

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 December 2006 (07.12.2006)

PCT

(10) International Publication Number
WO 2006/128554 A1

(51) International Patent Classification:

C11D 3/20 (2006.01) *C11D 1/825* (2006.01)
C11D 1/72 (2006.01) *C11D 1/83* (2006.01)

(21) International Application Number:

PCT/EP2006/004345

(22) International Filing Date: 1 May 2006 (01.05.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

0511313.9 3 June 2005 (03.06.2005) GB

(71) Applicant (for AE, AG, AU, BB, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, KE, KN, LC, LK, LS, MN, MW, NA, NG, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London Greater London EC4P 4BQ (GB).

(71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KM, KP, KR, KZ, LR, LT, LU, LV, LY, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NI, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SM, SN, SY, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, Mumbai 400 020 (IN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BOEREFIJN,**

Renee [NL/NL]; Van Linden van den Heuvelsingel 15, 3135 KH Vlaardingen (NL). **CHAPPLE, Andrew, Paul** [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB). **DOMBURG, Bastiaan** [NL/NL]; Unilever R & D Vlaardingen, Olivier Van Noortlaan 120, NL-3133 AT Vlaardingen (NL).

(74) Agents: **BRISTOW, Stephen, Robert** et al.; Unilever Patent Group, Colworth House, Sharnbrook, Bedfordshire MK44 1LQ (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: INCORPORATION OF ANTIOXIDANT IN DETERGENT COMPOSITION

(57) Abstract: A process for incorporation of up to 2% antioxidant into a granular detergent formulation comprising at least 5% organic surfactant, including the steps of: a) dissolving the antioxidant in an organic surfactant selected from the group comprising anionic surfactant, nonionic surfactant and mixtures thereof, provided that the organic surfactant contains less than 5% by weight, preferably less than 3% by weight soap and most preferably is soap free; and b) adding the solution formed in step a) to the detergent formulation and use of the granular laundry detergent composition to confer improved deposition of the antioxidant onto rubber during a wash process.

WO 2006/128554 A1

INCORPORATION OF ANTIOXIDANT IN DETERGENT COMPOSITION

The present invention relates to a process for the incorporation of an antioxidant in a granular detergent
5 composition, especially to the incorporation of BHT in a granular laundry detergent composition.

BHT (2,6 ditert-butyl-4-methyl phenol) is an antioxidant. Anti-oxidants such as BHT or propyl gallate are added to
10 laundry detergent formulations to reduce or prevent the effects of oxidation processes. These effects can manifest themselves during storage or during use of the formulation. Examples of the unwanted effects of oxidation processes are:
15 malodour, discoloration, perfume degradation, deactivation of ingredients such as organic surfactants, bleach, enzymes and change in properties of rubber based materials.

Antioxidants are usually provided as water insoluble, non-dispersible solids. This poses a problem if they are to be
20 dispersed efficiently in wash liquor in order to protect fabrics from oxidative effects. BHT is soluble in ethanol. Use of ethanol in a detergent formulation is not ideal because of the volatility of ethanol.

25 One process used to incorporate BHT in laundry detergent compositions is by co-formulating it with a perfume. However, this is a manufacturing constraint due to the fixed ratio of anti-oxidant to perfume in such a component, which makes it difficult to vary the level of one ingredient
30 independently of the other. This fixed ratio results either in overdosing of one of the ingredients or in a larger

- 2 -

number of the mixed ingredient raw materials having different ratios needing to be stocked. It also has an impact on the types of perfume that may be used to avoid possible interaction of the perfume with the antioxidant; for example, BHT gives unwanted discoloration with some perfumes on storage. Combining antioxidant and perfume in this way may also cause problems for obtaining new sources of perfume. It is therefore desirable to seek other ways to incorporate antioxidants, especially BHT, in laundry detergent formulations.

In WO2005054422 Tinogard® (a BHT derivative) is incorporated into a detergent formation to reduce malodour. The Tinogard® is added to the formulation by premixing it with zeolite.

