

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 July 2011 (21.07.2011)

(10) International Publication Number
WO 2011/087767 A1

(51) International Patent Classification:

C08L 83/04 (2006.01) *C08F 283/12* (2006.01)
C09D 183/04 (2006.01) *C08J 3/03* (2006.01)

(21) International Application Number:

PCT/US2010/061433

(22) International Filing Date:

21 December 2010 (21.12.2010)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/289,171 22 December 2009 (22.12.2009) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, 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, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, 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, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))
- of inventorship (Rule 4.17(iv))

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))



WO 2011/087767 A1

(54) Title: SILICONE RESIN-ORGANIC EMULSIONS

(57) Abstract: Methods for preparing emulsion compositions are disclosed by (i) preparing a silicone resin emulsion by emulsion polymerization of silane monomers containing at least one trialkoxysilane; (ii) adding to the emulsion in (i) components for preparing an emulsion containing an organic polymer by free radical emulsion polymerization of one or more ethylenically unsaturated organic monomers; and (iii) heating the emulsion from (ii).

SILICONE RESIN-ORGANIC EMULSIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001] This application claims the benefit of US Application No. 61/289171, as filed on 22 December, 2009.

BACKGROUND OF THE INVENTION

[0002] The prior art is replete with patents relating to emulsions containing silicone-organic copolymers. Representative of the state of the art relevant to this invention is US Patent
10 3,575,910 (April 20, 1971). The '910 patent, for example, describes aqueous emulsions of certain siloxane-acrylate copolymers. However, the siloxane in the '910 patent used to make the copolymer contains trifunctional T units $\text{RSiO}_{3/2}$ to provide reaction of the siloxane with an organic acrylate. Therefore it can be seen that the emulsion in the '910 patent essentially
15 contains resinous type siloxanes and copolymers formed from siloxanes and organic monomers.

BRIEF SUMMARY OF THE INVENTION

20 [0003] We have found that it is possible to make silicone-organic emulsion polymers that contain phase separated particles which are essentially blends of the siloxane and organic polymers. Depending on the compatibility of the particular silicone resin composition with the organic polymer composition, various particle morphologies can be obtained, including lobed, core-shell, or microdomains. The use of vinyl functional silanes was not necessary to
25 obtain siloxane-organic emulsion polymers useful in coatings and other applications.

[0004] The present silicone resin-organic hybrid polymers and blends emulsions are useful in various coating compositions, particularly latex. The present emulsions can be applied, for example, to metals, plastics, wood, paper, composition board, and other cellulosic materials.
30 The present emulsions are particularly useful to provide coating compositions which provide greatly improved weathering characteristics and find special utility in industrial applications.

The present emulsions may also be used in sealant compositions, molding compositions, and adhesive compositions.

DETAILED DESCRIPTION OF THE INVENTION

5

[0005] The present disclosure provides a method of making an emulsion composition comprising:

(i) preparing a silicone resin emulsion by emulsion polymerization of silane monomers containing at least one trialkoxysilane having the formula $R^1Si(OR^2)_3$

10 where R^1 is a monovalent hydrocarbon group containing 1 to 12 carbon atoms, R^2 is selected from the group consisting of hydrogen, alkyl groups containing 1 to 4 carbon atoms, $CH_3C(O)-$, $CH_3CH_2C(O)-$, $HOCH_2CH_2-$, $CH_3OCH_2CH_2-$, and $C_2H_5OCH_2CH_2-$,

wherein the silicon resin emulsion is stabilized by a combination of anionic and non-ionic surfactants or a surfactant containing both anionic and non-ionic functional groups;

15

(ii) adding to 100 parts by weight of the emulsion in (i) 30 to 150 parts by weight components for preparing an emulsion containing an organic polymer by free radical polymerization of one or more ethylenically unsaturated organic monomers; and

(iii) heating the emulsion from (ii).

20

[0006] Step (i) in the present process involves preparing a silicone resin emulsion by emulsion polymerization of silane monomers. As used herein, the term *emulsion polymerization* refers to its accepted meaning in the art, for example, any of the polymerization processes represented by processes described in US Patents US 2,891,920 (June 23, 1959), US 3,294,725 (December 27, 1966), US 4,999,398 (March 12, 1991), US 25 5,502,105 (March 26, 1996), US 5,661,215 (August 26, 1997), and US 6,316,541 (November 13, 2001).

