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(54) **Title:** AQUEOUS SILYLATED POLYMER EMULSION AND ITS PREPARATION METHOD AND USES THEREOF

(57) **Abstract:** The present invention relates to an aqueous silylated polymer emulsion and its preparation method and uses. The present emulsion comprises silylated polymer, hydrolysable silane, water, optional nano silica and optional emulsifying agent. By using the preparation methods of the invention, a stable silylated polymer emulsion could be obtained. The prepared emulsion has a solid content of ≤ 85 wt%, particularly the obtained polysiloxane emulsion has a solid content of ≤75 wt%; and has a particle size of less than 3 µm. The emulsion is stable when stored at room temperature. After volatilization of water, the emulsion can crosslink to form an elastomer. In use, the emulsion can be directly diluted with water. The emulsion can be used for formulating coatings, adhesives, sealants, inks, release agents, skin care products and detergents.

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Title

Aqueous Silylated Polymer Emulsion and Its Preparation Method and Uses Thereof

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a stable silylated polymer emulsion. More particularly, the present invention relates to an aqueous silylated polymer emulsion, which comprises silylated polymer, water, hydrolysable silane, optional nano silica and optional emulsifying agent. The present invention also relates to a method for preparing the aqueous silylated polymer emulsion and to uses of the same. Use of the invention can be made in the field of adhesives, sealants, coatings, inks, release agents, skin care products and detergents, among others.

Brief Description of Related Technology

A silylated polymer, e.g., a polymer having hydrocarbyloxysilyl groups at chain end(s) and/or pendant on the chain(s), can self-crosslink with moisture in air or react with a curing agent to obtain a crosslinked polymer, owing to the presence of the reactive hydrocarbyloxysilyl groups therein. The crosslinked polymer possesses excellent properties. It is widely used in various fields such as adhesives, sealants, coatings, inks, skin care products and detergents. However, during its application, the general situation is that organic solvent is used as a carrier. It is desirable to prepare an aqueous emulsion of the above polymer, following increasingly stricter regulatory constraints on volatile organic compound content.

For polymers insoluble in water, "post-emulsification" is often used to prepare aqueous emulsions of the polymers. This is done by dispersing already-prepared polymer in water under high shear speed to prepare an aqueous polymer emulsion. The emulsifier attaches itself to the surface of the polymer droplets through its lipophilic groups, whereas its hydrophilic groups extend to the water. Owing to charge repulsion or spatial shielding therein, the polymer emulsion particles are prevented from approaching and re-aggregating with each other. U.S. Patent Nos. 6,713,558 and 6,831,128 reportedly introduce a high solid-content silylated viscoelastic polymer emulsion, wherein a silylated polybutadiene polymer, a plasticizer, a surfactant, a low molecular weight acid and water were used for the preparation of an aqueous polymer emulsion having a solid content of greater than 75% and an average particle diameter of less than 5 μm. However, due to the high viscosity of the polymer, a large quantity of emulsifier, low molecular weight plasticizer or co-solvent was used to obtain the aqueous polymer emulsion. Since the emulsifier or plasticizer is mostly a low molecular weight compound, by adding it to the polymer in a large quantity the properties of the crosslinked polymer would be compromised, depending on the application at hand. Further, the addition of a co-solvent would increase the content of VOC in the emulsion, thereby raising questions of environmental compatibility. Moreover, latex particles in the aqueous polymer emulsion obtained by the above method were observed to have an irregular particle shape and a broad particle size distribution, thereby causing phase separation and poor emulsion stability.

"Self-emulsification" may also be used for polymers insoluble in water to prepare aqueous emulsions by introducing hydrophilic groups onto the polymer molecule. For example, U.S. Patent No. 5,466,729 reportedly introduced an aqueous dispersion of a silylated epoxy resin. The silylated epoxy resin was obtained by reacting a silane having both a hydrolysable group and a secondary amine group with an epoxy resin. The aqueous dispersion was directly prepared from the silylated epoxy resin under a high shear speed, which can be used in metal coating and glass adhesive. Aqueous polymer emulsion prepared by chemical modification was featured with a small particle size of disperse phase in the range of about tens to hundreds of nanometers, but the preparation process is difficult to control and the product cost is relatively higher. Moreover, due to the change in the molecular structure of polymer in the aqueous polymer emulsion prepared by this method, the properties of the product were somewhat influenced.

Chinese Patent Document No. CN 1140186A discloses a high viscosity polysiloxane dispersion that could be crosslinked via condensation, addition or free radical reactions. Surfactants and low amounts of water were added to prepare a gel of solid content greater than 75 wt%. A certain amount of silane could be added into the polysiloxane dispersion for carrying out a curing reaction, and the added silane acted as curing agent and crosslinking agent. Different from an emulsion, the gel of high solid content was unable to be used in the situations requiring fluids of flowing ability.

Chinese Patent Document No. CN 200510133811.X discloses a stable silylated polymer emulsion and its preparation methods. By taking advantage of the interaction between hydroxyl groups on the surface of nano silica and reactive groups on the molecular chain of silylated polymer, and by using post-emulsification process, a stable silylated polymer emulsion could be obtained only by adding a small quantity of surfactant to the system, or even without the use of surfactant. Further, the addition of nano silica seemingly enhances the mechanical strengths of the films formed from the emulsion. Nevertheless, some silylated polymers do not benefit from the addition of inorganic particles during emulsion preparation therewith.

Accordingly, it would be still desirable to provide stable silylated polymer emulsions.

The present invention could solely use a silane compound to obtain a stable silylated polymer emulsion, or when needed, use nano silica and silane compounds for a synergism action to obtain the emulsion. By virtue of a charge or bonding action of hydroxysilyl formed between the polymer and silane or silane as well as nano silica, a stable silylated polymer emulsion can be obtained. The silane compound solely or silane and nano silica synergistically act on the emulsion as a surfactant or stabilizer, and further act as a curing and crosslinking agent during the curing process upon water volatilization.

SUMMARY OF THE INVENTION

The invention thus provides an aqueous silylated polymer emulsion. The stable emulsion can be obtained using a small quantity of surfactant, if desired. After volatilization of the water in the emulsion, the polymer can be cured to form a crosslinked elastic film having excellent properties. The emulsion may include low volatile organic compounds (referred to as low VOC hereinafter).

