



(43) International Publication Date
5 June 2014 (05.06.2014)

(10) International Publication Number
WO 2014/082981 A1

(51) International Patent Classification:

C08K 3/16 (2006.01) *C08K 5/17* (2006.01)
C08K 3/22 (2006.01) *C08L 71/02* (2006.01)
C08G 65/26 (2006.01) *C08L 95/00* (2006.01)

(21) International Application Number:

PCT/EP2013/074670

(22) International Filing Date:

26 November 2013 (26.11.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12194681.8 28 November 2012 (28.11.2012) EP
61/730,721 28 November 2012 (28.11.2012) US

(71) Applicant: **AKZO NOBEL CHEMICALS INTERNATIONAL B.V.** [NL/NL]; Stationsstraat 77, NL-3811 MH Amersfoort (NL).

(72) Inventors: **HAGBERG, Daniel**; Bergsfoten 1, S-436 40 Askim (SE). **SELSE, Dennis**; Korvettgränd 4, S-471 61 Myggenäs (SE). **JAMES, Alan Duncan**; P.O. Box 4728, Chicago, Illinois 60680 (US).

(74) Agent: **AKZO NOBEL IP DEPARTMENT**; Association No. 485, Velperweg 76, NL-6824 BM Arnhem (NL).

(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, LT, 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, 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))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: A BITUMEN EMULSION CONTAINING POLYALUMINUM COMPOUNDS

(57) Abstract: The invention relates to an additive for a bitumen emulsion, which is a specific mixture of alkoxyiated compounds with low and high amounts of alkylene oxide units, in combination with a polyaluminum compound. Using this additive it is possible to prepare an aqueous slow-setting bitumen emulsion-aggregate mix suitable for cold paving of roads, parking places, sidewalks, and the like.



WO 2014/082981 A1

A BITUMEN EMULSION CONTAINING POLYALUMINUM COMPOUNDS

Field of the invention

5 The present invention relates to the manufacture of an aqueous bitumen-aggregate mix suitable for cold paving of roads, parking places, sidewalks, and the like. The bitumen-aggregate mix is manufactured by mixing aggregate and a bitumen emulsion containing an additive as an emulsifying and cohesion-increasing agent.

Background of the invention

10 Bitumen-in-water emulsions are used for road construction and repair, as well as in the construction industry as coatings and sealers. The asphalt properties are obtained after the emulsions set or cure, when the droplets of bitumen coalesce and adhere to the substrate and water is removed.

15 The rate of this setting process depends on the reactivity of the emulsion and the reactivity of the substrate. Emulsions are classified as rapid, medium and slow-setting types depending on their reactivity. Slow-setting emulsions find use in applications such as cold mix, where the emulsion is mixed with aggregates, and the mixture is used to pave roadways.

20 It is well-known in the art to prepare bitumen emulsions and to mix such emulsions with aggregates. When aggregates and the bitumen emulsion are mixed, the emulsion will "break" due to the attraction between the bitumen droplets and the aggregate surfaces. The bitumen droplets will deposit on the aggregate surfaces and be bonded to the aggregates by the electrostatic action at the interface between the bitumen droplets and the aggregates, and the residual bitumen will recover its macroscopic properties and act as a binder for the material with which it is used. This breaking speed must be adapted to suit the type of application intended for the emulsion. Slow setting emulsions have a slow breaking/setting of the emulsion in contact with aggregate and allow sufficient mixing of the emulsion and aggregate and also paving with these mixtures before it breaks. It is thus desired that the mixture retains a suitable consistency for paving for at least some hours after mixing. In addition, a strong cohesion between the bitumen and the aggregates as well as between the bitumen and the surface paved is advantageous. Further, a dense bitumen coating on the aggregates is desired.

25

30

A variety of amines and polyamines, and ethoxylated and/or quaternised derivatives thereof, has been used or suggested for use as emulsifiers and/or anti-stripping agents in bitumen emulsions.

5 WO 03/048256 relates to a bitumen-based, cold paving/coating formulation comprising water, a cationic bitumen emulsion, at least one first compound selected from the group consisting of alkali metal salts, alkali metal hydroxides, ammonium salts and ammonium hydroxide; and at least one second compound selected from the group consisting of Group IIA salts, Group IIIA salts, Group IIIB salts, copper salts, zinc salts, cadmium salts, manganese salts, iron salts, cobalt salts and nickel salts.

10 JP 58021448 relates to a high-viscosity bitumen emulsion prepared by emulsifying bitumen using an emulsifier composition containing a cationic emulsifier for bitumen and polyaluminum chloride. Among the cationic emulsifiers ethoxylated amines and polyamines are mentioned.

15 However, the bitumen residues (i.e. after curing of the emulsion) from slow-setting emulsions often show poor adhesion to silica-rich aggregates, such as quartzite. The result is poor durability of road materials prepared using these emulsions. Thus there is a need for improved slow-setting emulsion compositions giving a better adhesion of bitumen to the aggregates.

