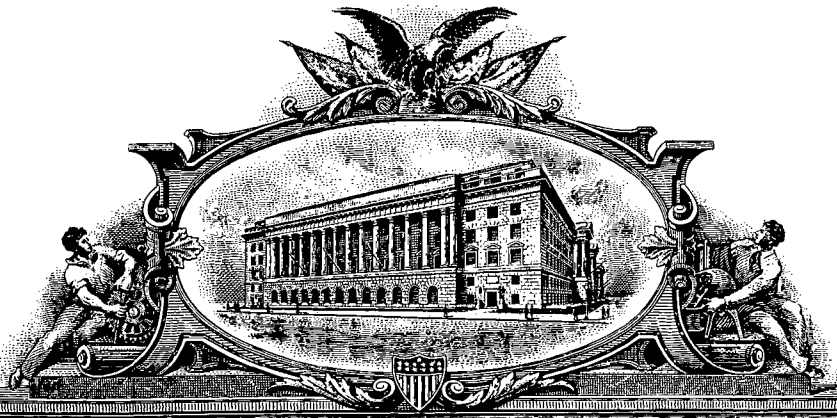


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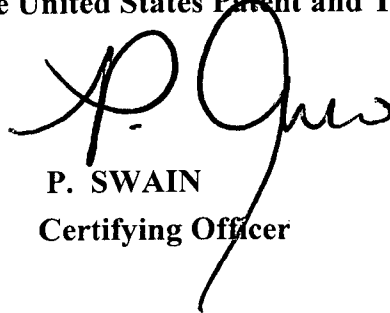
APPLICATION NUMBER: 62/308,532

FILING DATE: *March 15, 2016*

THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS *US62/308,532*

**By Authority of the
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P. SWAIN
Certifying Officer

Electronic Acknowledgement Receipt

EFS ID:	25202790
Application Number:	62308532
International Application Number:	
Confirmation Number:	8885
Title of Invention:	USE OF DIPA-ESTERQUAT DEBONDER FOR TISSUE AND FLUFF PULP MANUFACTURING
First Named Inventor/Applicant Name:	Deborah J. LEWIS
Customer Number:	22850
Filer:	Bradley Davis Lytle/Pamela Lockley
Filer Authorized By:	Bradley Davis Lytle
Attorney Docket Number:	468907US106PROV
Receipt Date:	15-MAR-2016
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Application Type:	Provisional

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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		468907US_Prov_App.pdf	136055 ac859a50b754d3fc336a57b8ee9ceb59506a307d	yes	21

Multipart Description/PDF files in .zip description

Document Description	Start	End
Provisional Cover Sheet (SB16)	1	1
Application Data Sheet	2	7
Specification	8	19
Claims	20	21

Warnings:**Information:**

2	Fee Worksheet (SB06)	fee-info.pdf	30510 db887780c13e2991fb4c913d817ed89b44ad7e51	no	2
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Warnings:**Information:**

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National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53(c).

Docket Number 468907US106PROV

INVENTOR(s)/APPLICANT(s)

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☐ Additional inventors are named on separately numbered sheets attached hereto.

TITLE OF THE INVENTION (500 CHARACTERS MAX)

USE OF DIPA-ESTERQUAT DEBONDER FOR TISSUE AND FLUFF PULP MANUFACTURING

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ENCLOSED APPLICATION PARTS

- ☒ Specification *Number of Pages:* 14 ☐ CD(s), Number
☐ Drawing(s) *Number of Sheets:* ☐ Other (specify):
☒ Application Data Sheet

METHOD OF PAYMENT

- ☐ Application Size Fee (\$400 per each additional 50 sheets over 100): Number of Pages Filed: _____
☐ Applicant claims small entity status. See 37 CFR 1.27.
☒ Credit card payment is being made online (if electronically filed), or is attached hereto (if paper filed), to cover the Provisional Filing Fees.
☒ The Director is hereby authorized to charge filing fees and credit any overpayment to Deposit Account Number 15-0030.

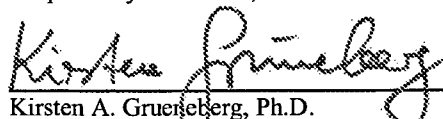
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AMOUNT **\$260.00**

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No.

☐ Yes, the name of the U.S. Government agency and the Government contract number are:

Respectfully Submitted,


Kirsten A. Gruenberg, Ph.D.

Registration No. 47,297

March 15, 2016
DATE

(OMMN 11/08)

PROVISIONAL APPLICATION FILING ONLY

Use of DIPA-Esterquat debonder for tissue and fluff pulp manufacturing

Background of the Invention:

5 Debonders are used in the manufacture of fluff pulp, tissue paper and other forms of paper. In tissue paper, paper toweling and other forms of paper, debonders can be used to decrease density of the fiber sheet. Decreasing the density of the sheet can among other things change the absorption properties and printability of different types of paper and tissue. This allows the paper manufacturer to achieve desired end use
10 properties.

There are two main types of chemicals used as debonders for fluff pulp and tissue. The first group of materials are di-alkyl dimethyl ammonium chloride where the alkyl groups are from 8 to 20 carbons long. The second type are materials based on quaternized imidazolines-

15 US 3,755,220 disclose that certain chemical additives known as debonding agents interfere with the natural fiber-to-fiber bonding that occurs during sheet formation in papermaking processes. This reduction in bonding leads to a softer, or less harsh, sheet of paper. Freimark et al. go on to teach the use of wet strength resins to enhance the wet strength of the sheet in conjunction with the use of debonding agents to off-set
20 undesirable effects of the wet strength resin. These debonding agents do reduce dry tensile strength, but there is also generally a reduction in wet tensile strength.

US 3,821,068 also disclose that chemical debonders can be used to reduce the stiffness, and thus enhance the softness, of a tissue paper web.

Chemical debonding agents have been disclosed in various references such as US
25 3,554,862.

These materials include quaternary ammonium salts such as trimethylcocoammonium chloride, trimethyloleylammonium chloride, di(hydrogenated) tallow dimethyl ammonium chloride and trimethylstearyl ammonium chloride.

US 4,144,122 disclose the use of complex quaternary ammonium compounds such as bis(alkoxy(2-hydroxy)propylene) quaternary ammonium chlorides to soften webs. The authors also attempt to overcome any decrease in absorbency caused by the debonders through the use of nonionic surfactants such as ethylene oxide and propylene oxide adducts of fatty alcohols.

WO 1993/021382 disclose that the use of dimethyl di(hydrogenated) tallow ammonium chloride in combination with fatty acid esters of polyoxyethylene glycols may impart both softness and absorbency to tissue paper webs.

Conventional quaternary ammonium compounds such as the well known dialkyl dimethyl ammonium salts (e.g. ditallow dimethyl ammonium chloride, ditallow dimethyl ammonium methyl sulfate, di(hydrogenated) tallow dimethyl ammonium chloride etc.) are effective chemical debonding agents. Unfortunately, these quaternary ammonium compounds are not biodegradable.

It is an object of the present invention to achieve a debonder which is dispersible at room temperature and which is readily biodegradable.

Surprisingly, the quaternary ammonia compounds of the invention solve at least one problem of the prior art.

