



(51) International Patent Classification:

C11D 3/42 (2006.01) C11D 3/22 (2006.01)

Published:

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

(21) International Application Number:

PCT/US2017/049069

(22) International Filing Date:

29 August 2017 (29.08.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

16187539.8 07 September 2016 (07.09.2016) EP

(71) Applicant: **THE PROCTER & GAMBLE COMPANY**
[US/US]; One Procter & Gamble Plaza, Cincinnati, Ohio
45202 (US).

(72) Inventors: **PICKERING, Carly**; Procter & Gamble Technical Centres Limited, Whitley Road, Longbenton, Newcastle upon Tyne NE12 9TS (GB). **BROOKER, Alan, Thomas**; Procter & Gamble Technical Centres Limited, Whitley Road, Longbenton, Newcastle upon Tyne NE12 9TS (GB). **SOMERVILLE-ROBERTS, Nigel, Patrick**; Procter & Gamble Technical Centres Limited, Whitley Road, Longbenton, Newcastle upon Tyne NE12 9TS (GB). **URE, Colin**; Procter & Gamble Technical Centres Limited, Whitley Road, Longbenton, Newcastle upon Tyne NE12 9TS (GB).

(74) Agent: **KREBS, Jay A.**; c/o THE PROCTER & GAMBLE COMPANY, Global IP Services, One Procter & Gamble Plaza, C9, Cincinnati, Ohio 45202 (US).

(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, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: USE OF CATIONICALLY MODIFIED POLYSACCHARIDE POLYMER FOR IMPROVED BRIGHTENER DEPOSITION

(57) Abstract: The present invention is the use of a cationically modified polysaccharide for improved brightener deposition.



USE OF CATIONICALLY MODIFIED POLYSACCHARIDE POLYMER FOR IMPROVED BRIGHTENER DEPOSITION

FIELD OF THE INVENTION

5 The present invention is the use of a cationically modified polysaccharide polymer for improved brightener deposition.

BACKGROUND OF THE INVENTION

Optical brighteners have been used in laundry detergent compositions for some time.

10 They make white fabrics appear whiter. Especially as white cotton items are ageing they tend to yellow, a color shift which is compensated through brightener deposition.

An issue with brighteners is achieving sufficient deposition onto fabrics during the wash operation.

In order to get desired brightener deposition onto fabrics during the wash operation it is
15 often necessary to use higher levels of brightener in the laundry detergent composition than is desired on the understanding that a proportion of said brightener will deposit and a proportion will be lost in the wash operation. This is inefficient and costly especially when there is limited formulation space available for detergent ingredients.

Known deposition aids could be used, but these again are inefficient as they take up
20 valuable formulation space that the formulator would prefer to use for ingredients that provide cleaning and fabric care benefits.

Thus, there is a need in the art for improved brightener deposition onto fabrics.

It was surprisingly found that the use of a cationic polysaccharide polymer according to the present invention provided improved brightener deposition. It was also surprisingly found
25 that the use of a cationically modified polysaccharide polymer and a second cellulosic polymer according to the present invention gave even better brightener deposition than with the cationically modified polysaccharide alone. Furthermore, advantageously, the cationically modified polysaccharide and second cellulosic polymers also provided cleaning and/or care benefits to fabrics and did not act solely as deposition aids for the brightener.

30

SUMMARY OF THE INVENTION

The present invention discloses the use of a first polymer to provide deposition of an optical brightener onto fabrics during a wash operation;

wherein the first polymer and the optical brightener are present in a wash liquor during the wash operation; and

wherein the first polymer is a cationically modified polysaccharide.

5 DETAILED DESCRIPTION OF THE INVENTION

Use

The present invention discloses a use of a first polymer to provide deposition of an optical brightener onto fabrics during a wash operation. The first polymer is described in more detail below. The optical brightener is described in more detail below.

10 Those skilled in the art will be aware of suitable wash operations. A fabric wash operation involves washing fabrics in a wash liquor comprising water and other cleaning ingredients. The wash liquor may be prepared as part of a hand wash operation, or as part of an automatic wash operation. In an automatic wash operation the wash liquor is prepared in the drum of an automatic washing machine. The automatic washing machine may be a top loader or
15 a front loader machine.