20 **Summary of the invention**

The object of the present invention is to at least partly meet the needs in the art, and to provide a slow-setting bitumen emulsion, where the bitumen residues after curing of the emulsion show good adhesion to aggregates, in particular to silica-rich aggregates.

25 It has now been found that by adding a specific mixture of alkoxyated compounds with low and high amounts of alkyleneoxy units, in combination with a polyaluminum compound, especially polyaluminum chloride (PAC), it is possible to prepare an aqueous slow-setting bitumen emulsion-aggregate mix suitable for cold paving. The bitumen residues from the slow-setting emulsion of the invention show excellent adhesion, notably better than shown by the residues derived from slow-setting cationic emulsions prepared with only amine ethoxylate mixtures. The cold mix asphalt has an
30 open time (i.e. the time interval from the addition of the emulsion to the aggregates, to when the mixture becomes unworkable) of at least two hours and within about 1 week

develops a high cohesion between the bitumen and the surface of the aggregates as well as between the bitumen and the paved surface. It also provides a dense bituminous coating of the solid surfaces.

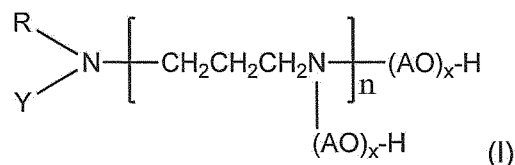
As used in the present invention the term "asphalt" refers to a mixture comprising bitumen and aggregate.

Detailed description of the invention

In a first aspect the invention relates to an additive for a bitumen emulsion containing

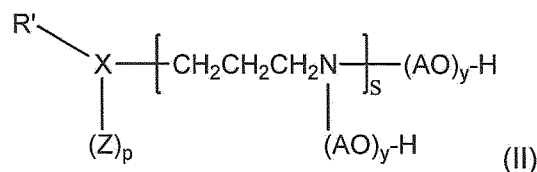
i) a polyaluminum compound, preferably polyaluminum chloride

ii) an alkoxyated amine having the formula



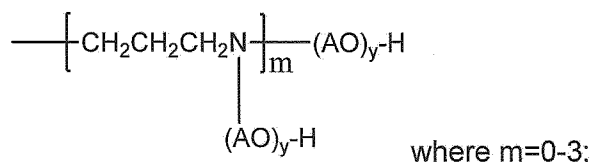
where R is a hydrocarbyl group having at least 10, preferably at least 12, and most preferably at least 14 carbon atoms; and at most 24, preferably at most 22, carbon atoms; $n=0-3$, preferably 0 or 1; each AO is independently ethyleneoxy or propyleneoxy, Y is a hydrocarbyl group having 1-24, preferably 1-4, and most preferably 1 carbon atoms, or a group $(\text{AO})_x\text{H}$; and the sum of all x in (I) is at least 0.5, preferably at least 1, more preferably at least 1.5 and most preferably at least 2, and at most 10, preferably at most 9, more preferably at most 8, even more preferably at most 7, still more preferably at most 6, still more preferably at most 5, still more preferably at most 4 and most preferably at most 3; and

iii) an alkoxyated compound having the formula



where R' is a hydrocarbyl group having at least 8, preferably at least 10, more preferably at least 12, and most preferably at least 14 carbon atoms; and at

most 24, preferably at most 22, carbon atoms; X is N, C(=O)O or O; s=0-3, preferably 0 or 1; p = 0 or 1; provided that when X is N, then p is 1 and when X is C(=O)O or O, then p is 0; and Z is a hydrocarbyl group having 1-24, preferably 1-4, and most preferably 1 carbon atoms, or a group



where each AO independently is ethyleneoxy or propyleneoxy, the sum of all y in (II) is at least 12, preferably at least 14, more preferably at least 20, even more preferably at least 30, still more preferably at least 40, and at most 200, preferably at most 150 and most preferably at most 100; or castor oil that has been alkoxyated with at least 12, preferably at least 14, more preferably at least 20, even more preferably at least 30, still more preferably at least 40, and at most 200, preferably at most 150 and most preferably at most 100 moles of ethyleneoxide and/or propylene oxide oxide per mole of castor oil (III).

In one embodiment, AO in the alkoxyated amine (I) is ethyleneoxy. In another embodiment, AO in the alkoxyated amine (I) is propyleneoxy. In yet another embodiment, both ethyleneoxy units and propyleneoxy units are present in the groups (AO)_x, for example such that from 10 to 90 % of the total number of AO-units in the alkoxyated amine (I) are ethyleneoxy units.

In the alkoxyated compounds (II) and (III), preferably at least 50, more preferably at least 60, even more preferably at least 70, still more preferably at least 80, and most preferably at least 90, or 100% of the total number of AO-units are ethyleneoxy units. The ethyleneoxy and the propyleneoxy units in the groups (AO)_y may be present in any order, such as in random order, or in block arrangement, preferably in poly(PO)-*block*-poly(EO) arrangement.

The additive preferably has a weight ratio ii:iii of from 1:25 to 4:1, preferably 1:20 to 1:1, and most preferably 1:15 to 1:2, and a weight ratio between the polyaluminum

compound and the sum of ii+iii of from 1:30 to 1:2, preferably from 1:20 to 1:5. Water will normally be present in the additive.