[0007] The silicone resin emulsions useful in the present disclosure may be prepared according to the techniques as taught in WO 2006/016968, which is incorporated herein by reference.

5 [0008] The silane monomers used to prepare the silicone resin emulsion must contain at least one trialkoxysilane having the formula $R^1Si(OR^2)_3$

where R^1 is a monovalent hydrocarbon group containing 1 to 12 carbon atoms, alternatively R^1 is an aromatic group, alternatively R^1 is phenyl.

10 R^2 is selected from the group consisting of hydrogen, alkyl groups containing 1 to 4 carbon atoms, $CH_3C(O)-$, $CH_3CH_2C(O)-$, $HOCH_2CH_2-$, $CH_3OCH_2CH_2-$, and $C_2H_5OCH_2CH_2-$,

[0009] The silane monomers may further contain a dialkoxydialkylsilane having the formula $R^1_2Si(OR^2)_2$ where R^1 and R^2 are the same as described above. Typically, the
15 dialkoxydialkylsilane is dimethoxydimethylsilane.

[0010] The amount of dialkoxydialkylsilane combined with the trialkoxysilane may vary to produce a silicone resin composed of 0 to 45 mol percent R^1_2SiO units and 55 to 100 mol percent $R^1SiO_{3/2}$ units; alternatively 5 to 45 mol percent R^1_2SiO units and 55 to 95 mol
20 percent $R^1SiO_{3/2}$ units.

[0011] The emulsion polymerization reaction is carried out in an aqueous medium containing the surfactant, and it is catalyzed by a siloxane condensation catalyst. Condensation polymerization catalysts which can be used include (i) strong acids, such as substituted
25 benzenesulfonic acids, aliphatic sulfonic acids, hydrochloric acid, and sulfuric acid; and (ii) strong bases such as quaternary ammonium hydroxides, and alkali metal hydroxides. Some ionic surfactants, such as dodecylbenzenesulfonic acid, can additionally function as a catalyst.

[0012] The silicone resin emulsions useful in the present invention can contain anionic surfactants and nonionic surfactants. Alternatively, the emulsion may contain a surfactant containing both anionic and nonionic functionality. The anionic surfactants include sulfonic acids and their salt derivatives. Some examples of anionic surfactants are alkali metal sulfosuccinates; sulfonated glyceryl esters of fatty acids such as sulfonated monoglycerides of coconut oil acids; salts of sulfonated monovalent alcohol esters such as sodium oleyl isothionate; amides of amino sulfonic acids such as the sodium salt of oleyl methyl tauride; sulfonated products of fatty acid nitriles such as palmitonitrile sulfonate; sulfonated aromatic hydrocarbons such as sodium alpha-naphthalene monosulfonate; condensation products of naphthalene sulfonic acids with formaldehyde; sodium octahydro anthracene sulfonate; alkali metal alkyl sulfates; ether sulfates having alkyl groups of eight or more carbon atoms such as sodium lauryl ether sulfate; and alkylaryl sulfonates having one or more alkyl groups of eight or more carbon atoms such as neutral salts of hexadecylbenzene sulfonic acid and C₂₀ alkylbenzene sulfonic acid.

15

[0013] Commercial anionic surfactants which can be used include the sodium salt of dodecylbenzene sulfonic acid sold under the trademark SIPONATE® DS-10 by Alcolac Inc., Baltimore, Maryland; sodium n-hexadecyl diphenyloxide disulfonate sold under the trademark DOWFAX® 8390 by The Dow Chemical Company, Midland, Michigan; the sodium salt of a secondary alkane sulfonate sold under the trademark HOSTAPUR® SAS 60 by Clariant Corporation, Charlotte, North Carolina; N-acyl taurates such as sodium N-lauroyl methyl taurate sold under the trademark NIKKOL LMT® by Nikko Chemicals Company, Ltd., Tokyo, Japan; and linear alkyl benzene sulfonic acids sold under the trademark BIO-SOFT® S-100 by the Stepan Company, Northfield, Illinois. Compositions of the latter type such as dodecylbenzene sulfonic acid, although a catalyst as noted above, can also function as the anionic surfactant when neutralized.