The present invention accordingly provides cellulose fiber materials containing 0.01 to 0.5 % by weight of ammonia compounds of formula (I) based on the dry weight of cellulose fiber material



wherein

R^1 independently an alkyl group consisting of 1 to 6 carbon atoms;

R^2 independently an unsaturated or saturated acyl group;

A independently an oxyalkyl radical consisting of at least 3 carbon atoms;

a 1 to 3;

where the radicals R^2 consist of 60% to 99% (w/w) of unsaturated acyl groups;

B is an anion selected from consisting of chloride, acetate, methyl sulfate, and mixtures thereof;

where the compounds of the formula (I) are biodegradable at a degree of at least 60% according the OECD 301F method;

5 The invention further provides an absorbent material consisting of the debonded cellulose fibers according the invention.

The invention further provides a process for producing the debonded cellulose fibers according the invention.

The invention further provides a method of debonding cellulose fibers using ammonia
10 compounds of the formula (I).

The invention further provides a method of lubricating cellulose fibers using liquid ammonia compounds of the formula (I).

It is advantage that the inventive compounds are biodegradable. Another advantage is that the inventive compounds are liquid at room temperature.

15 Especially advantageous is that the compounds of the invention allow a dose dependent change of properties, particularly the absorbance and the burst index.

Absorbency is the measure of the ability of a product, and its constituent webs, to absorb quantities of liquid, particularly aqueous solutions or dispersions. Overall
20 absorbency as perceived by the human consumer is generally considered to be a combination of the total quantity of liquid a given mass of tissue paper will absorb at saturation as well as the rate at which the mass absorbs the liquid.

Debonding is the masking of hydrogen bonds between the individual cellulosic fibers. The tissue formed has finally enhanced flexibility and lubrication between the individual
25 fibers and is not stiff and rough.

The subject-matter provided by the invention is illustratively described hereinbelow without any intention to limit the invention to these illustrative embodiments. Where ranges, general formulae or compound classes are specified hereinbelow, these shall

include not just the corresponding ranges or groups of compounds that are explicitly mentioned but also all sub-ranges and sub-groups of compounds which can be obtained by extracting individual values (ranges) or compounds. When documents are cited in the context of the present description, the contents thereof, particularly with regard to the
5 subject-matter that forms the context in which the document has been cited, are considered in their entirety to form part of the disclosure content of the present invention. Unless stated otherwise, percentages are figures in per cent by weight. When average values are reported herein below, the values in question are weight averages, unless stated otherwise. When parameters which have been determined by
10 measurement are reported hereinafter, they have been determined at a temperature of 25°C and a pressure of 101 325 Pa, unless stated otherwise.

Preference is given to quaternary ammonia compounds of formula (I) which are liquid at ambient temperature, preferable have a melting point of melting range between - 20°C to +20°C, more preferable between -10 to + 15°C, particularly preferable between 0 to
15 10°C.

The advantage of liquid quaternary ammonia compounds of formula (I) is that these compounds are able to penetrate deeper into the cellulose fibers, that they remain liquid even on dry products made of the cellulose fibers thus making these products more flexible and soft. A further advantage is that the energy upload of a hammer mill used for
20 subsequent fiberizing a raw cellulose fiber containing product in order to get a fluff pulp is lowered, thus the temperature of the product within the hammering process is lowered.

Preference is given to quaternary ammonia compounds of formula (I) where R2 is preferably independently of one another identical or different acyl radicals of saturated
25 or unsaturated fatty acids, where the fatty acids include 4 up to 40 carbon atoms, more preferably, the fatty acids are unsaturated selected from among palmitoleic acid ((Z)-9-hexadecenoic acid), oleic acid ((Z)-9-hexadecenoic acid), elaidic acid ((E)-9-octadecenoic acid), cis-vaccenic acid ((Z)-11-octadecenoic acid), linoleic acid ((9Z,12Z)-9,12-octadecadienoic acid), alpha-linolenic acid ((9Z,12Z,15Z)-9,12,15-
30 octadecatrienoic acid), gammalinolenic acid ((6Z,9Z,12Z)-6,9,12-octadecatrienoic acid), di-homo-gamma-linolenic acid ((8Z,11Z,14Z)-8,11,14-eicosatrienoic acid), arachidonic

acid ((5Z,8Z,11Z,14Z)-5,8,11,14-eicosatetraenoic acid), erucic acid ((Z)-13-docosenoic acid), nervonic acid ((Z)-15-tetracosenoic acid), ricinoleic acid, and undecenoic acid, and mixtures, such as, for example, rapeseed oil acids, soya fatty acids, sunflower fatty acids, peanut fatty acids and tall oil fatty acids. Especially preferred in this context are radicals of oleic acid.

- More especially preferred are the quaternary ammonia compounds of formula (I) which are liquid, and where the acyl radicals are of fatty acid mixtures comprising oleic acid, stearic acid, palmitic acid and gamma-linolenic acid, where these abovementioned fatty acids preferably amount to at least 85% by weight in the fatty acid mixture.
- Especially preferred are the quaternary ammonia compounds according to the invention which are liquid where the acyl radicals of fatty acid mixtures comprise oleic acid at least 70% by weight, preferably at least 75% by weight, more preferably at least 80% by weight, even more preferably at least 85% by weight, particularly preferably at least 90% by weight and especially preferably at least 95% by weight, the sum total of all fatty acids being 100% by weight.

Preference is given to quaternary ammonia compounds of formula (I) wherein R¹ is independently selected from the group of hexyl, pentyl, n-butyl, i-butyl, n-propyl, i-propyl, ethyl and methyl, especially preferably methyl;

- A further advantage of the quaternary ammonia compounds according to the invention is their biodegradability.

The biodegradability is preferably determined by the OECD 301 F method. More preferably, the biodegradability is determined as specified in 28 d of OECD 301 F.

- The quaternary ammonia compounds according to the invention preferably have a biodegradability of at least 50%, even more preferably of at least 55% and especially preferably of at least 60%, the maximum biodegradability value being 100%.

Preference is given to quaternary ammonia compounds of formula (I) which are miscible with organic solvents, preferably without miscibility gap at ambient temperature, preferable between 0 to 20°C.

Solvents are any non-toxic, non-ecotoxic organic compounds having at least one hydroxyl group, preferably mono hydroxyl aliphatic compounds, di hydroxyl aliphatic compounds, oligo hydroxyl aliphatic compounds which can be oligomeric or polymeric. More preferably the solvents are selected from alcohols, glycols, oligo or poly alcoxylene compounds, more preferably selected from poly oxyethylene or poly oxypropylene compounds, particularly those poly oxyalcoxylenes which are terminated on one end with an unsaturated fatty acid as defined above.

Preferably the solvents according the invention are biodegradable wherein biodegradable is understood as before mentioned.

- 10 Miscibility in the context of the invention is understood to mean the quaternary ammonia compounds of formula (I) having a solubility of at least 10 g/l, preferably at least 20 g/l, 50 g/l, 100 g/l and especially preferably of at least 150 g/l solvent at a temperature of 20°C. The upper solubility limit is preferably up to and including 900 g/l, more preferably 800 g/l, 700 g/l and especially preferably up to and including 600 g/l solvent at 20°C.
- 15 Determining the -solubility is comprehensible to the skilled person, who determines it preferably according to Regulation EC 440/2008 Part A.6, more preferably by the flask method of Regulation EC 440/2008 Part A.6.