The invention also provides simple, flexible and easy-to-operate methods for the preparation of the stable silylated polymer emulsion.

The invention also provides a method to prepare a stable aqueous silylated polymer emulsion by using silane compounds.

The invention also provides a method to prepare a stable aqueous silylated polymer emulsion by virtue of the synergism action of silane with nano silica.

The invention further provides a method for homogeneously dispersing nano silica into a silylated polymer.

The invention still further provides the stable silylated polymer emulsion for use as a raw material in the fields of coatings, adhesives, sealants, inks, skin care products, detergents and the like.

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 is a sectional SEM of a crosslinked polymer sample obtained from the silylated polymer emulsion containing 7 wt% silane compound obtained in Example 1 after volatilization of water, it is enlarged by 20,000 times, from which it can be seen that the crosslinked polymer formed a homogeneous film.

Fig. 2 is a sectional SEM of a crosslinked polymer sample obtained from the silylated polymer emulsion containing 10 wt% silane compound and 8 wt% nano silica obtained in Example 2 after volatilization of water, it is enlarged by 20,000 times, from which it can be seen that the nano silica was homogeneously dispersed in the crosslinked polymer.

Fig. 3 is a view of the particle size distribution of the silylated polymer emulsion containing 15 wt% silane compound obtained in Example 3, from which it can be seen that the average particle size of the emulsion is 340 nm and having a narrow distribution of particle size.

Fig. 4 is schematic flow diagram of the inventive method A to prepare the stable aqueous silylated polymer emulsion (Simultaneous-Addition-of-Silane method), wherein silylated polymer is first mixed with other components, and then silane compound is added into the obtained mixture to complete the emulsion process.

Fig. 5 is schematic flow diagram of the inventive method B to prepare the stable aqueous silylated polymer emulsion (Pre-Addition-of-Silane method), wherein silane compound is first mixed with silylated polymer, and then other components are added into the obtained mixture to complete the emulsion process.

Fig. 6 is schematic flow diagram of the inventive method C to prepare the stable aqueous silylated polymer emulsion (Post-Addition-of-Silane method), wherein silylated polymer is pre-emulsified with other components, and finally silane compound is added to complete the emulsion process.

Fig. 7 is schematic diagram for describing the inventive process to produce the stable aqueous silylated polymers.

DETAILED DESCRIPTION OF THE INVENTION

The term "Pickering emulsifying agent" used herein means solid fine particles added for stabilizing emulsion during the preparation of an emulsion. See *Pickering, S.U.J. Chem. Soc., Chem. Commun, 1907, 91, 2001*; and *B.P. Binks and S.O. Lumsdon Langmuir, 2001, 17, 4540-4547.*

The term "polysiloxane" used herein means a polymer with backbone of repeating Si-O units and organic group(s) directly attached to the silicon atom therein.

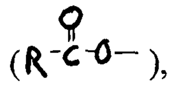
The term "silylated polymer" used herein means a polymer with silane functional group at the chain ends or pendant on the chain.

The term "silylated polysiloxane" used herein means a polymer with backbone of repeating Si-O units and organic group(s) directly attached to the silicon atom therein, and with a hydrocarbyloxysilyl group (≡Si-O-R) at the chain ends or pendant on the chain.

The term "post-emulsification" used herein means a method of preparing an aqueous polymer emulsion by first preparing a polymer via a conventional process and then dispersing the polymer into water.

The term "stable emulsion" used herein means that the emulsion is in a dispersed situation of thermodynamic stability, and could be placed as still under room temperature (25°C) for more than 1 month without visual phase separation, but with its reactive properties kept within this period.

The term "low VOC" used herein means the content of VOC in the emulsion is below 1wt%.

The inventors of the present invention found that: by using silane compounds with hydrocarbyloxy (-OR, R is hydrocarbyl, the same hereinafter unless indicated otherwise), acryloxy ( $R-\overset{\overset{O}{\|}}{C}-O-$), ketoximino (-O-N-CRR'), at their molecules, hydroxysilane compounds (or silanol) could be formed in the water, or the formed hydroxysilane compounds are further condensed to form silane oligomer or polysiloxane (see Figure 7). Hydroxysilyl and/or hydrocarbyloxy present at the surface of the formed hydroxysilane and/or polysiloxane would react with the reactive groups such as hydrocarbyloxysilyl (≡Si-O-R) and/or hydroxysilyl groups (≡Si-OH) on the molecular chain of a silylated polymer, and thus a large quantity of hydroxysilyl would be adsorbed on the surface of the silylated polymer latex particles by using post-emulsification process. The hydroxysilyl therein can not only stabilize the polymer latex particles, but also inhibit the self-crosslinking of the silylated polymer in water. Then, a stable silylated polymer emulsion can be obtained only by adding a small quantity of surfactant, or even no surfactant, to the system, while no organic solvent is needed herein.

The inventors of the present invention further found that: by additionally adding nano silica during the preparation of the silylated polymer emulsion where nano silica acts as Pickering emulsifier, the polymer latex particles could be further stabilized.

Based on these, the inventors accomplished the present invention.

Silylated polymer emulsion

Specifically, the present invention provides an aqueous silylated polymer emulsion, which comprises: (1) silylated polymer, (2) water, (3) hydrolysable silane compound, (4) optional nano silica, and (5) optional emulsifying agent.

The aqueous silylated polymer emulsion herein has a solid content of preferably 20- 85 wt%, more preferably 30 to 75 wt%, and in case that the silylated polymer is polysiloxane, the solid content is preferably 20- 75 wt%, more preferably 30 to 75 wt%. The emulsion obtained can be further diluted with water to desired extents in view of concrete intended uses. By adjusting its solid content, emulsifying agent, emulsifying aid and the like, the emulsion can be made as either oil-in-water or water-in-oil type emulsion.

The emulsion herein has average latex particle size of preferably less than 3 μm, more preferably less than 1 μm, determined by laser particle size analyzer.

The emulsion herein has a pH value of preferably 4 to 10, more preferably 5 to 9.