The first polymer and the optical brightener are present in the wash liquor during the wash operation. They may be added to the wash liquor in any suitable form. For example they may be added as part of a laundry detergent composition, or a laundry care composition. The laundry detergent or care composition may be a liquid, a solid or a mixture thereof. The laundry
20 detergent or care composition may be in the form a water-soluble unit dose article wherein said article comprises a liquid, a solid or a mixture thereof.

Preferably, the use further comprises a second polymer together with the first polymer to provide deposition of an optical brightener onto fabrics during a wash operation. In other words, the present invention may be to the use of a first polymer and a second polymer to provide
25 deposition of an optical brightener on fabrics during a wash operation. In such a use, the first polymer, the second polymer and the brightener are present in the wash liquor. The second polymer is described in more detail below.

Preferably, the first polymer is present at a concentration of between 0.5ppm and 15ppm, preferably between 1ppm and 12ppm, more preferably between 2ppm and 10ppm in the wash
30 liquor.

Preferably, the second polymer is present at a concentration of between 1ppm and 30 ppm, preferably between 1.5ppm and 25ppm, more preferably between 2ppm and 20ppm in the wash liquor.

Preferably, the brightener is present at a concentration of between 1ppm and 15ppm, preferably between 2ppm and 12ppm, more preferably between 3ppm and 10ppm in the wash liquor.

Preferably, the wash liquor comprises less than 300ppm, preferably less than 200ppm, more preferably less than 100ppm, most preferably essentially no fatty acid, neutralised fatty acid or a mixture thereof. Without wishing to be bound by theory, it is believed that lower fatty acid levels results in further improved brightener deposition.

Preferably, the wash liquor comprises less than 200ppm, preferably less than 150ppm, more preferably less than 100ppm, most preferably less than 75ppm of a non-ionic surfactant. The wash liquor may comprise essentially no non-ionic surfactant. The non-ionic surfactant may be selected from a fatty alcohol alkoxylate, an oxo-synthesised fatty alcohol alkoxylate, Guerbet alcohol alkoxylates, alkyl phenol alcohol alkoxylates or a mixture thereof. Preferably, the non-ionic surfactant comprises a fatty alcohol ethoxylate.

The wash liquor may comprise a non-soap anionic surfactant, preferably selected from linear alkylbenzene sulphonate, alkyl sulphate, alkoxylated alkyl sulphate or a mixture thereof.

Preferably, the non-soap surfactant is neutralised with an amine, preferably selected from monoethanolamine, diethanolamine, triethanolamine or a mixture thereof, more preferably monoethanolamine. Preferably the wash liquor comprises from about 100 to about 800ppm, preferably from about 200 to about 600ppm of the amine neutralized linear alkylbenzene sulphonate. Preferably the wash liquor comprises from about 100 to about 600ppm, preferably from about 150 to about 400ppm of the amine neutralized alkyl sulphate, alkoxylated alkyl sulphate, or mixtures thereof. Preferably the wash liquor comprises from about 300 to about 1200ppm, preferably from about 400 to about 1000ppm, more preferably from about 500 to about 800ppm of the total amine neutralized non soap anionic surfactant.

The wash liquor may comprise an adjunct ingredient selected from polymers, builders, dye transfer inhibiting agents, dispersants, enzyme stabilizers, catalytic materials, bleach, bleach activators, polymeric dispersing agents, anti-redeposition agents, suds suppressors, aesthetic dyes, opacifiers, perfumes, perfume delivery systems, structurants, hydrotropes, processing aids, pigments and mixtures thereof.

The wash liquor may be at any suitable temperature. The wash liquor may be at between 5°C and 90°C, preferably between 10°C and 65°C. more preferably between 15°C and 40°C.

First polymer

The first polymer is a cationically modified polysaccharide. Preferably, the first polymer is selected from cationic guar gums, cationic cellulosic polymers, and mixtures thereof, most preferably cationic cellulosic polymers.