Preference is given to quaternary ammonia compounds of formula (I) where the fatty acid or fatty acid mixture has iodine number between 105 and 130, preferably between 20 110 and 125.

Iodine numbers [g of iodine/100 g of sample] are determined by the method of Hanus, known as method DGF C-V 11 a (53) of the German Society for Fats, and arithmetically converted into the molar masses MW_{IN} for the respective fatty acid or fatty acid mixture.

Preference is given to cellulose fiber materials containing 0.02 to 0.3 % by weight of quaternary ammonia compounds of formula (I) based on the dry weight of cellulose fiber material, wherein

R^1 is independently selected from the group of hexyl, pentyl, n-butyl, i-butyl, n-propyl, i-propyl, ethyl and methyl, especially preferably methyl;

R² independently an unsaturated or saturated acyl group where the radicals R² consist of 60% to 99% (w/w) of unsaturated acyl group and where the unsaturated acyl group consist of at least in 70% of oleic acid;

a is 1;

5 A is independently – CH₂CH(CH₃) - O – or – CH(CH₃) CH₂ - O –;

B is MeOSO₃⁻.

More preferred are cellulose fiber materials containing 0.02 to 0.3 % by weight of quaternary ammonia compounds of formula (I) based on the dry weight of cellulose fiber material, wherein

10 R¹ is methyl

R² independently an unsaturated or saturated acyl group with a iodine number between 105 and 130, preferably between 110 and 125;

a is 1;

A is independently – CH₂CH(CH₃) - O – or – CH(CH₃) CH₂ - O –;

15 B is MeOSO₃⁻.

Particularly preference is given to cellulose fiber materials containing 0.03 to 0.2 % of liquid ammonia compounds of formula (I) based on the dry weight of cellulose fiber material, wherein R¹ is Methyl, R² is oleic acid, a is 1, A is – CH₂CH(CH₃) - O – or – CH(CH₃) CH₂ - O –, B is MeOSO₃⁻; where the iodine number of R² is between 110 and 130; and where the biodegradability is at least 60% according the OECD 301F method.

20 Preference is given to cellulose fiber materials selected from paper, tissue paper, paper toweling or non-woven material made of debonded cellulose fibers.

Preference is given to absorbent material with a higher water absorbance as the same material without the use of ammonia compounds of formula (I).

25 Due to the strong adhesion to the fiber surface ammonia compounds of formula (I) are advantageous because food contamination is prevented,

Another advantage of the ammonia compounds of formula (I) is the low surface tension watery solutions, this causes a good penetration into the cellulose fibers.

The quaternary debonder helps to manufacture in a high speed industrial process generating a tissue weight of $< 50 \text{ g/m}^2$, that is mainly used for paper towels or even tissue sheets with a weight of $12\text{-}20 \text{ g/m}^2$ that is typically used as toilet tissue.

5 Examples

Allgemeine Methoden und Materialien:

Table 1: test compounds, all products are commercially available and trademarks of Evonik, Germany

entry	tradename	melting range [°C]
ex 1	Adogen® 442	60 - 70
ex 2	REWOQUAT V 10036 (ZWVarisoft 3690)	30 – 50
ex 3	REWOQUAT DEEDMAC	55 – 65
ex 4	REWOQUAT CR 3099	5 – 10 °C

REWOQUAT V 10036 ZW is the active ingredient of Varisoft 3690.

10

Preparation or tissue sheets:

Untreated fluff pulp from a Scandinavian mill was obtained from the high density chest. This fluff pulp was used to form hand sheets with a Rapid Köthen hand sheet former as supplied by Frank PTI using ISO 5269-2. Four hand sheets were made for each experimental condition, including four sheets that were not treated with any debonder. The sheets were then tested for burst index, absorbency, density and softness. The data reported represents the average of each condition. The method for preparing the debonder samples and subsequently treating the fiber used to make hand sheets is as follows.

20 The pulp received was 7.29% (w/w) consistency in water. The consistency needed for preparation of sheets should be 0.18% by weight. In order to achieve this, the water to pulp ratio was using pulp as supplied in amount of 2.467% and water 97.533% by

weight based on the sum of 100% by weight. This was mixed for one hour at 400 rpm with an overhead mixer resulting in a fluff pulp slurry.

The debonders were dissolved in propylene glycol by mixing 40 g of pure debonder in 60 g of propylene glycol. In case of the dialkyldimethyl ammonium chlorid (Adogen 442) this compound was melted and then added to warm ($T = 50 - 80^{\circ}\text{C}$) propylene glycol and held at this temperature until dispersed in water.

These debonder solutions were dispersed in city water using 0.625 g of the above debonder solution in propylene glycol and 99.375 g of city water by mixing this for 90 minutes at 400 rpm resulting in sample A consisting of Adogen 442, sample B consisting of Varisoft 3690 and sample C consisting of the compound according the invention REWOQUAT CR 3099.

To 3 500 mL of the above fluff pulp slurry different amounts of samples A, B and C were added as indicated in table 2. The dose is based on the use of the above debonder solution in kg per dry weight of the pulp in ton. The resulting concentration is weight of pure debonder base on the weight or dry pulp.

table 2: Definition of the attempts

entry	Debonder dose; [kg/ton]	mL to add	Resulting concentration; [% (w/w)]
1	0	0	0
2	1	6.4	0.04
3	3	19.2	0.12
4	4	25.6	0.16

The resulting mixtures were stirred for 5 minutes at 500 rpm at room temperature.

The preparation of the hand sheets was performed with a Rapid Köthen Sheet Machine (FRANK-PTI) according to the product sheet number 95854 of company FRANK-PTI with some amendments.

The individual steps were carried out manually via the selector switch. At first water was introduced into the forming column. When it has been filled to the 4 liter mark, 800 ml the suspensions of table 1 were added. When the 7 liter mark was reached, the flow of water was stopped manually and agitation begins under pressure of compressed air.

5 After the agitation was completed, the suspension came to rest for 5 seconds and the draining process started (approximately 20 seconds) by decompression of the suction chamber. The hand sheet was formed on the screen frame.

A carrier board was placed with its smooth side downwards centrally on the wet sheet. Then a couch roll was rolled back and forth over the sheet for a 2-second period without

10 additional pressure, once in each of two directions at right angles to each other. The couch roll had been placed on the edge of the screen but not on the wet sheet. After removing the sheet-forming screen together with the wet sheet and the carrier board from the supporting screen it was hit with the edge slightly inclined to the horizontal against the silicon rubber underlay releasing the board to which the wet sheet was

15 attached on the underlay.

After placing the round metal plate onto the center of the wet sheet the sheet was peeled from the carrier board and air dried. The hand sheets were further prepared for the tests by storing under controlled climate (72°F, 50% relative humidity) until constant weight.

20

Properties of the tissue sheets:

Burst testing is performed on the Vantage Tensile Tester (Thwing-Albert Instrument Company, USA) utilizing the Tissue Burst attachment. The lower the burst index, the

25 weaker the test sample, which equates to better debonding.