The silylated polymer emulsion herein can be cured to obtain a crosslinked elastomer after volatilization of water. The silane compounds added also act as crosslinking agent for filming-forming polymers. The addition of nano silica in the emulsion plays a role of enhancing the mechanical strengths of the crosslinked film-forming polymer.

Silylated polymer

The silylated polymer used herein is preferably a polymer functionalized by at least one hydrocarbyloxysilyl groups, more preferably a polymer having two hydrocarbyloxysilyl groups at chain end(s) and/or pendant to the chain(s).

More specifically, the silylated polymer includes but is not limited to: hydrocarbyloxysilyl polyether, hydrocarbyloxysilyl polyester, hydrocarbyloxysilyl polysiloxane, hydrocarbyloxysilyl polyacrylate, hydrocarbyloxysilyl polycarbonate, hydrocarbyloxysilyl polyurethane, hydrocarbyloxysilyl polyamide, hydrocarbyloxysilyl polyimide, hydrocarbyloxysilyl polyolefins and any combinations thereof.

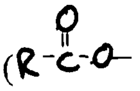
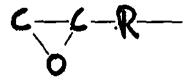
The non-limiting examples of the silylated polymer include: methyldiethoxysilyl polyethylene oxide ether, vinyldimethoxysilyl polypropylene oxide ether, triethoxysilyl polydimethylsiloxane, vinyldimethoxysilyl polydimethylsiloxane, methylethylmethoxysilyl polydimethylsiloxane, vinyldimethoxysilyl polymethylphenylsiloxane, vinyldimethoxysilyl polyester resin, vinyldiethoxysilyl polyester, methyldimethoxysilyl polyacrylate resin, methyldiethoxysilyl polycarbonate, methyldiacetoxysilyl polyurethane, triethoxysilyl polyurethane, propyldimethoxysilyl polyimide, and methyldiethoxysilyl polyethylene and the like. Said silylated polymer could be prepared according to the general methods disclosed in, for example U.S. Patent Nos. 5,300,608; 3,971,751; 4,374,237; 6,803,412; 5,986,014; 6,420,492 and CN 1100809C.

The silylated polymer as used herein has preferably a viscosity of 0.01 to 10,000 Pa.s (25°C), more preferably 0.05 to 2,000 Pa.s (25°C).

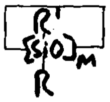
Said silylated polymers used in the present invention have preferably a weight average molecular weight (Mw) from 1000-200000, more preferably 5000-100000; molecular weight distribution index (Mw/Mn) preferably from 1-3, determined by GPC method.

The silylated polymer is present in the emulsion in an amount of preferably 20 to 84 wt%, more preferably 30 to 74 wt%, based on the total weight of the emulsion, and particularly in case that the silylated polymer is polysiloxane, the silylated polymer is present in the emulsion in an amount of preferably 20 to 74 wt%, more preferably 30 to 74 wt%.

Hydrolysable silane compound

Said hydrolysable silane compound is organic silicon compound containing group(s) capable to form a hydroxysilyl by virtue of hydrolysis, and could be represented by the general formula: Y_nSiX_{4-n}, wherein X is selected from C1-C16 hydrocarbyloxy (-OR), C1-C16 acyloxy ( $R-\overset{O}{\overset{\|}{C}}-O-$), C3-C16 ketoximino (-O-N=CRR'),and any of their combinations; Y is selected from: hydrogen (-H), hydroxyl (-OH), C1-C16 hydrocarbyl (-R), amino ($-NH_2$), C1-C16 hydrocarbylamino (-NHR, -NRR'), C1-C16 halohydrocarbyl (-RZ, Z is halogen), C1-C16 mercaptohydrocarbyl (-RSH), C1-C16 hydroxyhydrocarbyl (-ROH), C1-C16 aminohydrocarbyl (-RNH), C3-C16 epoxyhydrocarbyl (), C4-C16 acryloxyhydrocarbyl (CH_2=CRCOOR'-), C3-C16 (hydrocarbyl)phosphatohydrocarbyl ($-R_3PO_4$) and any of their combinations, and wherein R and R' are the same or different hydrocarbyls of certain carbon number ranges that meet the defined carbon number ranges in relation to the aforesaid groups, and n is an integer from 0-3;

Said silane compound could also be cyclic organosilicon compound



$\left[\overset{R'}{\underset{R}{Si}}O\right]_m$, R and R' are the same or different, and are hydrogen or C1-C10 hydrocarbyls, m is an integer from 3-10, which would form hydroxysilyls by hydrolysis.

Said hydrocarbyl is preferably alkyl.

More particularly, said silane compound is selected from: hydroxyl silane, hydrocarbyl hydrocarbyloxy silane, hydrocarbyl epoxy silane, amino hydrocarbyloxy silane, halohydrocarbyl hydrocarbyloxy silane, mercaptohydrocarbyl hydrocarbyloxy silane, hydroxyhydrocarbyl hydrocarbyloxy silane, aminohydrocarbyl hydrocarbyloxy silane, epoxyhydrocarbyl hydrocarbyloxy silane, (meth)acryloxyhydrocarbyl hydrocarbyloxy silane, hydrocarbyl acyloxy silane, hydrocarbyl ketoximino silane, (hydrocarbyl)phosphatohydrocarbylsilane, hydrocarbyl cyclosiloxane and any of their combinations. The non-limiting examples of said silane compound include: γ-chloropropyl triethoxy silane, chloropropyl methyl diethoxy silane, bromopropyl methyl diethoxy silane, tetraethyl orthosilicate, tetra-n-butyl orthosilicate, methyl diethoxy silane, methyl trimethoxy silane, methyl triethoxy silane, ethyl triethoxy silane, dimethyl diethoxy silane, propyl trimethoxy silane, allyl triethoxy silane, methyl ethyl dimethoxy silane, phenyl triethoxy silane, phenyl tripropoxy silane, phenyl triisopropoxy silane, phenyl tri-n-butoxy silane, diphenyl dimethoxy silane, diphenyl diethoxy silane, methyl phenyl dimethoxy silane, methyl phenyl diethoxy silane, ethyl phenyl diethoxy silane, decamethylcyclopentasiloxane,diethylphosphatoethyltriethoxysilane,vinyl triethoxy silane, vinyl tri (β – methoxyethoxy) silane, γ-aminopropyl triethoxy silane, γ-(β-aminoethyl)-aminopropyl methyl dimethoxy silane, γ-(β-aminoethyl)-aminopropyl trimethoxy silane, γ-(β-hydroxyethyl aminoethyl)-aminopropyl methyl dimethoxy silane, N,N-diethyl-γ-aminopropyl trimethoxy silane, N-methyl-3-aminopropyl trimethoxy silane, 3-cyclohexyl-aminopropyl methyl dimethoxy silane, γ-glycidyloxypropyl trimethoxy silane, γ-glycidyloxypropyl triethoxy silane, γ-glycidyloxypropyl methyl diethoxy silane, γ-methacryloxypropyl trimethoxy silane, γ-methyl acryloyloxy methyl dimethoxy silane, 3-ureidopropyl trimethoxy silane, γ-mercaptopropyl triethoxy silane, γ-mercaptopropyl trimethoxy silane, anilinomethyl triethoxy silane, hydroxyethyl dimethyl phenyl silane, dihydroxypropyl dimethyl silane, tetracetoxy silane, methyl triacetoxy silane, methyl tripropionyloxy silane, triphenyl acetoxy silane, vinyl tributanoneoximino silane, methyl triacetoneoximino silane, chloropropyl tributanoneoximino silane, and the like.

