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(54) **Oil and grease resistant treatment compositions**

Öl- und fettbeständige Behandlungszusammensetzungen

Compositions de traitement résistantes à l'huile et à la graisse

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Description*Technical Field*

[0001] The present invention relates to aqueous oil and grease resistant treatment compositions for cellulosic materials comprising a fluorocarbon resin, a guar gum and an inorganic phosphate salt.

[0002] The present invention also relates to a method for imparting oil and grease resistance to cellulose materials comprising the step of applying to said cellulosic materials said aqueous oil and grease resistant treatment compositions.

Background of the Art

[0003] The coating of cellulosic materials, such as paper products, with fluorocarbon resins to impart grease, oil, wax and solvent repellency (resistance) is well known. For example, Schwartz, in "Oil Resistance Utilizing Fluorochemicals", TAPPI, Seminar Notes, 74, 71-75, (1987), discloses the use of commercially available fluorochemicals to impart resistance to low surface tension fluids on various substrates. U.S. Pat. No. 4,426,466 discloses treatment compositions containing fluorochemical carboxylic acids and cationic epoxy-resin to impart oil and water repellency to cellulosic materials. U.S. Pat. No. 7,252,740 discloses carboxylic acids comprising perfluoropolyether chains capable of imparting oleo-repellence to various artificial or natural substrata, especially to paper. U.S. Pat. No. 5,370,919 discloses fluorochemical compositions for imparting oil and water repellency to various substrates.

[0004] Fluorine-containing polymers have been used to impart oleo-repellency to paper. For example, U.S. Pat. No. 5,247,008 describes finishing agents for textiles, leather, paper and mineral substrates which are aqueous dispersions of a copolymer of a perfluoroalkyl acrylate or methacrylate, an alkyl acrylate or methacrylate and an aminoalkyl acrylate or methacrylate.

[0005] US 4,529,658 discloses fluorochemicals copolymers for use as wet-end papermaking additives which impart oil and water repellency and food stain resistance to ovenable paperboard, but it does not mention the use of a guar gum and an inorganic phosphate salt in the additives, or in the related paperboard treatment.

[0006] It is also known how to confer oleo-repellence to paper by treatment with perfluoropolyether derivatives having a polyurethane structure (see for example EP 1 273 704).

[0007] Partial esters of phosphoric or phosphonic acid, such as salts of fluoroalkyl or (per)fluoropolyether phosphates or salts of N-alkyl fluoroalkane sulfonamidoalkyl phosphates, are known as oil-repellent agents for paper, in order to render the sheet more resistant to the penetration of oils. Such conventional oil proof agents, described for example in EP 0 280 115 or in EP 1 327 649, are applied to paper either by internal addition (internal sizing), which comprises dissolving or dispersing the agent in a pulp suspension or in a slurry for paper making, or by external addition (surface sizing), by dipping a sheet of paper in an aqueous solution or dispersion of the agent or by brushing on the sheet with the solution or dispersion to coat the surface of paper with the agent. Fluorocarbon resins, including all the different fluorine containing compounds that are commercially available as oil-repellent agents, are very excellent in imparting chemical resistance and solvent resistance and, further, good in heat resistance, weather resistance, gas impermeability, etc. Fluorocarbon resins are, however, poor in processability (e.g. film formability), they may require a baking treatment at high temperatures and, consequently, they tend to cause film defects, such as pin holes and the like.

[0008] Moreover, the cost of fluorocarbon resins conferring oleo-repellency represents a high fraction of the final cost of the finished product. Said fluorinated compounds indeed, although they are usually present in the final product in amounts ranging from about 0.1 to 2% by weight, represent from 10% up to 50% of the total costs of the final product (including the process water, the energy and the cellulosic substrate).

[0009] Since they have a low adhesion to substrate, the fluorocarbon resins are usually applied in combination with one or more sizing agents, which help to reduce the cost of the treatment by increasing the quantity of resin retained by the substrate. The sizing agent may be a natural sizing agent, such as animal glue, wax emulsion, rosin, starch; a semi-synthetic sizing agent, such as a fatty acid salt or complex, a fortified rosin, e.g. trisodium maleopimaric acid salt, sodium alginate, starch or modified starch, or sodium carboxymethylcellulose; or a synthetic sizing agent such as an alkylketene dimer, polyvinyl alcohol, a styrene-maleic anhydride polymer, and the like. Also, mixtures of the above sizing agents may be used.

