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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 August 2010 (12.08.2010)

PCT

(10) International Publication Number
WO 2010/091035 A1

(51) International Patent Classification:
C07C 409/00 (2006.01) *C01B 15/055* (2006.01)

(21) International Application Number:
PCT/US2010/022959

(22) International Filing Date:
3 February 2010 (03.02.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/149,445 3 February 2009 (03.02.2009) US

(71) Applicant *(for all designated States except US)*: **ARKEMA INC.** [US/US]; 2000 Market Street, Philadelphia, Pennsylvania 19103 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **GRAVELLE, Joseph, M.** [US/US]; 308 S. Haverfield Drive, Spring City, Pennsylvania 19475 (US). **KOZEL, Thomas, H.** [US/US]; 626 W. Hoffecker Road, Pottstown, Pennsylvania 19465 (US).

(74) Agents: **BOYD, Steven, D.** et al.; Arkema Inc., 2000 Market Street, Philadelphia, Pennsylvania 19103 (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, BR, BW, BY, BZ, CA, CH, CL, 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, PE, PG, PH, PL, PT, RO, RS, RU, 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, 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, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

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

WO 2010/091035 A1

(54) **Title**: THIXOTROPIC ANHYDROUS SHEAR THINNING PEROXIDE DISPERSIONS

(57) **Abstract**: Provided are dispersions which comprise more than about up to 55 percent by weight or more of an organic peroxide which is normally solid in an anhydrous liquid phase such as dibutyl maleate or dioctyl adipate, with about 5 % by weight or more fumed silica to provide a thixotropic, storage stable organic peroxide paste. Addition of about 5 weight % or more of fumed silica was found to result in the formation of a shear thinning anhydrous dispersion of organic peroxide which was storage stable.

THIXOTROPIC ANHYDROUS SHEAR THINNING PEROXIDE DISPERSIONS

FIELD OF INVENTION

The present invention relates to anhydrous pastes of organic peroxides. The pastes are phthalate free and exhibit thixotropic properties. That is, the pastes are shear thinning so as to be pumpable/pourable when mixed or stirred which makes their handling and use easier.

BACKGROUND

Peroxides have, as a general property, a tendency to be flammable and explosive with some peroxides exhibiting such properties to a greater extent than others. For example, benzoyl peroxide may decompose when dry due to shock, friction, or static electricity. This property carries with it the obvious hazards to the users of these materials as well as to the manufacturers and intermediate handlers thereof. One particularly burdensome aspect of this property occurs during shipment of the peroxides. Accordingly, it has long been an object to provide flame resistant organic peroxide compositions. For example, U.S. Pat. No. 3,507,800 is directed to providing a flame resistant peroxide composition consisting essentially of three components--water, peroxide and solvent wherein the water is at least about 18 percent of the composition.

The safety and end-use advantage provided by water-soluble or water-emulsifiable peroxides is recognized. U.S. Pat. No. 3,825,509 describes a process for the suspension polymerization of vinyl chloride wherein the initiator is an aqueous emulsion of an organic peroxide in which the peroxide is present in an amount up to 19 weight percent. The surfactant used to prepare the aqueous peroxide emulsion is a combination of polyvinyl alcohol and polyoxyethylene sorbitan monolaurate. However, emulsions containing greater than about 19 percent by weight of organic peroxide are described as being too viscous and therefore difficult to handle.

There have been attempts in the past to make peroxide dispersions. U.S. Pat. Nos. 4,039,475 and 4,092,470 disclose stable, pumpable aqueous suspensions of organic peroxides using a mixture of a) nonionic emulsifiers having a maximum HLB value

of 12.5 and b) nonionic emulsifiers having a minimum HLB value of 12.5 or anionic emulsifiers. U.S. Pat. No. 4,734,135 discloses aqueous suspensions of solid organic peroxides using a protective colloid, a surface active agent and water. U.S. Pat. No. 4,440,885 teaches emulsions of a solid organic peroxide using an emulsifier having an HLB value from about 9 to about 20, a hydrocarbon solvent and water.

Organic peroxides are used as initiators in polymerization operations such as for acrylic and polyester polymerizations. The organic peroxides such as benzoyl peroxide are commercially available as solutions/dispersions in phthalates such as dimethyl phthalate and dibutyl phthalate. Due to a perception of toxicity issues with phthalates, there is a current effort to discontinue their use in the production of polymers for certain uses.