5 In a second aspect the invention relates to a bitumen emulsion comprising bitumen, water and the above-mentioned additive.

The emulsion preferably has a pH value below 8.

The bitumen emulsion suitably comprises

10 50-75% (w/w) bitumen
0.002-1.5% (w/w) of a polyaluminum compound, preferably polyaluminum chloride
0.05-3, preferably 0.1-2.5, more preferably 0.3-2.0% (w/w) of ii+iii
0-20, preferably 0-10, and most preferably 0-5% (w/w) of other conventional
15 components and
balance water.

Polyaluminum compounds are based on aluminum, hydroxyl groups and anions, they are termed basic and in aqueous solutions they are polynuclear complexes.
20 Polyaluminum compounds, such as polyaluminum chloride and polyaluminum chloride containing sulfate, are in themselves well-known compounds. As examples of suitable compounds can be mentioned polyaluminum compounds having the general formula $Al_n(OH)_mX_{3n-m}$ wherein X is a negative ion, such as chloride or acetate, and both n and m are positive integers so that $3n-m$ is greater than 0. Preferably $X=Cl^-$ and such
25 polyaluminum compounds are known as polyaluminum chlorides (PAC). Polyaluminum chlorides may be produced by adding base to aluminum chloride until an empirical formula of $Al(OH)_p(Cl)_{3-p}$, suitably with p from 1.0 to 2.5, is obtained. Polyaluminum chlorides can also contain anions from sulfuric acid, phosphoric acid, polyphosphoric acid, chromic acid, dichromic acid, silicic acid, citric acid, carboxylic acids or sulfonic
30 acids. The basicity of polyaluminum compounds of the above given formula is defined as the ratio $m/3n \cdot 100$. The basicity is suitably within the range from 10 to 90% and preferably within the range from 20 to 85%.

To obtain the desired species of polyaluminum compound, the pH of the bitumen emulsion should suitably be below 8, preferably below 7.5, more preferably below 7.0,

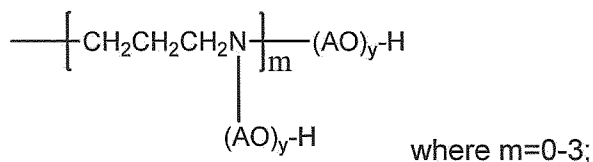
even more preferably below 6.5, still more preferably below 6.0 and most preferably below 5.5. The most preferred pH range for the emulsion is 4.0-5.5.

Acids may also be added to the composition. These acids may be organic or inorganic and monovalent or polyvalent. Examples of organic acids are carboxylic acids, such as formic acid, acetic acid, oxalic acid, malonic acid, tartaric acids, maleic acid, succinic acid, and citric acid. Other organic acids are alkyl esters of phosphoric acid. Examples of inorganic acids are hydrochloric acid, sulfuric acids, ortophosphoric acid, and phosphorous acid. Especially preferred acids are hydrochloric acid, orthophosphoric acid, formic acid, acetic acid and propionic acid.

The alkoxyated amines having formula (I) could be based on mono- or dialkylamines, preferably monoalkylamines, as starting materials, and the hydrocarbyl group(s) could be straight or branched, saturated or unsaturated. Examples of suitable hydrocarbyl groups are decyl, dodecyl, myristyl, cetyl, stearyl, oleyl, coco alkyl, tallow alkyl, tall alkyl, rapeseed alkyl, linseed alkyl, as well as hydrogenated unsaturated hydrocarbyl groups, such as hydrogenated tallow alkyl. The two hydrocarbyl groups of the dialkylamines could be the same or different. The latter compounds are the so-called asymmetrical amines, e.g. alkyl methylamines. Further, the starting amines could be mono- (n=0), di- (n=1), tri- (n=2) or tetraamines (n=3), preferably diamines, such as N-oleyl-aminopropylamine.

The alkoxyated compounds of formula (II) where X is N and p is 1 could be based on the same type of amines as the compounds of formula (I).

When Z is the group



for the sub-group of compounds where m=1-3, the amine is a so-called Y-amine, for example alkoxyated N,N-bis(3-aminopropyl)dodecylamine.

When X in formula (II) is O, p is 0, and the compound is an alkoxyated alcohol (when s=0) or an alkoxyated etheramine (when s=1-3).

When X in formula (II) is C(=O)O, p is 0, and the compound is an alkoxyated carboxylic acid, such as an alkoxyated fatty acid of natural origin. Such a product will normally be a mixture of a monoester between the carboxylic acid and polyalkylene glycol, where alkylene is ethylene or propylene, which compound is encompassed by formula (II), a diester between the acid and polyalkylene glycol, and unesterified polyalkylene glycol.

The above compounds are obtainable by methods well known in the art. For manufacturing of primary fatty amines and polyamines see Chapter "Fatty Amines" in *Kirk Othmer Encyclopedia of Chemical Technology*, Vol. 2, pp. 518-537, electronic edition, published online: Aug. 15, 2003.

