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(54) Title: LIQUID STABILIZER MIXTURES

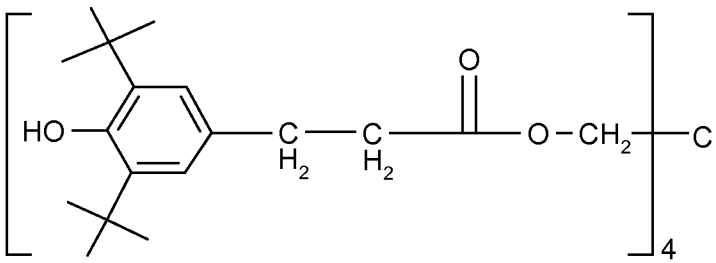
(57) Abstract: The present invention relates to two processes for providing stable liquid blends of a) pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, b) octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and c) tris-(2,4-di-tert-butylphenyl)phosphite. The first process comprises preparing a solid mixture comprising about 2 parts to about 3 parts by weight a), about 2 parts to about 3 parts by weight b) and about 2 parts to about 12 parts by weight c), heating the mixture to 185°C or higher for a sufficient time to obtain a clear liquid blend of a), b) and c), cooling the liquid blend to a temperature of from 90°C to 140°C and maintaining the liquid blend at a temperature of from 90°C to 140°C. The second process comprises preparing a solid mixture comprising about 2 parts to about 3 parts by weight a) and about 2 parts to about 3 parts by weight b), heating the mixture to 90°C or higher for a sufficient time to obtain a clear liquid mixture of a) and b), adding about 2 parts to about 12 parts by weight c) thereto to obtain a clear liquid blend of a), b) and c) and maintaining the liquid blend at a temperature of from 90°C to 140°C. The liquid blends of a), b) and c) are stable at the temperature at which they are maintained for greater than 120 hours.

Liquid Stabilizer Mixtures

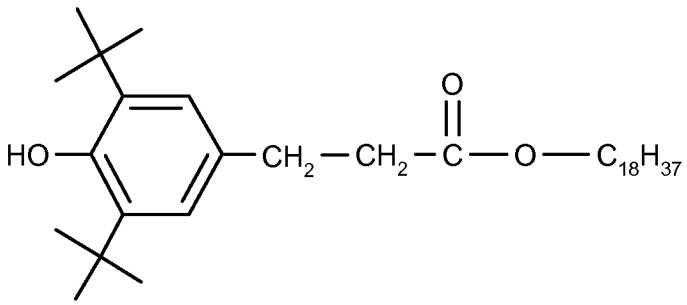
The present invention relates to processes for providing stable liquid blends of a) pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate,
b) octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and
c) tris-(2,4-di-tert-butylphenyl)phosphite. The liquid blends of stabilizers are useful as stabilizers for organic materials, for instance synthetic polymer stabilization.

Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and tris-(2,4-di-tert-butylphenyl)phosphite are well known polymer stabilizers, commercially available as IRGANOX 1010, IRGANOX 1076 and IRGAFOS 168 respectively. IRGANOX 1010 and IRGANOX 1076 are hindered phenolic antioxidants and IRGAFOS 168 is a phosphite processing stabilizer.

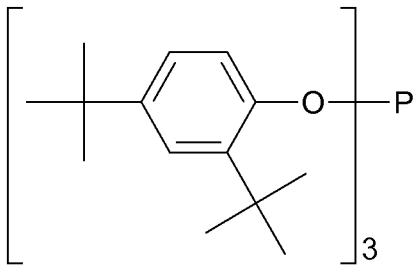
Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, IRGANOX 1010 is:



Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, IRGANOX 1076 is:



Tris-(2,4-di-tert-butylphenyl)phosphite, IRGAFOS 168 is:



The stabilizers are all solids at room temperature. IRGANOX 1010 has a melting point of ca. 120°C. IRGANOX 1076 has a melting point of ca. 56°C. IRGAFOS 168 melts at ca. 185°C.