[0010] However, it is still difficult to produce cellulosic materials where the oil resistance, wet strength and web drainage at the time of production, are all enhanced at the same time.

[0011] The present invention aims to overcome the difficulties mentioned above, providing aqueous oil and grease resistant treatment compositions for cellulosic materials comprising a fluorocarbon resin, a guar gum and an inorganic phosphate salt.

[0012] US 4,320,226 describes the use of a phosphate ester of a guar gum as sizing agent for the preparation of oil and grease resistant paper. This ester, which has a degree of substitution from 0.1 to 0.5, is obtained by reaction of a guar gum and phosphoric acid at high temperature in the presence of a base.

[0013] Now we have surprisingly found that substrates having outstanding oil and grease resistance can be produced by using a physical mixture of a guar gum and an inorganic phosphate salt as the sizing agent, in combination with a fluorocarbon resin.

[0014] US 2,868,664 describes compositions comprising a mannogalactan gum, a hydrophobising and a neutralizing agent which are easy dispersible in water, and their use in the paper making process; the mannogalactan gum is typically guar and the neutralizing agent may be an inorganic phosphate salt. Nonetheless, the composition US 2,868,664 are added to the paper furnish prior to the formation of the web to increase the wet and dry resistance of paper and they are not used in combination with a fluorocarbon resin to improve oil and grease repellency.

[0015] WO 99/53139 describes a sizing composition comprising a polyaluminium phosphate sulphate compound and, possibly a protective colloid or retention agent that may be guar gum, but it does not mention the use of fluorocarbon resins.

SUMMARY OF THE INTENTION

[0016] It is therefore an object of the present invention an aqueous oil and grease resistant treatment compositions for cellulosic materials comprising:

- a) from 0.1 to 10% by weight (wt) of a fluorocarbon resin;
- b) from 0.05 to 7.0 % wt of a guar gum;
- c) from 0.01 to 1.0 % wt of an inorganic phosphate salt.

[0017] Also, the present invention provides a method for imparting oil and grease repellency to cellulosic materials, comprising the step of applying to the cellulosic materials the above-described aqueous compositions in such an amount that the fluorocarbon resin is applied to said cellulosic materials in an amount between 0.08 and 5.0 % by weight on the weight of the cellulosic material.

[0018] Another object of the present invention is the use of the above described aqueous compositions for the manufacture of paper and paperboard for food packaging and food contact. In addition, the present invention provides paper or paperboard articles treated with the above-described aqueous oil and grease resistant treatment compositions useful in food grade applications.

DETAILED DESCRIPTION OF THE INVENTION

[0019] The method for treating cellulosic materials of the disclosure comprises the preparation of the aqueous compositions described above by mixing the ingredients from a) to c) with water, or with a water/solvent mixture. The mixture is preferably carried out at room temperature, and anyway in such conditions that no esterification reaction takes place between the guar gum and the inorganic phosphate salt.

[0020] Preferably the aqueous oil and grease resistant treatment compositions for cellulosic materials of the invention comprise:

- a) from 0.2 to 3.0% by weight (wt) of a fluorocarbon resin;
- b) from 0.1 to 5.0 % wt of a guar gum;
- c) from 0.02 to 0.6 % wt of an inorganic phosphate salt.

[0021] The fluorocarbon resin may be any fluorine containing compound or composition which is known in the art and is useful for oleo-repellent treatments, examples of which can be found in "Sizing with Fluorochemicals", R. D. Howells, 1997 Sizing Short Course, Nashville, TN, Apr. 14-16, TAPPI Press, or in "Fluorochemical Sizing", Olson C.C. et al. in "The Sizing of Paper", 3rd Edition, pag. 151-177, edited by Gess, J.M. and Rodriguez, J.M., TAPPI Press, 2005.

[0022] By way of example, suitable fluorine containing compounds may include fluorochemical copolymers.

[0023] Suitable commercially available fluorine containing compositions include MASURF FS 130 EB (perfluoro alkyl ethyl phosphate), a trademark of Mason Chemical Company, UNIDYNE TG 8711 and Unidyne TG 8111 (registered trademark of DAIKIN Inc.). Similar fluorine containing compositions include SOLVERA PT 5045 (water-based formulation containing a perfluoropolyether-phosphate derivative), a trademark of Solvay Solexis. Another suitable fluorine containing composition include Cartafluor UHC, from Clariant.