25

[0014] Commercially available nonionic surfactants which can be used include compositions such as 2,6,8-trimethyl-4-nonyloxy polyethylene oxyethanols (6EO) and (10EO) sold under the trademarks TERGITOL® TMN-6 and TERGITOL® TMN-10; alkyleneoxy polyethylene oxyethanol (C₁₁₋₁₅ secondary alcohol ethoxylates 7EO, 9EO, and

30

15EO) sold under the trademarks TERGITOL® 15-S-7, TERGITOL® 15-S-9, TERGITOL®
15-S-15; other C₁₁₋₁₅ secondary alcohol ethoxylates sold under the trademarks
TERGITOL® 15-S-12, 15-S-20, 15-S-30, 15-S-40; and octylphenoxy polyethoxy ethanol
(40EO) sold under the trademark TRITON® X-405. All of these surfactants are sold by
5 Union Carbide Corporation, Danbury, Connecticut.

[0015] Other useful commercial nonionic surfactants are nonylphenoxy polyethoxy ethanol
(10EO) sold under the trademark MAKON® 10 by Stepan Company, Northfield, Illinois;
polyoxyethylene 23 lauryl ether (Laureth-23) sold commercially under the trademark BRIJ®
10 35L by ICI Surfactants, Wilmington, Delaware; and RENEX® 30, a polyoxyethylene ether
alcohol sold by ICI Surfactants, Wilmington, Delaware.

[0016] In one embodiment, the surfactant is a surfactant containing both anionic and non-
ionic functional groups, such as Rhodapex® EST-30/BLB which is sodium trideceth(3)
15 sulfate.

[0017] Step (ii) of the present process involves adding to 100 parts by weight of the emulsion
from step (i) 30 to 150 parts by weight components for preparing an emulsion containing an
organic polymer by free radical polymerization of one or more ethylenically unsaturated
20 organic monomers. These components include a free radical catalyst and an ethylenically
unsaturated organic monomer. Alternatively for every 100 parts by weight of the emulsion
from step (i), 50 to 100 parts by weight components for preparing an emulsion containing an
organic polymer by free radical polymerization of one or more ethylenically unsaturated
organic monomers may be added.

25
[0018] Various types of ethylenically unsaturated and/or vinyl containing organic monomers
can be used for the organic phase including acrylates, methacrylates, substituted acrylates,
substituted methacrylates, vinyl halides, fluorinated acrylates, and fluorinated methacrylates,
for example. Some representative compositions include acrylate esters and methacrylate
30 esters such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl
methacrylate, decyl acrylate, lauryl acrylate, isodecyl methacrylate, lauryl methacrylate, and

butyl methacrylate; substituted acrylates and methacrylates such as hydroxyethyl acrylate, perfluorooctyl acrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, and hydroxyethyl methacrylate; vinyl halides such as vinyl chloride, vinylidene chloride, and chloroprene; vinyl esters such as vinyl acetate and vinyl butyrate; vinyl pyrrolidone;

5 conjugated dienes such as butadiene and isoprene; vinyl aromatic compounds such as styrene and divinyl benzene; vinyl monomers such as ethylene; acrylonitrile and methacrylonitrile; acrylamide, methacrylamide, and N-methylol acrylamide; and vinyl esters of monocarboxylic acids with up to 10 carbon atoms such as compositions sold under the trademarks VeoVa-9® and VeoVa-10® by Shell Chemical Oil Company, Houston, Texas. Some preferred

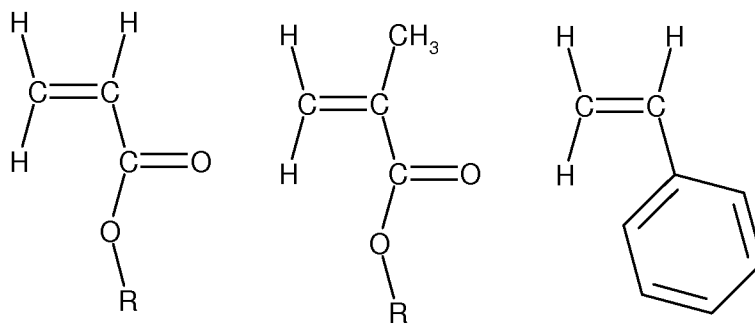
10 ethylenically unsaturated organic monomers useful herein and a simplified depiction of their polymerization are shown below wherein R can represent methyl, ethyl, 2-ethylhexyl, 2-hydroxyethyl, or 2-hydroxypropyl groups.