The amine compounds of formula (I) and (II) are obtainable by alkoxyating a suitable alkyl amine, dialkylamine, alkyl polyamine, or alkyl Y-amine, such as a primary (fatty alkyl)monoamine, a secondary di(fatty alkyl)monoamine or (fatty alkyl)methylamine, a (fatty alkyl)aminopropyl amine or a (fatty alkyl) Y-triamine.

The number of moles of alkylene oxide reacting with the amine compounds, with the alcohols or with the fatty acids need not be an integer and represents the number average degree of polymerization of the ethylene oxide in the product (see "Nonionic Surfactants: Organic Chemistry" in *Surfactant science series* volume 72, 1998, p 1ff, edited by Nico M. van Os; Marcel Dekker, Inc).

In a third aspect the invention relates to a process for the manufacture of an aqueous bitumen-aggregate mix by

- a) providing a bitumen emulsion as described above; and
- b) mixing said emulsion with aggregate.

In a fourth aspect the invention relates to an aqueous bitumen-aggregate mix comprising

2-40, preferably 2-15, more preferably 2-10% by weight of bitumen emulsion as described above; and

60-98, preferably 85-98, more preferably 90-98% by weight of aggregate.

The bitumen emulsions may be mixed with aggregate in a central plant, whereupon the final mixture is stored before paving, or be mixed with aggregate in a mobile mixer-paver on-site and paved directly. The aggregates may be pre-wetted with water or with water comprising the polyaluminum compound.

5

The aggregate are typically of a solid material, often minerals, such as crushed rock, gravel and sand, blast furnace slag and/or reclaimed asphalt, preferably a densely graded mineral such as granite, limestone, quartzite, and dolomite. The type of aggregates suitable for use in the present invention is sometimes referred to in the art as "construction aggregate". The particle size distribution suitably includes both fines and coarser particles.

10

Suitable kinds of bitumen for use in the present invention are those commonly used in paving of roads, sidewalks, airport runways and parking lots, and in the techniques of cold emulsion mix, slurry seal, microsurfacing, and the like. The bitumen used in the present invention can be petroleum straight asphalt, semiblow asphalt, cut-back asphalt, natural asphalt, petroleum tar, pitch, heavy oil, and a mixture of two or more of these products. The bitumen can also be modified with polymers such as SBS (styrene-butadiene-styrene block copolymer) and EVA (ethylene-vinylacetate copolymer).

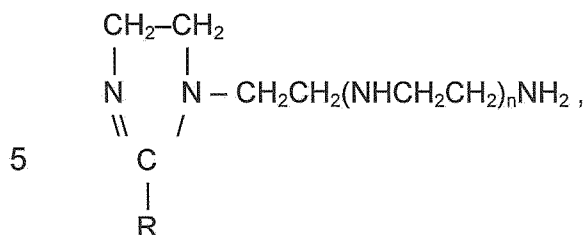
15

20

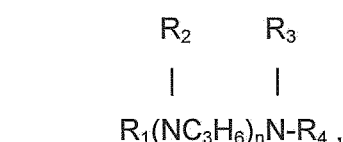
Also other conventional components can be present in the aqueous bitumen-aggregate mix and in the bitumen emulsion. Thus, the bitumen emulsion may contain organic solvents, such as white spirit, RME (rape seed methyl ester) and fuel oil, inorganic salts, such as calcium chloride, stabilizers, such as lignin amine, polysaccharide ethers, e.g. cellulose ethers, or other stabilizing polymers, and other emulsifiers which are nonionic or cationic surfactants containing at least one hydrocarbon group of 6-22 carbon atoms, preferably 8-22 carbon atoms, such as amide compounds, ethyleneoxy-containing amide compounds, acidified amidoamines, ethyleneoxy-containing amidoamines, imidazolines, polyamines, and quaternary ammonium compounds, and mixtures thereof. Specific examples of other emulsifiers are salts between acids, suitably polyvalent acids, such as a polyvalent phosphoric acid, and an imidazoline compound of the formula

25

30



10 wherein R is an alkyl group of 5-21, preferably 7-19 carbon atoms, and n is a number from 0-3; or an amidoamine compound of the formula



20 wherein one or two of the groups R₁, R₂, R₃, and R₄ are an acyl group of 6-22, preferably 8-20 carbon atoms and the remaining groups R₁, R₂, R₃, and R₄ are lower alkyl groups of 1-4 carbon atoms, preferably methyl, hydroxyethyl, hydroxypropyl or hydrogen, and n is a number from 1 to 4, with the proviso that at least one nitrogen atom is part of an amino group.

25 The aqueous bitumen-aggregate mix can also contain an additional organic binder, for example latex, selected from the group consisting of SBR, polychloroprene, and natural latex, and mixtures thereof. The latex can be incorporated into the bitumen emulsion or directly into the mix. It may be necessary to use cationic or nonionic grades of latex compatible with the emulsion, as is well known in the art of emulsion formulation. The latex binder may impart desirable properties to the cured mixture including improved durability. The bitumen aggregate mix can also contain other components such as fibres and pigments.

