred to use starch-based carriers which comply with international guidelines and regulations for food contact paper and cardboard and which can be applied onto a fibrous web using surface treatment devices. Specifically, this means there is a need for a starch based carrier which is not stabilized by esterification or etherification and which improves the performance of a fluorochemical to impart oil and grease resistance of a surface treatment composition. These and other objectives are met in the present invention.

Detailed description

[0008] The present invention provides a paper-pulp based solid substrate, comprising an anionic fluorochemical and a degraded root or tuber starch or starch blend, which degraded root or tuber starch or starch blend comprises 90-100 wt.%, based on the total weight of the starch or starch blend, of amylopectin, and which root or tuber starch or starch blend is characterized by a molecular weight of $0.5 - 20 \cdot 10^6$ Da, and a viscosity, determined on a 15 wt.% aqueous solution by a Brookfield LVF viscometer at 60 rpm and at 50 °C, of 20 - 150 cP.

[0009] A paper-pulp based solid substrate in this context is a cellulosic material. Specifically, it is a solid material comprising a network of cellulosic fibers, which are intertwined to provide a degree of coherency. Most notably, the paper-pulp based solid materials of the invention can be paper or cardboard, preferably paper. Any type of paper-pulp based solid substrate can be treated as described herein, to obtain an oil and grease-resistant paper-pulp based solid substrate. How to obtain a paper-pulp based solid substrate is well-known in the art.

[0010] A paper-pulp based solid substrate of the invention comprises an anionic fluorochemical. Anionic fluorochemicals are known in the art of providing oil- and grease resistant paper. Anionic fluorochemicals are polymers or oligomers comprising CF_2 and/or CF_3 groups. Preferably, at least 50 wt.% of the molecular mass can be attributed to CF_2 and/or CF_3 -groups, more preferably at least 60 wt.%. Alternatively or additionally, 40-90 wt.% of the molecular mass of the anionic fluorochemical is attributed to covalently bound fluor (F) atoms. Such polymers are well-known and commercially available.

[0011] Any type of anionic fluorochemical can be used. Preferred are an anionic fluoropolyether or an anionic perfluoropolyether, or copolymers comprising an anionic fluoropolyether or an anionic perfluoropolyether. Furthermore, fluorinated or perfluorinated carboxylic acids (perfluoroacids), including perfluorinated fatty acids, are suitable fluorochemicals for use according to the invention. These anionic fluorochemicals can include fluorocarboxylic acids having

an ether bond (perfluoro-ether acids). Further preferably, the anionic fluorochemical comprises a phosphate, sulfate or carboxylate anionic group.

[0012] In preferred embodiments, the molecular weight of the anionic fluorochemical is between 200 and 20000 Da, preferably between 300 and 15000 Da. For carboxyl anionic fluorochemicals, a preferred molecular weight is between 500 and 10000 Da. For phosphate anionic fluorochemicals, the molecular weight is preferably between 350 and 8000 Da.

[0013] An example of a suitable anionic fluorochemical is the Solvera PFPE product line of Solvay, which are products based on a perfluoropolyether (PFPE) backbone that is functionalized in order to graft the material to the substrate being treated. One suitable, exemplary compound is Solvera PT 5045PG.

[0014] The anionic fluorochemical can be applied to a single side of a paper-pulp based solid substrate, or to both sides. The paper-pulp based solid substrate of the invention preferably comprises a quantity of anionic fluorochemical of 0.01 - 0.5 g/m² per side of the paper-pulp based solid substrate, more preferably 0.015 - 0.3 g/m² per side, more preferably 0.02 - 0.2 g/m² per side, even more preferably 0.01 - 0.1 g/m² per side, even more preferably 0.015 - 0.05 g/m² per side. The total loading of anionic fluorochemical on the paper can be from 0.01 - 1 g/m², preferably 0.015 - 0.6 g/m², more preferably from 0.02 - 0.4 g/m², even more preferably 0.02 - 0.2 g/m², even more preferably from 0.03 - 0.1 g/m². It can be tested whether the anionic fluorochemical is present on one or on two sides of the paper-pulp based solid substrate by electron spectroscopy chemical analysis, as is known in the art.

[0015] Alternatively, the quantity of anionic fluorochemical on the paper-pulp based solid substrate is 0.5 - 5 kg/ton, preferably 0.8 - 4 kg/ton, more preferably 1 - 3 kg/ton.

[0016] One objective of the invention is to improve the performance of fluorochemicals by increasing the starch/fluorochemical ratio ("SF-ratio"). The SF-ratio is defined as the ratio of the quantity of starch per m² and the quantity of anionic fluorochemical (per m²). By increasing the SF-ratio, the oil and grease resistance of a paper-pulp based solid substrate can be increased. Alternatively, the quantity of anionic fluorochemical can be reduced to attain the same OGR at lower cost. Without being bound by theory, the inventors found that the starch functions as a carrier for the fluorochemical.

[0017] The paper-pulp based solid substrate further comprises a degraded root or tuber starch or starch blend, which degraded root or tuber starch or starch blend comprises 90-100 wt.%, based on the total weight of the starch or starch blend, of amylopectin.

[0018] The root or tuber starch (or starch blend) of the invention may be (a blend of starches of) of any root or tuber source. Root or tuber in this context includes the species of potato (*Solanum tuberosum* or Irish potato), sweet potato (*Ipomoea batatas*), cassava (also known as tapioca, *Manihot esculenta*, syn. *M. utilissima*), yuca dulce (*M. palmata*, syn. *M. dulcis*), yam (*Dioscorea spp.*), yautia (*Xanthosoma spp.*, including *X. sagittifolium*), taro (*Colocasia esculenta*), arracacha (*Arracacia xanthorrhiza*), arrowroot (*Maranta arundinacea*); chufa (*Cyperus esculentus*), sago palm (*Metroxylon spp.*), oca and ullucu (*Oxalis tuberosa* and *Ullucus tuberosus*), yam bean and jicama (*Pachyrhizus erosus* and *P. angulatus*), mashua (*Tropaeolum tuberosum*) and Jerusalem artichoke or topinambur (*Helianthus tuberosus*).