[0024] Another suitable commercially available fluorocarbon resin is "SEQUAPEL 1422" (a registered trademark of Sequa Chemicals, Inc.) Other suitable commercially available fluorocarbon resins include "LODYNE P-201" and "LODYNE P-208E", which are registered trademarks of Ciba-Geigy Corporation, Greensboro, N.C.

[0025] Guar gum, or simply guar, is a polysaccharide belonging to the family of galactomannans. It is extracted from, *Cyamopsis Tetragonolobus*, a leguminosae plant that grows in the semi-dry region of tropical countries, particularly in India and in Pakistan. The polysaccharide contained in guar seeds consists of a main chain of mannose units linked

together by 1-4-[beta]-glycosidic linkages from which single galactose units branch by means of 1-6-[alpha]-glycosidic linkages. The ratio of galactose units to mannose units can vary from one source to another. In the case of the polysaccharide contained in guar seeds the ratio is about 1:2. This polysaccharide forms highly viscous solutions in water at low concentrations, thus, 1 percent solutions of non-depolymerized guar gum in water usually have a viscosity of between

about 1,000 and about 9,000 mPa·s at 25 °C, when measured with a Brookfield RVT® viscometer at 20 rpm.

[0026] It is well known that, in some applications, the presence of manufacturing by-products or materials not expressly added and controlled, variable from batch to batch, even if in minimal amounts, can create problems during the use of products having natural origin, such as guar.

[0027] In the preparation of the aqueous compositions of the disclosure, the use of purified guar is thus preferred. Commonly, guar can be purified by extraction with water-solvent mixtures or, for crosslinked products, simply with water (R.L. Whistler, Industrial Gums, 3rd edition).

[0028] In an embodiment, the use of depolymerised guar is preferred.

[0029] In another embodiment, the use of depolymerised guar having low ash content is preferred.

[0030] In its natural state, in fact, the average molecular weight of guar galactomannans is very high. Conventionally, it can be reduced by depolymerising the polymer in oxidative conditions to generate shorter chain lengths.

[0031] Preferred guar gums have a Brookfield® RVT viscosity comprised between 10 to 10000 mPa·s in aqueous solution at 2% by weight measured at 20 °C and 20 rpm.

[0032] Particularly preferred for the realization of the present invention are guar gums having Brookfield® RVT viscosity between 20 and 500 mPa·s in aqueous solution at 2% by weight, 20°C and 20rpm, and ash content below 5.5% by weight.

[0033] Inorganic phosphate salt that may be used are, by way of example: phosphates, hydrogen phosphates, dihydrogen phosphates; polyphosphates such as pyrophosphate and triphosphate, and ring or chain metaphosphates, with 1-6 phosphorus atom, and mixture thereof. Suitable inorganic phosphate salts include orthophosphate, metaphosphate, hexametaphosphate, pyrophosphate, tripolyphosphate, tetrapolyphosphate and polyphosphate salts of alkali metals. Preferably the inorganic phosphate salt is a sodium or potassium salt of tripolyphosphate or hexametaphosphate; more preferably it is sodium or potassium tripolyphosphate.

[0034] The aqueous oil and grease resistant treatment compositions for cellulosic materials of this invention can further comprise at least another sizing agent commonly used for the sizing of cellulosic material such as starch and starch derivatives, alkylketene dimers and carboxymethyl cellulose. This additional sizing agent can be present in an amount comprised between 0.5 and 6% wt. Preferred additional sizing agents are starch and starch derivatives.

[0035] In the present text with the expression "cellulosic materials" we designate paper, paperboard and textile products derived from cellulose.

[0036] The aqueous oil and grease resistant treatment compositions for cellulosic materials are applied to cellulosic materials such as paper or textiles, in the form of solution, emulsion or dispersion in a suitable carrier (e.g., an aqueous medium or a mixture of water and organic solvents), in accordance with known methods. The solvent can be any solvent or solvent combination that is suitable to dissolve or disperse the composition and/or other components of the composition. In some cases, a solventless medium may be preferred but in others, it may be desirable to add solvents, such as alcohols, that evaporate quicker. Accordingly, some aqueous oil and grease resistant sizing composition according to the disclosure can be applied as a single phase system (e.g., aqueous phase system) or a metastable system, i.e. a system that does not undergo substantial phase separation on the time-scale of formulation preparation and/or application on the substrate.