The sheets were test for water absorbency on a M/K Systems model 251 GATS (Gravimetric Absorption Testing System) instrument which tests Horizontal wicking. This instrument determines rate of absorption and capacity of the test substrate by placing a sample of known weight on a porous plate attached to an instrument and analytical

30 balance. The porous plate is attached to a water reservoir placed on an analytical

balance. The instrument measures the rate of absorption and capacity by measuring the quantity and speed of water leaving the reservoir that supplies the porous plate.

The density of the sheets were measured with a Messmer micrometer Model 172M.

The sheets were analyzed for softness using a TSA (Tissue Softness Analyzer) supplied
 5 by Emtec Electronic GmbH, Germany. The tissue softness values are expressed as "hand feel". A two point increase in hand feel is considered significant and can be perceived by the average human.

Table 3: results of the property determination

entry	sample	Burst index; [Pa*m ² /g]	Density; [mg/mL]	Absorption Rate; [g/sec]	Hand Feel
0	-	31.7	249.27	2.031	63
1	A	27.7	243.27	1.563	64
1	B	28.8	245.02	1.774	64
1	C	30.2	244.71	2.216	62
2	A	20.3	240.91	1.105	65
2	B	15.5	246.54	1.328	69
2	C	15.5	243.52	1.490	67
3	A	17.9	246.98	1.034	66
3	B	12.8	249.01	1.492	70
3	C	12.7	241.11	1.355	72

10

The results show the advantage of the compounds of the invention. The burst index is effectively lowered and not only better than the blank but at higher concentrations also better than the compounds of the art. The density is comparable to those of the art but clearly effectively lowered at high concentrations. The absorption rate is being modified
 15 in a wide range.

Table 4: certain eco toxicological data according different OECD methods

	OECD method	442	10036	3099	deed
Fish; aqua tox	203; 96h; LC50 [mg/L]	10.1	1.8	>10	5.2
Aquatotoxicity, invertebrates	202; <i>Daphnia magna</i> ; 48 h; EC50 [mg/L]	0.19	0.105	>8.8	14.8
Biodegradation	301 *	3% (A)	13% (B)	>60% (F)	>60% (B)

Claims:

1. Cellulose fiber materials containing 0.01 to 0.5 % by weight of ammonia compounds of formula (I)



wherein

R^1 independently an alkyl group consisting of 1 to 6 carbon atoms;

R^2 independently an unsaturated or saturated acyl group;

A independently an oxyalkyl radical consisting of at least 3 carbon atoms;

a 1 to 3;

where the radicals R^2 consist of 60% to 99% (w/w) of unsaturated acyl groups;

B is an anion selected from consisting of chloride, acetate, methyl sulfate, and mixtures thereof;

where the compounds of the formula (I) are biodegradable at a degree of at least 60% according the OECD 301F method;

2. Cellulose fiber materials selected from paper, tissue paper, paper toweling or non-woven material made of debonded cellulose fibers according to claim 1.

3. Absorbent material consisting of debonded cellulose fibers according to claim 1.

4. A method of debonding cellulose fibers using ammonia compounds of the formula (I)



wherein

R^1 independently an alkyl group consisting of 1 to 6 carbon atoms;

R^2 independently an unsaturated or saturated acyl group;

A independently an oxyalkyl radical consisting of at least 3 carbon atoms;

a 1 to 3;

where the radicals R² consist of 60% to 99% (w/w) of unsaturated acyl groups;

B is an anion selected from consisting of chloride, acetate, methyl sulfate,
and mixtures thereof;

where the compounds of the formula (I) are biodegradable at a degree of at least 60% according the OECD 301F method;

5. Method of improving the softness of cellulose fiber materials according to claim 4.

6. Method of decreasing the density and/or increasing the porosity of cellulose fiber materials according to claim 4.

7. The invention further provides a method of lubricating cellulose fibers using liquid ammonia compounds of the formula (I).

8. Method of modifying the absorptive properties of cellulose fiber materials according to claim 4.

9. A process for producing debonded cellulose fibers consisting of the steps
(a) optionally dissolving the ammonia compounds of the formula (I) in a solvent
(b) ...

Application Data Sheet 37 CFR 1.76		Attorney Docket Number	468907US106PROV
		Application Number	NEW APPLICATION
Title of Invention	USE OF DIPA-ESTERQUAT DEBONDER FOR TISSUE AND FLUFF PULP MANUFACTURING		

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76. This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

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Legal Name

Application Data Sheet 37 CFR 1.76		Attorney Docket Number	468907US106PROV
		Application Number	NEW APPLICATION
Title of Invention	USE OF DIPA-ESTERQUAT DEBONDER FOR TISSUE AND FLUFF PULP MANUFACTURING		

Prefix	Given Name	Middle Name	Family Name	Suffix
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Enter either Customer Number or complete the Correspondence Information section below. For further information see 37 CFR 1.33(a).	
☐ An Address is being provided for the correspondence information of this application.	
Customer Number	22850
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Application Information:

Title of the Invention	USE OF DIPA-ESTERQUAT DEBONDER FOR TISSUE AND FLUFF PULP MANUFACTURING		
Attorney Docket Number	468907US106PROV	Small Entity Status Claimed ☐	
Application Type	Provisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	0	Suggested Figure for Publication (if any)	

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").		
For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).		
Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Application Data Sheet 37 CFR 1.76		Attorney Docket Number	468907US106PROV
		Application Number	NEW APPLICATION
Title of Invention	USE OF DIPA-ESTERQUAT DEBONDER FOR TISSUE AND FLUFF PULP MANUFACTURING		

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not be** the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32). Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One: ☒ Customer Number ☐ US Patent Practitioner ☐ Limited Recognition (37 CFR 11.9)

Customer Number 22850

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) or indicate National Stage entry from a PCT application. Providing this information in the application data sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.

When referring to the current application, please leave the application number blank.

Prior Application Status			
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX) the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Application Number	Country	Filing Date (YYYY-MM-DD)	Access Code (if applicable)

**Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File)
Transition Applications**

Application Data Sheet 37 CFR 1.76		Attorney Docket Number	468907US106PROV
		Application Number	NEW APPLICATION
Title of Invention	USE OF DIPA-ESTERQUAT DEBONDER FOR TISSUE AND FLUFF PULP MANUFACTURING		

This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after ☐ March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78 this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant must opt-out of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

Application Data Sheet 37 CFR 1.76		Attorney Docket Number	468907US106PROV
		Application Number	NEW APPLICATION
Title of Invention	USE OF DIPA-ESTERQUAT DEBONDER FOR TISSUE AND FLUFF PULP MANUFACTURING		

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

- ☐ Assignee
 ☐ Legal Representative under 35 U.S.C. 117
 ☐ Joint Inventor
- ☐ Person to whom the inventor is obligated to assign.
 ☐ Person who shows sufficient proprietary interest

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor :

If the Applicant is an Organization check here. ☐

Prefix	Given Name	Middle Name	Family Name	Suffix

Mailing Address Information For Applicant:

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Address 2			
City		State/Province	
Country		Postal Code	
Phone Number		Fax Number	
Email Address			

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

If the Assignee or Non-Applicant Assignee is an Organization check here. ☐

Application Data Sheet 37 CFR 1.76		Attorney Docket Number	468907US106PROV
		Application Number	NEW APPLICATION
Title of Invention	USE OF DIPA-ESTERQUAT DEBONDER FOR TISSUE AND FLUFF PULP MANUFACTURING		

Organization Name	Evonik Degussa GmbH		
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Address 2			
City	Essen	State/Province	
Country	Germany	Postal Code	45128
Phone Number		Fax Number	
Email Address			

Signature:

NOTE: This Application Data Sheet must be signed in accordance with 37 CFR 1.33(b). However, if this Application Data Sheet is submitted with the INITIAL filing of the application and either box A or B is not checked in subsection 2 of the "Authorization or Opt-Out of Authorization to Permit Access" section, then this form must also be signed in accordance with 37 CFR 1.14(c).