[0019] Preferably, the root or tuber is a potato, sweet potato, cassava or yam, more preferably potato, sweet potato or cassava, and most preferably the root or tuber is a potato (*Solanum tuberosum*).

[0020] Regarding production possibilities and properties, there are significant differences between potato starch on the one hand, and cereal starches on the other hand. This particularly applies to waxy maize starch, which is commercially by far the most important waxy cereal starch. The cultivation of waxy maize, suitable for the production of waxy maize starch is not commercially feasible in countries having a cold or temperate climate, such as The Netherlands, Belgium, England, Germany, Poland, Sweden and Denmark. The climate in these countries, however, is suitable for the cultivation of potatoes. Tapioca starch, obtained from cassava, may be produced in countries having a warm climate, such as is found in regions of South East Asia and South America.

[0021] The composition and properties of root and tuber starch, such as potato starch and tapioca starch, differ from those of the waxy cereal starches. Potato starch has a much lower content of lipids and proteins than the waxy cereal starches. Problems regarding odor and foaming, which, because of the lipids and/or proteins, may occur when using cereal or waxy cereal starch products (native and modified), do not occur, or occur to a much lesser degree when using corresponding potato starch products. In contrast to the waxy cereal starches, potato starch contains chemically bound phosphate groups. As a result, potato starch products in a dissolved state have a distinct polyelectrolyte character.

[0022] According to the present invention, the oxidized starch is a root or tuber starch. It has been found that the presence of the lipids and proteins adversely affects the oxidation reaction, leading to by-products because of which the oxidized starch is not of sufficient quality. Furthermore, the presence of lipids and proteins leads to an unacceptably high AOX level, wherein the AOX level is defined as the amount of material that adsorbs to active carbon when the oxidized starch is brought into contact with said active carbon. The AOX level provides an indication of the amount of halogenic material, such as chlorine, in the oxidized starch.

[0023] Starch is essentially composed of two molecule types, amylose and amylopectin. Amylose consists of unbranched or slightly branched molecules having an average degree of polymerization of 1000 to 5000, depending on the starch type (average molecular weight approximately $0.18 - 0.9 \cdot 10^6$ Da). Amylopectin consists of very large, highly branched molecules having an average degree of polymerization of 1.000.000 or more (average molecular weight about

180 • 10⁶ Da or more).

[0024] Natural, regular starch comprises about 70-85 wt.% of amylopectin and about 15-30 wt.% of amylose. However, amylopectin-rich starch ("waxy" starch) is also known, which generally comprises more than 95 wt.%, preferably more than 98 wt.%, based on the weight of the starch, of amylopectin.

[0025] The root or tuber starch or starch blend comprises 90-100 wt.%, based on the total weight of the starch, of amylopectin. A root or tuber starch of the invention may thus be a waxy starch, having an amylopectin content of more than 95 wt.%, preferably more than 98 wt.%, based on the weight of the starch, of amylopectin. A starch of the invention may also be a starch blend, comprising waxy starch with an amylopectin content of more than 95 wt.%, based on the weight of the starch, and regular starch with an amylopectin content of 70-85 wt.%, based on the weight of the starch. Blends of more than two types of starches are also possible. In case the starch of the invention is a starch blend, the ratio between the waxy starch and the regular starch is chosen so as to achieve an (overall) amylopectin content of 90-100 wt.%, based on the total weight of the starch blend. The weight ratio between the natural starch and the waxy starch may be between 3:1 and 1:3, preferably between 1:1 and 1:2.

[0026] The root or tuber starch or starch blend has been degraded. In case of starch blends, the starch types present in the blend may have been degraded separately, after which blending of the starch types results in the starch blend. Alternatively, the starch blend may have undergone the degradation process already blended.

[0027] Various degradation methods can be applied to the starch or starch blend to obtain the degraded starch. Suitable methods include oxidation, acid degradation and enzymatic degradation, which are all known in the art. Combinations of degradation methods may also be applied. It is preferred if the degraded starch has at least been oxidized. Oxidized starch is preferred. The advantage of using oxidized starch over using other types of degraded starches is presumed to lie in the increased presence of carbonyl groups, which impart special characteristics to the starch in the context of interaction with fluorochemical and/or paper-pulp based solid substrate.

[0028] In preferred embodiments, the starch or starch blend has been degraded by oxidation. Thus, the degraded starch or starch blend preferably comprises an oxidized starch.

[0029] In a first preferred embodiment, the oxidation to obtain an oxidized starch for use in the present invention is carried out using hypochlorite as described in WO 00/006607. This results in hypochlorite-oxidized starch. In this embodiment, the oxidation is carried out with an alkali metal hypochlorite as oxidizing agent. Preferably, sodium hypochlorite is used as an oxidizing agent. Alkali metal hypochlorites are relatively cheap and have a relatively large oxidizing power, thus leading to a very efficient and fast oxidizing process.

[0030] The amount in which the oxidizing agent is added may vary between 0.001 and 0.4 moles of alkali metal hypochlorite per mole starch, preferably between 0.0025 and 0.15 moles of alkali metal hypochlorite per mole starch. The skilled person will be aware that the alkali metal hypochlorite should be added to the starch in a controlled manner.

[0031] In a preferred embodiment, the oxidation of starch is performed at pH between 6 and 10, more preferably between 6.5 and 9.5, even more preferably between 7.5 and 9. It has been found that by working at a pH in these ranges particularly small amounts of oxidizing agent suffice in order to obtain an oxidized starch having excellent properties.

[0032] In order to maintain the pH at a desired value, it may be necessary to add an acid or a base to the reaction mixture. For this purpose, suitable acids and bases may be chosen such that they have substantially no negative effect on the oxidation reaction or on the oxidized starch. Preferably, hydrochloric acid or sodium hydroxide is used.