30

The invention is further illustrated by the working examples below. Comparison examples are marked with an (*)

General procedure

35

The emulsions were produced using a Scanroad Emulsion Plant 0.3R (SEP 0.3R) with an emulsion manufacturing capacity of 3 – 5 kg/minute. It is equipped with temperature

controlled pots for bitumen and water, flow controllers for bitumen and water, controlled speed of the emulsion mill and pressure control of the emulsion production.

5 The CSS screening test consisted of two sets of mixes of aggregate, water and emulsion. One was mixed for 30 seconds (30 s mix) and the other one was mixed for 3 minutes (3 minutes mix).

30s mix was divided in three portions and evaluated with respect to coating, workability and adhesion.

10 Coating test

1/3 of the 30 s mix was spread out on the table and the state of the coated aggregates was visually inspected. By this inspection, the area percentage of the aggregates coated by the bitumen was estimated.

15 Workability test

1/3 of the 30 s mix was placed in a plastic bag and stored over night. The workability was estimated by checking the stiffness of the mix in the bag (1=good workability, not stiff/emulsion unbroken, 3=poor workability, stiff/emulsion broken).

20 Adhesion test

1/3 of the 30 s mix was spread out on a metal plate and stored in the oven (60°C) over night.

25 The mix was thereafter put in boiling water for 10 minutes and the state of the coated aggregates was visually inspected. By this inspection, the area percentage of the aggregates coated by the bitumen was estimated.

30 The 3 minutes mix was divided in two portions. One portion was spread out on a table and state of the coated aggregates was visually inspected. By this inspection, the area percentage of the aggregates coated by the bitumen was estimated. The other portion was rinsed under pouring water until the water phase was not brownish anymore and the state of the coated aggregates was visually inspected. By this inspection, the area percentage of the aggregates coated by the bitumen was estimated.

All amounts of the components in the compositions are given as weight percent based on the total weight of the composition, unless otherwise is explicitly indicated.

Example 1

- 5 Aqueous bitumen-aggregate mixes were prepared by mixing
- a) 500 grams of aggregate of granite, consisting of the following fractions:
0-0.5 mm: 10 wt%; 0.5-2 mm: 15 wt%; 2-4 mm: 10 wt%; 4-8 mm: 20 wt%;
8-11 mm: 45 wt%;
 - b) 12 grams of water; and
 - 10 c) 40 grams of an oil-in-water bitumen emulsion containing 62% by weight of bitumen and emulsifiers in an amount in accordance with Table 1, at a temperature of about 20°C.

Table 1

Components	Emulsion no	
	1*	2*
Bitumen	62.0	62.0
Lignin Amine (ex Innventia AB)	0.097	0.097
N-Tallow alkyltrimethylenediamine + 15EO	0.078	0.078
N-oleyltrimethylenediamine + 2.5EO	0.023	0.023
Hydrogenated tallow alkylamine + 50EO	0.26	0.26
Water	To 100	To 100
Production data		
pH water phase	2.3	2.8
Bitumen flow, l/h	197,9	197,9
Water phase flow, l/h	114	114
Temp. water, °C	50	51
Temp. Bitumen, °C	140	140
Emulsion temperature, °C	90	91
Mill speed, rpm	9120	9120
Pressure after mill, barg	1.2	1.2

PAC was post added to the emulsions. 4.40g of ATC 8210 (10% PAC solution; ex Akzo Nobel) were post added to one litre of emulsion and mixed for 5 minutes with an IKA mixer RW 20 DZM at 200rpm.

5 The result is presented in table 2.

Table 2

Emulsion	1*	1 + PAC	2*	2 + PAC
30s mix. Coating [%]	100	100	100	100
30s mix. Workability	1	1	1	1
30s mix. Adhesion after boiling [%]	20	80	20	80
3 minutes mix. Coating [%]	100	100	100	100
3 minutes mix. Coating after rinsing [%]	0	0	0	0

10 Example 2

Aqueous bitumen-aggregate mixes were prepared by mixing

- a) 166.7 grams of an aggregate of granite, consisting of the following fractions:
0-0.5 mm: 10 wt%; 0.5-2 mm: 15 wt%, 2-4 mm: 10 wt%; 4-8 mm: 20 wt%; 8-11 mm: 45 wt%;
- 15 b) 4 grams of water; and
- c) 13.3 grams of an oil-in-water bitumen emulsion containing 62% by weight of bitumen and emulsifiers in an amount in accordance with Table 3, at a temperature of about 20°C.