This Application Data Sheet must be signed by a patent practitioner if one or more of the applicants is a juristic entity (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, all joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of all joint inventor-applicants.

See 37 CFR 1.4(d) for the manner of making signatures and certifications.

Signature			Date (YYYY-MM-DD)	2016-03-15	
First Name	Kirsten A.	Last Name	Grueneberg, Ph.D.	Registration Number	47,297

From the INTERNATIONAL BUREAU

PCTNOTIFICATION CONCERNING SUBMISSION,
OBTENTION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

EVONIK DEGUSSA GMBH
CI-IPM-PAT Bau 1042A/PB 15
Paul-Baumann-Strasse 1
45764 Marl
ALLEMAGNE

Date of mailing (day/month/year) 21 March 2017 (21.03.2017)	
Applicant's or agent's file reference 2015P00200WO	IMPORTANT NOTIFICATION
International application No. PCT/EP2017/054712	International filing date (day/month/year) 01 March 2017 (01.03.2017)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 15 March 2016 (15.03.2016)
Applicant EVONIK DEGUSSA GMBH	

The applicant is hereby notified of the date of receipt (or of obtaining by the International Bureau) of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to the date of receipt, **the priority document concerned was submitted or transmitted to or obtained by the International Bureau in compliance with Rule 17.1(a), (b) or (b-bis)**. This Form replaces any previously issued notification concerning submission, transmittal or obtaining of priority documents.

Priority datePriority application No.Country or regional Office
or PCT receiving OfficeDate of receipt
of priority document

15 March 2016 (15.03.2016)

62/308,532

US

18 March 2017 (18.03.2017)

The letters "NR" denote a priority document which, on the date of mailing of this Form, had not yet been received or obtained by the International Bureau in compliance with Rule 17.1(a), (b) or (b-bis). Where the applicant has failed to either submit, request to prepare and transmit, or to request the International Bureau to obtain the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

An asterisk "*" next to a date of receipt, denotes a priority document submitted or transmitted to or obtained by the International Bureau but not in compliance with Rule 17.1(a), (b) or (b-bis) (the priority document was received after the time limit prescribed in Rule 17.1(a); the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b) or the request to the International Bureau to obtain the priority document was made after the applicable time limit under Rule 17.1(b-bis)). Even though the priority document was not furnished in compliance with Rule 17.1(a), (b) or (b-bis), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

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(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
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TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
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GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to the applicant's entitlement to claim the priority of the
earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

(54) Title: USE OF DIPA-ESTERQUAT DEBONDER FOR TISSUE AND FLUFF PULP MANUFACTURING

(57) Abstract: The present invention relates to cellulose fiber materials containing 0.01 to 0.5 % by weight of ammonia compound comprising oxyalkyl radicals consisting of at least 3 carbon atoms which are biodegradable at a degree of at least 60% according the OECD 301F method and a process for producing debonded cellulose fibers.



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Use of DIPA-Esterquat debonder for tissue and fluff pulp manufacturing

The present invention relates to cellulose fiber materials containing 0.01 to 0.5 % by weight of ammonia compound comprising oxyalkyl radicals consisting of at least 3 carbon atoms which are biodegradable at a degree of at least 60% according the OECD 301F method and a process for producing debonded cellulose fibers.

Debonders are used in the manufacture of fluff pulp, tissue paper and other forms of paper. In tissue paper, paper toweling and other forms of paper, debonders can be used to decrease density of the fiber sheet. Decreasing the density of the sheet can among other things change the absorption properties and printability of different types of paper and tissue. This allows the paper manufacturer to achieve desired end use properties.

There are two main types of chemicals used as debonders for fluff pulp and tissue. The first group of materials are di-alkyl dimethyl ammonium chloride where the alkyl groups are from 8 to 20 carbons long. The second type are materials based on quaternized imidazolines-

US 3,755,220 disclose that certain chemical additives known as debonding agents interfere with the natural fiber-to-fiber bonding that occurs during sheet formation in papermaking processes. This reduction in bonding leads to a softer, or less harsh, sheet of paper. Freimark et al. go on to teach the use of wet strength resins to enhance the wet strength of the sheet in conjunction with the use of debonding agents to off-set undesirable effects of the wet strength resin. These debonding agents do reduce dry tensile strength, but there is also generally a reduction in wet tensile strength.

US 3,821,068 also disclose that chemical debonders can be used to reduce the stiffness, and thus enhance the softness, of a tissue paper web.

Chemical debonding agents have been disclosed in various references such as US 3,554,862.

These materials include quaternary ammonium salts such as trimethylcocoammonium chloride, trimethyloleylammonium chloride, di(hydrogenated) tallow dimethyl ammonium chloride and trimethylstearyl ammonium chloride.

US 4,144,122 disclose the use of complex quaternary ammonium compounds such as bis(alkoxy(2-hydroxy)propylene) quaternary ammonium chlorides to soften webs. The authors also attempt to overcome any decrease in absorbency caused by the debonders through the use of nonionic surfactants such as ethylene oxide and propylene oxide adducts of fatty alcohols.

WO 1993/021382 disclose that the use of dimethyl di(hydrogenated) tallow ammonium chloride in combination with fatty acid esters of polyoxyethylene glycols may impart both softness and absorbency to tissue paper webs.

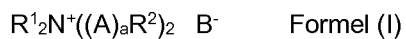
Conventional quaternary ammonium compounds such as the well known dialkyl dimethyl ammonium salts (e.g. ditallow dimethyl ammonium chloride, ditallow dimethyl ammonium methyl sulfate, di(hydrogenated)

tallow dimethyl ammonium chloride etc.) are effective chemical debonding agents. Unfortunately, these quaternary ammonium compounds are not biodegradable.

It is an object of the present invention to achieve a debonder which is dispersible at room temperature and which is readily biodegradable.

- 5 Surprisingly, the quaternary ammonia compounds of the invention solve at least one problem of the prior art.

The present invention accordingly provides cellulose fiber materials containing 0.01 to 0.5 % by weight of ammonia compounds of formula (I) based on the dry weight of cellulose fiber material



- 10 wherein

R^1 independently an alkyl group consisting of 1 to 6 carbon atoms;

R^2 independently an unsaturated or saturated acyl group;

A independently an oxyalkyl radical consisting of at least 3 carbon atoms;

a 1 to 3;

- 15 where the radicals R^2 consist of 60% to 99% (w/w) of unsaturated acyl groups;

B is an anion selected from consisting of chloride, acetate, methyl sulfate, and mixtures thereof;

where the compounds of the formula (I) are biodegradable at a degree of at least 60% according to the OECD 301F method.

- 20 The invention further provides an absorbent material consisting of the debonded cellulose fibers according to the invention.

The invention further provides a process for producing the debonded cellulose fibers according to the invention.