[0033] The temperature at which the starch, in accordance with the invention, is treated with an oxidizing agent is preferably chosen between 20 and 50°C, more preferably between 25 and 40°C.

[0034] The oxidation reaction may be carried out as a suspension or solution reaction in water. Preferably, the reaction is carried out as a suspension reaction in water, as this leads to a granular oxidized starch. To this end, the starch to be oxidized is suspended in water in an amount ranging between 0.5 and 1.5 kg of dry starch per liter water.

[0035] Optionally, a catalyst or a combination of catalysts may be used in the oxidation reaction. Suitable catalysts include bromide, cobalt, iron, manganese and copper salts. The catalyst or catalysts will be applied in catalytic amounts, which will be no higher than 10 wt.%, with respect to the amount of alkali metal hypochlorite.

[0036] Preferably, the reaction product of the above-described oxidation reaction is subjected to an alkaline treatment. This treatment comprises keeping the product for at least 15 minutes at a temperature of 20-50°C and a pH higher than 10. The alkaline treatment has a beneficial effect on the properties, especially the viscosity stability, of the oxidized starch. An oxidized starch according to the invention may be stored at increased temperatures, e.g. 80°C, for prolonged periods of time without substantially any change in the viscosity of the product being observed.

[0037] Preferably, the alkaline treatment lasts at least 30, more preferably at least 60 minutes. Although there is no critical upper limit for the duration of the alkaline treatment, it will usually not be carried out for more than 6 hours in order to prevent that too much of the desired product dissolves in the water. The pH at which the alkaline treatment is carried out is preferably higher than 10.5. Further preferred is that the pH is kept below 12. It has been found that according to these preferred embodiments, an even higher viscosity stability may be achieved.

[0038] In a second preferred embodiment, the oxidation is carried out using hydrogen peroxide as described in US 5,833,755. In this embodiment, the amount of hydrogen peroxide employed is preferably from about 0.0075 to 15.0

wt.%, more preferably about 0.01 to 2.0 wt.%, and even more preferably about 0.25 to 1.5 wt.% anhydrous hydrogen peroxide on dry substance of the starch. The hydrogen peroxide will normally be used in the form of an aqueous solution, as commonly supplied in commerce.

[0039] Preferably, the oxidation reaction is performed in a solution, dispersion or suspension of the starch in water, to which the hydrogen peroxide, or an aqueous solution thereof, is added. Preferably, the hydrogen peroxide is added batchwise or dropwise.

[0040] Suitable concentrations of the starch in said solution, dispersion or suspension lie between 10 and 50, preferably between 20 and 40 wt.%, based on the weight of the solution, dispersion or suspension. The pH during the oxidation reaction is between pH 10 and 12.5, preferably between 11 and 12. When the desired degree of oxidation is achieved, the pH will be adjusted to a level of pH 5-6. The temperature during the oxidation reaction in a suspension will preferably be below 60°C, more preferably between 20 and 50°C. When the reaction is carried out in a solution or dispersion, the temperature will usually be chosen between 60 and 200°C, preferably between 100 and 160°C. In order to carry out the reaction at a temperature higher than 100°C, use is preferably made of a jet cooker.

[0041] In accordance with the present invention, the oxidation of the specific starch described above is preferably performed in the presence of a catalyst. The catalyst preferably comprises divalent copper ions or a manganese complex. The use of a manganese complex as catalyst is particularly preferred.

[0042] In case the catalyst comprises divalent copper ions, it will preferably be used in the form of a salt. In principle, any copper(II)-salt which is soluble in water may be used. Suitably, the anion of the salt may be chosen from the group of chloride, sulfate, phosphate, nitrate, acetate, bromide and combinations thereof. Preferably, the quantity of copper used ranges from about 5 ppb to about 5000 ppb, more preferably from about 100 to about 1000 ppb, on dry substance of starch. When the oxidation reaction is carried out in a solution or a dispersion, the quantity of copper may be lower (e.g. between 5 and 1000 ppb) than when the reaction is performed in a suspension. In a preferred embodiment, the action of the divalent copper ions is enhanced by calcium, vanadium, manganese, iron and/or tungsten ions. The counterions for these ions may be of the same type as those of the copper catalyst. These additional salts will preferably be used in an amount between about 100 and about 2000 ppm, on dry substance of starch.

[0043] In case the catalyst comprises a manganese complex, the oxidation may also be carried out as disclosed in US 2012/0070554. In this embodiment, oxidation is carried out in the presence of a homogeneous manganese-based complex coordination catalyst. The homogeneous manganese-based complex coordination catalyst is typically a mononuclear or dinuclear complex of a Mn(III) or Mn(IV) transition metal. It will usually contain at least one organic ligand containing at least three nitrogen atoms that coordinate with the manganese, for example 1,4,7-triazacyclononane (TACN), 1,4,7-trimethyl-1,4,7-triazacyclononane (Me-TACN), 1,5,9-triazacyclododecane, 1,5,9-trimethyl-1,5,9-triazacyclododecane (Me-TACD), 2-methyl-1,4,7-triazacyclononane (Me/TACN), 2-methyl-1,4,7-trimethyl-1,4,7-triazacyclononane (Me/Me-TACN), N,N',N''-(2-hydroxyethyl) 1,4,7-triazacyclononane. In a preferred embodiment, the ratio of the manganese atoms to the nitrogen atoms is 1:3.

[0044] A suitable catalyst may also contain from 0 to 6 coordinating or bridging groups per manganese atom. When the homogeneous manganese based complex coordination catalyst is a mononuclear complex, coordinating groups are for example selected from -OMe, -O-CH₂-CH₃, or -O-CH₂-CH₂-CH₃. When the homogeneous based complex coordination catalyst is a dinuclear complex, bridging groups may be selected, among others, from -O-, -O-O-, or -O-CH(Me)-O-. The manganese catalyst may also contain one or more monovalent or multivalent counterions leading to a charge neutrality. The number of such monovalent or multivalent counterions will depend on the charge of the manganese complex which can be 0 or positive. The type of the counterions needed for the charge neutrality of the complex is not critical and the counterions may be selected for example from halides such as chlorides, bromides and iodides, pseudohalides, sulphates, nitrates, methylsulphates, phosphates, acetates, perchlorates, hexafluorophosphates, or tetrafluoroborates.

