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(54) Title: OIL AND GREASE REPELLANT AQUEOUS DISPERSIONS, OIL AND GREASE REPELLANT CELLULOSE FIBER ARTICLES, AND METHODS OF MAKING THE SAME

(57) Abstract: An oil and grease repellent aqueous dispersion for treating various papers, paperboard, and cellulose fiber products is disclosed. The dispersion provides superior oil and grease resistance when compared to known fluorochemical, waxes, and silicone treatments. The dispersion comprises clay nanoparticle components and fluorochemicals that can be applied to the paper, paperboard, and cellulose products using known methods.



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**OIL AND GREASE REPELLANT AQUEOUS DISPERSIONS, OIL AND
GREASE REPELLANT CELLULOSE FIBER ARTICLES,
AND METHODS OF MAKING THE SAME**

FIELD OF THE INVENTION

[0001] The invention relates to paper treatment aqueous dispersions comprising a colloidal dispersion of clay nanoparticles and an aqueous fluorochemical that can be applied to or in paper and paperboard products and cellulose fiber products. Paper and paperboard products and cellulose fiber products that have been modified by these aqueous dispersions, which result in having improved oil and grease penetration properties, are also disclosed.

BACKGROUND OF THE TECHNOLOGY

[0002] Waxes and fluorochemicals have been applied topically to cellulose fiber products, such as paper and paperboard, in the past to provide oil and grease resistance, but have suffered from high cost accompanying the conversion from C8 telomer fluorochemicals to C6 telomer and perfluoropolyether (PFPE) fluorochemicals. These newer fluorochemicals are thought to have lower risk of degradation into products harmful to the environment but are also less efficient.

SUMMARY OF THE INVENTION

[0003] There is a desire to reduce the overall usage of fluorochemicals for environmental and cost reasons. Thus, it can be understood that oil and grease

resistant compositions that reduce the amount of fluorochemicals used, but still retain good oil and grease resistance, are in demand.

[0004] Therefore, it is desirable to further extend the effectiveness of fluorochemicals and to produce a paper or paperboard or cellulose fiber product with improved stiffness, print clarity, adhesion, release and friction characteristics while still retaining desirable oil and grease repellency and holdout attributes.

[0005] The invention disclosed herein provides oil and grease resistant aqueous dispersions comprising aqueous dispersions of clay nanoparticles that can be combined with traditional paper fluorochemicals. Paper and paperboard and cellulose fiber products treated with the disclosed dispersions show superior oil and grease resistance properties over prior fluorochemical and silicone treated papers and paperboard and cellulose fiber products. Treated paper and paperboard and cellulose fiber products also show improved stiffness, print clarity, adhesion, release and friction characteristics over prior fluorochemical or silicone treated papers and paperboard and cellulose fiber products. The nanoparticles are shown to act as a fluorochemical extender allowing oil and grease resistant properties on the papers and paperboard and cellulose fiber products at reduced fluorochemical levels on the weight of papers and paperboard and cellulose fiber products.

[0006] Clay nanoparticles can be effective extenders for fluorochemicals in fluorochemical water and oil and grease resistance treatment compositions directed to papers and paperboard and cellulose fiber products. Specifically, the amount of fluorochemical required for a given oil and grease resistance effect is

surprisingly reduced by inclusion of clay nanoparticles in the fluorochemical formulation or emulsion, resulting in effective oil and grease resistance at substantially reduced fluorine levels compared to the prior formulations. When papers and paperboard and cellulose fiber products are treated with the disclosed aqueous dispersions, the clay particles are essentially hydrophilic but are still effective as extenders of the hydrophobic properties that would otherwise be expected to depend on the fluorochemical concentration alone. Under certain conditions, aqueous dispersions of clay nanoparticles are shown to impart many of the same benefits expected from fluorochemicals alone.

[0007] In one aspect, an aqueous dispersion for oil and grease resistance is provided comprising at least one clay nanoparticle component and a fluorochemical is provided. The clay nanoparticle component can be either natural or synthetic. The fluorochemical can comprise any chemical containing a carbon-fluorine moiety.

[0008] In another aspect, a cellulose fiber substrate comprising a surface treatment comprising at least one clay nanoparticle component and a fluorochemical is provided. The cellulose fiber substrate can be any paper or paperboard type material.