Said silane compound is present in the emulsion in an amount of preferably 1-20 wt%, more preferably 1-15 wt%.

Water

Water is present in the emulsion in an amount of preferably 15 to 78 wt%, more preferably 20 to 68 wt%, based on the total weight of the emulsion, and particularly in case that the silylated polymer is polysiloxane, the water is present in the emulsion in an amount of preferably 25 to 78 wt%, more preferably 25 to 68 wt%.

Emulsifying agent

The emulsifying agent as used herein could be any conventional emulsifying agent that serves to stabilize the silylated polymer in the aqueous silylated polymer emulsion. Preferably, the emulsifying agent is selected from the group consisting of anionic surfactant, nonionic surfactant, and any combinations thereof. More preferably, the emulsifying agent is selected from anionic surfactant having a HLB value of 3 to 50, nonionic surfactant having a HLB value of 3 to 50, and any combinations thereof.

More specifically, the emulsifying agent is preferably selected from the group consisting of C8-C22 alkyl sulfonates, C8-C22 alkyl benzene sulfonates, C8-C22 alkyl sulfates, phosphates, polyether-type surfactants such as C8-C22 fatty alcohol polyethylene oxide ether and C8-C22 alkyl phenol polyethylene oxide ether, C8-C22 fatty amide-polyethylene oxide, hydrophilic block polymer containing emulsified silylated polymer segment, and any combinations thereof.

The non-limiting examples of the emulsifier include: sodium dodecyl sulphonate (HLB=11-12), sodium cetyl sulphonate (HLB=12.1), sodium dodecyl benzenesulphonate (HLB=14.8), ammonium dodecyl benzenesulphonate (HLB=14.8), isopropyl amine dedecyl benzenesulphonate (HLB=11.7), sodium octyl sulfate (HLB=42.0), Triethanolamine dodecyl benzenesulphonate, sodium dodecyl diphenyl ether disulfonate, sodium nonyl phenol polyoxyethylene (4) ether sulfate, ammonium nonyl phenol polyoxyethylene (4) ether sulfate, sodium octyl sulfate (HLB=42), sodium dodecyl sulfate (HLB=42.0), ammonium dodecyl sulfate (HLB=42.0), monoethanolamine dodecyl sulfate (HLB=42.0), ammonium dodecyl polyoxyethylene (2) ether sulfate (HLB=42.0), ammonium C_{12-15} alkyl polyoxyethylene (1-4) ether sulfate (Standapol AP-60, Witcolate AE-3, HLB=42.0), sodium dodecyl polyoxyethylene(4) ether phosphate (HLB=42.0), tridecyl polyoxyethylene (6) ether phosphate (HLB=42.0), oleyl polyoxyethylene (3) ether phosphate (HLB=42.0), sodium nonyl phenol polyoxyethylene (9) ether phosphate (HLB=42.0), dinonyl phenol polyoxyethylene (10) ether phosphate (HLB=42.0), sodium diisobutyl sulfosuccinate (HLB=42.0), sodium divalerate sulfosuccinate (HLB=42.0), disodium dodecyl sulfosuccinate (HLB=42.0), sodium dicyclohexyl sulfosuccinate (HLB=42.0), sodium di-tridecyl sulfosuccinate (HLB=42.0), disodium dodecyl polyoxyethylene (1-4) ether sulfosuccinate (for example Alconate L-3, HLB=42.0), disodium oleylamido polyoxyethylene (2) ether sulfosuccinate (HLB=42.0), disodium nonyl phenol polyoxyethylene (10) ether sulfosuccinate (HLB=42.0), disodium oleylamido sulfosuccinate,(HLB=42.0), disodium N-monococoamido sulfosuccinate (HLB=42.0), dodecyl polyoxyethylene (2) ether (HLB=9.5), dodecyl polyoxyethylene (7) ether (HLB=11.0), dodecyl polyoxyethylene (12) ether (HLB=14.8), dodecyl polyoxyethylene (15) ether (HLB=15.5), dodecyl polyoxyethylene (23) ether (HLB=16.9), C_{9-11} alkyl polyoxyethylene (6) ether (for example Neodol 91-6, HLB=12.5), C_{12-14} alkyl polyoxyethylene (7) ether (for example Imbentin-AG/124/070, Marlipal, HLB=12.0), C_{12-15} alkyl polyoxyethylene (12) ether (for example Alkasurf LA-12, Tergitol 25-L-12, HLB=14.4), tridecyl polyoxyethylene (6) ether (HLB=11.4), tridecyl polyoxyethylene (10) ether (HLB=13.8), tridecyl polyoxyethylene (15) ether (HLB=15.5), hexadecyl polyoxyethylene (15) ether (HLB=15.5), hexadecyl polyoxyethylene (20) ether (HLB=17.0), hexadecyl polyoxyethylene (30) ether (HLB=19.5), isohexadecyl polyoxyethylene (20) ether(HLB=15.7), hexadecyl /octadecyl polyoxyethylene (12) ether (for example Incropol CS-12, HLB=12.0), hexadecyl /octadecyl polyoxyethylene (30) ether (for example Incropol CS-30, HLB=16.7), stearyl polyoxyethylene (20) ether (HLB=15.3), stearyl polyoxyethylene (40) ether (HLB=17.4), oleyl alcohol polyoxyethylene (20) ether (HLB=15.5), nonyl phenol polyoxyethylene (9) ether (HLB=13.5), nonyl phenol polyoxyethylene (10) ether (HLB=14.0), nonyl phenol polyoxyethylene(12) ether (HLB=14.6), nonyl phenol polyoxyethylene(30) ether (HLB=17.5), nonyl phenol polyoxyethylene(40) ether (HLB=18.0), nonyl phenol polyoxyethylene(70) ether (HLB=18.7), nonyl phenol polyoxyethylene(5) ether (HLB=10.0), nonyl phenol polyoxyethylene(8) ether (HLB=12.4), nonyl phenol polyoxyethylene(10) ether (HLB=13.3), nonyl phenol polyoxyethylene(30) ether (HLB=18.1), nonyl phenol polyoxyethylene (100) ether (HLB=19.1), cocoamine polyoxyethylene (15) ether (HLB=15.7), ethylenediamine polyoxyethylene polyoxypropylene polyoxyethylene polyether (HLB=12-18), glycol (8) dilaurate (HLB=10.8)), glycol (20) dilaurate (HLB=10.8), glycol (40) stearate (HLB=16.9), glycol (100) stearate (HLB=18.5), polyoxyethylene (20) glyceryl monostearate (HLB=13.1), polyoxyethylene (5) Sorbitan monooleate (HLB=10.0).