SUMMARY OF THE INVENTION

The present invention is direct toward an anhydrous, phthalate free, peroxide paste which exhibits thixotropic properties. The anhydrous, phthalate free, peroxide paste of the present invention allows for the transportation and handling of a peroxide paste having a high concentration of peroxide which paste is shear thinning so it can be easily pumped/poured and is also is resistant to separation upon standing. The anhydrous, phthalate free, peroxide paste of the present invention is a paste of organic peroxide and fumed silica in a liquid phase. The liquid phase could be based upon diesters made from diacids such as C2-C10, saturated or unsaturated, and alcohols ranging from C1 to C10. It was discovered that the addition of anhydrous fumed silica to an anhydrous benzoyl peroxide in dibutyl maleate or dioctyl adipate pastes resulted in an anhydrous paste which was shear thinning, i.e. thixotropic.

DESCRIPTION OF PREFERRED EMBODIMENTS

The anhydrous pastes of the present invention comprises an organic peroxide, which is normally solid, in a phthalate free, liquid phase such as dibutyl maleate or dioctyl adipate the mixture also includes anhydrous fumed silica. By phthalate free, within the scope of the present invention, is meant substantially free of phthalates and that phthalates are not intentional add to the paste. It is intended that phthalate free herein include pastes which contain trace amounts of phthalates.

Exemplary of suitable organic peroxides are aromatic diacyl peroxides, such as benzoyl peroxide, o-methylbenzoyl peroxide, o-methoxybenzoyl peroxide, o-ethoxy benzoyl peroxide, o-chlorobenzoyl peroxide and 2, 4-dichlorobenzoyl peroxide; aliphatic diacyl peroxides, such as decanoyl peroxide, lauroyl peroxide and myristoyl peroxide; ketone peroxides, such as 1-hydroxy cyclohexyl peroxide and 1-hydroperoxycyclohexyl peroxide; aldehyde peroxides such as 1-hydroxy heptyl peroxide; peroxy dicarbonates such as dicetyl peroxydicarbonate, di(4-t-butylcyclohexyl) peroxydicarbonate and acylperoxy alkylcarbonates, such as acetyl peroxy stearyl carbonate and the like.

The pastes of the present invention comprise about 40 percent or more by weight of organic peroxide. One of the features of the present invention is that it enables the preparation of pastes containing about 40 or more percent by weight of organic peroxide which pastes are pumpable because they are shear thinning. Heretofore it has been difficult to make pumpable pastes containing about 40 or more percent by weight organic peroxide. In this description, shear thinning means that viscosity drops as the shear rate increases. Thus, the viscosity of the peroxide pastes of the present invention will drop as the paste is stirred or mixed and it becomes pourable or pumpable easing use.

The organic peroxide is formed into a paste in a liquid phase such as a solvent/plasticizer such as dibutyl maleate or dimethyl maleate. Preferably the paste comprises about 40% and more preferably, 55% by weigh benzoyl peroxide in dibutyl maleate or dioctyl adipate. The organic peroxide paste is mixed with fumed silica in amounts greater than about 5% by weight to provide a thixotropic paste. It was found that when less than 5% of fumed silica was added to a 55 wt % benzoyl peroxide in dibutyl maleate or dioctyl adipate paste, phase separation occurred after a few days. However, when about 5% by weight of fumed silica was added, an extremely viscous paste form which did not separate over time and exhibited thixotropic properties.

The anhydrous, phthalate free peroxide paste of the present invention is formed by simple mixing of the organic peroxide with the liquid phase followed by addition of the fumed silica. The fumed silica is a very light fluffy power which is preferably added in multiple steps, typically three steps, in order to facilitate dispersion of the fumed silica throughout the organic peroxide paste. Upon addition of the full amount

of fumed silica to the organic peroxide paste, the paste is poured into a suitable shipping container where it will thicken. The thickened paste can be easily removed from the container for use by mixing or stirring whereupon it becomes pourable.

The advantageous properties of this invention can be observed by reference to the following examples, which illustrate but do not limit the invention.