[0037] The aqueous oil and grease resistant treatment compositions for cellulosic materials can also be prepared in the form of emulsion. An emulsifying aid, such as a surfactant, can be added as well, to help stabilize the emulsion.

[0038] Adjuvants such as dyes, inhibitors, defoamers, fillers (such as clay or calcium carbonate), whiteners, silica, antioxidants, and the like can be added to the aqueous composition, if desired.

[0039] Since cations in hard water may cause precipitation, it is common to add to the compositions a chelating agent, such as ethylenediaminetetracetic acid (EDTA) or one of its salts, to soften the water.

[0040] The aqueous oil and grease resistant treatment compositions for cellulosic materials according to the invention can be applied on the cellulosic materials using any known application technique as part of the making process (such as by addition to the cellulose pulp or on the textile fibers/yarns) or as a surface post-treatment (application by size-press of a laminated paperboard or of a woven fabric).

[0041] Preferably the compositions of the invention are applied by spraying, extrusion, padding, immersion or foaming.

[0042] Preferably the compositions of the invention are applied in such an amount that the fluorocarbon resin is applied to the cellulosic material in an amount between 0.15 and 1.5 % by weight on the weight of the cellulosic material.

[0043] The aqueous oil and grease resistant treatment compositions for cellulosic materials can be applied to any cellulosic material, but they are particularly suited for paper and paperboard that represent the preferred cellulosic materials. As used herein, "paper" and "paperboard" refers to a paper based substrate resulting from the mixing of fibers that can include, at least in part, vegetable and/or wood fibers, such as cellulose, hemicelluloses, lignin; and/or synthetic fibers.

[0044] The aqueous oil and grease resistant treatment compositions for cellulosic materials according to the invention can be applied to the pre-formed paper or cardboard by coating, or can be applied during their manufacturing process. The aqueous oil and grease resistant treatment compositions for cellulosic materials of this invention can be used in combination with paper and paperboard manufacturing adjuvants such as natural and synthetic wax emulsions, alum, retaining agents, buffering agents, fireproofing agents, fungicidal agents, antistatic agents, dyes, optical bleaching agents, sequestering agents, mineral salts, swelling agents, and fillers such as clay, talc, and titanium dioxide.

[0045] The aqueous oil and grease resistant treatment compositions for cellulosic materials of this invention can be used both in the acidic and in the alkaline paper and paperboard manufacturing process.

[0046] Grease and oil resistant cellulosic materials prepared with the aqueous compositions according to the invention can be used in all the applications for which this kind of material is conventionally used. For example, treated paper and paperboard can be utilized in food processing, including baking, or in food packaging, and treated cellulosic textiles can be utilized for carpet, upholstery and other similar applications.

[0047] Preferably, the paper and paperboard treated with the aqueous oil and grease resistant treatment compositions for cellulosic materials of this invention are used in food packaging and food processing, because they are suitable for food contact.

[0048] Some examples of preferred applications of the treated paper and paperboard include fast food packaging, food packaging for microwave oven, pizza boxes, candy wrappers, pet-food bags and boxes, packaging for fatty foods in general, and the like.

[0049] The use of the aqueous compositions comprising: a) from 0.1 to 10% wt of a fluorocarbon resin; b) from 0.05 to 7.0 % wt of a guar gum; c) from 0.01 to 1.0 % wt of an inorganic phosphate salt for the manufacture of paper and paperboard for food packaging and food contact is another object of the present invention.

[0050] The following non-limiting examples are provided to further illustrate the invention.

EXAMPLES

[0051] The grease and oil resistance of paper treated with the different aqueous compositions was measured according to the procedure TAPPI UM-557.

Examples 1-7

[0052] 100 g mixtures made from guar gum and inorganic phosphate salts (sodium salt) were prepared mixing together the appropriate amount of the ingredients as shown in Table 1 (in grams).

[0053] Guar 1 is a depolymerized guar gum. The product has a RVT Brookfield Viscosity, 20 °C and 20 rpm, 2% by weight water solution of 160 mPa*s and ash content of about 13%.

[0054] Guar 2 is a depolymerized guar gum having a RVT Brookfield Viscosity, 20 °C and 20 rpm, 2% water solution of 150 mPa.s and ash content < 5%.