- 25 The invention further provides a method of debonding cellulose fibers using ammonia compounds of the formula (I).

The invention further provides a method of lubricating cellulose fibers using liquid ammonia compounds of the formula (I).

It is an advantage that the inventive compounds of the formula (I) are biodegradable. Another advantage is that the inventive compounds are liquid at room temperature.

- 30 Especially advantageous is that the compounds of the invention allow a dose dependent change of properties, particularly the absorbance and the burst index.

Absorbency is the measure of the ability of a product, and its constituent webs, to absorb quantities of liquid, particularly aqueous solutions or dispersions. Overall absorbency as perceived by the human consumer is generally considered to be a combination of the total quantity of liquid a given mass of tissue paper will absorb at saturation as well as the rate at which the mass absorbs the liquid.

- 5 Debonding is the masking of hydrogen bonds between the individual cellulosic fibers. The tissue formed has finally enhanced flexibility and lubrication between the individual fibers and is not stiff and rough.

The subject-matter provided by the invention is illustratively described herein below without any intention to limit the invention to these illustrative embodiments. Where ranges, general formulae or compound classes are specified herein below, these shall include not just the corresponding ranges or groups of compounds
10 that are explicitly mentioned but also all sub-ranges and sub-groups of compounds which can be obtained by extracting individual values (ranges) or compounds. When documents are cited in the context of the present description, the contents thereof, particularly with regard to the subject-matter that forms the context in which the document has been cited, are considered in their entirety to form part of the disclosure content of the present invention. Unless stated otherwise, percentages are figures in per cent by weight. When
15 average values are reported herein below, the values in question are weight averages, unless stated otherwise. When parameters which have been determined by measurement are reported hereinafter, they have been determined at a temperature of 25°C and a pressure of 101 325 Pa, unless stated otherwise.

Preference is given to quaternary ammonia compounds of formula (I) which are liquid at ambient temperature, preferable have a melting point of melting range between – 20°C to +20°C, more preferable
20 between -10 to + 15°C, particularly preferable between 0 to 10°C.

The advantage of liquid quaternary ammonia compounds of formula (I) is that these compounds are able to penetrate deeper into the cellulose fibers, that they remain liquid even on dry products made of the cellulose fibers thus making these products more flexible and soft. A further advantage is that the energy upload of a hammer mill used for subsequent fiberizing a raw cellulose fiber containing product in order to get a fluff
25 pulp is lowered, thus the temperature of the product within the hammering process is lowered.

Preference is given to quaternary ammonia compounds of formula (I) where R² is preferably independently of one another identical or different acyl radicals of saturated or unsaturated fatty acids.

Preferred fatty acids include 4 up to 40 carbon atoms, more preferably, the fatty acids are unsaturated selected from among palmitoleic acid ((Z)-9-hexadecenoic acid), oleic acid ((Z)-9-hexadecenoic acid),
30 elaidic acid ((E)-9-octadecenoic acid), cis-vaccenic acid ((Z)-11- octadecenoic acid), linoleic acid ((9Z,12Z)-9,12- octadecadienoic acid), alpha-linolenic acid ((9Z,12Z,15Z)-9,12,15-octadecatrienoic acid), gammalinolenic acid ((6Z,9Z,12Z)-6,9,12-octadecatrienoic acid), di-homo-gamma-linolenic acid ((8Z,11Z,14Z)- 8,11,14-eicosatrienoic acid), arachidonic acid ((5Z,8Z,11Z,14Z)-5,8,11,14-eicosatetraenoic acid), erucic acid ((Z)-13-docosenoic acid), nervonic acid ((Z)-15-tetracosenoic acid), ricinoleic acid, and
35 undecenoic acid, and mixtures, such as, for example, rapeseed oil acids, soya fatty acids, sunflower fatty acids, peanut fatty acids and tall oil fatty acids. Especially preferred in this context are radicals of oleic acid.

More especially preferred are the quaternary ammonia compounds of formula (I) which are liquid, and where the acyl radicals are of fatty acid mixtures comprising oleic acid, stearic acid, palmitic acid and gamma-linolenic acid, where these abovementioned fatty acids preferably amount to at least 85% by weight in the fatty acid mixture.

- 5 Especially preferred are the quaternary ammonia compounds according to the invention which are liquid where the acyl radicals of fatty acid mixtures comprise oleic acid at least 70% by weight, preferably at least 75% by weight, more preferably at least 80% by weight, even more preferably at least 85% by weight, particularly preferably at least 90% by weight and especially preferably at least 95% by weight, the sum total of all fatty acids being 100% by weight.

- 10 Preference is given to quaternary ammonia compounds of formula (I) wherein R¹ is independently selected from the group of hexyl, pentyl, n-butyl, i-butyl, n-propyl, i-propyl, ethyl and methyl, especially preferably methyl;

A further advantage of the quaternary ammonia compounds according to the invention is their biodegradability.

- 15 The biodegradability is preferably determined by the OECD 301 F method. More preferably, the biodegradability is determined as specified in 28 d of OECD 301 F.

The quaternary ammonia compounds according to the invention preferably have a biodegradability of at least 60%, even more preferably of at least 70% and especially preferably of at least 75%, the maximum biodegradability value being 100%.

- 20 Preference is given to quaternary ammonia compounds of formula (I) which are miscible with organic solvents, preferably without miscibility gap at ambient temperature, preferable between 0 to 20°C.

Solvents are any non-toxic, non-ecotoxic organic compounds having at least one hydroxyl group, preferably mono hydroxyl aliphatic compounds, di hydroxyl aliphatic compounds, oligo hydroxyl aliphatic compounds which can be oligomeric or polymeric. More preferably the solvents are selected from alcohols, glycols, oligo
25 or poly oxyalkylene compounds, more preferably selected from or poly oxypropylene compounds, further more preferably selected from poly oxyethylene or poly oxypropylene compounds with Mw 200 to 1000 g/mol, particularly those poly oxyalkoxylenes which are terminated on one end with an unsaturated fatty acid as defined above.

- 30 Preferably the solvents according to the invention are biodegradable wherein biodegradable is understood as before mentioned.

- Miscibility in the context of the invention is understood to mean the quaternary ammonia compounds of formula (I) having a solubility of at least 10 g/l, preferably at least 20 g/l, 50 g/l, 100 g/l and especially preferably of at least 150 g/l solvent at a temperature of 20°C. The upper solubility limit is preferably up to and including 900 g/l, more preferably 800 g/l, 700 g/l and especially preferably up to and including 600 g/l
35 solvent at 20°C. Determining the solubility is comprehensible to the skilled person, who determines it

preferably according to Regulation EC 440/2008 Part A.6, more preferably by the flask method of Regulation EC 440/2008 Part A.6.

Preference is given to quaternary ammonia compounds of formula (I) where the fatty acid or fatty acid mixture has iodine number between 105 and 130, preferably between 110 and 125.

- 5 Iodine numbers [g of iodine/100 g of sample] are determined by the method of Hanus, known as method DGF C-V 11 a (53) of the German Society for Fats, and arithmetically converted into the molar masses MW_{IN} for the respective fatty acid or fatty acid mixture.