The emulsifying agent is preferably present in the emulsion in an amount of 0 to 4 wt%, more preferably 0 to 2 wt%, based on the total weight of the emulsion.

nano silica

Nano silica as used herein has a particle size of preferably 10 to 300 nm, more preferably 10 to 200 nm. nano silica as used herein has preferably BET specific surface area of $30m^2/g$ to $400m^2/g$.

Nano silica as used herein is of hydroxyl groups on the surface, such as various types of hydrophilic nano silica, which include, but are not limited to, nano silica powder such as precipitated nano silica and fumed nano silica, and nano silica hydrosol. The non-limiting examples of said nano silica include: nano silica hydrosol Nyacol® 9950, Nyacol® 2040, Nyacol® 830C, Nyacol® 2034DI, Bindzil® CC40, Bindzil® CC30 manufactured by EKA Chemical Corporation (Germany); nano silica hydrosol CH83-120, CH83-125, CH83-130 manufactured by Guolian Chemical Ltd., Jiangyin city, Jiangsu province; nano silica hydrosol GS-15, GS-20, GS-25, GS-30, GS-40, GS-301, GS-302, GS-303, GS-304, GS-305 manufactured by Yuda Chemical Ltd., Zhejiang province; precipitated nano silica Ultrasil® 360, S320DS, S325C manufactured by

Degussa Corporation, Germany; fumed nano silica Aerosil® R816, Aerosil® 130, Aerosil® 150, Aerosil® 200, Aerosil® 300, Aerosil® 380 manufactured by Degussa Corporation, Germany; fumed nano silica CAB-O-SIL® M-5, CAB-O-SIL® H-5, CAB-O-SIL® HS-5 manufactured by Cabot Corporation, USA; fumed nano silica N20 manufactured by Wacker Corporation, Germany; and fumed nano silica QS20LS, QS102, QS40, DM-10 manufactured by TOKUYAMA Corporation, Japan.

The nano silica is present in the emulsion in an amount of 0 to 20 wt%, preferably 0 to 10 wt%, based on the total weight of the emulsion.

Emulsifying aid

If desired, for instance, when it is desired to increase the hydrophilicity of the used polymers, consistency or stability of the emulsions, the emulsion herein may further comprise various suitable emulsifying aids so long as they bring no substantial adverse influence on the emulsion. The non-limiting examples of the emulsifying aid include hydrophilic aids, thickening agents, stabilizer, pH regulator, and any combinations thereof.

More specifically, the hydrophilic aid is preferably selected from water-soluble polymeric compounds, more preferably selected from the group consisting of polyvinyl pyrrolidone, polyethylene glycol, polyvinyl alcohol, polyvinyl methyl ether, and any combinations thereof.

The thickening agent is preferably selected from aqueous thickening agents, more preferably selected from the group consisting of hydroxymethyl cellulose, hydroxyethyl cellulose, bentonite, active clay, and any combinations thereof.

The stabilizer for emulsion includes thermal stabilizer and freeze-thaw stabilizer.

The pH regulator includes acid, base, or salt of low molecular weight, and any combinations thereof. More preferably, the pH regulator is selected from hydrochloric acid, sulfuric acid, nitric acid, ammonia water, ammonium carbonate, sodium carbonate, ammonium chloride and any combinations thereof.

The emulsifying aid is present in the emulsion in an amount of preferably from 0 to 5 wt%, more preferably from 0 to 3 wt%, based on the total weight of the emulsion.

Other optional ingredients

The emulsion herein may further comprise other optional ingredients so long as they bring no substantial adverse influence on the emulsion. The non-limiting examples of the optional ingredients include pigments, filler, defoaming agents, levelling agents, antioxidants, tackifiers, UV absorbents, and any combinations thereof.

More specifically, the optional ingredients include conventional pigments, filler (including inorganic materials in the form of nano particle and inert to the present inventive system, such as nano silica, nano titanium dioxide, nano aluminum oxide, nano iron oxide, nano zirconium oxide, nano zinc oxide, nano calcium carbonate, and the like), defoaming agents, levelling agents, antioxidants, tackifiers and UV absorbents that are conventionally used in the products such as coatings, adhesives, sealants, cosmetics, and any combinations thereof.

Method for preparing the aqueous silylated polymer emulsion

The present invention uses a specific silane compound to prepare the stable aqueous silylated polymer emulsion, and the preparation is diversified, but is simple, flexible and easy-to-operate.