20

Table 3

Components	Emulsion no			
	3*	4 ^a	5 ^b	6 ^c
Bitumen	62.0	62.0	62.0	62.0
Lignin Amine	0.097	0.097	0.097	0.097
N-Tallow alkyltrimethylenediamine + 15EO	0.078	0.078	0.078	0.078
N-oleyltrimethylenediamine + 2.5EO	0.023	0.023	0.023	0.023
Hydrogenated tallow alkylamine + 50EO	0.26	0.26	0.26	0.26
PAC (10%)	-	0.42	0.42	0.42
Water	To 100	To 100	To 100	To 100
Production data				
pH water phase	3.8	3.4	3.6	3.6
Bitumen flow, l/h	196	196	196	196
Water phase flow, l/h	114	114	114	114
Temp. water, °C	47	47	47	47
Temp. Bitumen, °C	145	145	145	145
Emulsion temperature, °C	90	90	90	90
Mill speed, rpm	9120	9120	9120	9120
Pressure after mill, barg	1.2	1.2	1.2	1.2

^aWater phase with emulsifiers and PAC was produced one day in advance of emulsification

5 ^bPAC and Emulsifiers were mixed and stored at room temperature during 2 months

^cPAC and Emulsifiers were added to water phase just before emulsification.

The result is presented in table 4.

Table 4

Emulsion	3*	3 + PAC	4 ^a	5 ^b	6 ^c
30s mix. Coating [%]	100	100	100	100	100
30s mix. Adhesion after boiling [%]	10	80	85	95	90
3 minutes mix. Coating [%]	100	100	100	100	100
3 minutes mix. Coating after rinsing [%]	0	0	0	0	0

Emulsion "3 + PAC" was prepared according to the following: PAC was post added to the emulsion (3): 4.40g of ATC 8210 (10% PAC solution; ex Akzo Nobel) were post added to one litre of the emulsion and mixed for 5 minutes with an IKA mixer RW 20 DZM at 200rpm.

Example 3

Aqueous bitumen-aggregate mixes were prepared by mixing

- 10 a) 166.7 grams of an aggregate of granite, consisting of the following fractions:
0-0.5 mm: 10 wt%; 0.5-2 mm: 15 wt%, 2-4 mm: 10 wt%; 4-8 mm: 20 wt%; 8-11 mm: 45 wt%;
- b) 4 grams of water,
- 15 c) 13.3 grams of an oil-in-water bitumen emulsion containing 62% by weight of bitumen and emulsifiers in an amount in accordance with Table 5, at a temperature of about 20°C.

Table 5

Components	Emulsion no		
	7	8	9
Bitumen	62.0	62.0	62.0
PAC (20%) (Ekoflock 54, ex Feralco Nordic AB)	0.2	0.2	0.2
Lignin Amine	-	0.097	-
N-Tallow alkyltrimethylenediamine + 15EO	0.078	0.078	0.078
N-oleyltrimethylenediamine + 2.5EO	0.023	0.023	0.023
Hydrogenated tallow alkylamine + 50EO	0.26	0.26	0.26
Methyl hydroxyethyl cellulose	-	-	0.1
Water	To 100	To 100	To 100
pH water phase	3.33	3.63	3.35

The result is presented in table 6.

5 Table 6

Emulsion	7	8	9
Adhesion	70%	80%	80%
Workability	1	1	1

Example 4

Aqueous bitumen-aggregate mixes were prepared by mixing

- 10 a) 166.7 grams of an aggregate of granite, consisting of the following fractions:
0-0.5 mm: 10 wt%; 0.5-2 mm: 15 wt%, 2-4 mm: 10 wt%; 4-8 mm: 20 wt%; 8-11 mm: 45 wt%;
- b) 4 grams of water,
- 15 c) 13.3 grams of an oil-in-water bitumen emulsion containing 62% by weight of bitumen and emulsifiers in an amount in accordance with Table 7, at a temperature of about 20°C.

Table 7

Components	Emulsion no							
	10	11	12	13	14	15	16	17
Bitumen	62.0	62.0	62.0	62.0	62.0	62.0	62.0	62.0
PAC (20%)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
N-Tallow alkyltrimethylenediamine + 15EO	0.11	-	0.11	-	0.11	-	0.11	-
N-oleyltrimethylenediamine + 2.5EO	-	0.11	-	0.11	-	0.11	-	0.11
Hydrogenated tallow alkylamine + 50EO	0.26	0.26	-	-	-	-	-	-
C ₁₆₋₂₂ alcohol+ 80EO	-	-	0.26	0.26	-	-	-	-
Decanoic acid monoethanolamide + 50EO	-	-	-	-	0.26	0.26	-	-
Castor Oil + 40EO	-	-	-	-	-	-	0.26	0.26
Water	To 100	To 100	To 100	To 100	To 100	To 100	To 100	To 100
pH water phase	3.65	3.8	3.5	3.7	3.3	3.4	3.5	3.7

The result is presented in table 8.

5 Table 8

Emulsion	10	11	12	13	14	15	16	17
Emulsification	Ok	Ok	Ok	Ok	Ok	Ok	Ok	Ok
Stability over night	Ok	Ok	Ok	Ok	Ok	Ok	Ok	Ok
Adhesion	30%	60%	20%	60%	30%	70%	20%	90%
Workability	1	1	1	1	1	1	1	1

Example 5

Aqueous bitumen-aggregate mixes were prepared by mixing

- a) 166.7 grams of an aggregate of granite, consisting of the following fractions:
0-0.5 mm: 10 wt%; 0.5-2 mm: 15 wt%, 2-4 mm: 10 wt%; 4-8 mm: 20 wt%; 8-11 mm: 45 wt%;
- b) 4 grams of water,
- c) 13.3 grams of an oil-in-water bitumen emulsion containing 62% by weight of bitumen and emulsifiers in an amount in accordance with Table 9, at a temperature of about 20°C.