Preference is given to cellulose fiber materials containing 0.02 to 0.3 % by weight of quaternary ammonia compounds of formula (I) based on the dry weight of cellulose fiber material, wherein

- 10 R^1 is independently selected from the group of hexyl, pentyl, n-butyl, i-butyl, n-propyl, i-propyl, ethyl and methyl,, especially preferably methyl;

R^2 independently an unsaturated or saturated acyl group where the radicals R^2 consist of 60% to 99% (w/w) of unsaturated acyl group and where the unsaturated acyl group consist of at least in 70% of oleic acid;

a is 1;

- 15 A is independently $-\text{CH}_2\text{CH}(\text{CH}_3) - \text{O} -$ or $-\text{CH}(\text{CH}_3) \text{CH}_2 - \text{O} -$;

B is MeOSO_3^- .

More preferred are cellulose fiber materials containing 0.02 to 0.3 % by weight of quaternary ammonia compounds of formula (I) based on the dry weight of cellulose fiber material, wherein

R^1 is methyl

- 20 R^2 independently an unsaturated or saturated acyl group with a iodine number between 105 and 130, preferably between 110 and 125;

a is 1;

A is independently $-\text{CH}_2\text{CH}(\text{CH}_3) - \text{O} -$ or $-\text{CH}(\text{CH}_3) \text{CH}_2 - \text{O} -$;

B is MeOSO_3^- .

- 25 Particularly preference is given to cellulose fiber materials containing 0.03 to 0.2 % of liquid ammonia compounds of formula (I) based on the dry weight of cellulose fiber material, wherein R^1 is Methyl, R^2 is oleic acid, a is 1, A is $-\text{CH}_2\text{CH}(\text{CH}_3) - \text{O} -$ or $-\text{CH}(\text{CH}_3) \text{CH}_2 - \text{O} -$, B is MeOSO_3^- ; where the iodine number of R^2 is between 110 and 130; and where the biodegradability is at least 60% according the OECD 301F method.

- 30 Preference is given to cellulose fiber materials selected from paper, tissue paper, paper toweling or non-woven material made of debonded cellulose fibers.

Preference is given to absorbent material with a higher water absorbance as the same material without the use of ammonia compounds of formula (I).

Preference is given to a process for producing debonded cellulose fibers consisting of the steps

- (a) optionally dissolving the ammonia compounds of the formula (I) in a solvent
- 5 (b) diluting the ammonia compounds of the formula (I) in water
- (c) adding the water solution (b) to cellulose fiber materials.

Due to the strong adhesion to the fiber surface ammonia compounds of formula (I) are advantageous because food contamination is prevented,

10 Another advantage of the ammonia compounds of formula (I) is the low surface tension watery solutions, this causes a good penetration into the cellulose fibers.

The quaternary debonder helps to manufacture in a high speed industrial process generating a tissue weight of $< 50 \text{ g/m}^2$, that is mainly used for paper towels or even tissue sheets with a weight of $12\text{-}20 \text{ g/m}^2$ that is typically used as toilet tissue.

15 Examples

Methods and materials

Table 1: test compounds, all products are commercially available and trademarks of Evonik, Germany

entry	tradename	melting range [°C]
ex 1	Adogen® 442	60 - 70
ex 2	REWOQUAT V 10036 ZW (Varisoft 3690)	30 – 50
ex 3	REWOQUAT DEEDMAC	55 – 65
ex 4	REWOQUAT CR 3099	5 – 10 °C

REWOQUAT V 10036 ZW is the active ingredient of Varisoft 3690.

20 Preparation or tissue sheets:

Untreated fluff pulp from a Scandinavian mill was obtained from the high density chest. This fluff pulp was used to form hand sheets with a Rapid Köthen hand sheet former as supplied by Frank PTI using ISO 5269-2. Four hand sheets were made for each experimental condition, including four sheets that were not treated with any debonder. The sheets were then tested for burst index, absorbency, density and softness. The data reported represents the average of each condition. The method for preparing the debonder samples and subsequently treating the fiber used to make hand sheets is as follows.

25 The pulp received was 7.29% (w/w) consistency in water. The consistency needed for preparation of sheets should be 0.18% by weight. In order to achieve this, the water to pulp ratio was using pulp as supplied in

amount of 2.467% and water 97.533% by weight based on the sum of 100% by weight. This was mixed for one hour at 400 rpm with an overhead mixer resulting in a fluff pulp slurry.

The debonders were dissolved in propylene glycol by mixing 40 g of pure debonder in 60 g of propylene glycol. In case of the dialkyldimethyl ammonium chloride (Adogen 442) this compound was melted and then added to warm (T = 50 - 80°C) propylene glycol and held at this temperature until dispersed in water.

These debonder solutions were dispersed in city water using 0.625 g of the above debonder solution in propylene glycol and 99.375 g of city water by mixing this for 90 minutes at 400 rpm resulting in sample A consisting of Adogen 442, sample B consisting of REWOQUAT V 10036 ZW and sample C consisting of the compound according to the invention REWOQUAT CR 3099.

To 3 500 mL of the above fluff pulp slurry different amounts of samples A, B and C were added as indicated in table 2. The dose is based on the use of the above debonder solution in kg per dry weight of the pulp in ton. The resulting concentration is weight of pure debonder base on the weight or dry pulp.

table 2: Definition of the attempts

entry	Debonder dose; [kg/ton]	mL to add	Resulting concentration; [% (w/w)]
1	0	0	0
2	1	6.4	0.04
3	3	19.2	0.12
4	4	25.6	0.16

The resulting mixtures were stirred for 5 minutes at 500 rpm at room temperature.

The preparation of the hand sheets was performed with a Rapid Köthen Sheet Machine (FRANK-PTI) according to the product sheet number 95854 of company FRANK-PTI with some amendments.

The individual steps were carried out manually via the selector switch. At first water was introduced into the forming column. When it has been filled to the 4 liter mark, 800 ml the suspensions of table 1 were added.

When the 7 liter mark was reached, the flow of water was stopped manually and agitation begins under pressure of compressed air. After the agitation was completed, the suspension came to rest for 5 seconds and the draining process started (approximately 20 seconds) by decompression of the suction chamber. The hand sheet was formed on the screen frame.

A carrier board was placed with its smooth side downwards centrally on the wet sheet. Then a couch roll was rolled back and forth over the sheet for a 2-second period without additional pressure, once in each of two directions at right angles to each other. The couch roll had been placed on the edge of the screen but not on the wet sheet. After removing the sheet-forming screen together with the wet sheet and the carrier

board from the supporting screen it was hit with the edge slightly inclined to the horizontal against the silicon rubber underlay releasing the board to which the wet sheet was attached on the underlay.

After placing the round metal plate onto the center of the wet sheet the sheet was peeled from the carrier board and air dried. The hand sheets were further prepared for the tests by storing under controlled climate (72°F, 50% relative humidity) until constant weight.

Properties of the tissue sheets:

Burst testing is performed on the Vantage Tensile Tester (Thwing-Albert Instrument Company, USA) utilizing the Tissue Burst attachment. The lower the burst index, the weaker the test sample, which equates to better debonding.

The sheets were test for water absorbency on a M/K Systems model 251 GATS (Gravimetric Absorption Testing System) instrument which tests Horizontal wicking. This instrument determines rate of absorption and capacity of the test substrate by placing a sample of known weight on a porous plate attached to an instrument and analytical balance. The porous plate is attached to a water reservoir placed on an analytical balance. The instrument measures the rate of absorption and capacity by measuring the quantity and speed of water leaving the reservoir that supplies the porous plate.