[0009] In a further aspect, a process of making an oil and grease resistant cellulose fiber substrate using the oil and grease resistant aqueous dispersions discussed above is provided. Such process comprises applying said aqueous dispersions onto said cellulose fibers on the dry end (size press or coater) or wet end of a papermaking process in an amount resulting in said at least one clay

nanoparticle component present in an amount from about 100 ppm (parts per million - particle weight per weight of the dry paper fiber) to about 4000 ppm OWPF, including from about 500 ppm to about 1500 ppm OWPF, from about 500 ppm to about 1000 ppm OWPF, from about 1000 ppm to about 1500 ppm, from about 1000 ppm to about 2000 ppm OWPF, and from about 1500 ppm to about 2000 ppm OWPF, on the surface of the cellulose fiber substrate; and said fluorochemical present in an amount that results in an elemental fluorine content of from about 25 ppm to about 1000 ppm OWPF, including from about 25 to about 500 ppm OWPF, from about 75 ppm to about 150 ppm OWPF, from about 75 ppm to about 200 ppm OWPF, from about 100 ppm to about 200 ppm OWPF, and from about 140 ppm to about 150 ppm OWPF, on the surface of said cellulose substrate. The fluorochemical and clay nanoparticle can be added to the wet end or dry end of a paper process. The treated cellulose fiber substrate is then cured. (Curing refers to the process of drying the solvent used to carry the solution onto the substrate and/or melt spreading the fluorochemical. This can optionally be done using a heating step.).

DEFINITIONS

[00010] While mostly familiar to those versed in the art, the following definitions are provided in the interest of clarity.

[00011] Nanoparticle: A multidimensional particle in which one of its dimensions is less than 100 nm in length.

[00012] OWPF (On weight of paper fiber): The amount of solids that were applied after drying off the solvent.

[00013] WPU (Wet Pick-up): The amount of solution weight that was applied to the paper fiber before drying off the solvent.

DETAILED DESCRIPTION OF THE INVENTION

[00014] An oil and grease resistance aqueous dispersion is disclosed comprising at least one clay nanoparticle component and a fluorochemical. The clay nanoparticle component can refer to particles substantially comprising minerals of the following geological classes: smectites, kaolins, illites, chlorites, and attapulgites. These classes include specific clays such as montmorillonite, bentonite, pyrophyllite, hectorite, saponite, sauconite, nontronite, talc, beidellite, volchonskoite, vermiculite, kaolinite, dickite, antigorite, anauxite, indellite, chrysotile, bravaisite, suscovite, paragonite, biotite, corrensite, penninite, donbassite, sudoite, pennine, sepiolite, and polygorskyte. The clay nanoparticles can be either synthetic or natural, including synthetic hectorite, and Laponite® from Rockwood Additives Ltd. The Laponite® clay nanoparticles can be Laponite RD®, Laponite RDS®, Laponite JS®, and Laponite S482®.

[00015] The fluorochemicals can include any liquid containing at least one dispersed or emulsified fluorine containing polymer or oligomer. The liquid can also contain other non-fluorine containing compounds. Examples of fluorochemical compositions used in the disclosed composition include anionic, cationic, or nonionic fluorochemicals such as the fluorochemical allophanates

disclosed in U.S. Pat. No. 4,606,737; fluorochemical polyacrylates disclosed in U.S. Pat. Nos. 3,574,791 and 4,147,85; fluorochemical urethanes disclosed in U.S. Pat. No. 3,398,182; fluorochemical carbodiimides disclosed in U.S. Pat. No. 4,024,178; and fluorochemical guanidines disclosed in U.S. Pat. No. 4,540,497. The above listed patents are hereby incorporated by reference in their entirety. A short chain fluorochemical with less than or equal to six fluorinated carbons per fluorinated side-chain bound to the active ingredient polymer or surfactant can also be used. The short chain fluorochemicals can be made using fluorotelomer raw materials or by electrochemical fluorination. Another fluorochemical that can be used in the disclosed composition is a fluorochemical emulsion sold as Capstone® P-600 or P-620 or P-623 or P-640 (all referred to as "Capstone®") from DuPont.