It would be advantageous for industry to be able to provide a liquid blend of these well known stabilizers. A liquid blend could be pumped to be incorporated into a polymer during melt processing or during solution polymerization. Dosing would be more accurate and incorporation would be easier to perform.

Two processes have now been found for forming a stable liquid blend of a) pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate,
b) octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and
c) tris-(2,4-di-tert-butylphenyl)phosphite.

First process.

Disclosed is a process for forming a stable liquid blend of

a) pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate,
b) octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and
c) tris-(2,4-di-tert-butylphenyl)phosphite,

which process comprises preparing a solid mixture comprising about 2 parts to about 3 parts by weight a), about 2 parts to about 3 parts by weight b) and about 2 parts to about 12 parts by weight c), heating the mixture to 185°C or higher for a sufficient time to obtain a clear liquid blend of a), b) and c), cooling the liquid blend to a temperature of from 90°C to 140°C and maintaining the liquid blend at a temperature of from 90°C to 140°C,

where the liquid blend of a), b) and c) is stable at the temperature at which it is maintained for greater than 120 hours.

Preferably, the process comprises preparing a solid mixture comprising about 5 parts to about 11 parts by weight c).

More preferably, the process comprises preparing a solid mixture comprising about 8 parts to about 11 parts by weight c).

Preferably, the liquid blend of a), b) and c) is maintained at a temperature of from 90°C to 125°C.

More preferably, the liquid blend of a), b) and c) is maintained at a temperature of from 90°C to 110°C.

Second Process.

Further disclosed is a process for forming a stable liquid blend of

a) pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate,
b) octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and

c) tris-(2,4-di-tert-butylphenyl)phosphite,

which process comprises preparing a solid mixture comprising about 2 parts to about 3 parts by weight a) and about 2 parts to about 3 parts by weight b), heating the mixture to 90°C or higher for a sufficient time to form a clear liquid mixture of a) and b), adding about 2 parts to about 12 parts by weight c) thereto to obtain a clear liquid blend of a), b) and c) and maintaining the liquid blend at a temperature of from 90°C to 140°C,

where the liquid blend of a), b) and c) is stable at the temperature at which it is maintained for greater than 120 hours.

Preferably, the process comprises adding about 5 to about 11 parts by weight c) to the liquid mixture of a) and b).

More preferably, the process comprises adding about 8 to about 11 parts by weight c) to the liquid mixture of a) and b).

Preferably, the liquid blend of a), b) and c) is maintained at a temperature from 90°C to 125°C.

More preferably, the liquid blend of a), b) and c) is maintained at a temperature from 90°C to 110°C.

Cooling may be active cooling or allowing slowly to cool at ambient conditions.

Stable means no observed precipitation or solids at a certain temperature for greater than a certain length of time.

Example 1

10 gram samples of IRGANOX 1010/IRGANOX 1076/IRGAFOS 168 are dry mixed and placed in a glass vial in a 200°C oven for half an hour. Clear liquid blends are achieved. The clear liquid blends are then transferred to ovens set at 150°C, 140°C

and 135°C to observe if any precipitation occurs at these temperatures at 24, 48, 72, 96 and 120 hour time periods.

The following results are observed at 120 hours:

Formulation	1	2	3	4	5
IRGANOX 1010 wt.%	9	11	13.8	16	18
IRGANOX 1076 wt.%	22	20	17.2	15	13
IRGAFOS 168 wt.%	69	69	69	69	69
Precipitation Temp. (°C)	>140	>140	<135	<135	<135

Formulations 3-5 are very stable liquid blends. Higher levels of IRGANOX 1010 are advantageous even though its melting point is much higher than IRGANOX 1076.

Example 2

Example 1 is repeated, except that in this case, glass vials containing mixtures of IRGANOX 1010 and IRGANOX 1076 are placed in an oil bath and heated to greater than 90°C to obtain a clear liquid. IRGAFOS 168 is slowly added to the liquid with stirring to obtain a clear liquid blend. The liquid blends are transferred to ovens set at 150°C, 140°C and 135°C to observe if any precipitation occurs at these temperatures at 24, 48, 72, 96 and 120 hour time periods.