5 The cationic guar gum may comprise guar hydroxypropyl trimonium chloride

 Preferably the cationically modified cellulose polymer is selected from cationically modified hydroxyethyl cellulose, cationically modified hydroxypropyl cellulose, cationically and hydrophobically modified hydroxyethyl cellulose, cationically and hydrophobically modified hydroxypropyl cellulose, or a mixture thereof, more preferably cationically modified
10 hydroxyethyl cellulose, cationically and hydrophobically modified hydroxyethyl cellulose, or a mixture thereof.

 By “hydrophobically modified” we herein mean that one or more hydrophobic groups are bound to the polymer. By “cationically modified” we herein mean that one or more cationically charged groups are bound to the polymer.

15 The cationically modified hydroxyethyl cellulose preferably is hydroxyethyl cellulose derivatised with trimethyl ammonium substituted epoxide.

 The first polymer can be synthesized in, and are commercially available in, a number of different molecular weights. In order to achieve optimal softening performance from the product, it is desirable that the cationic polymer used in this invention be of an appropriate molecular
20 weight. Without wishing to be bound by theory, it is believed that polymers that are too high in mass can entrap soils and prevent them from being removed. The use of cationic polymers with an average molecular weight of less than 1,250,000 daltons, or with an average molecular weight of less than 850,000 daltons, and especially those with an average molecular weight of less than 500,000 daltons can help to minimise this effect without significantly reducing the softening
25 performance of properly formulated products. On the other hand, polymers with a molecular weight of about 10,000 daltons or less are believed to be too small to give an effective softening benefit. Therefore the cationic polymer according to the invention preferably has a molecular weight of from about 10,000 daltons to about 1,250,000 daltons, preferably from about 30,000 daltons to about 850,000 daltons, more preferably from about 50,000 daltons to about 750,000
30 daltons, even more preferably from about 100,000 daltons to about 600,000 daltons, most preferably from about 200,000 daltons to about 500,000 daltons.

 The cationic polymers according to the invention may also have a cationic charge density ranging from about 0.1meq/g to about 5meq/g, preferably from about 0.12meq/g to about 4

meq/g, more preferably from about 0.14meq/g to about 2.5 meq/g, even more preferably from about 0.16meq/g to about 1.5 meq/g, most preferably from about 0.18 meq/g to about 0.7 meq/g, at the pH of intended use of the laundry composition. As used herein the “charge density” of the cationic polymers is defined as the number of cationic sites per polymer gram atomic weight (molecular weight), and can be expressed in terms of meq/gram of cationic charge. In general, adjustments of the proportions of amine or quaternary ammonium moieties in the polymer in function of the pH of the liquid laundry formulation in the case of amines, will affect the charge density. Without intending to be bound by theory, cationic polymers with a too high charge density are thought to be too sensitive to precipitate out with anionic compounds in the formulation, while cationic polymers with a too low charge density are thought to have a too low affinity to fabrics, compromising softness accordingly. Any anionic counterions can be used in association with cationic polymers. Non-limiting examples of such counterions include halides (e.g. chlorine, fluorine, bromine, iodine), sulphate and methylsulfate, preferably halides, more preferably chlorine.

The cationic polymer according to the invention might be “hydrophobically modified”. We herein mean that one or more hydrophobic groups are bound to the polymer. Without intending to be bound by theory we believe that hydrophobic modification can increase the affinity of the polymer towards the fabric. Without intending to be limiting, the one or more hydrophobic groups can be independently selected from C₁-C₃₂ preferably C₅-C₃₂ alkyl; C₁-C₃₂ preferably C₅-C₃₂ substituted alkyl, C₅-C₃₂ alkylaryl, or C₅-C₃₂ substituted alkylaryl, (poly)alkoxy C₁-C₃₂ preferably C₅-C₃₂ alkyl or (poly)alkoxy substituted C₁-C₃₂ preferably C₅-C₃₂ alkyl or mixtures thereof. Hydrophobic substitution on the polymer, preferably on the anhydroglucose rings or alternatively on the nitrogen of the cationic substitution of the cationic polymer may range from 0.01% to 5% per glucose unit, more preferably from 0.05% to 2% per glucose unit, of the polymeric material.

Those skilled in the art will be aware of ways to make the first polymer using conventional chemical techniques. The first cationic cellulosic polymer may be lightly cross-linked with a dialdehyde, such as glyoxal, to prevent forming lumps, nodules or other agglomerations when added to water at ambient temperatures.