EXAMPLES

Example 1

A sample of paste in accordance with the present invention was prepared by combining anhydrous benzoyl peroxide and dibutyl maleate in a high shear mixer. After the peroxide was thoroughly dispersed, fumed silica (AEROSIL® 972 available from Evonik) was slowly added (typically in three portions). The final paste was then mixed in a high shear blender for 30 to 60 seconds. The sample was the placed in a 25°C oven overnight. The following morning, the sample was removed from the oven and stirred vigorously. The viscosity was measured over the following three hours.

Paste Composition:

Dibutyl Maleate	45% by weight
Benzoyl Peroxide	50% by weight
AEROSIL® 972	5% by weight

Apparatus: Brookfield Model DV-II+ Viscometer
Spindle: T-C @ 2 rpm (helipath used)
Temperature: 25°C

Viscosity:

Time (Minutes)	Viscosity (cP)
0	4,500
5	55,000
10	81,500
30	124,500
60	156,000
120	212,000
180	227,000

Example 2

A sample of paste in accordance with the present invention was prepared by combining anhydrous benzoyl peroxide and dioctyl adipate in a high shear mixer. After the peroxide was thoroughly dispersed, fumed silica (AEROSIL® 972 available from Evonik) was slowly added (typically in three portions). The final paste was then mixed in a high shear blender for 30-60 seconds. The viscosity was measured over a two-hour period at 22.5°C (Room Temperature).

Paste Composition:

Dioctyl Adipate	45% by weight
Benzoyl Peroxide	50% by weight
AEROSIL® 972	5% by weight

Apparatus: Brookfield Model DV-II+ Viscometer
Spindle: T-C @ 2 rpm (helipath used)
Temperature: 22.5°C

Experimental results:

Time (Minutes)	Viscosity (cP)
0	2,500
5	20,000
10	31,000
30	44,500
60	56,000
120	67,000

The data in examples 1 and 2 shows that the viscosity of the mixture increased significantly with time after the string is stopped, i.e. the mixture was thixotropic. No phase separation was observed over time in either example.

Having described the invention, we now claim the following and their equivalents.

CLAIMS

What is claimed is:

1. An anhydrous dispersion comprising about 40% by weight or more of an organic peroxide in an anhydrous liquid phase and 5 % by weight or more of fumed silica.

2. The anhydrous dispersion of claim 1 which phthalate free.

3. The anhydrous dispersion of claim 1, wherein said organic peroxide is selected from the group consisting of diacyl peroxides, aliphatic diacyl peroxides, ketone peroxides aldehyde peroxides peroxy dicarbonates, acylperoxy alkylcarbonates and mixtures thereof.

4. The anhydrous dispersion of claim 3, wherein said diacyl peroxides is selected from the group consisting of benzoyl peroxide, o-methylbenzoyl peroxide, o-methoxybenzoyl peroxide, o-ethoxy benzoyl peroxide, o-chlorobenzoyl peroxide and 2, 4-dichlorobenzoyl peroxide.

5. The anhydrous dispersion of claim 3, wherein said aliphatic diacyl peroxides is selected from the group consisting of decanoyl peroxide, lauroyl peroxide and myristoyl peroxide.

6. The anhydrous dispersion of claim 3, wherein said ketone peroxides is selected from the group consisting of 1-hydroxy cyclohexyl peroxide and 1-hydroperoxycyclohexyl peroxide.

7. The anhydrous dispersion of claim 3, wherein said aldehyde peroxides is 1-hydroxy heptyl peroxide.

8. The anhydrous dispersion of claim 3, wherein said peroxy dicarbonates is selected from the group consisting of dicetyl peroxydicarbonate and di(4-t-butylcyclohexyl) peroxydicarbonate.

9. The anhydrous dispersion of claim 3, wherein said acylperoxy alkylcarbonate is acetyl peroxy stearyl carbonate.

10. The anhydrous dispersion of claim 1, wherein said anhydrous liquid phase comprises C2-C10, saturated or unsaturated diesters made from diacids or C1 to C10 alcohols.

11. The anhydrous dispersion of claim 10, wherein said diesters made from diacids is selected from the group consisting of dibutyl maleate and dioctyl adipate.

12. The anhydrous dispersion of claim 1, wherein said anhydrous dispersion comprises about 55% by weight or more of said organic peroxide.