In WO9606151 BHT was added to a PAS formulation by two alternative processes. In the preferred process, the BHT was added to the base powder in the high-speed mixer/granulator as a non-ionic surfactant/soap/BHT mixture. In the second alternative method it was post dosed in powder form. It was also suggested to add a dispersion or solution of antioxidant to the base powder by dissolving or dispersing it into a nonionic surfactant. Alternatively, the postdosed method may be adapted to form granules on a carrier material with a binder. There is no suggestion to postdose the nonionic variant. This patent application is concerned with the problem of preventing oxidation of PAS at high temperatures during production. Hence, the preference to add the antioxidant to the base powder and to post dose after the antioxidant is present.

- 3 -

In EP 1302 442 a liquid detergent composition containing hydrogen peroxide is stabilised by addition of sterically hindered amines. The compositions may contain surfactant and, in a comparative example, BHT is used. It is added to the liquid composition dissolved in nonionic surfactant (a C₁₃₋₁₅ fatty alcohol ethoxylated with an average of 7 moles of ethylene oxide). The amount of nonionic surfactant added is 0.5wt% of the full composition to deliver 0.02wt% BHT. Thus, the loading of BHT in the nonionic surfactant is 4wt%.

According to the present invention a process for incorporation of up to 2% antioxidant into a granular detergent formulation comprising at least 5% organic surfactant, includes the steps of

- a) dissolving the antioxidant in an organic surfactant selected from the group comprising anionic surfactant, nonionic surfactant and mixtures thereof, provided that the organic surfactant contains less than 5% by weight, preferably less than 3% by weight soap and most preferably is soap free; and
- b) adding the solution formed in step a) to the detergent formulation.

The organic surfactant is preferably water free and highly saturated. The organic surfactant used in step a) advantageously comprises less than 1% free water and furthermore it desirably contains no ethylenic unsaturation.

More preferably, the surfactant is anionic or nonionic. Nonionic surfactants are the most preferred due to these

- 4 -

surfactants being commonly available in a water-free form. Ethoxylated fatty alcohols are the preferred class of nonionic surfactants because of their ability to dissolve up to 40wt% of the antioxidant, particularly BHT. It is
5 advantageous to dissolve at least 20wt% antioxidant into the surfactant so that to get a typical loading of 0.02wt% antioxidant into the granular detergent composition it is necessary to add as little as 0.05 and typically about 0.1wt% of organic surfactant to the powder in the
10 incorporation step. The nonionic surfactant preferably has from 5 to 40 ethylene oxide units. It also preferably has from 8 to 45 carbon atoms in its backbone.

The ratio of surfactant to antioxidant in step a) is in the
15 range 1000:1 to 1:1, preferably 10:1 to 2:1.

The antioxidant is preferably selected from the group comprising BHT and propyl gallate, most preferably BHT.

20 The organic surfactant may be pre-heated to assist in the dissolution of the antioxidant.

Throughout this specification references to antioxidants also include free radical scavengers, except where the
25 context would make this impossible.

Suitable free radical scavengers for use herein include the well-known substituted mono and dihydroxy benzenes and their
analogs, alkyl and aryl carboxylates and mixtures thereof.
30 Preferred such radical scavengers for use herein include di-tert-butyl hydroxy toluene (BHT), hydroquinone, ditert-butyl

- 5 -

hydroquinone, mono-tert-butyl hydroquinone, tert-butyl-hydroxy anisole, benzoic acid, toluic acid, catechol, t-butyl catechol, benzylamine, 1,1,3-tris(2-methyl-4-hydrox-5-t-butylphenyl)butane, n-propyl-gallate or mixtures thereof
5 and highly preferred is di-tert-butyl hydroxy toluene. Such radical scavengers like N-propyl-gallate may be commercially available from Nipa Laboratories under the trade name Nipanox S1®. Radical scavengers when used, are typically present herein in amounts ranging from up to 10% and
10 preferably from 0.001% to 0.5% by weight of the total composition.

