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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 November 2015 (26.11.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/176984 A1

(51) International Patent Classification:
C09D 5/02 (2006.01) *C11D 1/825* (2006.01)
C09G 1/00 (2006.01) *C09G 1/18* (2006.01)
C09G 1/14 (2006.01) *C09K 3/10* (2006.01)
C09G 1/16 (2006.01)

(21) International Application Number:
PCT/EP2015/060345

(22) International Filing Date:
11 May 2015 (11.05.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
14169554.4 23 May 2014 (23.05.2014) EP

(71) Applicant: **BASF SE** [DE/DE]; 67056 Ludwigshafen (DE).

(72) Inventors: **SILVA, Luiz Antonio Martins Da**; 2050 Costa Barros, CEP-03210 São Paulo (BR). **DA SILVA, Juraci Marques**; 2050 Costa Barros St, BL. 03/1603, CEP-03210-001 SPaulo-SP (BR).

(74) Agent: **BERNHARDT, Wolfgang**; BASF Schweiz AG, - IP Department -, P.O. Box, 4002 Basel (CH).

(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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, 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.

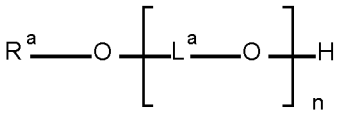
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, 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).

Published:

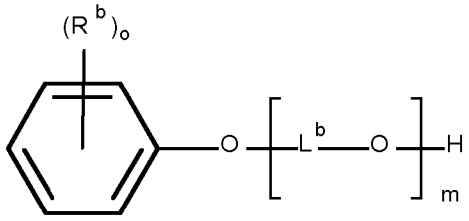
— *with international search report (Art. 21(3))*

WO 2015/176984 A1

(54) Title: MULTI PURPOSE ADDITIVE FOR FLOOR COATING FORMULATION



(A)



(B)

(57) Abstract: The present invention provides blends containing i) a compound of formula (A) or a mixture of compounds of formula (A), wherein R^a is C_{6-30}-alkyl, L^a is C_{2-6}-alkylene, and n is an integer from 1 to 10, and ii) a compound formula (B) or a mixture of compounds of formula (B), wherein R^b is C_{1-10}-alkyl, L^b is C_{2-6}-alkylene, m is an integer from 1 to 12, and o is an integer from 1 to 5, as well as floor coating compositions comprising these blends.

Multi Purpose Additive for Floor Coating Formulation

Description

Floor coating formulations require various additives to guarantee coalescence, leveling, plasticizing, wetting and drying control properties. Tributoxyethyl phosphate (TBEP) is a fire retardant but also a well known plasticizer and leveling agent with a reasonable performance in floor coating formulations. As tributoxyethyl phosphate (TBEP) contains phosphate, it is not welcome in terms of sustainability and eco-efficiency. Therefore, in the last years a lot of efforts have been done by the floor coating formulators to replace TBEP.

US 4,460,734 describes a polymer composition comprising a polyalkoxylated linear aliphatic alcohol as leveling agent and a polymer, usually in form of a water insoluble latex polymer prepared by emulsion polymerisation and dispersed in the aqueous medium. This polymer composition may be used to formulate aqueous polishes, in particular aqueous floor polishes. It is preferred that the linear aliphatic alcohol is polyalkoxylated with at least one compound selected from the group consisting of ethylene oxide, propylene oxide and epichlorohydrin. It is more preferable that the leveling agent is at least one compound selected from the group consisting of polyalkoxylated linear alcohols of formula $CH_3(CH_2)_mO(CH_2CH_2O)_nH$, wherein m and n are integers and n is greater than one. Preferably, m is an integer from 9 to 15, and n is an integer from 2 to 6. The leveling agent may be composed of mixtures of polyalkoxylated linear aliphatic alcohols. In one embodiment it is preferred that the average value of m is about 12.5 and the average value of n is from 2 to 4. It is more preferable that the average value of n is 3. Examples 5, 6 and 7 describe the performance of aqueous floor polishes comprising polyethoxylated linear aliphatic alcohols. Comparative example 3 describes the performance of aqueous floor polishes comprising Triton® X-45, which is ethoxylated octylphenol, having an average number ethylene oxide units of 7 to 8.