Table 9

Components	Emulsion no				
	18	19*	20	21*	22
Bitumen 160/220	62.0	62.0	62.0	62.0	62.
PAC (20%)	0.2	0.2	0.2	0.2	0.2
Lignin Amine	0.097	0.097	0.13	0.097	0.097
N-Tallow alkyltrimethylenediamine + 15EO	0.078	-	0.1	-	0.279
N-oleyltrimethylenediamine + 2.5EO	0.023	0.31	0.03	-	0.0822
Hydrogenated tallow alkylamine + 50EO	0.26	-	-	0.31	-
NonylPhenol + 50EO	-	-	0.32	-	-
Water	To 100	To 100	To 100	To 100	To 100
pH water phase	3.63	3.87	3.8	3.7	3.5

The result is presented in table 10.

Table 10

Emulsion	18	19	20	21	22
Emulsification	Ok	Ok	Ok	-	Ok
Stability over night	Ok	Ok	Ok	-	Ok
Adhesion	75%	90%	75%	-	75%
Workability	1	3	1	-	1

Example 6

Aqueous bitumen-aggregate mixes were prepared by mixing

a) 166.7 grams of an aggregate of granite, consisting of the following fractions:

5 0-0.5 mm: 10 wt%; 0.5-2 mm: 15 wt%, 2-4 mm: 10 wt%; 4-8 mm: 20 wt%; 8-11 mm: 45 wt%;

b) 4 grams of water,

c) 13.3 grams of an oil-in-water bitumen emulsion containing 62% by weight of bitumen and emulsifiers in an amount in accordance with Table 9, at a
10 temperature of about 20°C.

Table 11

Components	Emulsion no					
	23*	24	25*	26	27	28
Bitumen	62.0	62.0	62.0	62.0	62.0	62.0
PAC (20%)	-	0.20	-	0.20	0.20	0.20
Lignin Amine	0,104	0,104	0,104	0,104	0,104	0,104
N-Tallow alkyltrimethylenediamine + 15EO	0,081	0,081	0,081	0,081	0,081	0,081
N-oleyltrimethylenediamine + 2.5EO	0,023	0,023	-	-	-	0,023
N-oleyltrimethylenediamine + 2PO	-	-	0,023	0,023	0,023	-
Hydrogenated tallow alkylamine + 50EO	0.25	0.25	0.25	0.25	-	-
C ₁₆₋₂₂ alcohol + 80EO	-	-	-	-	0.25	-
Hydrogenated tallow alkylamine + 4PO + 40EO	-	-	-	-	-	0.25
Water	To 100	To 100	To 100	To 100	To 100	To 100
pH water phase	3.5	3.6	3.4	3.5	3.5	3.6

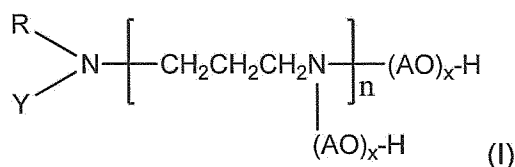
The result is presented in table 12.

Table 12

Emulsion no	23	24	25	26	27	28
30s mix. Coating [%]	100	100	100	100	100	100
30s mix. Adhesion after boiling [%]	40	85	25	85	85	85
30s mix. Workability	1	1	1	1	1	1
3 minutes mix. Coating [%]	100	100	100	100	100	100
3 minutes mix. Coating after rinsing [%]	0	0	0	0	0	0

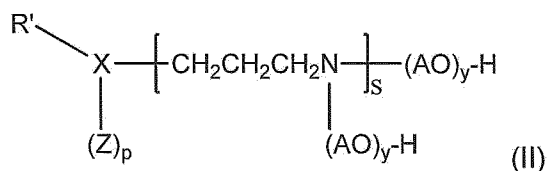
CLAIMS

1. An additive for a bitumen emulsion containing
- 5 i) a polyaluminum compound, preferably polyaluminum chloride;
- ii) an alkoxyated amine having the formula

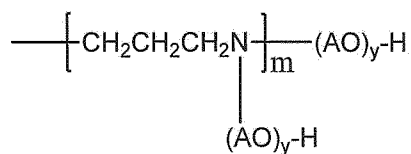


10 where R is a hydrocarbyl group having from 10 to 24 carbon atoms; n=0-3; each AO is independently ethyleneoxy or propyleneoxy, Y is a hydrocarbyl group having 1-24 carbon atoms, or a group (AO)_xH; and the sum of all x in (I) is 0.5-10; and

- iii) an alkoxyated compound having the formula



15 where R' is a hydrocarbyl group from 8 to 24 carbon atoms; X is N, C(=O)O or O; s=0-3; p = 0 or 1; provided that when X is N, then p is 1 and when X is C(=O)O or O, then p is 0; and Z is a hydrocarbyl group having 1-24 carbon atoms, or a group



20 where m=0-3;

where each AO independently is ethyleneoxy or propyleneoxy, and the sum of all y in (II) is from 12 to 200; or

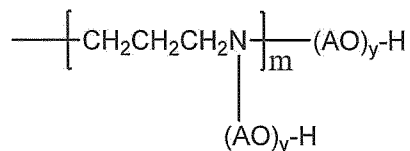
25 castor oil that has been alkoxyated 12 to 200 moles of ethylene oxide and/or propylene oxide per mole of castor oil (III).