15

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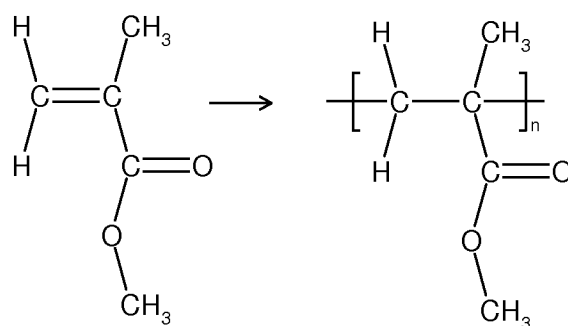
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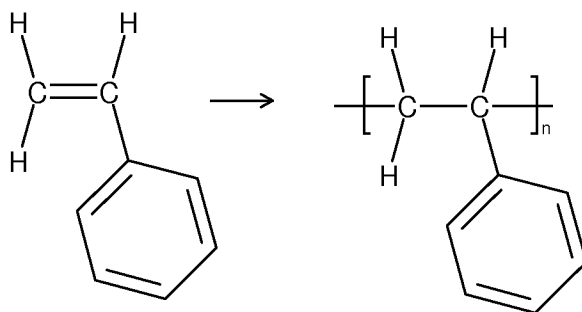
Acrylate Ester

Methacrylate Ester

Styrene



Free Radical Polymerization of Methyl Methacrylate to Poly(methylmethacrylate)



Free Radical Polymerization of Styrene to Polystyrene

5

[0019] Any organic acrylate can be employed in making the polymers of this invention. Thus, for example, acrylic acid and methacrylic acid or their derivatives such as the esters, nitriles, and amides can be employed. The esters are the preferred compound. The specific examples of acrylates that can be employed are methyl methacrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, vinyl acrylate, allyl acrylate, benzyl acrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, ethylcyano acrylate, ethylene

glycol, diacrylate, glycerol triacrylate, ethyl methacrylate, butyl methacrylate, hexyl methacrylate, allyl methacrylate, benzyl methacrylate, diethylene glycol dimethacrylate. It is understood by those skilled in the art that either a single acrylate or various combinations of acrylates can be employed in making the hybrid polymer or polymer blend. The particular
5 choice of acrylate will be determined by the intended use of the polymer. Thus, for example, methyl methacrylate by itself tends to give a hard and somewhat brittle product which can be used in making automobile finishes, whereas ethyl acrylate by itself tends to give a soft and somewhat sticky product which would not be useful as an automobile finish but instead would find utility in another field such as treating textiles or making adhesives. Generally
10 speaking, it is preferred to employ a blend of acrylates in making the copolymers since it is seldom possible to find a single compound which will give a product having the optimum properties desired for a particular application.

[0020] One process embodiment for preparing the present emulsions is a *semi-continuous*
15 *process* while another process embodiment for preparing the present emulsions is a *monomer swell process*. According to the semi-continuous process, the procedure commences with the preparation of the silicone resin emulsion by emulsion polymerization as describe above. In the second stage, the organic monomer(s) are then introduced to a reactor continuously over a period of several hours at a temperature of 80-90 °C. A water-soluble free radical initiator
20 such as sodium persulfate is then added to the reactor in a separate stream over a period of several hours during addition of the organic monomer(s). In the monomer swell process, it also commences with preparation of a silicone resin emulsion by emulsion polymerization as described above. However, the organic monomer(s) and an organic free radical azo-type initiator are introduced to the reactor simultaneously and allowed to swell the silicone resin
25 emulsion particles for a brief period of time. Heating is then increased to activate the initiator, causing the organic monomer(s) to polymerize within the silicone emulsion particles.

[0021] Thermal or redox initiation processes are used in the preparation of the organic polymer phase. Conventional thermal free radical initiators which can be used include
30 hydrogen peroxide, sodium peroxide, potassium peroxide, t-butyl hydroperoxide, cumene hydroperoxide, ammonium and/or alkali metal persulfates, sodium perborate, perphosphoric

acid and salts thereof, potassium permanganate, and ammonium or alkali metal salts of peroxydisulfuric acid. These initiators are typically used at a level of 0.01-3.0 percent by weight based on the total weight of monomer. Redox initiators which can be used are typically an oxidant plus a reducing agent in combinations effective to generate free radicals, including the same free radical initiators listed above as the oxidant; and a suitable reductant such as sodium sulfoxylate formaldehyde, ascorbic acid, isoascorbic acid, alkali metal and ammonium salts of sulfur-containing acids such as sodium sulfite, bisulfite, thiosulfate, hydrosulfite, sulfide, hydrosulfide or dithionite, formamidine sulfinic acid, hydroxymethane sulfonic acid, acetone bisulfite; amines such as ethanolamine, glycolic acid, glyoxylic acid hydrate, lactic acid, glyceric acid, malic acid, tartaric acid, as well as salts of the preceding acids which may be used.