JP 6-080933 describes a floor polish composition comprising a polymer, a wax and an adipic ester.

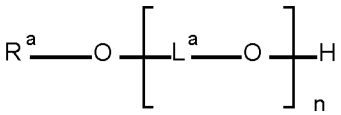
JP 2004-107586 describes a floor polish composition containing (i) R_a-O-$(PO)_m$-$(EO)_n$-H (I) or R_b-C_6H_4-O-$(PO)_m$-$(EO)_n$-H (II), wherein R_a and R_b denote alkenyl or linear or branched alkyl group of 6 to 22 carbon atoms, PO represents a propylenoxide unit, EO represents an ethylene oxide unit, m is 0 to 3 and n is 1 to 8, and (ii) one or more kinds of compounds of formulae (1) to (8). Exemplified is, for example, a floor coating composition comprising (i) a polyoxyethylene lauryl ether, a compound of formula (I), wherein $R_a = C_{12}H_{25}$, m = 0 and n = 3, and (ii) 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, a compound of formula (3).

US 7,378,381 B2 describes floor coating compositions comprising a C_{7-10} aliphatic monocarboxylic acid monoester of a diol, or 2) a C_{7-10} aliphatic monocarboxylic acid monoester or diester of a triol.

It was the object of the present invention to provide an additive suitable for floor coating compositions, which additive shows a well-balanced combination of levelling properties, plasticizing properties and water-spot resistance properties.

The object is solved by blends containing

i) a compound of formula



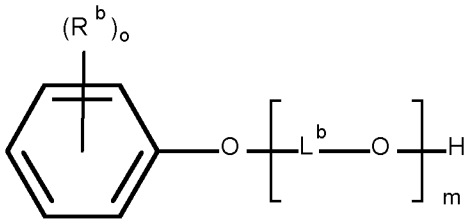
(**A**)

or a mixture of compounds of formula (**A**),

wherein
R^a is C_{6-30}-alkyl,
L^a is C_{2-6}-alkylene, and
n is an integer from 1 to 10,

and

ii) a compound formula



(**B**)

or a mixture of compounds of formula (**B**),

wherein
R^b is C_{1-10}-alkyl,
L^b is C_{2-6}-alkylene,
m is an integer from 1 to 12, and
o is an integer from 1 to 5.

C_{1-3}-alkyl, C_{1-5}-alkyl, C_{1-10}-alkyl, C_{10-15}-alkyl, C_{8-20}-alkyl and C_{6-30}-alkyl can be branched or unbranched. Examples of C_{1-3}-alkyl are methyl, n-ethyl, n-propy and isopropyl. Examples of C_{1-5}-alkyl are C_{1-3}-alkyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl and isopentyl. Examples

of C_{1-10}-alkyl are C_{1-5}-alkyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, 1,1-dimethyl-3,3-dimethylbutyl, n-nonyl and n-decyl. Examples of C_{10-15}-alkyl are n-decyl, n-undecyl, n-dodecyl, n-tridecyl, iso-tridecyl, n-tetradecyl and n-pentadecyl. Examples of C_{8-20}-alkyl are n-octyl, 2-ethylhexyl, 1,1-dimethyl-3,3-dimethylbutyl, n-nonyl, C_{10-15}-alkyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl. Examples of C_{6-30}-alkyl are n-hexyl, n-heptyl, C_{8-20}-alkyl, n-docosyl, n-tetracosyl, n-hexacosyl, n-octacosyl and n-triacontyl.

C_{2-3}-alkylene and C_{2-6}-alkylene can be branched or unbranched. Examples of C_{2-3}-alkylene are ethylene, propylene and (1-methyl)ethylene. Examples of C_{2-6}-alkylene are C_{2-3}-alkylene and butylene, (1-methyl)propylene, (2-methyl)propylene, pentylene and hexylene.