In one embodiment of method for preparing the silylated polymer emulsion herein (Scheme A, simultaneous-addition of silane), the method comprises the following steps (see Fig. 4):

(1) blending silylated polymer, optional emulsifying agent and optional emulsifying aid together, to form Component AI;

(2) optionally mixing silane compound, water and optional nano silica together, to form Component AII;

(3) with stirring, adding the Component AII obtained in step (2) to the Component AI obtained in step (1), or simultaneously adding silane compound, water and optional nano silica separately, to carry out post-emulsification; and

(4) optionally, after finishing the post-emulsification, regulating the pH of the resultant emulsion to 4-10, thereby preparing the present silylated polymer emulsion.

In the preparation method, the amounts of various ingredients are controlled so as to prepare a stable oil-in-water or water-in-oil type silylated polymer emulsion. Based on the total weight of the emulsion, the amounts of various ingredients are preferably controlled as follows: 20 to 84 wt% of the silylated polymer, and in case that the silylated polymer is polysiloxane, the silylated polymer is present in the emulsion in an amount of preferably 20 to 74 wt%, more preferably 30 to 74 wt%; 1-20 wt% of silane compound; 15 to 78 wt% of water, and in case that the silylated polymer is polysiloxane, the water is present in the emulsion in an amount of preferably 25 to 78 wt%, more preferably 25 to 68 wt%; 0 to 4 wt% of the emulsifying agent; 0 to 20 wt% of nano silica; and from 0 to 5 wt% of the emulsifying aid.

In step (1), at a temperature of preferably 20-95°C, the silylated polymer, the optional emulsifying agent and the optional emulsifying aid are blended in a high-speed mixer with stirring at, preferably, 1,000-3,000 rpm for, preferably, 1-30 minutes.

In step (2), at a temperature of preferably 0-95°C, a homogeneous

Component AII containing silane compound, water and optional nano silica is formed in a mixer with stirring at, preferably, 100 -3,000 rpm for preferably 1-30 minutes.

In step (3), by controlling the system temperature at preferably 20-95°C, the Component AII that is already mixed homogeneously in advance and includes silane compound, water and optional nano silica is added in a high-speed mixer with stirring at, preferably, 2,000-5,000 rpm within preferably 0.05-3 hours; more preferably, after finishing the addition, the system may be further stirred at, preferably, 1,000-5,000 rpm for preferably 0.05-2 hours, while controlling the system temperature at preferably 20-95°C, thereby accomplishing the post-emulsification.

Alternatively, in step (3), by controlling the system temperature at preferably 20-95°C, the silane compound, water and optional nano silica is added simultaneously but separately with stirring at, preferably, 2,000-5,000 rpm within preferably 0.05-3 hours; more preferably, after finishing the addition, the system may be further stirred at, preferably, 1,000-5,000 rpm for preferably 0.05-2 hours, while controlling the system temperature at preferably 20-95°C, thereby accomplishing the post-emulsification.

In step (4), a pH regulator is preferably used to regulate the pH value of the silylated polymer emulsion. The non-limiting examples of the preferred pH regulator include acid, base, or salt of low molecular weight, and any combinations thereof. The non-limiting examples of the suitable pH regulator include hydrochloric acid, sulfuric acid, nitric acid, ammonia water, ammonium carbonate, sodium carbonate, ammonium chloride and the like. The pH regulator is used in an amount depending on the desired pH value of the emulsion.

The above preparation method A is preferably suitable for the silylated polymer emulsion using a water-soluble silane compound or its oligomer (for example γ-aminopropyltriethoxysilane, γ-(β-aminoethyl)-aminopropyl trimethoxy silane , diethylphosphatoethyltriethoxysilane).

In another embodiment of method for preparing the silylated polymer emulsion herein (Scheme B, Pre-addition of silane), the method comprises the following steps (see Fig. 5):

(1) blending silylated polymer, silane compound, optional emulsifying agent and optional emulsifying aid together, to form Component BI;

(2) mixing water and optional nano silica together, to form Component BII;

(3) with stirring, adding the Component BII obtained in step (2) to the Component BI obtained in step (1), to carry out post-emulsification; and

(4) optionally, after finishing the post-emulsification, regulating the pH of the resultant emulsion to 4-10, thereby preparing the present silylated polymer emulsion.

In the preparation method, the amounts of various ingredients are controlled in the same way as indicated in Scheme A, so as to prepare a stable oil-in-water or water-in-oil type silylated polymer emulsion.

In step (1), at a temperature of preferably 20-95°C, the silylated polymer, silane compound, the optional emulsifying agent and the optional emulsifying aid are blended in a high-speed mixer with stirring at, preferably, 1,000-3,000 rpm for, preferably, 1-30 minutes, to form Component BI.

In step (2), at a temperature of preferably 20 -95°C, a homogeneous Component BII containing water and optional nano silica is formed in a mixer with stirring at, preferably, 1000 -3,000 rpm for preferably 1-30 minutes, and/or preferably ultrasonic dispersion for 2-20 minutes.

In step (3), by controlling the system temperature at preferably 20-95°C, the Component BII that is already mixed homogeneously in advance and includes water and optional nano silica is added in a high-speed mixer with stirring at, preferably, 2,000-5,000 rpm within preferably 0.05-3 hours; more preferably, after finishing the addition, the system may be further stirred at, preferably, 1,000-5,000 rpm for preferably 0.05-2 hours, while controlling the system temperature at preferably 20-95°C, thereby accomplishing the post-emulsification.

In step (4), a pH regulator as indicated above is preferably used to regulate the pH value of the silylated polymer emulsion. The pH regulator is used in an amount depending on the desired pH value of the emulsion.

The above preparation method B is preferably suitable for the silylated polymer emulsion using a silane compound well compatible with the polymer (for example methytriethoxysilane, methylphenyldimethoxysilane).

In yet another embodiment of method for preparing the silylated polymer emulsion herein (Scheme C, Post-Addition of Silane), the method comprises the following steps (see Fig. 6):

(1) blending silylated polymer, optional emulsifying agent and optional emulsifying aid together, to form Component CI;

(2) with stirring, adding water and optional nano silica together to Component CI obtained in step (1), to form Component CII;

(3) with stirring, adding silane compound to the Component CII obtained in step (2), to carry out post-emulsification; and

(4) optionally, after finishing the post-emulsification, regulating the pH of the resultant emulsion to 4-10, thereby preparing the present silylated polymer emulsion.

