(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
5 February 2009 (05.02.2009)

PCT

(10) **International Publication Number**
WO 2009/016073 A1

(51) **International Patent Classification:**
C08K 5/00 (2006.01) ***C08K 5/134*** (2006.01)

(21) **International Application Number:** PCT/EP2008/059624

(22) **International Filing Date:** 23 July 2008 (23.07.2008)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
60/962,837 1 August 2007 (01.08.2007) US

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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, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, 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, 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, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, 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*

(54) **Title:** LIQUID ANTIOXIDANT MIXTURES

(57) **Abstract:** The present invention provides for liquid antioxidant mixtures of octylated/butylated diphenylamine, phenothiazine and octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate. The antioxidant mixtures are useful for polyurethane stabilization.

WO 2009/016073 A1

Liquid antioxidant mixtures

The present invention is aimed at a liquid mixture of specific antioxidant additives for plastics. The antioxidants are octylated/butylated diphenylamine, phenothiazine and octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate. The liquid antioxidant mixture is useful for the stabilization of polyurethane.

Octylated/butylated diphenylamine is a known antioxidant for a variety of organic materials. This is taught for example in U.S. 4,824,601.

Phenothiazine is a known antioxidant for organic materials.

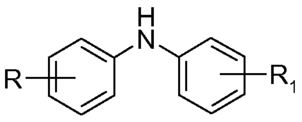
Octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate is a well known phenolic antioxidant for organic materials. This is disclosed for example in U.S. 4,228,297.

Liquid mixtures of antioxidant packages are desirable for plastics manufacturing purposes. Two part mixtures of octylated/butylated diphenylamine and phenothiazine are not stable liquids under ambient conditions. Surprisingly, it has been found that addition of low levels of the further antioxidant octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate allow the mixture to be liquid at certain temperatures.

Disclosed is a liquid antioxidant mixture comprising octylated/butylated diphenylamine, phenothiazine and octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate.

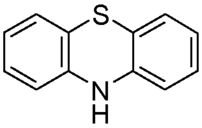
Also disclosed is a method for providing a liquid antioxidant mixture, which method comprises adding octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate to a two part mixture of octylated/butylated diphenylamine and phenothiazine and stirring and optionally heating the mixture.

The preparation of octylated/butylated diphenylamine is disclosed for example in U.S. Pat. No. 4,824,601. It is the reaction product of diphenylamine with diisobutylene (2,4,4-trimethylpentene). The structure is:



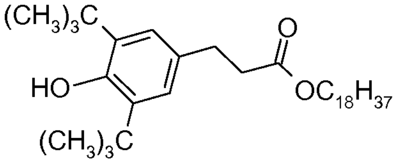
where R and R_1 are independently H, C_4H_9 or C_8H_{17}. This compound mixture is a liquid at room temperature.

Phenothiazine is commercially available, for example from Sigma-Aldrich. It is:



Phenothiazine has a melting point of 182-187°C.

Octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate is:



The preparation of octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate is disclosed in for example U.S. 4,228,297. Octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate has a melting point of 50-55°C.

The three part antioxidant mixtures are liquid for example at ambient temperature and pressure. The mixtures are liquid for example from about 25°C to about 60°C at ambient pressure. The mixtures are liquid for example from about 40°C to about 60°C at ambient pressure.

Ambient conditions are about 25°C and about 1 atmosphere of pressure.

Disclosed is a liquid antioxidant mixture comprising from 74.4 to 79.0 weight percent octylated/butylated diphenylamine, from 3.0 to 3.6 weight percent phenothiazine and from 18.0 to 22.0 weight percent octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate, where the total weight of antioxidants is 100%. Such liquid mixtures are stable at 40°C.

The liquid antioxidant mixture in particular comprises 76.7 weight percent octylated/butylated diphenylamine, 3.3 weight percent phenothiazine and 20.0 weight percent octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate.

Also disclosed is a liquid antioxidant mixture comprising from 84.8 to 87.5 weight percent octylated/butylated diphenylamine, from 3.4 to 4.1 weight percent phenothiazine and from 9.1 to 11.1 weight percent octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate, where the total weight of antioxidants is 100%. Such liquid mixtures are stable at 60°C.

The liquid antioxidant mixture in particular comprises 86.2 weight percent octylated/butylated diphenylamine, 3.8 weight percent phenothiazine and 10.0 weight percent octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate.