Preferably, R^a is C_{8-20}-alkyl.
More preferably, R^a is C_{10-15}-alkyl.
Most preferably, R^a is n-decyl, n-dodecyl, n- tridecyl, iso- tridecyl, n-tetradecyln or n-pentadecyl.

Preferably, L^a is C_{2-3}-alkylene.
Most preferably L^a is ethylene.

Preferably, n is an integer from 1 to 5.
More preferably, n is an integer from 2 to 4.

Preferably, R^b is C_{1-5}-alkyl.
More preferably, R^b is C_{1-3}-alkyl.
Most preferably, R^b is methyl.

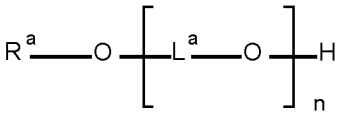
Preferably, L^b is C_{2-3}-alkylene.
More preferably, L^b is C_3-alkylene.
In particular, L^b is (1-methyl)ethylene.

Preferably, m is an integer from 2 to 10.
More preferably, m is an integer from 4 to 8.

Preferably, o is 1 or 2.
More preferably, o is 1.

Preferred blends contain

i) a compound of formula



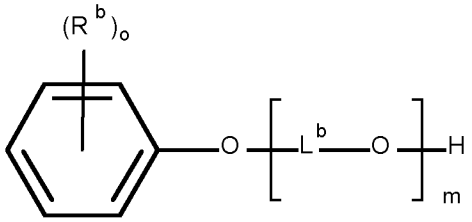
(**A**)

or a mixture of compounds of formula (**A**),

wherein
R^a is C_{8-20}-alkyl,
L^a is C_{2-3}-alkylene, and
n is an integer from 1 to 5,

and

ii) a compound formula



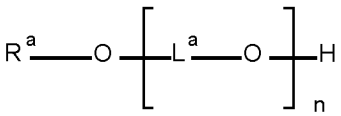
(**B**)

or a mixture of compounds of formula (**B**),

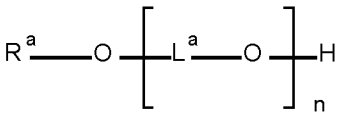
wherein
R^b is C_{1-5}-alkyl,
L^b is C_{2-3}-alkylene,
m is an integer from 2 to 10, and
o is an integer from 1 to 2.

More preferred blends contain

i) a compound of formula



(**A**)



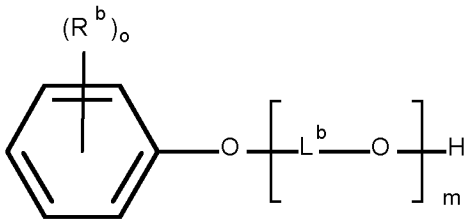
(A)

or a mixture of compounds of formula (A),

wherein
R^a is C_{10-15}-alkyl,
L^a is ethylene, and
n is an integer from 2 to 4,

and

ii) a compound formula



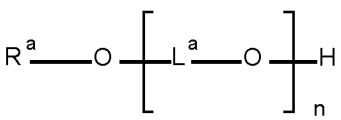
(B)

or a mixture of compounds of formula (B),

wherein
R^b is C_{1-3}-alkyl,
L^b is C_3-alkylene,
m is an integer from 4 to 8, and
o is 1.

Most preferred blends contain

i) a compound of formula



(A)

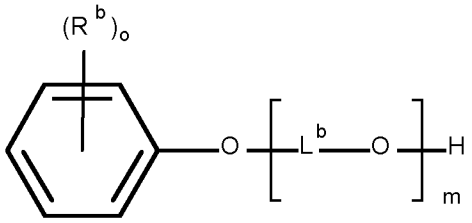
or a mixture of compounds of formula (A),

wherein

R^a is n-decyl, n-dodecyl, n- tridecyl, iso- tridecyl, n-tetradecyln or n-pentadecyl,
L^a is ethylene, and
n is 2 to 4,

and

ii) a compound formula



(B)

or a mixture of compounds of formula (**B**),

wherein
R^b is methyl,
L^b is (1-methy)ethylene,
m is 4 to 8, and
o is 1.