The density of the sheets were measured with a Messmer micrometer Model 172M.

The sheets were analyzed for softness using a TSA (Tissue Softness Analyzer) supplied by Emtec Electronic GmbH, Germany. The tissue softness values are expressed as "hand feel". A two point increase in hand feel is considered significant and can be perceived by the average human.

Table 3: results of the property determination

Entry ref table 2	sample	Burst index; [Pa*m ² /g]	Density; [mg/mL]	Absorption Rate; [g/sec]	Hand Feel
0	-	31.7	249.27	2.031	63
1	A	27.7	243.27	1.563	64
1	B	28.8	245.02	1.774	64
1	C	30.2	244.71	2.216	62
2	A	20.3	240.91	1.105	65
2	B	15.5	246.54	1.328	69
2	C	15.5	243.52	1.490	67
3	A	17.9	246.98	1.034	66
3	B	12.8	249.01	1.492	70
3	C	12.7	241.11	1.355	72

The results show the advantage of the compounds of the invention. The burst index is effectively lowered and not only better than the blank but at higher concentrations also better than the compounds of the art.

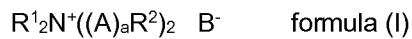
- 5 The density is comparable to those of the art but clearly effectively lowered at high concentrations. The absorption rate is being modified in a wide range.

Table 4: certain eco toxicological data according different OECD methods

method (OECD)	Adogen 442	V 10036	CR 3099	DEEDMAC
Fish; aqua tox (203); 96h; LC50 [mg/L]	10.1	1.8	>10	5.2
Aquatoxicity, invertebrates, <i>Daphnia magna</i> ; (202)48 h; EC50 [mg/L]	0.19	0.105	>8.8	14.8
Biodegradation (301 *)	3% (A)	13% (B)	>60% (F)	>60% (B)

Claims:

1. Cellulose fiber materials containing 0.01 to 0.5 % by weight of ammonia compounds of formula (I)



wherein

R^1 independently an alkyl group consisting of 1 to 6 carbon atoms;

R^2 independently an unsaturated or saturated acyl group;

A independently an oxyalkyl radical consisting of at least 3 carbon atoms;

a 1 to 3;

where the radicals R^2 consist of 60% to 99% (w/w) of unsaturated acyl groups;

B is an anion selected from consisting of chloride, acetate, methyl sulfate, and mixtures thereof;

where the compounds of the formula (I) are biodegradable at a degree of at least 60% according to the OECD 301F method.

2. Cellulose fiber materials according to claim 1 where the ammonia compounds of formula (I) are liquid at ambient temperature, preferably have a melting point of melting range between -20°C to $+20^\circ\text{C}$, more preferably between -10 to $+15^\circ\text{C}$, particularly preferably between 0 to 10°C .

3. Cellulose fiber materials according to any of claims 1 or 2 where the ammonia compounds of formula (I) where R^2 is independently of one another identical or different acyl radicals of saturated or unsaturated fatty acids where preferably, the fatty acids are unsaturated selected from among palmitoleic acid ((Z)-9-hexadecenoic acid), oleic acid ((Z)-9-hexadecenoic acid), elaidic acid ((E)-9-octadecenoic acid), cis-vaccenic acid ((Z)-11-octadecenoic acid), linoleic acid ((9Z,12Z)-9,12-octadecadienoic acid), alpha-linolenic acid ((9Z,12Z,15Z)-9,12,15-octadecatrienoic acid), gamma-linolenic acid ((6Z,9Z,12Z)-6,9,12-octadecatrienoic acid), di-homo-gamma-linolenic acid ((8Z,11Z,14Z)-8,11,14-eicosatrienoic acid), arachidonic acid ((5Z,8Z,11Z,14Z)-5,8,11,14-eicosatetraenoic acid), erucic acid ((Z)-13-docosenoic acid), nervonic acid ((Z)-15-tetracosenoic acid), ricinoleic acid, and undecenoic acid, and mixtures, such as, for example, rapeseed oil acids, soya fatty acids, sunflower fatty acids, peanut fatty acids and tall oil fatty acids.

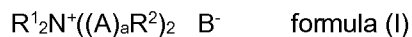
4. Cellulose fiber materials according to any of claims 1 to 3 where the ammonia compounds of formula (I) are liquid where the acyl radicals of fatty acid mixtures comprise oleic acid at least 70% by weight, preferably at least 75% by weight, more preferably at least 80% by weight, even more preferably at least 85% by weight, particularly preferably at least 90% by weight and especially preferably at least 95% by weight, the sum total of all fatty acids being 100% by weight.

5. Cellulose fiber materials according to any of claims 1 to 4 where the ammonia compounds of formula (I) miscible with organic solvents, preferably without miscibility gap at ambient temperature, preferable between 0 to 20°C.

6. Cellulose fiber materials selected from paper, tissue paper, paper toweling or non-woven material made of debonded cellulose fibers according to any of claims 1 to 5.

7. Absorbent material consisting of debonded cellulose fibers according to any of claims 1 to 6.

8. A method of debonding cellulose fibers using ammonia compounds of the formula (I)



wherein

R^1 independently an alkyl group consisting of 1 to 6 carbon atoms;

R^2 independently an unsaturated or saturated acyl group;

A independently an oxyalkyl radical consisting of at least 3 carbon atoms;

a 1 to 3;

where the radicals R^2 consist of 60% to 99% (w/w) of unsaturated acyl groups;

B is an anion selected from consisting of chloride, acetate, methyl sulfate, and mixtures thereof;

where the compounds of the formula (I) are biodegradable at a degree of at least 60% according the OECD 301F method.

9. Method according to claim 8 for improving the softness of cellulose fiber materials.

10. Method according to claim 8 for decreasing the density and/or increasing the porosity of cellulose fiber materials according to claim 4.

11. A method of lubricating cellulose fibers using liquid ammonia compounds of the formula (I).

12. Method according to claim 8 for modifying the absorptive properties of cellulose fiber materials.

13. A process for producing debonded cellulose fibers consisting of the steps

- 5 (a) optionally dissolving the ammonia compounds of the formula (I) in a solvent
 (b) diluting the ammonia compounds of the formula (I) in water
 (c) adding the water solution (b) to cellulose fiber materials.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/054712

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	D21C9/00 D21H17/07	D06M13/463 D21H21/22
	D21H11/16	D21H11/18 D21H11/22
ADD.		
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) D21C D06M D21H		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 415 737 A (PHAN DEAN V [US] ET AL) 16 May 1995 (1995-05-16) the whole document	1-13
X	US 5 981 044 A (PHAN DEAN VAN [US] ET AL) 9 November 1999 (1999-11-09) column 3, line 25 - column 2, line 49; claims	1-13
X	WO 00/77303 A1 (PROCTER & GAMBLE [US]) 21 December 2000 (2000-12-21) page 8, line 5 - page 11, line 14; claims	1-13
☐ 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 another 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 28 April 2017		Date of mailing of the international search report 09/05/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Koegler-Hoffmann, S

INTERNATIONAL SEARCH REPORT

Information on patent family members

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