[0045] A particularly preferred catalyst is compound (I), di-manganese(IV)-tris(mu-oxo)-di(1,4,7-trimethyl-1,4,7-triazacyclononane)-bis(acetate) or [(Me-TACN)₂Mn^{IV}2(μ-O)3](CH₃COO)₂, known as Dragon's blood or Dragon A350.

[0046] The manganese catalyst may be present in a total amount of from 10 to 1,000 ppm based on the weight of the starch, preferably from 20 to 500 ppm, more preferably from 30 to 200 ppm.

[0047] Alternatively, the degraded starch may be an acid-degraded starch, or an enzymatically degraded starch. How to perform acid- and enzymatic degradation of starch is well-known in the art.

[0048] By acid catalyzed hydrolysis, the length of the molecular chains in the granule is reduced. Acid treatment can be conducted in a starch slurry (wet), dry, or semi-dry conditions. When applying slurry conditions, the acid treatment is performed using an approximately 40% starch slurry in diluted hydrochloric or sulphuric acid and heated to 25-55°C. The final properties of the resulting starch depend on the temperature, length of the treatment, type of acid and concentration. Slurry converted starches are known in food industry as thin-boiling starches. They exhibit a low hot-paste viscosity after cooking and develop good gel properties when cooled.

[0049] Enzymatic degradation of unmodified starch is known as enzymatic conversion. Starch slurry is mixed with alpha-amylase and then gradually heated to 60-90°C. The required temperature depends on the pasting temperature

of the starch and the type of enzyme. Tuber starches have a lower pasting temperature than cereal starches. Enzymatic hydrolysis can start earlier when the pasting temperature is lower. Temperature and pH play are important factors for enzyme activity. An increase in temperature will speed up the rate of hydrolysis, but may also destroy part of the catalytic capacity. Optimum temperature and pH differ with enzyme source and should be based on the manufacturer specifications. The presence of minerals is another factor influencing the enzyme activity. Calcium ions promote enzyme activity, whereas the presence of copper can inhibit enzyme activity. Time, temperature and pH depend the final viscosity of the degraded starch solution. Finally, the enzyme activity is stopped when the required viscosity is reached. This can be done by denaturation of the enzyme by heat or reducing the pH using a mineral or organic acid.

[0050] The degraded root or tuber starch can be stabilized by etherification or esterification. Preferably however, the degraded root or tuber starch has not been further modified, such as by etherification or esterification. The degraded root or tuber starch according to the invention is not crosslinked.

[0051] The degraded root or tuber starch or starch blend is characterized by a molecular weight of $0.5 - 20 \cdot 10^6$ Da ($0.5 - 20$ MDa). The molecular weight, in this context, is a weight-average molecular weight, determined as described in the examples. Preferably, the molecular weight is $0.75 - 18 \cdot 10^6$ Da, more preferably $1 - 17 \cdot 10^6$ Da.

[0052] The degraded root or tuber starch or starch blend is characterized by a viscosity, determined on a 15 wt.% aqueous solution by a Brookfield LVF viscometer at 60 rpm and at 50°C , of $20 - 150$ cP. The type of spindle used to determine the viscosity is generally known from instruction manuals with a specific type of viscometer. A preferred viscosity is $25 - 140$ cP, more preferably $30 - 135$ cP.

[0053] In a paper-pulp based solid substrate of the invention, the starch (or starch blend) is preferably present in a quantity of $0.3 - 5$ g/m², preferably $0.3 - 2.5$ g/m², preferably $0.4 - 2$ g/m², even more preferably $0.5 - 1.8$ g/m², even more preferably $0.6 - 1.5$ g/m² per side of the paper-pulp based solid substrate. That is, starch (or starch blend) can be present on the paper in a (total) quantity of $0.3 - 10$ g/m² (single- or double sided application of the starch), preferably $0.3 - 5$ g/m², preferably $0.4 - 4$ g/m², even more preferably $0.5 - 3.6$ g/m², even more preferably $0.6 - 3$ g/m². It can be tested whether the paper comprises starch on one or on two sides by iodine staining, which is well-known in the art.

[0054] In a paper-pulp based solid substrate of the invention, the ratio between the quantity per surface area of starch and the quantity per surface area of anionic fluorochemical (SF-ratio) is from $10 - 80$, preferably $15 - 75$, more preferably from $15 - 70$, even more preferably $20 - 65$, even more preferably $25 - 60$. These ratio's ensure good grease- and oil resistance at relatively low fluorochemical loading.

[0055] The paper may furthermore comprise a chelating agent, such as for example an alkali metal salt of ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentacetic acid (DTPA), nitrilotriacetic acid, N-hydroxyethyl ethylenediaminetriacetic acid, oxalic acid, citric acid, boric acid, hexametaphosphate, pyrophosphate, phosphate or carbonate.

[0056] The invention further pertains to an aqueous composition for improving the oil and grease resistance of a paper-pulp based solid substrate, comprising

- $2 - 20$ wt.%, preferably $3 - 18$ wt.%, more preferably $4 - 16$ wt.%, of a degraded root or tuber starch or starch blend, which degraded root or tuber starch or starch blend comprises $90 - 100$ wt.%, based on the total weight of the starch or starch blend, of amylopectin, and which root or tuber starch or starch blend is characterized by a molecular weight of $0.5 - 20 \cdot 10^6$ Da, and a viscosity, determined on a 15 wt.% aqueous solution by a Brookfield LVF viscometer at 60 rpm and at 50°C , of $20 - 150$ cP;
- $0.04 - 2$ wt.%, preferably $0.1 - 1.5$ wt.%, more preferably $0.15 - 1.25$ wt.%, of an anionic fluorochemical;
- optionally a chelating agent.

[0057] The degraded root or tuber starch or starch blend and the anionic fluorochemical have been described above.