The weight ratio of compound of formula (**A**) or mixtures of compounds of formula (**A**)/compounds of formula (**B**) or mixtures of compounds of formula (**B**) is preferably 20/80 to 80/20, more preferably 30/70 to 70/30, even more preferably 40/60 to 60/40 and most preferably 45/55 to 55/45.

The compounds of formula (**A**) and the compounds of formula (**B**) are commercially available or can be prepared by methods known in the art.

The blends can be prepared by mixing the compound of formula (**A**) or mixtures of compounds of formula (**A**) with compounds of formula (B) or mixtures of compounds of formula (**B**), preferably at a temperature in the range of 25 to 50 °C.

Also part of the present invention are floor coating compositions comprising the inventive blends.

The floor coating compositions usually comprise 0.01 to 10%, preferably 0.5 to 5%, more preferably 1 to 4%, by weight of the blends of the present invention based on the weight of the floor coating composition.

The floor coating composition may comprise additional ingredients such as polymers, waxes, surfactants, anti-foam agents, mineral oils, preservatives and fragrances.

Examples of polymers are acrylic polymers. Examples of waxes are polypropylene-maleic anhydride graft polymers and oxidized polyethylene polymers. Examples of surfactants are fluorosurfactants. Examples of a preservatives are benzoisothiazolinon and mixtures of methylisothiazolinon and chloroisothiazolin.

Preferably, the coating composition comprises the blends of the present invention, polymers, waxes, surfactants, anti-foam agents and preservatives. It is preferred that the coating composition does not comprise alkali soluble resins. The dry mass ratio of polymer/wax is usually between 99/1 to 50/50, preferably between 95/5 to 70/30, more preferably between 90/10 to 85/15.

The pH of the floor coating composition is usually in the range of 8 to 9.

The coating composition may be prepared by mixing the blend of the present invention with the additional ingredients of the coating composition, preferably at a temperature in the range of 25 to 50 °C. After the mixing, the pH of the coating composition may be adjusted, for example using ammonium hydroxide solution.

Also part of the present invention is the use of the blends of the present invention as leveling, plasticizing and water-spot resistance agents in floor coating compositions.

The blends of the present invention show a well-balanced combination of leveling properties, plasticizing properties and water-spot resistance properties.

In particular, the inventive blends 1 to 5 all show at the same time a leveling of at least 4 as determined by ASTM D3153-87, a Pencil Hardness of at least 3H as determined by ASTM D3363-05, a Pendulum Hardness of maximum 32 as determined by DIN EN 1522 (2007) a water-spot resistance of at least 4 as determined by ASTM D1793-92.

Examples

Example 1

Preparation of blends containing at least one compound of formula (**A**) and at least one compound of formula (**B**)

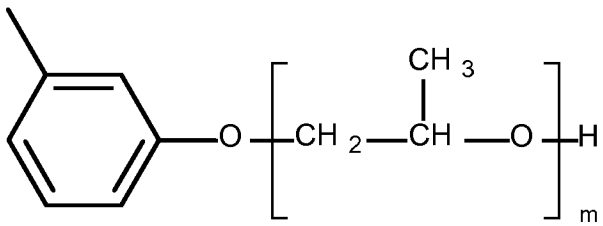
Ingredients	Blend 1[1]	Blend 2[1]	Blend 3[1]	Blend 4[1]	Blend 5[1]
Compound A					
mixture of $C_{13}H_{27}$-O(CH_2CH_2O)$_3$-H (**A1**) and $C_{15}H_{31}$-O(CH_2CH_2O)$_3$-H (**A2**)	50	---	---	25	20
iso-$C_{13}H_{27}$-O(CH_2CH_2O)$_3$-H (**A3**)	---	50	---	---	10
2-propylheptyyl-O(CH_2CH_2O)$_3$-H (**A4**)	---	---	---	---	20
mixture of $C_{12}H_{25}$-O(CH_2CH_2O)$_3$-H (**A5**) and $C_{14}H_{29}$-O(CH_2CH_2O)$_3$-H (**A6**)	---	---	50	25	---
Compound B					
mixture of **B1** and **B2**[2]	---	50	---	---	50
mixture of **B1** and **B2**[2]	50	---	50	50	