[0022] Redox reaction catalyzing metal salts of iron, copper, manganese, silver, platinum, vanadium, nickel, chromium, palladium, or cobalt, may optionally be used. The initiator or initiator system can be added in one or more additions, continuously, linearly, or not, over the reaction period, or as combinations thereof. Several azo-type organic free radical initiators which can be used in the monomer swell process such as azobis-isobutyronitrile and azobispropionitrile, which are sold under the trademark VAZO® by E.I. du Pont de Nemours Company.

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EXAMPLES

[0023] The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventor to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention. All percentages are in wt. %. All measurements were conducted at 23°C unless indicated otherwise.

Example 1

Preparation of a Silicone Resin Emulsion by Emulsion Polymerization

[0024] To a one liter glass reactor fitted with a Teflon® paddle stirrer, condenser, Dean Stark trap, and three addition ports, was added 360.71 grams of water, 64.05 grams of sodium ether (4 EO) lauryl sulfate (30.5% active), 29.33 grams of sodium ether (30 EO) lauryl sulfate (33.4% active), and 0.91 grams of a 10% solution of potassium hydroxide. The mixture was heated to 90°C with mixing. When the temperature reached 90°C, 203.84 grams of phenyltrimethoxysilane and 41.16 grams of dimethyldimethoxysilane were fed in over 60 minutes and methanol collected in the trap over several hours until no more methanol was collected. The emulsion was cooled to room temperature with stirring. The resulting silicone resin emulsion had a non-volatile content of 34.5 percent and an average particle size of 27 nanometer (0.027 micron).

Example 2*Preparation of Silicone Resin Emulsion by Emulsion Polymerization*

[0025] To a one liter glass reactor fitted with a Teflon® paddle stirrer, condenser, Dean Stark trap, and three addition ports, was added 363.09 gram of water, 63.00 gram of anionic/nonionic combination surfactant sodium tridecyl ether sulfate (31% actives), and 0.91 gram of 10% solution of potassium hydroxide. The mixture was heated to 90°C with mixing. When the temperature reached 90°C, 273.0 grams of phenyltrimethoxysilane were fed in over 60 minutes and methanol collected in the trap over several hours until no more methanol was collected. The emulsion was cooled to room temperature with stirring. The resulting silicone resin emulsion had a non-volatile content of 35.1 percent and a particle size of 27 nanometer (0.027 micron).

Example 3*Silicone Resin-Poly (Ethyl Acrylate/Methyl Methacrylate/Methacrylic Acid) Emulsion using a Semi-Continuous Process*

[0026] A one liter reactor was charged with 317.04 gram of the silicone resin emulsion from Example 1, 155.42 grams of water, and 4.48 grams of Abex 18-S surfactant (35% active). The mixture was heated to 70°C with mixing. When the temperature reached 70°C, separate monomer and aqueous feeds were started, using liquid metering pumps. The monomer feed consisted of 142.24 grams of ethyl acrylate, 77.28 grams of methyl methacrylate, and 4.48 grams of methacrylic acid, which was added over 2 hours. The aqueous feed was added over 2.5 hours and consisted of 97.66 grams of deionized water, 1.05 grams of potassium persulfate, and 0.35 grams of sodium bicarbonate. After the aqueous feed was complete, the temperature was increased to 85°C and was stirred for an additional 2 hours. The emulsion was allowed to cool to room temperature with stirring. The final emulsion had a non-volatile content of 41.9 percent and a particle size of 47 nanometers (0.047 micron).