The first polymers according to the invention include those which are commercially available and further include materials which can be prepared by conventional chemical modification of commercially available materials. Commercially available cationic cellulose polymers according to the invention include those with the INCI name Polyquaternium 10, such

as those sold under the trade names: Ucare Polymer JR 30M, JR 400, JR 125, LR 400 and LK 400 polymers; Polyquaternium 67 such as those sold under the trade name Softcat SK TM, all of which are marketed by Amerchol Corporation, Edgewater NJ; and Polyquaternium 4 such as those sold under the trade name: Celquat H200 and Celquat L-200, available from National

5 Starch and Chemical Company, Bridgewater, NJ. Other suitable polysaccharides include hydroxyethyl cellulose or hydroxypropylcellulose quaternized with glycidyl C₁₂-C₂₂ alkyl dimethyl ammonium chloride. Examples of such polysaccharides include the polymers with the INCI names Polyquaternium 24 such as those sold under the trade name Quaternium LM 200 by Amerchol Corporation, Edgewater NJ. Commercially available guar gums include the N-

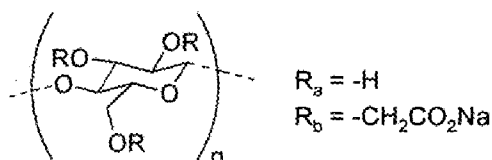
10 HANCE series from the Ashland Corporation.

Second polymer

The second polymer is a cellulosic polymer, preferably wherein the second cellulosic polymer is a carboxymethyl cellulosic polymer. Preferably, the second cellulosic polymer is

15 selected from carboxymethyl cellulose, a hydrophobically modified carboxymethyl cellulose or a mixture thereof. As used herein, the term "celluloses" includes natural celluloses and synthetic celluloses. Celluloses can be extracted from plants or produced by microorganisms.

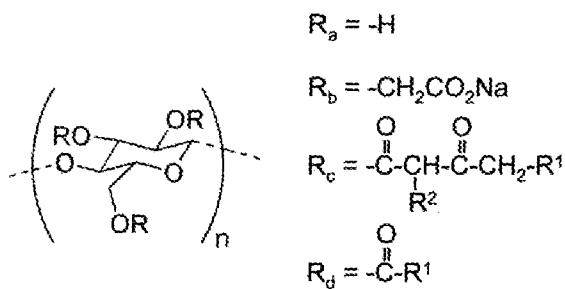
Suitable carboxymethyl cellulose has a structure according to the formula:



20 Cellulose has three groups (R) available for substitution per repeating unit. For carboxymethyl cellulose, each R group will comprise either R_a or R_b with the 'degree of substitution' being defined as the average number of R groups per repeating cellulose unit that comprise R_b. Obviously in the case of carboxymethylcellulose, not all R groups will be R_a. The R_b moiety is the carboxymethyl substituent. The carboxymethyl cellulose has an average degree

25 of carboxymethyl substitution of from 0.3 to 0.9, preferably from 0.4 and preferably to 0.8.

It may be preferred for the carboxymethyl cellulose to be further substituted with a hydrophobic moiety according to the following structure to give a hydrophobically modified carboxymethyl cellulose



wherein, each R group will comprise either R_a , R_b , R_c , or R_d in which R^1 and R^2 are independently selected from alkyl or alkenyl chains having from 5 to 22 carbon atoms. The R_b moiety is the carboxymethyl substituent. Obviously for hydrophobically modified

5 carboxymethylcellulose, at least one R_b group will be present. The R_c and R_d moieties are examples of possible hydrophobic substituents. Alternative hydrophobic substituents will be recognized by persons skilled in the art. The 'degree of carboxymethyl substitution' is defined as the average number of R groups per repeating cellulose unit that comprise R_b . The carboxymethyl cellulose has an average degree of carboxymethyl substitution of from 0.3 to 0.9,

10 preferably from 0.4 and preferably to 0.8. The 'degree of hydrophobic moiety substitution' is defined as the average total number of R groups per repeating cellulose unit that comprise R_c , and/or R_d . Preferably, the average degree of hydrophobic moiety substitution is in the range of from 0.001 to 0.2.