[00016] The disclosed oil and grease resistance aqueous dispersion can be made using various techniques. One technique comprises contacting at least one clay nanoparticle component with water to form an aqueous clay nanoparticle solution. Aqueous solvent mixtures containing low molecular weight alcohols (such as methanol, ethanol, isopropanol, and the like) can also be used to disperse the clay. The clay nanoparticle component can be present in an amount from about 0.01% to about 25% weight in solution, including about 1% to about 20%, about 0.05% to about 15%, about 0.01% to about 5%, about 0.05% to about 5%, about 0.5% to about 5%, and about 5% to about 15%. When Laponite® is used as the clay nanoparticle, the concentration is from about 0.05% to about 25% weight in solution, including from about 0.05% to 1% w/w

and from about 5% to about 15% w/w. The aqueous clay nanoparticle solution is then contacted with a fluorochemical to form the oil and grease resistant aqueous dispersion. The % elemental fluorine in the combined dispersion can be present in an amount from about 0.0001% to about 5% weight fluorine atoms present in dispersion, including about 0.001% to about 2%, about 0.001% to about 0.8%, about 0.005% to about 0.5%, about 0.005% to about 0.15%, about 0.01% to about 1%, about 0.025% to about 0.5%, and about 0.05% to about 0.5%. When Capstone® is used as the fluorochemical, the concentration is from about 0.005% to about 0.5%, including from about 0.005% to about 0.15% depending on the wet pick-up percentage of the application to the fibers. When formulating the aqueous dispersions, the weight percent of clay nanoparticle component should remain higher than the weight percent fluorine. Typical weight percent ratios of clay nanoparticles to fluorine range from about 5000:1 to about 2:1, including about 3000:1, about 1500:1, about 1000:1, about 500:1, about 100:1, about 50:1, about 25:1, and about 10:1.

[00017] The disclosed oil and grease resistant aqueous dispersion can be applied to various types of paper and paperboard and cellulose products as a surface treatment. The disclosed oil and grease resistant aqueous dispersions can be applied to a paper or paperboard or cellulose fiber structure using various techniques known in the art. Such techniques include spraying, dipping, coating, foaming, painting, brushing, and rolling the aqueous dispersion on to the cellulose substrate. After application, the paper or paperboard or cellulose is then heat cured at a temperature of from about 25°C to about 200°C, including

from about 30°C to about 125 °C; and a time of from about 1 second to about 40 minutes, including 5 minutes.

[00018] Once applied, the clay nanoparticle component can be present in an amount from about 200 ppm to about 4000 ppm OWPF, including from about 500 ppm to about 1500 ppm OWPF, from about 500 ppm to about 1000 ppm OWPF, from about 1000 ppm to about 1500 ppm OWPF, from about 1000 ppm to about 2000 ppm OWPF and from about 1500 ppm to about 2000 ppm OWPF, on the surface of the fiber, yarn or textile. The fluorochemical can also be present in an amount that results in an elemental fluorine content of from about 25 ppm to about 1000 ppm OWPF, including from about 25 ppm to about 500 ppm OWPF, from about 75 ppm to about 150 ppm OWPF, from about 75 ppm to about 200 ppm OWPF, from about 100 ppm to about 200 ppm OWPF, and from about 140 ppm to about 150 ppm OWPF, on the surface of the paper and paperboard and cellulose. When applying the aqueous dispersions, the OWPF of the clay nanoparticle component should remain higher than the OWPF of fluorine. Typical OWPF ratios of nanoparticles to fluorine can range from about 80:1 to about 1.5:1, including about 27:1, about 20:1, about 13:1, about 10:1, about 7.5:1, and about 5:1. Additional components can be added to the oil and grease resistant compositions disclosed above. Such components can include silicones, optical brighteners, antibacterial components, anti-oxidant stabilizers, coloring agents, light stabilizers, UV absorbers, wetting agents, starch, polyvinyl alcohol, retention aids and wet strength aids.

[00019] The nanoparticles are shown to act as a fluorochemical extender allowing oil and grease resistant properties on the paper and paperboard and cellulose at reduced fluorine levels on the weight of paper fiber.