[0058] The aqueous composition preferably comprises at least 50 wt.%, preferably at least 70 wt.%, more preferably at least 90 wt.% of water, and may furthermore comprise water-miscible organic solvents. Water-miscible organic solvents may be for example alcohols, preferably methanol, ethanol, isopropanol, t-butanol or ethylene glycol, propylene glycol, dipropyleneglycol, dipropyleneglycol monomethylether, or alternatively acetone.

[0059] The optional chelating agent can be for example an alkali metal salt of ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentacetic acid (DTPA), nitrilotriacetic acid, N-hydroxyethyl ethylenediaminetriacetic acid, oxalic acid, citric acid, boric acid, hexametaphosphate, pyrophosphate, phosphate or carbonate. The chelating agent may be present in a quantity of $0.01 - 0.2$ wt.%, preferably 0.03 wt.% - 0.16 wt.%, more preferably 0.05 wt.% - 0.12 wt.%.

[0060] The invention furthermore pertains to a method for improving the oil and grease resistance of a paper-pulp based solid substrate, comprising providing a composition as defined above, applying said composition to at least one side of the paper-pulp based solid substrate, and drying said paper-pulp based solid substrate.

[0061] The composition is applied to the paper-pulp based solid substrate so as to result after drying in $0.3 - 5$ g/m², preferably $0.3 - 2.5$ g/m², preferably $0.4 - 2$ g/m², even more preferably $0.5 - 1.8$ g/m², even more preferably $0.6 - 1.5$ g/m² degraded starch per side. This amounts to a total quantity of degraded starch on the paper, after single- or double sided application, of $0.3 - 10$ g/m², preferably $0.3 - 5$ g/m², preferably $0.4 - 4$ g/m², even more preferably $0.5 - 3.6$ g/m²,

even more preferably 0.6 - 3 g/m².

[0062] Furthermore, the composition is applied such so as to result after drying in 0.01 - 0.5 g/m² per side, more preferably 0.015 - 0.3 g/m² per side, more preferably 0.02 - 0.2 g/m² per side, even more preferably 0.01 - 0.1 g/m² per side, even more preferably 0.015 - 0.05 g/m² per side anionic fluorochemical. The total loading after single- or double sided application on the paper of anionic fluorochemical (after drying) can be from 0.01 - 1 g/m², preferably 0.015 - 0.6 g/m², more preferably from 0.02 - 0.4 g/m², even more preferably 0.02 - 0.2 g/m², even more preferably from 0.03 - 0.1 g/m².

[0063] The composition can be applied by well-known methods for applying liquid compositions to paper-pulp based solid substrates. For example, the composition can be applied by a horizontal size press, a declined size press, a film press, a gate roll coater, spray coater, curtain coater, air knife coater, a metering bar or a blade coater.

[0064] The invention furthermore pertains to use of the above composition for improving the oil and grease resistance of a paper-pulp based solid substrate. Potential uses include use for packaging, such as the packaging of food, pet food, cosmetics, vitamins, nutritional supplements, pharmaceuticals, or technical products.

[0065] For the purpose of clarity and a concise description features are described herein as part of the same or separate embodiments, however, it will be appreciated that the scope of the invention may include embodiments having combinations of all or some of the features described. The invention will now be illustrated by the following, non-limiting examples.

Examples

Methodology

Molecular weight determination

[0066] Prior to dissolution, a specific amount of a root or tuber starch sample (powder (as is)) was weighed into a glass vial (20 ml). Subsequently 20 ml eluent (50 mM NaNO₃) was added to obtain a concentration of 2 mg/ml. The vial was capped with an aluminum/silicone septum and fitted into a heating block. The vial was heated under continuous stirring during 60 minutes at 137 °C. After cooling to room temperature some of the obtained solution was collected with a syringe (5ml), and this quantity was subsequently filtered over a 5.0 µm cellulose acetate filter into a sample vial (1.5 ml; septum/screw cap).

[0067] Molecular weight (MW) of the samples was determined after separation by asymmetric field flow and detected with MALLS/RI detector. The MW and the molecular mass distribution (MMD) were determined by means of aF4/MALLS/RI. The aF4 system consisted of a Dionex HPLC system (quaternary pump, auto sampler including a 250 µl injection loop), thermostatic column compartment, light-scattering (LS) detector (Dawn Heleos II; Wyatt), and a refractive index (RI) detector (T-rex; Wyatt). The scattered light was detected at multiple angles (18) ranging from 13° to 158°. The multi angle laser light scattering (MALLS) was serially connected with the concentration (RI) detector. A sample is fractionated via a Frit Inlet channel with a permeable wall having a 5 kDa pore size. A pullulan DIN standard (50 kDa; 2 mg/ml) was used for normalization of the MALLS, and alignment of the MALLS and RI detector (correction for inter detector delay volume and bandbroadening). Samples were stored in the auto sampler at 25 °C to be processed automatically in a sequence overnight. Elution of the samples was carried out with an aqueous eluent (50 mM NaNO₃) at a specific flow regime at 25°C. The sample volume was set at 50 µl based on the average concentration of all samples. The data acquired during every run were collected and afterwards evaluated with the ASTRA software (version 6.1.2.84).

Starch dissolution

[0068] Starch is added in cold water in a tank, equipped with a suitable stirrer. The obtained starch slurry is then heated in a water bath with well-dispersed live steam to a temperature of 95 °C. This temperature was maintained for 20 minutes. The starch solution is stored at 50°C before use.

Preparation of starch mixtures

[0069] The starch solutions were diluted after cooking in tap water to the desired solids content of that series using hot water of about 60°C. EDTA solution was added in a quantity of 0.6 parts dry on 100 parts starch. Then the required amount of fluorochemical was added in parts dry on 100 parts dry starch, while stirring the solution using a mixer. For each experiment about 1000 g solution was prepared. The different mixtures were stored at 50°C before the experiments.