The carboxymethylcellulose preferably has a molecular weight of from 10,000 Da to

15 300,000 Da, preferably from 50,000 Da to 250,000 Da, most preferably from 100,000 Da to 200,000 Da.

In order to further improve the dissolution performance of the carboxymethyl cellulose, it may be preferred for a combination of smaller molecular weight and larger molecular weight carboxymethyl celluloses to be used, typically in such a manner so that a bimodal molecular

20 weight distribution is achieved. Preferably, the carboxymethyl cellulose has a bimodal molecular weight distribution, wherein the first molecular weight modal has a peak in the range of from 10,000 Da to below 100,000 Da, and wherein the second molecular weight modal has a peak in the range of from 100,000 Da to 300,000 Da. Preferably, the first molecular weight modal has a peak in the range of from 20,000 Da or from 30,000 Da, and preferably to 90,000 Da, or to

25 80,000 Da, or to 70,000 Da. Preferably, the second second molecular weight modal has a peak in the range of from 120,000 Da, or from 150,000 Da, and preferably to 250,000 Da, or to 200,000 Da.

It may also be preferred for the carboxymethyl cellulose to have a degree of substitution (DS) in the range of from 0.01 to 0.99 and a degree of blockiness (DB) such that the sum of DS+DB is at least 1.00, preferably at least 1.05, or at least 1.10, or at least 1.15, or at least 1.20, or at least 1.25, or at least 1.30, or at least 1.35, or at least 1.40, or at least 1.45, or at least 1.50.

5 Preferably, the carboxymethyl cellulose has a degree of substitution (DS) in the range of from 0.01 to 0.99 and a degree of blockiness (DB) such that the sum of $DB+2DS-DS^2$ is at least 1.20, or at least 1.25, or at least 1.30, or at least 1.35, or at least 1.40, or at least 1.45, or at least 1.50.

10 Preferably, the carboxymethyl cellulose is a hydrophobically modified carboxymethylcellulose having a degree of substitution (DS) of from 0.01 to 0.99 and a degree of blockiness (DB) such that either $DS+DB$ is of at least 1.00 and/or $DB+2DS-DS^2$ is at least 1.20.

A typical method to determine the degree of substitution (DS) of carboxymethyl cellulose (CMC) is described in more detail below. A typical method to determine the degree of blockiness (DB) of carboxymethyl cellulose (CMC) is described in more detail below.

15 Methods of producing carboxymethyl cellulose are well described in the art.

Various methods of producing hydrophobically modified carboxymethyl cellulose are disclosed in the art.

20 Carboxymethylcellulose polymers include Finnfix GDA (sold by CP Kelco), a hydrophobically modified carboxymethylcellulose, e.g. the alkyl ketene dimer derivative of carboxymethylcellulose sold under the tradename Finnfix SH1 (CP Kelco), or the blocky carboxymethylcellulose sold under the tradename Finnfix V (sold by CP Kelco).

25 Method to determine degree of carboxymethyl substitution (DS) of a carboxymethyl cellulose (CMC): The DS was determined by igniting CMC to ash at high temperature (650°C) for 45 minutes in order to remove all the organic material. The remaining inorganic ashes were dissolved in distilled water and methyl red added. The sample was titrated with 0.1M hydrochloric acid until the solution turned pink. The DS was calculated from the amount of titrated acid (b ml) and the amount of CMC (G g) using the formula below.

$$DS = 0.162 * \{(0.1*b/G) / [1-(0.08*0.1*(b/G))]\}$$

30 Alternatively, the DS of a substituted cellulose may be measured by conductimetry or ¹³C NMR.

Method to determine degree of blockiness (DB) of a carboxymethyl cellulose (CMC): In the case of a substituted cellulose, the DB may correspond to the amount (A) of non-substituted

glucose units released after a specific enzymatic hydrolysis with the commercial endoglucanase enzyme (Econase CE, AB Enzymes, Darmstadt, Germany) divided by the total amount of non-substituted glucose units released after acid hydrolysis (A+B). The enzymatic activity is specific to non-substituted glucose units in the polymer chain that are directly bounded to another non-substituted glucose unit.