Cloud Point[3] [°C]	< 0°C	39	38	33	39

Table 1:

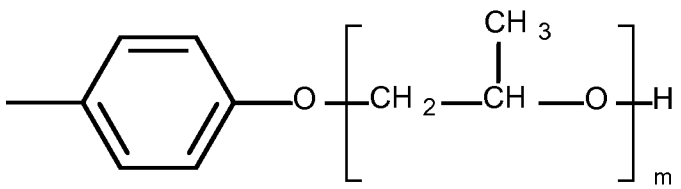
[1]The amount of the compounds **A** and compounds **B** of the blend are given in weight percent based on the weight of the blend.

[2]**B1** and **B2** have following formulae



(**B1**)

and



(**B2**)

wherein m is 4 to 8.

[3]The Cloud Point is determined by DIN EN 1890 (2006) method D (5 g of the blend containing at least one compound of formula (A) and at least one compound of formula (B) + 45 g of diethylene glycol monobutyl ether solution, 250 g/l).

Example 2

Preparation of comparative blends containing at least one compound of formula (A) or at least one compound of formula (B)

Ingredients	Comp. blend 1[1]	Comp. blend 2[1]	Comp. blend 3[1]	Comp. blend 4[1]
Compound A				
mixture of $C_{13}H_{27}$-O(CH_2CH_2O)$_3$-H (**A1**) and $C_{15}H_{31}$-O(CH_2CH_2O)$_3$-H (**A2**)	40	25	---	---
iso-$C_{13}H_{27}$-O(CH_2CH_2O)$_3$-H (**A3**)	20	25	---	---
2-propylheptyl-O(CH_2CH_2O)$_3$-H (**A4**)	40	25	---	---
mixture of $C_{12}H_{25}$-O(CH_2CH_2O)$_3$-H (**A5**) and $C_{14}H_{29}$-O(CH_2CH_2O)$_3$-H (**A6**)	---	25	---	---
Compound B				
Mixture of **B1** and **B2**[2]	---	---	50	70
Mixture of **B1** and **B2**[2]	---	---	50	30
Cloud Point[3] [°C]	38	48	49	24

Table 2. [1,2,3] see Table 1.

Example 3

Preparation of Floor Coating Formulations comprising the blends of example 1, the comparative blends of example 2 or TBEP

The following floor coating formulations comprising the blends of example 1, the comparative blends of example 2 or TBEP are prepared:

Ingredients	Solid content[1]	Amount Ingedient[2]
deionized water	0	42.34
diethylene glycol monoethyl ether	0	4.50
Blends of example 1, comparative blends of example 2[4] or TBEP[3,4]	99.5	2.00
fluorosurfactant	1	1.00
acrylic polymer emulsion	38,5	44.00
oxidized polyethylene homopolymer emulsion	35	3.50

polypropylene – maleic anhydride graft polymer emulsion	40	2.50
antifoam agent (blend of mineral oil, emulsifiers and silica derivatives)	100	0.06
Benzoisothiazolinon	20	0.10

Table 3: [1]The solid content is given in weight percent based on the weight of the ingredient. [2]The amount of the ingredients is given in weight percent based on the weight of the floor coating formulation. [3]TBEP is tributoxyethyl phosphate. [4]The floor coating formulation comprising the blends of example 2 or TBEP are comparative floor coating formulations.

The pH of the floor coating formulation is adjusted to pH 8-9 using ammonium hydroxide solution (25%).