Claims

1. A process for forming a stable liquid blend of

a) pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate,
b) octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and
c) tris-(2,4-di-tert-butylphenyl)phosphite,

which process comprises preparing a solid mixture comprising about 2 parts to about 3 parts by weight a), about 2 parts to about 3 parts by weight b) and about 2 parts to about 12 parts by weight c), heating the mixture to 185°C or higher for a sufficient time to obtain a clear liquid blend of a), b) and c), cooling the liquid blend to a temperature of from 90°C to 140°C and maintaining the liquid blend at a temperature of from 90°C to 140°C,

where the liquid blend of a), b) and c) is stable at the temperature at which it is maintained for greater than 120 hours.

2. A process according to claim **1** which comprises preparing a solid mixture comprising about 5 parts to about 11 parts by weight c).

3. A process according to claim **1** which comprises preparing a solid mixture comprising about 8 parts to about 11 parts by weight c).

4. A process according to claim **1** where the liquid blend of a), b) and c) is maintained a temperature of from 90°C to 125°C.

5. A process according to claim **1** where the liquid blend of a), b) and c) is maintained a temperature of from 90°C to 110°C.

6. A process for forming a stable liquid blend of

a) pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate,
b) octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and
c) tris-(2,4-di-tert-butylphenyl)phosphite,

which process comprises preparing a solid mixture comprising about 2 parts to about 3 parts by weight a) and about 2 parts to about 3 parts by weight b), heating the mixture to 90°C or higher for a sufficient time to obtain a clear liquid mixture of a) and b), adding about 2 parts to about 12 parts by weight c) thereto to obtain a clear liquid blend of a), b) and c) and maintaining the liquid blend at a temperature of from 90°C to 140°C,

where the liquid blend of a), b) and c) is stable at the temperature at which it is maintained for greater than 120 hours.

7. A process according to claim **6** which comprises adding about 5 to about 11 parts by weight c) to the liquid mixture of a) and b).

8. A process according to claim **6** which comprises adding about 8 to about 11 parts by weight c) to the liquid mixture of a) and b).

9. A process according to claim **6** where the liquid blend of a), b) and c) is maintained at a temperature from 90°C to 125°C.

10. A process according to claim **6** where the liquid blend of a), b) and c) is maintained at a temperature from 90°C to 110°C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/057501

A. CLASSIFICATION OF SUBJECT MATTER

C08K 5/00(2006.01)i, C08K 5/05(2006.01)i, C08K 5/52(2006.01)i, C08J 3/00(2006.01)i

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 5/00; B32B 1/08; C08K 5/1539; C08F 255/00; B29C 41/04; C08K 5/353; C08F 8/00; C08K 5/53

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: irganox 1010, irganox 1076, irgafos 168, liquid blend, mixture, melt.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2003-0146542 A1 (FATNES, ANNE MARIE et al.) 07 August 2003 See abstract; paragraphs [0001]-[0026]; claims 1-18.	1-10
A	US 2003-0078340 A1 (FATNES, ANNE MARIE et al.) 24 April 2003 See abstract; paragraphs [0001]-[0027]; claims 1-34.	1-10
A	US 2010-0233403 A1 (HO, THOI H. et al.) 16 September 2010 See abstract; paragraphs [0008]-[0013], [0026]-[0035]; claims 1-3.	1-10
A	EP 2163577 A1 (ARMACELL ENTERPRISE GMBH) 17 March 2010 See abstract; paragraphs [0016]-[0056]; claims 1-24.	1-10
A	US 2010-0160509 A1 (YAZDANI-PEDRAM, MEHRDAD et al.) 24 June 2010 See abstract; paragraphs [0011]-[0023], [0028]-[0036]; claims 1-6.	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

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

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"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
26 March 2013 (26.03.2013)	**29 March 2013 (29.03.2013)**
Name and mailing address of the ISA/KR Facsimile No. 82-42-472-7140	Authorized officer KIM, Dong Seok Telephone No. 82-42-481-8647

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2012/057501

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/057501

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