The enzymatic degradation is performed using the enzyme (Econase CE) in a buffer at pH 4.8 at 50°C for 3 days. To 25 ml of substituted cellulose sample, 250 mL of enzyme is used. The degradation is stopped by heating the samples to 90°C and keeping them hot for 15 minutes. The acid hydrolysis for both substitution pattern and blockiness is carried out in perchloric acid (15 min in 70% HClO₄ at room temperature and 3 hours in 6.4% HClO₄ at 120°C). The samples are analysed using Anion Exchange Chromatography with Pulsed Amperometric Detection (PAD detector: BioLC50 (Dionex, Sunnyvale, California, USA)). The HPAEC/PAD system is calibrated with ¹³C NMR. The monosaccharides are separated at 35°C using a flow rate of 0.2ml/min on a PA-1 analytical column using 100mM NaOH as eluent with increasing sodium acetate (from 0 to 1M sodium acetate in 30 mins). Each sample is analysed three to five times and an average is calculated. The number of unsubstituted glucose that were directly linked to at least one substituted glucose (A), and the number of unsubstituted glucose that were not directly linked to a substituted glucose (B) are deduced and the DB of the substituted cellulose sample is calculated: $DB = B/(A+B)$.

Method to determine degree of hydrophobic moiety substitution of a hydrophobically modified carboxymethyl cellulose (CMC): The degree of hydrophobically moiety substitution is determined using FT-IR spectroscopy.

Brightener

The brightener is preferably selected from stilbene brighteners, hydrophobic brighteners and mixtures thereof. The brightener may comprise brightener 36, brightener 49, brightener 15 or a mixture thereof, preferably brightener 49.

The brightener may comprise stilbenes, preferably selected from brightener 36, brightener 15 or a mixture thereof. Other suitable brighteners are hydrophobic brighteners, and brightener 49. The brightener may be in micronized particulate form, having a weight average particle size in the range of from 3 to 30 micrometers, or from 3 micrometers to 20 micrometers, or from 3 to 10 micrometers. The brightener can be alpha or beta crystalline form.

Suitable brighteners include: di-styryl biphenyl compounds, e.g. Tinopal® CBS-X, di-amino stilbene di-sulfonic acid compounds, e.g. Tinopal® DMS pure Xtra and Blankophor® HRH, and Pyrazoline compounds, e.g. Blankophor® SN, and coumarin compounds, e.g. Tinopal® SWN.

5 Preferred brighteners are: sodium 2 (4-styryl-3-sulfophenyl)-2H-naphthol[1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl)amino 1,3,5- triazin-2-yl)];amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate, and disodium 4,4'- bis(2-sulfostyryl)biphenyl. A suitable fluorescent brightener is C.I. Fluorescent Brightener 260, which may be used in its beta or alpha
10 crystalline forms, or a mixture of these forms.

EXAMPLES

Test Method :

In order to demonstrate the impact of formulating with a cationically modified
15 hydroxyethyl cellulose to provide improved deposition of an optical brightener onto fabrics a whiteness maintenance full scale test was been conducted. A short cotton cycle at 40°C and 6 gpg water hardness was been selected on a Miele washing machine (model 1714). Total run time was 1 hour 25 minutes. 2.5 kg cotton ballast loads (sourced from Warwick Equest Ltd. Unit 55, Consett Business Park, Consett, County Durham, DH8 6BN) were added together with a soiled
20 load (4 SBL2004 soiled ballast sheets ex wfk Testgewebe GmbH Christenfeld 10. D-41379 Brügggen-Bracht Germany order ref 10996). White fabric bundles (8 in total containing Terry Towel, Knitted Cotton, Flat Cotton, Polycotton and Polyester sourced from Warwick Equest Ltd. Unit 55, Consett Business Park, Consett, County Durham, DH8 6BN) were added to each machine and washed in either reference product only or reference product with the addition of
25 cationically modified hydroxyethyl cellulose. Four wash cycles were carried out, removing soiled ballast sheets each time and adding four more along with the addition of product. After repeating the wash process four times, whiteness bundles were removed and tumble dried in an electric Miele tumble dryer (Novotronic T430) set to “extra dry”.