Brookfield viscosity of a starch solution

[0070] Starch viscosity is measured in a 300 mL glass beaker with a Brookfield type LVF at 60 rpm and 50°C using the appropriate spindle, as indicated in the manual. The value is recorded when the viscosity is stable, or after 60 s.

Application of the composition to paper

[0071] The starch solutions (9% by weight of starch; temperature 50°C) were applied to both sides of the base paper (Mondi Lohja, 36 g/m² OGR base paper) using a horizontal size press (type T.H. Dixon; model 160-B; roll hardness 80 shore). The machine speed of the Dixon was 50 m/min and the line pressure was 7 kg/cm. The surface sized paper was thereafter dried to 5% by weight of moisture. The paper samples obtained were conditioned at 23°C and 50% relative humidity before testing. In all cases, the total amount applied to the paper is about 1.4 g/m² of starch and 0.06 g/m² of fluorochemical, resulting a weight ratio (per m²).

Fluorochemical quantity

[0072] The quantity of fluorochemical applied onto the paper is calculated from the amount of starch applied to the paper. Starch and fluorochemical are present in a composition in a known weight ratio (dry/dry), expressed as parts fluorochemical relative to 100 parts starch. The starch addition applied to the paper (in g/m²) therefore gives the amount of fluorochemical in g/m² applied to the paper.

Oil and grease resistance (OGR)

[0073] The oil and grease resistance (oleo-repellency) is generally assessed by the resistance of a substrate against the penetration of a hydrophobic liquid. The test describes a procedure for testing the degree of repellency and/or the antiwicking characteristics of paper or paperboard treated with fluorochemical sizing agents.

[0074] OGR was measured according to Tappi method T559 ("Kit-test") and expressed as a Kit value. The Kit test uses 12 different mixtures of hydrocarbon liquids with decreasing viscosity and surface tension. The highest numbered solution (the most aggressive) that remains on the surface of the paper without disrupting the paper structure and while providing oil and grease resistance is reported as the "kit rating".

[0075] The applied method results in the OGR of the top side of the paper, or the back side of the paper (wire side). Although the compositions of the invention are applied to both sides of the paper, the kit-rating of the different sides usually varies, due to varying processing conditions in the double-sided press for the top- and wire side of the paper. When the staining is not clear, a value between the two highest Kit ratings is given.

Starch determination in paper

[0076] Weigh 1.050 g of paper and put into a blender. Add 100 ml water and grind the paper. Add 25 g pulp into a plastic bottle and fill up to 97.5 g with hot tap water. Add 2.5 ml acetate buffer of pH 4.6 and 0.1 ml of a 1:1 mixture alpha-amylase and amyloglucosidase (both from Megazyme). Allow the starch to be converted into D-glucose using alpha-amylase by storing the bottle during 2 hours at 60 °C. The concentration D-glucose was then quantitatively determined using the D-glucose assay kit from Megazyme (K-GLUHK) and finally recalculated to the starch content in the paper as g/m².

Materials

[0077] Solvera PT5045PG is (per)fluoropolyether from Solvay Solexis with a dry solids content of about 20%. Dissolvine is a 40% EDTA solution from Akzo Nobel.

[0078] The following starches were used for the experiments:

Starch A

[0079] 1.0 kg of amylopectin potato starch (0.81 kg dry matter, Eliane® potato starch from AVEBE; amylopectin content >98%) was suspended in 1.0 kg of water. The temperature of the suspension was increased to 35°C. The pH was set at 9.0 by the addition of a 4.4 wt.% sodium hydroxide solution. 29.0 ml of a sodium hypochlorite solution containing 179 g/liter of active chlorine was added. During the oxidation the pH was maintained at 9.0 by the addition of a 4.4 wt.% sodium hydroxide solution. Once the reaction was complete, i.e. no chlorine was detectable with potassium iodide-starch paper, the pH was increased to 10.5 by the addition of a 4.4 wt.% sodium hydroxide solution. After one hour of alkaline

EP 3 301 220 A1

post-treatment 5 ml sodium hypochlorite solution was added for decoloration. The reaction mixture was neutralized to pH 5.5 by the addition of 10 N H₂SO₄, whereupon the product was dewatered and washed before drying.

Starch B

[0080] Starch B was prepared similarly as Starch A, but now 20.1 ml of a sodium hypochlorite solution containing 179 g/liter of active chlorine was added.

Starch C

[0081] Starch C was prepared similarly as Starch A, but now 63.7 ml of a sodium hypochlorite solution containing 179 g/liter of active chlorine was added.

Starch D

[0082] For Starch D a blend of 0.5 kg regular potato starch (0.41 kg dry matter, food grade potato starch from AVEBE; amylopectin content 81%) and 0.5 kg of amylopectin potato starch (0.41 kg dry matter, Eliane® potato starch from AVEBE; amylopectin content >98%) was suspended in 1.0 kg of water. The temperature of the suspension was increased to 35 °C. The pH was set at 9.0 by the addition of a 4.4 wt.% sodium hydroxide solution. 48.0 ml of a sodium hypochlorite solution containing 179 g/liter of active chlorine was added. During the oxidation the pH was maintained at 9.0 by the addition of a 4.4 wt.% sodium hydroxide solution. Once the reaction was complete, i.e. no chlorine was detectable with potassium iodide-starch paper, the pH was increased to 10.5 by the addition of a 4.4 wt.% sodium hydroxide solution. After one hour of alkaline post-treatment 5 ml sodium hypochlorite solution was added for decoloration. The reaction mixture was neutralized to pH 5.5 by the addition of 10 N H₂SO₄, whereupon the product was dewatered and washed before drying.

Starch E

[0083] Starch E was prepared similarly as Starch A, but now 111.7 ml of a sodium hypochlorite solution containing 179 g/liter of active chlorine was added.

Reference 1

[0084] An oxidized potato starch obtained from Avebe U.A. under the name Perfectamyl A4692.

Reference 2

[0085] A dextrin of a blend of waxy corn starch and regular corn starch obtained from Cargill, with an amylopectin content of approximately 25%, obtainable under the trade name C*iFilm 07412.