Also disclosed is a liquid antioxidant mixture comprising from 89.2 to 91.2 weight percent octylated/butylated diphenylamine, from 3.5 to 4.3 weight percent phenothiazine and from 5.3 to 6.5 weight percent octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate, where the total weight of antioxidants is 100%. Such liquid mixtures are stable at 60°C.

The liquid antioxidant mixture in particular comprises 90.3 weight percent octylated/butylated diphenylamine, 3.9 weight percent phenothiazine and 5.8 weight percent octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate.

The present invention relates also to a process for the stabilization of polyurethanes or their precursors against oxidative, thermal or light-induced degradation which comprises incorporating therein or applying thereto a liquid antioxidant mixture as outlined above.

A further embodiment of the present invention relates to the use of a liquid antioxidant mixture as outlined above for the stabilization of polyurethanes or their precursors against oxidative, thermal or light-induced degradation.

The liquid antioxidant mixture will preferably be added to the polyurethane to be stabilized in concentrations of from 0.0005 to 10 %, preferably 0.001 to 2 %, typically 0.01 to 2 %, based on the weight of the polyurethane.

The liquid antioxidant mixture likewise is used for polyurethane production, especially for preparing flexible polyurethane foams. In this context the liquid antioxidant mixture protects the products against degradation. In particular, scorching during foam production is avoided.

The polyurethanes are obtained from precursors, for example, by reacting polyethers, polyesters and polybutadienes which contain terminal hydroxyl groups with aliphatic or aromatic polyisocyanates.

Polyethers having terminal hydroxyl groups are known and are prepared, for example, by polymerizing epoxides such as ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, styrene oxide or epichlorohydrin with themselves, for example in the presence of BF_3, or by addition reaction of these epoxides, alone or as a mixture or in succession, with starting components containing reactive hydrogen atoms, such as water, alcohols, ammonia or amines, for example ethylene glycol, propylene 1,3- and 1,2-glycol, trimethylolpropane, 4,4'-dihydroxydiphenylpropane, aniline, ethanolamine or ethylenediamine. Sucrose polyethers are also suitable in accordance with the invention. In many cases preference is given to those polyethers which predominantly (up to 90% by weight, based on all the OH groups present in the polyether) contain primary OH groups. Furthermore, polyethers modified by vinyl polymers, as are formed, for example, by polymerizing styrene and acrylonitrile in the presence of polyethers, are suitable, as are polybutadienes containing OH groups.

These compounds generally have molecular weights of 400-10000 and are polyhydroxy compounds, especially compounds containing from two to eight hydroxyl groups, especially those of molecular weight from 800 to 10 000, preferably from 1000 to 6000, for example polyethers containing at least 2, generally 2 to 8, but preferably 2 to 4, hydroxyl groups, as are known per se for the preparation of homogeneous polyurethanes and cellular polyurethanes.

It is of course possible to employ mixtures of the above compounds containing at least two isocyanate-reactive hydrogen atoms, in particular with a molecular weight of 400 - 10 000.

Suitable polyisocyanates are aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates, for example ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-dodecane diisocyanate, cyclobutane 1,3-diisocyanate, cyclohexane 1,3- and -1,4-diisocyanate and also any desired mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane, 2,4- and 2,6-hexahydrotolylene diisocyanate and also any desired mixtures of these isomers, hexahydro-1,3- and/or -1,4-phenylene diisocyanate, perhydro-2,4'- and/or -4,4'-diphenylmethanediisocyanate, 1,3- and 1,4-phenylene diisocyanate, 2,4- and 2,6-tolylene diisocyanate, and also any desired mixtures of these isomers, diphenylmethane 2,4'- and/or -4,4'-diisocyanate, naphthylene 1,5-diisocyanate, triphenylmethane 4,4',4"-triisocyanate, polyphenyl-polymethylene polyisocyanates as are obtained by aniline-formaldehyde condensation followed by phosgenization, m- and p-isocyanatophenylsulfonyl isocyanates, perchlorinated aryl polyisocyanates, polyisocyanates containing carbodiimide groups, polyisocyanates containing allophanate groups, polyisocyanates containing isocyanurate groups, polyisocyanates containing urethane groups, polyisocyanates containing acylated urea groups, polyisocyanates containing biuret groups, polyisocyanates containing ester groups, reaction products of the abovementioned isocyanates with acetals, and polyisocyanates containing polymeric fatty acid radicals.

It is also possible to employ the isocyanate group-containing distillation residues, as they are or dissolved in one or more of the abovementioned polyisocyanates, which are obtained in the course of the industrial preparation of isocyanates. It is additionally possible to use any desired mixtures of the abovementioned polyisocyanates.