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Example 4*Silicone Resin-Poly (Methyl Acrylate) Emulsion using a Monomer Swell Process*

[0027] A one liter reactor was charged with 347.0 grams of a silicone resin emulsion having
5 essentially the same composition as the silicone resin emulsion from Example 2. It had a
particle size of 27 nm (0.027 micron) and a non-volatile content of 35.1 percent. With
continuous mixing, 289.82 grams of deionized water was added to the reactor. The monomer
mixture consisted of 112.5 grams of methyl acrylate and 0.68 grams of VAZO® 67 initiator.
The mixture was added to the silicone resin emulsion, and mixed for 4 hours at room
10 temperature. The temperature of the reactor was brought to 68°C to initiate polymerization.
After the exotherm was complete, the temperature of the reactor was brought to 90°C and
held for 3 hours, and then cooled to room temperature with stirring. The final emulsion had a
non-volatile content of 31.5 and a particle size of 46 nanometer (0.046 micron).

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Claims

1. A method of making an emulsion composition comprising:

(i) preparing a silicone resin emulsion containing 0 to 45 mol percent R^1_2SiO units
5 and 55 to 100 mol percent $R^1SiO_{3/2}$ units by emulsion polymerization of silane
monomers containing at least one trialkoxysilane having the formula $R^1Si(OR^2)_3$

where R^1 is a monovalent hydrocarbon group containing 1 to 12 carbon atoms,

R^2 is selected from the group consisting of hydrogen, alkyl groups containing
1 to 4 carbon atoms, $CH_3C(O)-$, $CH_3CH_2C(O)-$, $HOCH_2CH_2-$,

10 $CH_3OCH_2CH_2-$, and $C_2H_5OCH_2CH_2-$,

wherein the silicone resin emulsion is stabilized by a combination of anionic and non-ionic
surfactants or a surfactant containing both anionic and non-ionic functional groups;

(ii) adding to 100 parts by weight of the emulsion in (i) 30 to 150 parts by weight
components for preparing an emulsion containing an organic polymer by free radical
15 polymerization of one or more ethylenically unsaturated organic monomers; and

(iii) heating the emulsion from (ii).

2. The method of claim 1 wherein R^1 is a phenyl group.

20 3. The method of claim 1 wherein R^2 is a methyl group.

4. The method of claim 1 wherein the trialkoxysilane is phenyltrimethoxysilane.

5. The method of claim 1 wherein the silane monomers contain a dialkoxydialkylsilane.

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6. The method of claim 1 wherein the silane monomers contains dimethoxydimethylsilane.

7. The method of claim 1 wherein the silicone resin contains 5 to 45 mol percent R^1_2SiO
units and 55 to 95 mol percent $R^1SiO_{3/2}$ units.

8. The method of claim 1 wherein the surfactant is sodium trideceth(3) sulfate.
9. The method of claim 1 wherein the ethylenically unsaturated organic monomer is an
5 acrylate ester, a methylacrylate ester, a fluorinated acrylate, a fluorinated methacrylate,
acrylic acid, methacrylic acid, allyl methacrylate, dimethylaminoethyl methacrylate, a
vinyl halide, a vinyl ester, a vinyl aromatic compound, a vinyl ester of a monocarboxylic
acid, or a vinyl pyrrolidone.
- 10 10. The method of claim 1 wherein the ethylenically unsaturated organic monomer is mixture
of ethyl acrylate, methyl methacrylate, and methacrylic acid.
11. The method of claim 1 wherein step (ii) components contain an organic free radical
initiator.
- 15 12. The method of claim 1 wherein step (ii) components contain azobis-isobutyronitrile or
azobispropionitrile.
13. The emulsion prepared according to any one of claims 1 to 12.
- 20 14. A method of coating a substrate comprising applying to the substrate a film of the
emulsion from claim 13 and allowing the film to dry.
- 25

INTERNATIONAL SEARCH REPORT

International application No PCT/US2010/061433

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08L83/04 C09D183/04 C08F283/12 C08J3/03
 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)
 C08L C09D C08F C08J
 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
 EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 973 068 A (YAMAYA MASAOKI [JP] ET AL) 26 October 1999 (1999-10-26) column 14, lines 27-44; example 2; table 2 -----	1-14
X	US 5 223 586 A (MAUTNER KONRAD [DE] ET AL) 29 June 1993 (1993-06-29) column 4, lines 21-43; claim 3; examples 4,5 -----	1-14
A	US 2007/082478 A1 (LIND DAVID [AU] ET AL) 12 April 2007 (2007-04-12) claims 1-11 -----	1-14

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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.</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 26 April 2011	Date of mailing of the international search report 09/05/2011
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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 Buestrich, Ralf
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/061433

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