Reference 3

[0086] An oxidized potato starch from Chemigate Raisamyl 01121.

Reference 4

[0087] An oxidized regular potato starch from Avebe U.A., obtainable under the trade name Perfectamyl P255SH

Reference 5

[0088] 1.0 kg of regular potato starch (0.81 kg dry matter, food grade potato starch from AVEBE; amylopectin content 81%) was suspended in 1.0 kg of water. The temperature of the suspension was increased to 35°C. The pH was set at 9.0 by the addition of a 4.4 wt.% sodium hydroxide solution. 64.2 ml of a sodium hypochlorite solution containing 179 g/liter of active chlorine was added. During the oxidation the pH was maintained at 9.0 by the addition of a 4.4 wt.% sodium hydroxide solution. Once the reaction was complete, i.e. no chlorine was detectable with potassium iodide-starch paper, the pH was increased to 10.5 by the addition of a 4.4 wt.% sodium hydroxide solution. After one hour of alkaline post-treatment 5 ml sodium hypochlorite solution was added for decoloration. The reaction mixture was neutralized to pH 5.5 by the addition of 10 N H₂SO₄, whereupon the product was dewatered and washed before drying.

Reference 6

[0089] Reference 6 was prepared similarly as Reference 5, except that now 36.3 ml sodium hypochlorite solution containing 179 g/liter of active chlorine was added.

Table 1: starches used

Starch	Botanical source	Mw*10e6 [g/mole]	Viscosity [15%, 50°C, 60 rpm]
Reference 1	Potato starch	0.29	14
Reference 2	A dextrin of a blend of waxy corn starch and corn starch	0,07; 300	35
Reference 3	oxidized potato starch	0.24	20
Reference 4	oxidized potato starch	0.63	23
Reference 5	oxidized potato starch	1.8	solid gel
Reference 6	oxidized potato starch	4.8	solid gel
A	oxidized waxy potato starch	6.6	90
B	oxidized waxy potato starch	17	135
C	oxidized waxy potato starch	3	31
D	oxidized blend of waxy potato starch and potato starch (1:1 weight ratio)	4.8	66
E	oxidized waxy potato starch	1	22

Example 1

[0090] Table 1 shows that the high molecular weight products produced from pure potato starch are not stable and therefore cannot be used for surface treatment applications. Products produced from waxy potato starch or a blend of waxy potato starch are stable and can therefore be used. Only products with a relatively low molecular weight are stable enough for surface treatment compositions.

Example 2

[0091] Compositions based on different starches were applied in combination with a (per)fluoropolyether from Solvay (Solvay PT5045PG) at constant starch concentration of 9% and at a fixed (weight) ratio starch : fluorochemical of 4.2 parts fluorochemical per 100 parts starch.

Table 2

	Ref 1	Ref 3	Ref 4	A	B	C	D
M *10e6	1	0.24	0.63	6.6	17	3	4.8
Viscosity (cP)	14	20	23	90	135	31	66
Concentration [wt. % starch]	9%	9%	9%	9%	9%	9%	9%
EDTA [parts]	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Fluorochemical [parts]	4.2	4.2	4.2	4.2	4.2	4.2	4.2
Starch [g/m ²]	1.36	1.37	1.37	1.47	1.49	1.37	1.4
Fluorochemical [g/m ²]	0.057	0.058	0.058	0.062	0.064	0.058	0.06
SF-Ratio	23.9	23.6	23.6	23.7	23.3	23.6	23.3
Kit top side	4.5	5	6	7	7	6	7
Kit wire side	9	7	8	10	11	9	10

[0092] Table 2 shows that the compositions of the invention show higher oil and grease resistance at the same fluorochemical level as measured with Tappi T559.

Example 3

[0093] In this example the amount of fluorochemical added to the paper was changed by variation of the fluorochemical ratio to starch. The starches were applied in the same manner as described in Example 1. In all cases about 1.4 g/m² of starch was applied to the paper.

Table 3

	Ref 1	Ref 2	A	B
M *10e6	1	0.07;300	6.6	17
Viscosity (cP)	14	35	90	135
Concentration [wt. % starch]	10%	10%	9%	9%
EDTA [parts]	0.6	0.6	0.6	0.6
Fluorchemical [parts]	6	6	4.2	4.2
Starch [g/m ²]	1.39	1.27	1.47	1.49
Fluorchemical [g/m ²]	0.084	0.076	0.062	0.064
SF-ratio	16.5	16.7	23.7	23.3
Kit top side	7	7	7	7
Kit wire side	11	10	10	11

[0094] Table 3 shows that the compositions of the invention give the same oil and grease resistance using less fluorochemical as compared to the compositions with the reference starches as measured according to Tappi T559.

Example 4

[0095] In this example the compositions were either applied using low concentrated solutions (5-6 wt. %) and 12 parts fluorochemical, or using high concentrated solutions (9-10 wt. %) and 4.2 parts fluorochemical. In all cases the amount of fluorochemical was similar. The coatings were applied using a Dixon coater as described in Example 1.

Table 4

	Ref 1	Ref 1	Ref 2	Ref 2	A	A	B	B
M*10e6	1	1	0.07;300	0.07;300	6.6	6.6	17	17
Viscosity [cP]	14	14	35	35	90	90	135	135
Concentration[wt. % starch]	5%	10%	6%	10%	5%	9%	5%	9%
EDTA [parts]	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Fluorchemical [parts]	12	6	12	6	12	6	12	6
Starch [g/m ²]	0.69	1.39	0.66	1.27	0.73	1.49	0.7	1.38
Fluorchemical [g/m ²]	0.083	0.084	0.079	0.076	0.088	0.09	0.084	0.083
SF-ratio	8.3	16.5	8.4	16.7	8.3	16.6	8.3	16.6
Kit top side	7	7	7	7	7	9	7.5	10
Kit wire side	8	11	7	10	8	12	9	12

[0096] Table 4 shows that only the compositions of the invention show an improvement of the oil and grease resistance when the concentration increases while keeping the amount of fluorochemical at the same level. Oil and grease resistance was measured according to Tappi T559. Compositions with the reference starches do not show the improvement.