Particular preference is given in general to the polyisocyanates which are readily obtainable industrially, for example 2,4- and 2,6-tolylene diisocyanate and any desired mixtures of these isomers ("TDI"), polyphenyl-polymethylene-polyisocyanates as prepared by aniline-formaldehyde condensation followed by phosgenization ("crude MDI"), and polyisocyanates containing carbodiimide, urethane, allophanate, isocyanurate, urea or biuret groups ("modified polyisocyanates").

Examples:

Formulation 1: 115g of octylated/butylated diphenylamine
5g of phenothiazine
30g of octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate

The mixture is stirred with heating. The resultant liquid is stable at 40°C.

Formulation 2: 115g of octylated/butylated diphenylamine
5g of phenothiazine
13.5g of octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate

The mixture is stirred with heating. The resultant liquid is stable at 60°C.

Formulation 3: 115g of octylated/butylated diphenylamine
5g of phenothiazine
7.5g of octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate

The mixture is stirred with heating. The resultant liquid is stable at 60°C.

The term “stable” means that the liquid remains a liquid over a period of at least 4 days at the specified temperature. The liquid does not crystallize upon being subjected to a shock.

The viscosity of Formulation 1 is measured on a Brookfield Viscosity meter, spindle 31.

Tempurature	Speed	Viscosity	Dial	Factor
60°C	30	43	4.3	10
59.9°C	60	43	8.6	5
39.9°C	30	160	16	10
40°C	60	163	32.6	5

What is claimed is:

1. A liquid antioxidant mixture comprising octylated/butylated diphenylamine, phenothiazine and octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate.

2. A liquid antioxidant mixture according to claim 1 comprising from 74.4 to 79.0 weight percent octylated/butylated diphenylamine, from 3.0 to 3.6 weight percent phenothiazine and from 18.0 to 22.0 weight percent octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate, where the total weight of antioxidants is 100%.

3. A liquid mixture according to claim 2 comprising 76.7 weight percent octylated/butylated diphenylamine, 3.3 weight percent phenothiazine and 20.0 weight percent octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate.

4. A liquid mixture according to claim 2 that is stable at 40°C.

5. A liquid antioxidant mixture according to claim 1 comprising from 84.8 to 87.5 weight percent octylated/butylated diphenylamine, from 3.4 to 4.1 weight percent phenothiazine and from 9.1 to 11.1 weight percent octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate, where the total weight of antioxidants is 100%.

6. A liquid antioxidant mixture according to claim 5 comprising 86.2 weight percent octylated/butylated diphenylamine, 3.8 weight percent phenothiazine and 10.0 weight percent octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate.

7. A liquid antioxidant mixture according to claim 5 that is stable at 60°C.

8. A liquid antioxidant mixture according to claim 1 comprising from 89.2 to 91.2 weight percent octylated/butylated diphenylamine, from 3.5 to 4.3 weight percent phenothiazine and from 5.3 to 6.5 weight percent octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate, where the total weight of antioxidants is 100%.

9. A liquid antioxidant mixture according to claim 8 comprising 90.3 weight percent octylated/butylated diphenylamine, 3.9 weight percent phenothiazine and 5.8 weight percent octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate.

10. A liquid antioxidant mixture according to claim 8 that is stable at 60°C.

11. A method for providing a liquid antioxidant mixture, which method comprises adding octadecyl (3,5-di-tert-butyl-4-hydroxyphenyl)-propionate to a two part mixture of octylated/-butylated diphenylamine and phenothiazine and stirring and optionally heating the mixture.

12. A process for the stabilization of polyurethanes or their precursors against oxidative, thermal or light-induced degradation which comprises incorporating therein or applying thereto a liquid antioxidant mixture according to claim 1.

13. Use of a liquid antioxidant mixture according to claim 1 for the stabilization of polyurethanes or their precursors against oxidative, thermal or light-induced degradation.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/059624

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K5/00 C08K5/134

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)
C08K

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 2005/054328 A (CIBA SC HOLDING AG [CH]; MAEDER DIETMAR [DE]; SCHRINNER KERSTIN [SG];) 16 June 2005 (2005-06-16) claims; examples	1-13
A	US 4 228 297 A (HAEBERLI JOERG ET AL) 14 October 1980 (1980-10-14) claims; examples	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

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

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"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

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Date of the actual completion of the international search 22 October 2008	Date of mailing of the international search report 04/11/2008
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 Devriese, Karel

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2008/059624

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005054328 A	16-06-2005	BR PI0417261 A	06-03-2007
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US 4228297 A	14-10-1980	NONE	