Table 1

Ingredient	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6*	Ex. 7
Guar 1	90.58	90.58	90.58	90.58	90.58	100	-
Guar 2	-	-	-	-	-	-	90.58
Triphosphate	9.42	-	-	-	-	-	9.42
Trimetaphosphate	-	9.42	-	-	-	-	-
Pyrophosphate	-	-	9.42	-	-	-	-
Esametaphosphate	-	-	-	9.42	-	-	-
Monophosphate	-	-	-	-	9.42	-	-
* Comparative							

[0055] All the mixtures of Examples 1-7, were dissolved in demineralized water at a concentration of 2.7% wt with the addition of MASURF FS 130 EB (phosphate ester of perfluoropolymer, commercialized by MASON CHEMICAL COMPANY), to obtain aqueous oil and grease resistant treatment compositions for cellulosic materials with dry matter content of 3.45% wt.

[0056] About 200 ml of each solution were transferred in a laboratory Pad Batch device (pressure 2 Bar, rolls speed

4 m/min) and used to impregnate three A4 format untreated paper specimen (40 g/m²). The addition of oil and grease resistant composition on the paper specimen was about 0.5 g/m².

[0057] After 3 hours of conditioning at 23° C e 50% relative humidity, the grease and oil resistance of each paper specimen was determined using the method reported above.

[0058] The average results of the three replicate test are reported in Table 2. Higher values demonstrate a superior resistance to oil and grease.

Table 2

	Kit Test
Example 1	11
Example 2	9
Example 3	10
Example 4	10
Example 5	9
Example 6*	7
Example 7	11
* Comparative	

[0059] The results show that the addition of an inorganic phosphate salt to the sizing composition, in particular of a tripolyphosphate salt, increases the oil and grease resistance.

Examples 8-13

[0060] 100 g mixtures made of a guar and sodium tripolyphosphate were prepared mixing in a bag an appropriate amount of each ingredient as shown in Table 3. Guar 3 is a guar gum with a RVT Brookfield Viscosity of 5200 mPa*s at 25 °C, 20 rpm, 1% wt water solution.

Table 3

Ingredient	MIX A % w/w	MIX B % w/w	MIX C % w/w
Guar 1	90.58	-	-
Guar 2	-	90.58	-
Guar 3	-	-	90.58
Tripolyphosphate	9.42	9.42	9.42

[0061] Aqueous oil and grease resistant treatment compositions of the invention were obtained by dissolving MIX A and MIX B in demineralized water at a concentration of 3% wt together with MASURF FS 130 EB or UNIDYNE TG 8111 (water-based fluoropolymer emulsion, commercialized by DAIKIN INC.).

[0062] The aqueous compositions of the invention were compared with a aqueous composition containing oxidized corn starch, dispersed in cold demineralized water and then dissolved at 90° C in 30 minutes.

Table 4 shows the amount of active ingredients used to prepare 100 g of aqueous oil and grease resistant treatment compositions.

Table 4

Ingredient	Ex. 8	Ex. 9	Ex. 10*	Ex. 11	Ex. 12	Ex. 13*
MIX A	3g	-	-	3 g	-	-
MIX B	-	3 g	-	-	3 g	-
Oxidized Corn Starch	-	-	3 g	-	-	3 g
MASURF FS 130 EB	3 g	3 g	3 g	-	-	-

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(continued)

Ingredient	Ex. 8	Ex. 9	Ex. 10*	Ex. 11	Ex. 12	Ex. 13*
UNIDYNE TG 8111	-	-	-	3 g	3 g	3 g
Dry matter content	3.84%	3.84%	3.84%	3.60%	3.60%	3.60%
* Comparative						

[0063] About 200 ml of each solution were transferred in a laboratory Pad Batch device (pressure 2 Bar, rolls speed 4 m/min) and used to impregnate three A4 format untreated paper specimen (40 g/m²). The addition of oil and grease sizing composition on the paper specimen was about 0.5 g/m².

[0064] After 3 hours of conditioning at 23° C e 50% relative humidity, the grease and oil resistance of the paper specimen was determined using the method reported above. The average results are reported in Table 5.

Table 5

	Kit Test
Example 8	11
Example 9	15
Example 10*	7
Example 11	10
Example 12	15
Example 13*	10
* Comparative	

[0065] As can be seen from the values reported above better performances are obtained with a guar gum with low ash content.