[0097] Application of highly viscous degraded starches in combination with anionic fluorochemicals result in an increase in Kit-value when increasing the quantity of starch, relative to the quantity of fluorochemical. Low-viscous starches do not display this effect. It can be expected on this basis that stabilized starches, which have increased viscosity by the stabilization with e.g. ethers or esters, also display this effect.

Example 5

[0098] In this example compositions were applied onto paper using a Dixon coater as described in example 1. In this case a different base paper was used (OGR base paper, ex. Pfeleiderer Teisnach, 37 g/m²). The coatings were the same as described in Example 1 except that in this case a different base paper was used.

Table 5

	Ref 1	A
Concentration [wt.% starch]	10%	9%
Fluorochemical [parts]	3.5	3.5
Starch [g/m ²]	1.08	1.12
Fluorochemical [g/m ²]	0.038	0.039
SF-ratio	28.4	28.7
Kit top side	5	8
Kit wire side	6	7

[0099] Table 5 shows that a composition according to the inventions improves the oil and grease resistance of a different type of base paper.

Example 6

[0100] Compositions of the invention were applied at different concentrations. The fluorochemical/starch ratio was changed at a constant quantity of fluorochemical of between 0.08 and 0.09 g/m².

Table 6

	A	A	A	A
Concentration	5%	9%	11%	15%
EDTA [parts]	0.6	0.6	0.6	0.6
Fluorochemical [parts]	12	6	4.2	2
Starch [g/m ²]	0.73	1.49	1.91	3.28
Fluorochemical [g/m ²]	0.088	0.09	0.08	0.066
SF-ratio	8	17	24	50
Kit top side	7	9	10	12
Kit wire side	8	12	12	12

[0101] Table 6 shows that by increasing the ratio between starch and fluorochemical at constant quantity of fluorochemical, the kit rating of the paper increases.

Claims

1. A paper-pulp based solid substrate, comprising an anionic fluorochemical and a degraded root or tuber starch or starch blend, which degraded root or tuber starch or starch blend comprises 90-100 wt.%, based on the total weight of the starch or starch blend, of amylopectin, and which root or tuber starch or starch blend is **characterized by a**

molecular weight of $0.5 - 20 \cdot 10^6$ Da, and a viscosity, determined on a 15 wt.% aqueous solution by a Brookfield LVF viscometer at 60 rpm and at 50 °C, of 20 - 150 cP.

2. A paper-pulp based solid substrate according to claim 1, wherein the degraded starch or starch blend comprises potato starch.
3. A paper-pulp based solid substrate according to claim 1 or 2, wherein the degraded starch or starch blend comprises an oxidized starch.
4. A paper-pulp based solid substrate according to any of claims 1 - 3, wherein the degraded starch or starch blend is a starch blend, comprising waxy starch with an amylopectin content of more than 95 wt.%, based on the weight of the starch, and regular starch with an amylopectin content of 70-85 wt.%, based on the weight of the starch.
5. A paper-pulp based solid substrate according to any of claims 1 - 4, wherein the starch is present in a quantity of 0.3 - 5 g/m² per side of the paper-pulp based solid substrate.
6. A paper-pulp based solid substrate according to any of claims 1 - 5, wherein the quantity of anionic fluorochemical is 0.01 - 0.5 g/m² per side of the paper-pulp based solid substrate.
7. A paper-pulp based solid substrate according to any of claims 1 - 6, wherein the ratio between the quantity per surface area of starch and the quantity per surface area of anionic fluorochemical is from 10 - 80.
8. An aqueous composition for improving the oil and grease resistance of a paper-pulp based solid substrate, comprising
 - 2 - 20 wt.% of a degraded root or tuber starch or starch blend, which degraded root or tuber starch or starch blend comprises 90-100 wt.%, based on the total weight of the starch or starch blend, of amylopectin, and which root or tuber starch or starch blend is **characterized by** a molecular weight of $0.5 - 20 \cdot 10^6$ Da, and a viscosity, determined on a 15 wt.% aqueous solution by a Brookfield LVF viscometer at 60 rpm and at 50 °C, of 20 - 150 cP;
 - 0.04 - 2 wt.% of an anionic fluorochemical;
 - optionally a chelating agent.
9. A composition according to claim 8, wherein the chelating agent is an alkali metal salt of ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentacetic acid (DTPA), nitrilotriacetic acid, N-hydroxyethyl ethylenediaminetriacetic acid, oxalic acid, citric acid, boric acid, hexametaphosphate, pyrophosphate, phosphate or carbonate.
10. A method for improving the oil and grease resistance of a paper-pulp based solid substrate, comprising providing a composition as defined in claims 8 or 9, applying said composition to at least one side of the paper-pulp based solid substrate, and drying said paper-pulp based solid substrate.
11. A method according to claim 10, wherein the composition is applied to the paper-pulp based solid substrate so as to result after drying in 0.3 - 10 g/m² degraded starch and 0.01 - 1 g/m² anionic fluorochemical.
12. A method according to claim 10 or 11, wherein the composition is applied by a horizontal size press, a declined size press, a film press, a gate roll coater, spray coater, curtain coater, air knife coater, a metering bar or a blade coater.
13. A paper-pulp based solid substrate according to any of claims 1 - 7, a composition according to claim 8 or 9, or a method according to any of claims 10 - 12, wherein the anionic fluorochemical is an anionic fluoropolyether or perfluoropolyether.
14. Use of a composition as defined in claims 8 or 9 for improving the oil and grease resistance of a paper-pulp based solid substrate.
15. Use of a paper-pulp based solid substrate according to any of claims 1 - 7 for the packaging of food, pet food, cosmetics, vitamins, nutritional supplements, pharmaceuticals, or technical products.



EUROPEAN SEARCH REPORT

Application Number
EP 16 19 1852

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EP 16 19 1852

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