Fabric tracers were then analysed using a bench-top spectrophotometer Konica – Minolta
30 model CM-3630 which when combined with Polaris White Star software (ex Axiphos GmbH Arend-Braye Str. 42, D-79540 Loerrach, Germany) allows the extraction of reflectance data in the range of 360 -740 nm. In order to determine the impact of cationically modified hydroxyethylcellulose on deposition of optical brightener L a b measurements were taken (The

lightness, L^* , represents the darkest black at $L^* = 0$, and the brightest white at $L^* = 100$. The color channels, a^* and b^* , will represent true neutral grey values at $a^* = 0$ and $b^* = 0$. The red/green opponent colors are represented along the a^* axis, with green at negative a^* values and red at positive a^* values. The yellow/blue opponent colors are represented along the b^* axis, with blue at negative b^* values and yellow at positive b^* values) a more negative b value showing higher light emission in the blue region (420-470nm) which is a function of optical brightening agents as they absorb light in the ultraviolet/violet region (340-370nm) and re-emit in the blue.

Test products:

Table 1. Reference Base;

Reference base	Wt%		Wt%
Monopropylene Glycol	7.4	Amphiphilic graft copolymer	2.54
Glycerol	3.4	Opacifer OP301	3.03
Dipropylene Glycol	10.4	Perfume	2.4
8-METHYL-1-NONANOL PROPOXYLATE-BLOCKETHOXYLATE,HLB 11	6.4	Texcare Soil release polymer	0.3
DPNB glycol ether	7.4	Ethoxylated Polyethylenepolyamine	2.01
C12-14 ALKYL ETHOXYLATE SULPHATE	11.9	Water/ Minors	20.4
Editronic Acid, neutralised	3.06		
Sodium Linear Alkyl Benzene Sulfonate	17.8		
Enzymes	0.1		
Brightener 49 Tinopal® CBS-X	0.34		
Carboxymethyl cellulose	1.0		
Antifoaming Agent	0.12		

Table 2. Premix Composition;

Polypropylene glycol	60wt%
Cationically modified hydroxyethyl cellulose	37wt%
Acusol 880	3wt%

(wt% by weight of the premix composition)

Products Tested

- Composition A: Reference formulation described above; 27g of said product was added directly into the drum of the washing via a plastic weighing boat.
- 5 • Composition 1: 27g of reference formulation added as described above together with cationically modified hydroxyethyl cellulose delivered via the premix detailed above, 0.34g of said premix added directly into the machine with ballast and test items via a plastic weighing boat in addition to the 27g of reference formulation.

Results :

10 Table 3 below shows the L a b* values of the whiteness tracers.

Table 3

	Composition A			Composition 1			Delta 1 vs. A		
	L	a	b*	L	a	b*	dL	da	db*
Terry Towel Fabric	95.59	3.91	<u>-15.09</u>	95.52	4.04	<u>-16.00</u>	-0.07	0.13	-0.92

As can be seen from Table 3, composition 1 shows a more negative b value than composition A. This more negative b value results in brighter fabrics. In other words, the fabrics appear brighter due to increased brightener deposition.

15

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 mm” is intended to mean

20 “about 40 mm.”

CLAIMS

What is claimed is:

1. Use of a first polymer to provide deposition of an optical brightener onto fabrics during a wash operation;
wherein the first polymer and the optical brightener are present in a wash liquor during the wash operation; and
wherein the first polymer is a cationically modified polysaccharide.
2. The use according to claim 1 wherein the use further comprises a second polymer together with the first polymer to provide deposition of an optical brightener onto fabrics during a wash operation and wherein the second polymer is present in the wash liquor and wherein the second polymer is a cellulosic polymer.
3. The use according to claim 1 wherein the first polymer is present at a concentration of between 0.5ppm and 15ppm, preferably between 1ppm and 12ppm, more preferably between 2ppm and 10ppm in the wash liquor.
4. The use according to any preceding claims wherein the second polymer is present at a concentration of between 1ppm and 30 ppm, preferably between 1.5ppm and 25ppm, more preferably between 2ppm and 20ppm in the wash liquor.
5. The use according to any preceding claims wherein the brightener is present at a concentration of between 1ppm and 15ppm, preferably between 2ppm and 12ppm, more preferably between 3ppm and 10ppm in the wash liquor.
6. The use according to any preceding claims wherein the brightener is selected from brightener 49, brightener 15, brightener 36, or a mixture thereof.
7. The use according to any preceding claims wherein the first polymer is selected from a cationically modified polysaccharide, more preferably selected from cationic guar gums, cationic cellulosic polymers, and mixtures thereof, most preferably cationic cellulosic polymers.