CLAIMS

What I claim is:

1. An aqueous dispersion for oil and grease resistance comprising:
at least one clay nanoparticle component; and
a fluorochemical.
2. The aqueous dispersion of claim 1, wherein said at least one clay nanoparticle component is selected from the group consisting of:
smectites, kaolins, illites, chlorites, and attapulgites.
3. The aqueous dispersion of claim 1, wherein said at least one clay nanoparticle component is selected from the group consisting of:
montmorillonite, bentonite, pyrophyllite, hectorite, saponite, sauconite, nontronite, talc, beidellite, volchonskoite, vermiculite, kaolinite, dickite, antigorite, anauxite, indellite, chrysotile, bravaisite, suscovite, paragonite, biotite, corrensite, penninite, donbassite, sudoite, pennine, sepiolite, and polygorskyte.
4. The aqueous dispersion of claims 1 - 3, wherein said at least one clay nanoparticle component is synthetic.
5. The aqueous dispersion of claim 3, wherein said at least one clay nanoparticle component is synthetic hectorite.
6. The aqueous dispersion of claim 1, wherein said fluorochemical is selected from the group consisting of: fluorochemical allophanates, fluorochemical polyacrylates, fluorochemical urethanes, fluorochemical carbodiimides, and fluorochemical guanidines.

7. The aqueous dispersion of claim 1, wherein said fluorochemical has less than or equal to six fluorinated carbons per fluorinated side-chain.
8. The aqueous dispersion of claim 5, wherein said fluorochemical is a fluorochemical urethane.
9. The aqueous dispersion of claim 1, wherein said at least one clay nanoparticle component is present in an amount from about 0.01% to about 25% weight in dispersion.
10. The aqueous dispersion of claim 1, wherein said fluorochemical is present in an amount from about 0.0001% to about 5% weight fluorine atoms present in the dispersion.
11. The aqueous dispersion of claim 1, wherein said at least one clay nanoparticle component is synthetic hectorite present in an amount from about 0.05% to about 15% weight in the dispersion; and said fluorochemical has per fluorinated side-chains with less than or equal to six fluorinated carbons and is present in an amount from about 0.005% to about 0.5% weight fluorine atoms present in the dispersion; and further wherein the weight percent ratio of said clay nanoparticle component to said fluorine ranges from about 5000:1 to about 2:1.
12. A cellulose substrate comprising a surface treatment comprising at least one clay nanoparticle component and a fluorochemical.
13. The cellulose substrate of claim 12, wherein said at least one clay nanoparticle component is selected from the group consisting of: montmorillonite, bentonite, pyrophyllite, hectorite, saponite, sauconite, nontronite, talc, beidellite, volchonskoite, vermiculite, kaolinite, dickite, antigorite, anauxite, indellite, chrysotile, bravaisite, suscovite, paragonite, biotite, corrensite, penninite, donbassite, sudoite, pennine, sepiolite, and polygorskyte.

14. The cellulose substrate of claims 12 - 13, wherein said at least one clay nanoparticle component is synthetic.
15. The cellulose substrate of claim 13, wherein said at least one clay nanoparticle component is synthetic hectorite.
16. The cellulose substrate of claim 12 wherein said fluorochemical is selected from the group consisting of: fluorochemical allophanates, fluorochemical polyacrylates, fluorochemical urethanes, fluorochemical carbodiimides, and fluorochemical guanidines.
17. The cellulose substrate of claim 12, wherein said fluorochemical has less than or equal to six fluorinated carbons per fluorinated side-chain.
18. The cellulose substrate of claim 15, wherein said fluorochemical is fluorochemical urethane.
19. The cellulose substrate of claim 12, wherein said at least one clay nanoparticle component is present in an amount from about 200 ppm to about 4000 ppm OWPF on the surface of said cellulose substrate.
20. The fiber of claim 12, wherein said fluorochemical is present in an amount that results in a surface fluorine content from about 25 ppm to about 1000 ppm OWPF on the surface of said cellulose substrate.
21. The cellulose substrate of one of claims 12 – 13, or 15 – 20, wherein said cellulose substrate is selected from the group consisting of paper and paperboard.
22. The cellulose substrate of claim 12, wherein said at least one clay nanoparticle component is synthetic hectorite in an amount from about 500 ppm to about 1500 ppm OWPF on the surface of said cellulose substrate; and said fluorochemical has per fluorinated side-chains with

less than or equal to six fluorinated carbons and is present in an amount from about 75 ppm to about 200 ppm OWPF on the surface of the cellulose substrate.