Examples 14-17

[0066] MIX B, described above, was dissolved in demineralized water at a concentration of 2.7% wt with the addition of 0.6% wt, as active substance, of MASURF FS 130 EB and UNIDYNE TG 8111, to obtain aqueous oil and grease resistant treatment compositions for cellulosic materials according to the invention with a dry matter content of 3.3% wt.

[0067] The two aqueous compositions of the invention were compared with a aqueous composition containing oxidized corn starch previously described.

[0068] The amount of active ingredients used to prepare 100 g of aqueous oil and grease resistant treatment compositions for cellulosic materials are summarized in Table 6.

Table 6

Ingredient	Ex. 14	Ex. 15	Ex. 16*	Ex. 17*
MixB	2.7 g	2.7 g	-	-
Oxidized Corn Starch	-	-	2.7 g	2.7 g
MASURF FS 130 EB	2.14 g	-	2.14 g	-
UNIDYNE TG 8111	-	3.0 g	-	3.0 g
Dry Matter Content	3.3%	3.3%	3.3%	3.3%
* Comparative				

[0069] About 200 ml of each solution were transferred in a laboratory Pad Batch device (pressure 2 Bar, rolls speed 4 m/min) and used to impregnate three A4 format untreated paper specimen (40 g/m²). The addition of oil and grease resistant sizing composition on the paper specimen was about 0.5 g/m².

[0070] After 3 hours of conditioning at 23° C e 50% relative humidity, the grease and oil resistance of the paper

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specimen was determined using the method reported above. The average results are reported in Table 7.

Table 7

	Kit Test
Example 14	14
Example 15	15/16
Example 16*	7
Example 17*	10
* Comparative	

Examples 18-21

[0071] Another 15% water solution of oxidized corn starch was prepared as described above.

[0072] A 0.8% solution of CAMBEX SAH (Sodium Alginate, RVT Brookfield Viscosity 550 mPa*s, at 25 °C, 100 rpm, 1% water solution; commercialized by CAMBRIAN CHEMICALS Inc.) and a 0.8 % solution of MIX C in water were prepared dissolving an appropriate amount of powder in demineralized water.

[0073] Aqueous oil and grease resistant treatment compositions were prepared by mixing together the corn starch solution with 0.6 % wt of fluorocarbon resins (active substance) and with the alginate or guar gum solutions maintaining an active matter amount of 75% wt of starch - 25% wt of alginate or guar.

[0074] The amount of ingredients used to prepare 100 g of treatment compositions are summarized in Table 8.

Table 8

Ingredient	Ex.18*	Ex. 19*	EX. 20	Ex. 21
Oxidized Corn Starch (15% sol.)	13.5 g	13.5 g	13.5 g	13.5 g
Alginate (0.8% sol.)	84.4 g	84.4 g	-	-
MIX C (0.8% sol.)	-	-	84.4 g	84.4g
Demineralized Water	2.1 g	2.1 g	2.1 g	2.1 g
MASURF FS 130 EB	2.14 g	-	2.14 g	-
UNIDYNE TG 8111	-	3 g	-	3 g
Dry Matter Content	3.3%	3.3%	3.3%	3.3%
* Comparative				

[0075] About 200 ml of each solution, Example 20 - 23, were transferred in a laboratory Pad-Batch device (pressure 2 Bar, rolls speed 4 m/min) and used to impregnate three A4 format untreated paper specimen (40 g/m²). The addition of oil and grease resistant composition on the paper specimen was about 0.5 g/m².

[0076] After 3 hours of conditioning at 23° C e 50% relative humidity, the grease and oil resistance of each specimen was determined using the method reported above. The average results are reported in Table 9.

Table 9

	Kit Test
Example 18*	6
Example 19*	4
Example 20	11/12
Example 21	13/14
*Comparative	

[0077] The results reported in Table 5, 7, 9 demonstrate that the aqueous oil and grease resistant treatment compo-

sitions of the invention are able to impart higher oil and grease resistance to the paper compared to compositions of the prior art.