Example 4

Application of the floor coating formulations of example 3 on black PVC composite tiles

The floor coating formulations of example 3 are evaluated on black PVC composite tiles, 0.09 m^2, produced by Fademac. The application rate of the floor coating formulations is 33.3 g/m^2, equivalent to 3 mL of the floor coating formulations applied over the tile per coat

The applied floor coating formulations show the following performance.

Additive	Blend 1	Blend 2	Blend 3	Blend 4	Blend 5
60° Specular Gloss ASTM D-1455-87	83.2	83.4	81.9	82.1	82.4
Powdering ASTM D2048-10	none	none	none	none	none
Levelling ASTM D3153-87	4	4	4	4	4
Recoatability ASTM D3153-87	4	4	3	3	4-5
Water Spot Resistance ASTM D1793-92	4	4	4	4	4
Detergent Resistance ASTM D3207-92	4	3-4	4-5	4-5	4-5
Removability ASTM D1792-06	4	4-5	4-5	4	4
Slip Index, FSC 2000 ASTM D2047-11	0.37	0.38	0.39	0.38	0.43
Pencil Hardness ASTM D3363-05	3H	3H	2H	3H	3H

Pendulum Hardness DIN EN 1522 (2007)	32	29	32	31	28
Freeze/Thaw Stability ASTM D3209-93	UATC[1]	UATC[1]	UATC[1]	UATC[1]	UATC[1]
Accelerated Aging ASTM D1791-93	ok	ok	ok	ok	ok
Non-Volatile Content ASTM D2834-95	20.98	20.61	20.81	20.79	21.41
pH, ASTM E70-07	8.99	9.00	8.63	8.66	9.00
Viscosity LVF (cps) ASTM D2196-10	11	11	11	11	10

Table 4. [1]UATC means unchanged after three cycles.

Additive	**TBEP[2]**	**Comp. Blend 1**	**Comp. Blend 2**	**Comp. Blend 3**	**Comp. Blend 4**
60° Specular Gloss ASTM D-1455-87	82.3	84.6	79.5	82.5	84.3
Powdering ASTM D2048-10	none	none	none	none	none
Levelling ASTM D3153-87	4-5	4	4	3	3- 4
Recoatability ASTM D3153-87	3	5	3-4	4	4-5
Water Spot Resistance ASTM D1793-92	4	3-4	3-4	2-3	3-4
Detergent Resistance ASTM D3207-92	3-4	3-4	4-5	3	4
Removability ASTM D1792-06	4	4	5	4-5	5
Slip Index, FSC 2000 ASTM D2047-11	0.37	0,36	0,39	0,39	0,39
Pencil Hardness ASTM D3363-05	2H	2H	3H	4H	4H
Pendulum Hardness DIN EN 1522 (2007)	36	31	32	29	26
Freeze/Thaw Stability ASTM D3209-93	UATC[1]	UATC[1]	UATC[1]	UATC[1]	UATC[1]
Accelerated Aging ASTM D1791-93	ok	ok	ok	ok	ok

Non-Volatile Content ASTM D2834-95	20.69	20,52	20,54	20,85	20,57
pH, ASTM E70-07	9.06	8,99	8,63	9,01	9,05
Viscosity LVF (cps) ASTM D2196-10	10	10	11	10	11

Table 5. [1]UATC means unchanged after three cycles. [2]TBEP is tributoxyethyl phosphate.

The Pencil Hardness and the Pendulum Hardness describe the plasticizing properties of an additive. The higher the Pencil Hardness and the lower the Pendulum Hardness, the better are the plasticizing properties.

Table 4 shows that the inventive blends 1 to 5 all show at the same time good leveling properties, good plasticizing properties and good water-spot resistance properties. In particular, the inventive blends 1 to 5 all show at the same time a leveling of at least 4 as determined by ASTM D3153-87, a Pencil Hardness of at least 3H as determined by ASTM D3363-05, a Pendulum Hardness of maximum 32 as determined by DIN EN 1522 (2007) and a water-spot resistance of at least 4 as determined by ASTM D1793-92.