2. An additive according to claim 1, where the sum of all x in (I) is from 0.5 to 5.

3. An additive according to claim 1 or 2, where the sum of all y in (II) is from 14 to 100.
- 5 4. An additive according to any one of the preceding claims, wherein AO in (I) is ethyleneoxy.
5. An additive according to any one of the preceding claims, wherein AO in (I) is propyleneoxy.
- 10 6. An additive according to any one of the preceding claims, wherein at least 50% of the total number of AO-units in (II) or (III) is ethyleneoxy units.
- 15 7. An additive according to any one of the preceding claims, wherein AO in (II) is ethyleneoxy.
8. An additive according to any one of the preceding claims where the weight ratio ii:iii is 1:25 to 4:1, and where the weight ratio between polyaluminum compound and the sum ii+iii is 1:30 to 1:2.
- 20 9. A bitumen-in-water emulsion comprising an additive according to any one of the claims 1 to 8, bitumen and water.
- 25 10. A bitumen emulsion according to claim 9 comprising
50-75% (w/w) bitumen
0.002-1.5% (w/w) of a polyaluminum compound, preferably polyaluminum chloride
0.05-3% (w/w) of ii+iii
0-20% (w/w) of other conventional components and
30 balance water.
11. A bitumen emulsion according to claim 9 or 10, having a pH below 8.

12. A bitumen emulsion according to any one of the claims 9 to 11, where X in formula (II) is N and p is 1.

13. A bitumen emulsion according to claim 8 where Z is the group



where m=0-3.

14. A bitumen emulsion according to any one of the claims 9 to 13, where X in formula (II) is O, p is 0 and s is 0.

15. A process for the manufacture of an aqueous bitumen-aggregate mix by
a) providing a bitumen emulsion according to any one of the claims 9-14; and
b) mixing said emulsion with an aggregate.

16. An aqueous bitumen-aggregate mix comprising
2-40% by weight of bitumen emulsion according to any one of the claims 9-14;
and
60-98% by weight of an aggregate.

17. A method for paving a surface of a road, a sidewalk, a parking lot or an airport runway by spreading the bitumen-aggregate mix according to claim 16 on the surface, or by spreading the bitumen emulsion according to claim 9-14 on a surface at least partially covered by an aggregate.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/074670

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08K3/16 C08K3/22 C08G65/26 C08K5/17 C08L71/02
C08L95/00

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)

C08K C08G C08L

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 511 858 A (NICHIREKI CHEM IND CO) 24 May 1978 (1978-05-24) page 3, line 6 - line 22 -----	1-17
A	US 2010/101981 A1 (MOFFETT ROBERT HARVEY [US] ET AL) 29 April 2010 (2010-04-29) paragraphs [0029], [0045] -----	1-17
A	JP S58 21448 A (KAO CORP) 8 February 1983 (1983-02-08) cited in the application the whole document -----	1-17
A	WO 03/048256 A1 (BASF CORP [US]; TAKAMURA KOICHI [US]; GOLZAR BABAK [US]; ADAMS VANESSA) 12 June 2003 (2003-06-12) cited in the application the whole document -----	1-17



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

27 February 2014

Date of mailing of the international search report

21/03/2014

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

olde Scheper, Bernd

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/074670

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1511858	A	24-05-1978	CA 1053811 A1 01-05-1979
			DE 2553617 A1 12-08-1976
			FR 2292674 A1 25-06-1976
			GB 1511858 A 24-05-1978
			JP S5162186 A 29-05-1976
			JP S5342313 B2 10-11-1978
			US 4053401 A 11-10-1977

US 2010101981	A1	29-04-2010	AR 074183 A1 29-12-2010
			AU 2009314391 A1 20-05-2010
			CA 2684155 A1 29-04-2010
			CA 2734474 A1 20-05-2010
			CN 102203028 A 28-09-2011
			EP 2349945 A1 03-08-2011
			EP 2644579 A2 02-10-2013
			US 2010101981 A1 29-04-2010
			US 2010104744 A1 29-04-2010
			US 2010126910 A1 27-05-2010
			US 2013081981 A1 04-04-2013
			WO 2010056539 A1 20-05-2010

JP S5821448	A	08-02-1983	JP S617223 B2 05-03-1986
			JP S5821448 A 08-02-1983

WO 03048256	A1	12-06-2003	AU 2002360285 A1 17-06-2003
			CA 2420742 A1 20-05-2003
			WO 03048256 A1 12-06-2003