Claims

1. Aqueous oil and grease resistant treatment compositions for cellulosic materials comprising from 0.1 to 10% by weight (wt) of a fluorocarbon resin, **characterized by** the fact that the compositions further comprise:
 - a) from 0,05 to 7.0 % wt of a guar gum, and
 - b) from 0.01 to 1.0% wt of an inorganic phosphate salt.
2. The aqueous oil and grease resistant treatment compositions for cellulosic materials of claim 1 comprising from 0.2 to 3.0% wt of a fluorocarbon resin, from 0.1 to 5.0 % wt of a guar gum and from 0.02 to 0.6 % wt of an inorganic phosphate salt.
3. The aqueous oil and grease resistant treatment compositions for cellulosic materials according to claim 1 wherein the guar gum b) has a RVT Brookfield ® viscosity comprised between 20 and 500 mPa.s in aqueous solution at 2% by weight, measured at 20 °C and 20 rpm, and an ash content below 5.5 % by weight,
4. The aqueous oil and grease resistant treatment compositions for cellulosic materials according to claim 1 wherein the inorganic phosphate salt is sodium or potassium triphosphate.
5. The aqueous oil and grease resistant treatment compositions for cellulosic materials according to any of the preceding claims further comprising : c) from 0.5 and 6% wt of a sizing agent.
6. The aqueous oil and grease resistant treatment compositions for cellulosic materials according to claim 5 wherein the additional sizing agent is starch or a starch derivative.
7. Method for imparting oil and grease repellency to cellulosic materials comprising the step of applying to the cellulosic materials the aqueous compositions according to claim 1, in such an amount that the fluorocarbon resin is applied in an amount between 0.08 and 5.0 % by weight on the weight of the cellulosic material.
8. The method for treating cellulosic materials according to claim 7 wherein said fluorocarbon resin is applied in an amount between 0.15 and 1.5 % by weight on the weight of the cellulosic material.
9. The method according to claim 7, wherein the aqueous compositions are applied to the cellulosic materials as surface post-treatment or during the making process.
10. The method according to any of claims from 7 to 9, wherein the cellulosic materials are paper or paperboard.
11. The use of the aqueous compositions of any of claims from 1) to 6) for the manufacture of paper and paperboard for food packaging and food contact.

Patentansprüche

1. Wässrige fett- und ölbeständige Behandlungszusammensetzungen für zellulosehaltige Materialien mit einem Anteil eines Fluorkarbonharzes von 0,2 bis 10 % des Gewichts (wt), **dadurch gekennzeichnet, dass** die Zusammensetzung außerdem Folgendes enthält:
 - a) einen Anteil von 0,05 bis 7,0 % des Gewichts Guarkernmehl, und
 - b) einen Anteil von 0,01 bis 1,0% des Gewichts eines anorganischen Phosphatsalzes.
2. Die wässrige, öl- und fettbeständige Behandlungszusammensetzung für zellulosehaltige Materialien gemäß Patentanspruch 1 enthält 0,2 bis 3,0 % des Gewichts eines Fluorkarbonharzes, 0,1 bis 5,0 % des Gewichts Guarkernmehl sowie 0,02 bis 0,6 % des Gewichts eines anorganischen Phosphatsalzes.

3. Die wässrige, öl- und fettbeständige Behandlungszusammensetzung für zellulosehaltige Materialien gemäß Patentanspruch 1, bei der das Guarkernmehl b) mit einer Viskosität RVT Brookfield® zwischen 20 und 500 mPa.s in wässriger Lösung bei 2 % des Gewichts, gemessen bei 20 °C und 20 U/min und ein Aschegehalt von weniger als 5,5 % des Gewichts enthalten sind.
4. Die wässrige, öl- und fettbeständige Behandlungszusammensetzung für zellulosehaltige Materialien gemäß Patentanspruch 1, bei der das anorganische Phosphatsalz Natrium oder Kaliumtrypolyphosphat ist.
5. Die wässrige, öl- und fettbeständige Behandlungszusammensetzung für zellulosehaltige Materialien gemäß einem beliebigen der vorausgehenden Patentansprüche enthält außerdem:
 - c). ein Schlichtmittel von 0,5 bis 6 % des Gewichts.
6. Die wässrige, öl- und fettbeständige Behandlungszusammensetzung für zellulosehaltige Materialien gemäß Patentanspruch 5, bei der das zusätzliche Schlichtmittel Stärke oder ein Stärkederivat ist.
7. Methode zum Herstellen öl- und fettabweisender Eigenschaften bei zellulosehaltigen Materialien einschließlich dem Schritt des Auftragens der wässrigen Bestandteile gemäß Patentanspruch 1 auf das zellulosehaltige Material in einer Menge, dass das Fluorkarbonharz mit einem Anteil von 0,08 bis 5,0 % des Gewichts auf das zellulosehaltige Material aufgetragen wird.
8. Die Methode zur Behandlung zellulosehaltiger Materialien gemäß Patentanspruch 7, bei der das genannte Fluorkarbonharz mit einem Anteil von 0,15 bis 1,5 % des Gewichts auf das zellulosehaltige Material aufgetragen wird.
9. Die Methode gemäß Patentanspruch 7, bei der die wässrigen Zusammensetzungen auf das zellulosehaltige Material als Nachbehandlung der Oberfläche oder während des Herstellungsprozesses aufgetragen werden.
10. Die Methode gemäß einem beliebigen der Patentansprüche 7 bis 9, bei der es sich beim zellulosehaltigen Material um Papier oder Karton handelt.
11. Die Verwendung der wässrigen Zusammensetzungen eines beliebigen der Patentansprüche 1) bis 6) durch den Hersteller von Papier und Karton zur Verpackung von Nahrungsmitteln oder im Kontakt mit Nahrungsmitteln,