8. The use according to claim 7, wherein the first polymer is selected from cationically modified hydroxyethyl cellulose, cationically modified hydroxypropyl cellulose, cationically and hydrophobically modified hydroxyethyl cellulose, cationically and hydrophobically modified hydroxypropyl cellulose, or a mixture thereof, more preferably cationically modified hydroxyethyl cellulose, cationically and hydrophobically modified hydroxyethyl cellulose, or a mixture thereof.
9. The use according to any preceding claims wherein the second polymer is a carboxymethyl cellulosic polymer, preferably, selected from carboxymethyl cellulose, a hydrophobically modified carboxymethyl cellulose or a mixture thereof, more preferably a hydrophobically modified carboxymethylcellulose having a degree of substitution (DS) of from 0.01 to 0.99 and a degree of blockiness (DB) such that either $DS+DB$ is of at least 1.00 and/or $DB+2DS-DS^2$ is at least 1.20.
10. The use according to any preceding claims wherein the wash liquor comprises less than 300ppm, preferably less than 200ppm, more preferably less than 100ppm, most preferably essentially no fatty acid, neutralised fatty acid or a mixture thereof.
11. The use according to any preceding claims wherein the wash liquor comprises less than 200ppm, preferably less than 150ppm, more preferably less than 100ppm, most preferably less than 75ppm of a non-ionic surfactant, preferably wherein the non-ionic surfactant comprises a fatty alcohol ethoxylate.
12. The use according to any preceding claims, wherein the wash liquor comprises a non-soap anionic surfactant, preferably selected from linear alkylbenzene sulphonate, alkyl sulphate, alkoxylated alkyl sulphate or a mixture thereof.
13. The use according to claim 12, wherein the non-soap surfactant is neutralised with an amine, preferably selected from monoethanolamine, diethanolamine, triethanolamine or a mixture thereof, more preferably monoethanolamine.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/049069

A. CLASSIFICATION OF SUBJECT MATTER

INV. C11D3/42 C11D3/22
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)

C11D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/059079 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; LEVER HINDUSTAN LTD [IN]; CHEATER) 30 June 2005 (2005-06-30) page 20, line 12 - page 21, line 10; claims 1-10; example 1 page 30, line 21 - line 25 -----	1-13
A	WO 2010/072627 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN]; BULLEN G) 1 July 2010 (2010-07-01) table 1 -----	1-13
A	US 2011/034365 A1 (LANT NEIL JOSEPH [GB]) 10 February 2011 (2011-02-10) claims 1-15 -----	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

15 November 2017

Date of mailing of the international search report

23/11/2017

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

Richards, Michael

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/049069

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005059079	A1	30-06-2005	AR 046891 A1 28-12-2005
		AU 2004298516 A1 30-06-2005	
		BR PI0417715 A 03-04-2007	
		CA 2549373 A1 30-06-2005	
		CN 1894392 A 10-01-2007	
		EP 1694808 A1 30-08-2006	
		MX PA06006839 A 23-08-2006	
		US 2007203052 A1 30-08-2007	
		WO 2005059079 A1 30-06-2005	
WO 2010072627	A1	01-07-2010	AR 074849 A1 16-02-2011
		BR PI0923571 A2 23-08-2016	
		CN 102257116 A 23-11-2011	
		EP 2366008 A1 21-09-2011	
		ES 2393529 T3 26-12-2012	
		WO 2010072627 A1 01-07-2010	
		ZA 201104027 B 29-08-2012	
US 2011034365	A1	10-02-2011	BR 112012005245 A2 15-03-2016
		CN 102575198 A 11-07-2012	
		EP 2302025 A1 30-03-2011	
		US 2011034365 A1 10-02-2011	
		WO 2011031599 A1 17-03-2011	