In the preparation method, the amounts of various ingredients are controlled in the same way as indicated in Scheme A, so as to prepare a stable oil-in-water or water-in-oil type silylated polymer emulsion.

In step (1), at a temperature of preferably 20-95°C, the silylated polymer, the optional emulsifying agent and the optional emulsifying aid are blended in a high-speed mixer with stirring at, preferably, 1,000-3,000 rpm for, preferably, 1-30 minutes, to form Component CI.

In step (2), at a temperature of preferably 20-95°C, water and optional nano silica that are already mixed homogeneously in advance are added to Component CI in a high-speed mixer with stirring at, preferably, 2,000-5,000 rpm within preferably 0.05-3 hours, to form Component CII; more preferably, after finishing the addition, the system may be further stirred at, preferably, 1,000-5,000 rpm for preferably 0.05-2 hours, while controlling the system temperature at preferably 20-95°C.

In step (3), by controlling the system temperature at preferably 20-95°C, the silane compound, is added with stirring at, preferably, 2,000-5,000 rpm within preferably 0.05-3 hours; more preferably, after finishing the addition, the system may be further stirred at, preferably, 1,000-5,000 rpm for preferably 0.05-2 hours, while controlling the system temperature at preferably 20-95°C, thereby accomplishing the post-emulsification.

In step (4), a pH regulator as indicated above is preferably used to regulate the pH value of the silylated polymer emulsion. The pH regulator is used in an amount depending on the desired pH value of the emulsion.

The above preparation method C is widely suitable for the silylated polymer emulsion using a silane compound. This could simplify the process for silane addition, and alleviate the problem of inter-crosslinking of hydroxysily during the emulsion preparation, especially suitable for the emulsion preparation where a complicated processing step like heating is needed.

Anyone of the above three preparation methods could be used to prepare the aqueous silylated polymer emulsions.

The preparation process of the emulsion herein has no special requirement in pressure so long as it exerts no substantial adverse influence on the preparation method. Other operation conditions possibly involved but not mentioned in the present preparation method, may be identical with those conventionally used for preparing the silylated polymer emulsion. For example, see U.S. Patent Nos. 6,713,558 and 6,831,128.

The aqueous silylated polymer emulsion and its preparation method as set forth herein have the following advantages: (1) By using hydrolysable silane compounds with hydrocarbyloxy, acryloxy, or ketoximino and the like at their molecules, hydroxysilane compounds or polysiloxane could be formed in the water. Hydroxysilyl and/or hydrocarbyloxy present at the surface of the formed hydroxysilane and/or polysiloxane would react with the hydrocarbyloxysilyl and/or hydroxysilyl groups on the molecular chain of a silylated polymer, and thus a large quantity of hydroxysilyl would be adsorbed on the surface of the silylated polymer latex particles by using post-emulsification process. The hydroxysilyl can not only stabilize the polymer latex particles, but also inhibit the self-crosslinking of the silylated polymer in water. The silane compound actually acts as a surfactant or stabilizer, and further acts as a curing agent and crosslinking agent upon the water volatilization, in relation to the emulsion. Then, a stable silylated polymer emulsion can be obtained only by adding a small quantity of surfactant, or even no surfactant, to the system, while no organic solvent is needed herein.

(2) Nano silica is also allowed to be added during the preparation of emulsion, which could further stabilize polymer latex particles as a Pickering emulsifier.

(3) By using the methods as above described, nano silica can also be homogeneously dispersed in a silylated polymer. Also, without any

surface modification, nano silica can be directly added to the silylated polymer. It has good compatibility with the silylated polymer. Further, the addition of nano silica enhances the mechanical strengths of the crosslinked elastomer.

(4) The prepared silylated polymer emulsion has a solid content of ≤ 85 wt%, particularly, in case that the silylated polymer is polysiloxane, the solid content being ≤ 75 wt%, preferably 20-75 wt%; its particle size of less than 3 μm; and a shelf life of over one month when stored at room temperature. In use, the emulsion can be conveniently diluted directly with water to desired extent.

(5) The silylated polymer emulsion can be cured to obtain a crosslinked elastomer after volatilization of water. The obtained elastomer has a good mechanical property and is well used in formulating coatings, adhesives and sealants.

(6) The preparation methods as described herein include simultaneous-addition-of-silane method, pre-addition-of-silane method, and post-addition-of-silane method, which three methods are all useful for preparing a suitable aqueous silylated polymer emulsion, and simple, flexible and easy-to-operate.

Uses of the present emulsion

The stable low VOC silylated polymer emulsion prepared herein can be used as a raw material for coatings, adhesives, sealants, inks, release agents, skin care products, detergents and the like, and can be applied to the above products in a manner conventionally used by the silylated polymer emulsion. In use, the emulsion can be directly diluted with water to the desired extent in view of the concrete intended use.

All percentages and ratios used herein are based on weight, and all amounts of the ingredients in the emulsion are based upon the total weight of the emulsion, unless otherwise specified.

All cited publications are incorporated herein by reference in their entireties for all purposes.

EXAMPLES

The following examples further describe and demonstrate the preferred embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration, and are not to be construed as limitations of the present invention.

All steps for preparing the emulsion in the following examples are carried out under normal pressure, and the temperature involved is room temperature, unless otherwise specified.

The properties of the silylated polymer emulsion prepared herein are characterized as follows:

The viscosity of polymer is measured with NDJ-1A rotary viscometer (manufactured by Shende Technological Development Co., Ltd., China) at 25±1°C.

The molecular weight and its distribution of polymers are measured with Waters Breeze 1515 HPGPC (manufactured by Waters Co., USA).

The BET specific surface of nano silica was measured at 77K using an ASAP 2010 analyzer for nitrogen adsorption measurements and utilizing Barrett-Emmett-Teller (BET) for calculation of specific surface.

The average particle size of emulsion is determined with Coulter N4 Plus laser particle size analyzer (manufactured by Beckman Co., USA).

The appearance of crosslinked polymer is observed by XL30 Scanning Electron Microscopy ("SEM") (manufactured by Philips Co.).