The compositions made according to the invention may comprise further antioxidant or mixtures thereof.

15

Suitable further antioxidants to be used herein include organic acids like citric acid, ascorbic acid, tartaric acid, adipic acid and sorbic acid, or amines like lecithin, or amino acids like glutamine, methionine and cysteine, or
20 esters like ascorbil palmitate, ascorbil stearate and triethylcitrate, or mixtures thereof. Preferred antioxidants for use herein are citric acid, ascorbic acid, ascorbil palmitate, lecithin or mixtures thereof.

25 This manufacturing process has been shown to have the benefit of improving the efficacy of the anti-oxidant. Thus it can be used at a lower level to obtain the same efficacy or it can be used at the same level to obtain even better protection of detergent ingredients and laundry.

30

- 6 -

Furthermore, because the antioxidant can be dissolved into the surfactant easily during the detergent formulation manufacturing process, there is no longer the restriction of having to have two components like perfume and anti-oxidant in a fixed ratio. The only restriction is that there should be enough surfactant in the formulation to dissolve all the antioxidant. Typically, for nonionic surfactant, the minimum level is a 2:1 weight excess over the antioxidant although it is possible to dissolve up to 40wt% BHT in some surfactants. It is preferred for the surfactant to be selected from those already present in the formulation. However, an additional surfactant may also be employed. Incorporation of BHT by dissolution in nonionic has been found to give particularly good protection of rubber based materials from catalysed oxidation systems during the wash.

According to a second aspect of the invention there is provided the use of a granular laundry detergent comprising an antioxidant dissolved in ethoxylated nonionic surfactant to confer improved deposition of the antioxidant onto rubber during a wash process.

A preferred process for manufacture of a powdered detergent formulation is to add the antioxidant in a nonionic surfactant by spraying this mixture onto the powder whilst the powder is being mixed. A drum mixer or other suitable process may be used to perform this method of incorporation. Suitable alternative mixers include fluidised beds and double cone mixers.

- 7 -

The granular laundry detergent formulation, or powder, is not limited: provided it contains organic surfactant. It may comprise mixtures of organic surfactants such as anionic and nonionic surfactant. It may comprise builders and other
5 ingredients commonly found in detergent powder formulations. The composition may be low medium or high bulk density and may be produced by any of the processes known in the art.

The invention will now be further described with reference
10 to the following non-limiting examples.

Example 1

BHT was dissolved in a C12-15 fatty alcohol nonionic
15 surfactant ethoxylated with an average of 7 moles of ethylene oxide. It was found possible to dissolve up to 40wt% of BHT in the organic surfactant. In a variant of this procedure it was found easily possible to dissolve 30 wt% of the antioxidant in Synperonic AO5 nonionic
20 surfactant.

Example 2

A 30wt% solution of BHT in nonionic organic surfactant as
25 described in example 1 was sprayed in a drum mixer onto a phosphate built granular detergent composition containing LAS as anionic surfactant in an amount so as to give 0.02wt% of BHT in the finished granular detergent. Because so little nonionic surfactant was added in this way there was
30 no need for any further process operation.

- 8 -

Example 3

Control A: Laundry powder without BHT

Control B: Laundry powder with 0.02% BHT added in perfume

5 Example 4: Laundry powder with 0.02% BHT added in nonionic
surfactant as described in example 2.

The BHT was supplied by Fluka.

Two tests were carried out.

10

Test 1

In this test, we investigated the effect of the method of
incorporation of the BHT on the quantity of BHT found in the
15 wash liquor. This test indicates how well the composition
stores and then disperses the BHT into solution. Analysis
is done by means of ABTS. In each case, the wash liquor is
made up using 6FH water. ABTS reaction times of 15 mins on
solutions were used.