Revendications

1. Compositions de traitement aqueuses résistantes aux huiles et aux graisses pour matériaux celluloses, comprenant de 0,1 à 10 % en poids d'une résine fluorocarbonée, **caractérisées en ce que** les compositions comprennent également :
 - a) de 0,05 à 7,0 % en poids d'une gomme de guar, et
 - b) de 0,01 à 1,0 % en poids d'un sel phosphate inorganique.
2. Compositions de traitement aqueuses résistantes aux huiles et aux graisses pour matériaux celluloses selon la revendication 1, comprenant comprenant de 0,2 à 3,0 % en poids d'une résine fluorocarbonée, de 0,1 à 5,0 % en poids d'une gomme de guar et de 0,02 à 0,6 % en poids d'un sel phosphate inorganique.
3. Compositions de traitement aqueuses résistantes aux huiles et aux graisses pour matériaux celluloses selon la revendication 2, dans lesquelles la gomme de guar b) a une viscosité Brookfield® RVT comprise entre 20 et 500 mPa.s en solution aqueuse à 2 % en poids, mesurée à 20 °C et 20 tr/min, et un taux de cendres inférieur à 5,5 % en poids.
4. Compositions de traitement aqueuses résistantes aux huiles et aux graisses pour matériaux celluloses selon la revendication 1, dans lesquelles le sel phosphate Inorganique est du tripolyphosphate de sodium ou de potassium.
5. Compositions de traitement aqueuses résistantes aux huiles et aux graisses pour matériaux celluloses selon l'une quelconque des revendications précédentes, comprenant en outre :

c) de 0,5 à 6 % en poids d'un produit d'encollage

6. Compositions de traitement aqueuses résistantes aux huiles et aux graisses pour matériaux cellulosiques selon la revendication 5, dans lesquelles le produit d'encollage supplémentaire est de l'amidon ou un dérivé d'amidon.

7. Procédé visant à conférer une imperméabilisation aux huiles et aux graisses à des matériaux cellulosiques, comprenant l'étape consistant à appliquer sur les matériaux cellulosiques les compositions aqueuses selon la revendication 1, en une quantité telle que la résine fluorocarbonée est appliquée en une quantité comprise entre 0,08 et 5,0 % en poids par rapport au poids du matériau cellulosique.

8. Procédé de traitement de matériaux cellulosiques selon la revendication 7, dans lequel ladite résine fluorocarbonée est appliquée en une quantité comprise entre 0,15 et 1,5 % en poids par rapport au poids du matériau cellulosique.

9. Procédé selon la revendication 7, dans lequel les compositions aqueuses sont appliquées aux matériaux cellulosiques en tant que traitement de surface a posteriori ou pendant le procédé de fabrication.

10. Procédé selon l'une quelconque des revendications 7 à 9, dans lequel les matériaux cellulosiques sont du papier ou du carton.

11. Utilisation des compositions aqueuses selon l'une quelconque des revendications 1 à 6 pour fabrication de papier et de carton pour emballage alimentaire et contact alimentaire.

REFERENCES CITED IN THE DESCRIPTION

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