13. A process of imparting thixotropic properties to a phthalate free, anhydrous organic peroxide paste comprising 40% by weight or more of organic peroxide comprising mixing with said paste 5 % by weight or more of fumed silica.

14. The process of claim 13, wherein said organic peroxide is selected from the group consisting of diacyl peroxides, aliphatic diacyl peroxides, ketone peroxides aldehyde peroxides peroxy dicarbonates, acylperoxy alkylcarbonates and mixtures thereof.

15. The anhydrous dispersion of claim 14, wherein said diacyl peroxides is selected from the group consisting of benzoyl peroxide, o-methylbenzoyl peroxide, o-methoxybenzoyl peroxide, o-ethoxy benzoyl peroxide, o-chlorobenzoyl peroxide and 2, 4-dichlorobenzoyl peroxide.

16. The process of claim 14, wherein said aliphatic diacyl peroxides is selected from the group consisting of decanoyl peroxide, lauroyl peroxide and myristoyl peroxide.

17. The process of claim 14, wherein said ketone peroxide is selected from the group consisting of 1-hydroxy cyclohexyl peroxide and 1-hydroperoxycyclohexyl peroxide.

18. The process of claim 14, wherein said aldehyde peroxides is 1-hydroxy heptyl peroxide.

19. The process of claim 14, wherein said peroxy dicarbonates is selected from the group consisting of dicetyl peroxydicarbonate and di(4-t-butylcyclohexyl) peroxydicarbonate.

20. The process of claim 14, wherein said acylperoxy alkylcarbonate is acetyl peroxy stearyl carbonate.

21. The anhydrous dispersion of claim 13, wherein said anhydrous liquid phase comprises a C2-C10, saturated or unsaturated diester made from diacids, a C1 to C10 alcohols or mixtures thereof.

22. The anhydrous dispersion of claim 21, wherein said diester made from diacids is selected from the group consisting of dibutyl maleate and dioctyl adipate.

23. The anhydrous dispersion of claim 13, wherein said anhydrous dispersion comprises about 55% by weight or more of said organic peroxide.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 10/22959

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C07C 409/00; C01B 15/055 (2010.01)
USPC - 252/186.26; 252/186.25
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)
IPC- C07C 409/00; C01B 015/055 (2010.01);
USPC- 252/186.26; 252/186.25

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC- 252/186.26; 252/186.25 (text search)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWest (US Pat, PgPub, EPO, JPO: class, keyword), DialogClassic (Derwent, EPO, JPO, USPTO, WIPO: keyword), GoogleScholar; search terms: anhydride, anhydrous, organic, diacyl, ketone, aldehyde, carbonate, alkyl, acetyl, stearyl, fumed silica, suspension, dispersion, thixotropic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,690,856 A (MILLEVILLE et al.) 25 November 1997 (25.11.1997), col 3, ln 23 to col 5, ln 41; col 6, ln 1-48; col 7, ln 64 to col 8, ln 3	1-23
Y	US 5,632,996 A (RAMIREZ et al.) 27 May 1997 (27.05.1997), col 2, ln 17-20; col 3, ln 14-17; col 3, ln 27-31, col 3, ln 44; col 2, ln 22-25; col 3, ln 5-13	1-23
Y	US 4,387,044 A (SANCHEZ et al.) 07 June 1983 (07.06.1983), col 3, ln 3-6; col 2, ln 60	6, 8, 17, 19
Y	US 2,558,396 A (THOMAS) 26 June 1951 (26.06.1951), col 1, ln 1-38; col 6, ln 31-34	9, 20
A	US 2004/0260111 A1 (VAN DE BOVENKAMP-BOUWMAN et al.) 23 December 2004 (23.12.2004); Table 1; para [0010], [0016], [0023], [0042], [0045]-[0047], [0056], [0057], [0084]	1-23
A	US 2006/0204530 A1 (RAMIREZ et al.) 14 September 2006 (14.09.2006), entire document	1-23
A	US 2005/0281758 A1 (DODD et al.) 22 December 2005 (22.12.2005), entire document	1-23
A	US 2001/0044497 A1 (MYERS) 22 November 2001 (22.11.2001), entire document	1-23

☐ Further documents are listed in the continuation of Box C. ☐

* 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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"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	Date of mailing of the international search report
09 March 2010 (09.03.2010)	19 MAR 2010
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774