20

The results are shown in table 1 below:

Table 1

Ex	% BHT Nominal	Product dose g/l	% Recovered		
			5 mins	10 mins	20 mins
A	0	8	0	0	0
B	0.02	8	0	48	47
4	0.02	8	63	>98	>98

- 9 -

Comparison of the perfume route (B) with the nonionic route (4) shows much better availability of the BHT in the wash when added via the nonionic. NB that due to solubility constraints the wt% BHT in the perfume could only be about 6
5 wt% maximum. Thus, the amount of spray on needed to be much larger for example B than for example 4.

Test 2

10 For this test, the formulations used for Test 1 were used to wash rubber-based materials eight times each. BHT was then extracted from the material to see how much had been absorbed or deposited during the 8 washes, using the value for Example A as the base line. The results are given in
15 Table 2.

Table 2

Ex.	mMol BHT/kg
A	0
B	0
4	+0.4

20 It can be seen that the most effective process for incorporation is the process according to the invention - example 4. The use of the perfume process is clearly not as effective as the use of nonionic surfactant.

- 10 -

CLAIMS

1. A process for incorporation of up to 2% antioxidant
into a granular detergent formulation comprising at
5 least 5% organic surfactant, including the steps of
 - c) dissolving the antioxidant in an organic
surfactant selected from the group comprising
anionic surfactant, nonionic surfactant and
10 mixtures thereof, provided that the organic
surfactant contains less than 5% by weight,
preferably less than 3% by weight soap and most
preferably is soap free; and
 - d) adding the solution formed in step a) to the
15 detergent formulation.
2. A process as claimed in claim 1 wherein the organic
surfactant used in step a) comprises less than 1% free
water.
20
3. A process as claimed in claim 1 or claim 2 wherein the
organic surfactant used in step a) contains no
ethylenic unsaturation.
- 25 4. A process as claimed in claim 3 wherein the organic
surfactant is a nonionic surfactant.
5. A process as claimed in claim 4 wherein the nonionic
surfactant has from 5 to 40 ethylene oxide units.

- 11 -

6. A process as claimed in claim 5 wherein the nonionic surfactant has from 8 to 45 carbon atoms in its backbone.
- 5 7. A process as claimed in any preceding claim in which the organic surfactant is heated to dissolve the antioxidant.
8. A process as claimed in any preceding claim in which
10 the antioxidant is selected from the group comprising BHT and propyl gallate, preferably BHT.
9. A process as claimed in any preceding claim in which
15 the ratio of surfactant to antioxidant in step a) is in the range 1000:1 to 1:1, preferably 10:1 to 2:1.
10. Use of a granular laundry detergent composition comprising an antioxidant dissolved in ethoxylated nonionic surfactant to confer improved deposition of
20 the antioxidant onto rubber during a wash process.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/004345

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/20 C11D1/72 C11D1/825 C11D1/83

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96/06151 A (UNILEVER PLC; UNILEVER N.V) 29 February 1996 (1996-02-29) cited in the application page 1, lines 6-11 page 7, lines 10-33 claims 1,2,4-9,15; examples	1-10
A	US 3 580 850 A (JEAN DUPRE) 25 May 1971 (1971-05-25) column 6, lines 6-16; claims	1-10

☐ 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 document 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.
- *Z* document member of the same patent family

Date of the actual completion of the international search

21 July 2006

Date of mailing of the international search report

04/08/2006

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Péntek, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2006/004345

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9606151	A	29-02-1996	AU 2983095 A	14-03-1996
			BR 9508807 A	06-01-1998
			CA 2187311 A1	29-02-1996
			CZ 9700530 A3	16-07-1997
			EP 0777715 A1	11-06-1997
			HU 77100 A2	02-03-1998
			PL 318787 A1	07-07-1997
			SK 24097 A3	06-08-1997
			TR 960109 A2	21-06-1996
			ZA 9505934 A	17-01-1997
US 3580850	A	25-05-1971	NONE	