23. The cellulose substrate of claim 12, wherein said at least one clay nanoparticle component is synthetic hectorite in an amount from about 500 ppm to about 1000 ppm OWPF on the surface of said cellulose substrate; and said fluorochemical has per fluorinated side-chains with less than or equal to six fluorinated carbons and is present in an amount from about 75 ppm to about 200 ppm OWPF on the surface of the cellulose substrate.
24. The cellulose substrate of claim 12, wherein said at least one clay nanoparticle component is synthetic hectorite in an amount from about 1000 ppm to about 1500 ppm OWPF on the surface of said cellulose substrate; and said fluorochemical has per fluorinated side-chains with less than or equal to six fluorinated carbons and is present in an amount from about 75 ppm to about 200 ppm OWPF on the surface of the cellulose substrate.
25. The cellulose substrate of claim 12, wherein said at least one clay nanoparticle component is synthetic hectorite in an amount from about 1500 ppm to about 2000 ppm OWPF on the surface of said cellulose substrate; and said fluorochemical has per fluorinated side-chains with less than or equal to six fluorinated carbons and is present in an amount from about 75 ppm to about 200 ppm OWPF on the surface of the cellulose substrate.
26. A method of making an oil and grease resistant cellulose substrate using an oil and grease resistance aqueous dispersion from one of claims 1 – 11, comprising:

- a) applying said aqueous dispersion onto said cellulose substrate in an amount resulting in said at least one clay nanoparticle component present in an amount from about 1000 ppm to about 2000 ppm OWPF on the surface of the cellulose substrate, and said fluorochemical present in an amount that results in a surface fluorine content from about 25 ppm to about 500 ppm OWPF on the surface of the cellulose substrate; and
 - b) heat curing said cellulose substrate.
27. The method of claim 26, wherein said oil and grease resistant composition is applied using a technique selected from the group consisting of: spraying, dipping, coating, foaming, painting, brushing, and rolling.
28. The method of claim 27, wherein said oil and grease resistant composition is applied by spraying.

A. CLASSIFICATION OF SUBJECT MATTER**D21H 21/14(2006.01)i, D21H 27/00(2006.01)i, D21H 17/68(2006.01)i, D21H 17/63(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D21H 21/14; D04H 11/00; D06M 15/00; B05D 5/00; D21F 11/00; B41M 5/00; C07F 7/08; B32B 29/00; B32B 29/06; D21H 19/44; D21H 27/00; D21H 17/68; D21H 17/63

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: aqueous dispersion, oil resistance, clay nanoparticle, fluorochemical

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011-0311757 A1 (IVERSON, ISAAC KEENE et al.) 22 December 2011 See abstract; paragraphs [0007]–[0008]; claims 1–25.	1–25
X	US 2010-0215894 A1 (IVERSON, ISAAC KEENE et al.) 26 August 2010 See abstract; paragraph [0032]; claim 1.	1–5, 12–15
A		6–11, 16–25
X	US 2004-0099390 A1 (TROCHLIL, THOMAS R. et al.) 27 May 2004 See abstract; claims 1, 4 and 11.	1–4, 12–14
A		5–11, 15–25
A	WO 2007-140009 A2 (DOW REICHHOLD SPECIALTY LATEX, LLC) 6 December 2007 See abstract; claims 1–2 and 5–6.	1–25
A	US 2008-0003384 A1 (MURPHY, CHRISTOPHER B. et al.) 3 January 2008 See abstract; claims 1 and 10.	1–25



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

24 January 2014 (24.01.2014)

Date of mailing of the international search report

24 January 2014 (24.01.2014)

Name and mailing address of the ISA/KR


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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/064841

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 27-28
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 27-28 are unclear since they are referring to the multiple dependent claims which do not comply with PCT Rule 6.4(a).

3. ☒ Claims Nos.: 26
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/064841

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