The comparative additive tributoxyethyl phosphate (TBEP) shows a high leveling of 4 to 5, and a good water-spot resistance of 4, but the plasticizing properties are very poor. The Pencil Hardness is 2H and the Pendulum Hardness is 36.

The comparative blends 1 and 2 comprising at least one compound of formula **A**, but no compound of formula **B** show a good leveling of 4, but the water-spot resistance is only 3 to 4, and the Pencil Hardness of comparative blend 1 is only 2H.

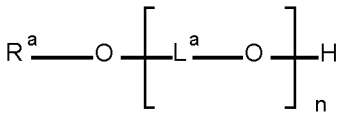
The comparative blends 3 and 4 comprising at least one compound of formula **B**, but no compound of formula **A** show high plasticizing properties, but a poor leveling of 3, respectively, 3 to 4, and a poor water-spot resistance of 3 to 4.

Thus the inventive blends of the present invention show well-balanced leveling, plasticizing and water-spot resistance properties.

Claims

1. Blends containing

i) a compound of formula



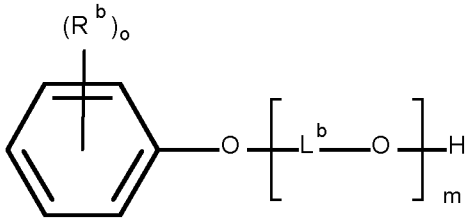
(**A**)

or a mixture of compounds of formula (**A**),

wherein
R^a is C_{6-30}-alkyl,
L^a is C_{2-6}-alkylene, and
n is an integer from 1 to 10,

and

ii) a compound formula



(**B**)

or a mixture of compounds of formula (**B**),

wherein
R^b is C_{1-10}-alkyl,
L^b is C_{2-6}-alkylene,
m is an integer from 1 to 12, and
o is an integer from 1 to 5.

2. The blends of claim 1, wherein
R^a is C_{8-20}-alkyl.

3. The blends of claim 1 or 2, wherein
R^a is C_{10-15}-alkyl and L^a is C_{2-3}-alkylene.

4. The blends of any of claims 1 to 3, wherein
L^a is ethylene.

5. The blends of any of claims 1 to 4, wherein
n is an integer from 2 to 4.

6. The blends of any of claims 1 to 5, wherein
R^b is C_{1-5}-alkyl.

7. The blends of any of claims 1 to 6, wherein
R^b is C_{1-3}-alkyl and L^b is C_{2-3}-alkylene

8. The blends of any of claims 1 to 7, wherein
R^b is methyl and L^b is C_3-alkylene.

9. The blends of any of claims 1 to 8, wherein
m is an integer from 4 to 8.

10. The blends of any of claims 1 to 9, wherein
o is an integer from 1 or 2.

11. The blends of any of claims 1 to 10, wherein
the weight ratio of compound of formula (**A**) or mixtures of compounds of formula (**A**)/compounds of formula (**B**) or mixtures of compounds of formula (**B**) is 30/70 to 70/30.

12. The blends of any of claims 1 to 10, wherein
the weight ratio of compound of formula (**A**) or mixtures of compounds of formula (**A**)/compounds of formula (**B**) or mixtures of compounds of formula (**B**) is 40/60 to 60/40.

13. A floor coating compositions comprising the blends of any of claims 1 to 10.

14. Use of the blends of any of claims 1 to 10 as leveling, plasticizing and water-spot resistance agents in floor coating compositions.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/060345

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/02 C09G1/00 C09G1/14 C09G1/16 C11D1/825
C09G1/18 C09K3/10
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)
C09D C09G C11D C09K

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 A	US 2011/233461 A1 (WASOW GUNTHER [DE] ET AL) 29 September 2011 (2011-09-29) claim 1; example 3	1-5, 10-12 6-9,13, 14
X	CH 464 413 A (STALEY MFG CO A E [US]) 31 October 1968 (1968-10-31) claim 1; example 2; table 1	1-14

☐ 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	Date of mailing of the international search report
17 July 2015	30/07/2015

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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/060345

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