The tensile strength and shearing strength of crosslinked polymer are determined by DXLL-10000 electron tensile tester (manufactured by

Shanghai Chemical Machinery Plant, China), in which the sample having a length of 20 mm is made according to ASTM-D412 standard, and the speed of extension is 50 mm/min.

Shore hardness of crosslinked polymer is determined by the TH-200 Shore hardometer manufactured by Tianjin Shidai Inc. of Shidai Group Corporation.

All of the determinations are conducted under ambient conditions, unless otherwise specified.

Example 1:

Formula 1 of aqueous silylated polymer emulsion (Scheme B)

Ingredients	Amount, gram
vinyl tri(β-methoxyethoxy) silane	7.0
vinyl diethoxysilyl terminated polydimethylsiloxane	33.0
water	57.0
ammonium lauryl polyoxyethylene (2) ether sulfate	2.0
hexadecyl polyoxyethylene (30) ether	1.0
polyoxyethylene (5) sorbitan monooleate	0.5

33.0 g vinyl diethoxysilyl terminated polydimethylsiloxane (having a molecular weight (Mw) of 12,000, see U.S. Patent No. 3,971,751. note: in this example and the following examples, the term "terminated" means that both ends of the polymer chain were terminated.), 7.0g vinyl tri(β-methoxyethoxy) silane, 2.0 g ammonium lauryl polyoxyethylene (2) ether sulfate , 1.0g hexadecyl polyoxyethylene (30) ether, and 0.5 g polyoxyethylene (5) sorbitan monooleate were added to a high speed mixer. At room temperature, the system was homogeneously mixed with stirring at 2,000 rpm for 10 minutes. By controlling the temperature at 30-40°C, 57.0g water was evenly dropped to the system within 2 hours with stirring at 3,000 rpm. After finishing the dropping, the system was continually stirred at the room temperature for 0.5 hour at 2,000 rpm, thereby resulting in an aqueous silylated polymer emulsion.

The prepared silylated polymer emulsion had a solid content of 39 wt%, an average latex particle diameter of 580 nm. When the aqueous silylated polymer emulsion obtained in the present example was used to bond glass sheets together, the shearing strength was 2.5 MPa. The emulsion had added silane compound content of 7 wt%. The emulsion could be placed as stable in room temperature over half a year, and could be diluted with water in use.

Example 2

Formula 2 of aqueous silylated polymer emulsion (Scheme B)

Ingredients	Amount, gram
isobutyl triethoxy silane	10.0
50 wt% nano silica hydrosol	16.0
triethoxysilyl terminated polydimethylsiloxane	59.0
sodium lauryl sulphate	0.5
Rhodia CO436	0.5
Rhodia CA 897	0.5
water	14.0
10 wt% Hydrochloric acid	to pH = 8

59.0 g triethoxysilyl polydimethylsiloxane (having a molecular weight (Mw) of 60,000, provided by Henkel KGaA, Duesseldorf, Germany, see

U.S. Patent No. 5,300,608), 10.0 g Isobutyl triethoxy silane, 0.5 g sodium lauryl sulfate, 0.5 g Rhodia CO436 (anionic surfactant, a polyethylene oxide (4) alkylphenol ether sulfate, manufactured by Rhodia Co.), and 0.5 g Rhodia CA897 (nonionic surfactant, a polyethylene oxide (40) nonyl phenol ether, manufactured by Rhodia Co.) were added to a high speed mixer. At room temperature, the system was homogeneously mixed with stirring at 2,000 rpm for 10 minutes. By controlling the temperature at 50-60°C, the mixed liquid of 14.0g water and 16.0 g 50 wt% nano silica hydrosol (Nyacol® 9950, having an average particle size of 100 nm, manufactured by EKA Chemical Co.) was evenly dropped to the system within 2 hours with stirring at 3,000 rpm. After finishing the dropping, the system was continually stirred for 0.5 hour at 2,000 rpm, while keeping the temperature at 50-60°C. Then, 10 wt% hydrochloric acid was added till pH = 8, thereby resulting in an aqueous silylated polymer emulsion.

The prepared silylated polymer emulsion had a solid content of 74 wt%, an average latex particle diameter of 1200 nm. The aqueous silylated polymer emulsion obtained in the present example after being dried to form a film at room temperature had a Shore hardness of 35 in the form of its dried film. The emulsion had added silane compound content of 10 wt% and nano silica content of 8 wt%. The emulsion could be placed as stable in room temperature over one month, and could be diluted with water in use.

Example 3:

Formula 3 of aqueous silylated polymer emulsion (scheme A)

Ingredients	Amount, gram

dodecamethyl cyclohexasiloxane	2.0
methyl diethoxy silane	13.0
methyl dimethoxysilyl terminated polyurethane	35.0
ICI Span 20	1.0
ICI Brij 97	0.8
ICI Brij 30	0.2
polyethylene glycol 8000	2.0
water	46.0

At room temperature, 2.0 g Dodecamethyl cyclohexasiloxane, 13.0 g Methyl diethoxy silane and 46.0 g water were homogeneously mixed in a mixer and ready for use in a dropping pipette. 35.0 g Methyl dimethoxysilyl terminated polyurethane (a molecular weight (Mw) 2200, see U.S. Patent No. 4,374,237), 1.0 g ICI Span 20 (a surfactant, manufactured by ICI Co.), 0.8 g ICI Brij 97 (a surfactant, manufactured by ICI Co.), 0.2 g ICI Brij 30 (a surfactant, manufactured by ICI Co.), and 2.0 g polyethylene glycol 8000 were added to a high speed mixer. At room temperature, the system was homogeneously mixed with stirring at 3,000 rpm for 30 minutes. The silane-containing mixed liquid obtained as above was evenly dropped to the system at room temperature within 2 hours with stirring at a 3,000 rpm. After finishing the dropping, the system was continually stirred for 0.5 hour at 3,000 rpm at room temperature, thereby resulting in an aqueous silylated polymer emulsion.

The prepared silylated polymer emulsion had a solid content of 49 wt%, an average latex particle diameter of 340 nm. When the aqueous silylated polymer emulsion obtained in the present example was used to bond aluminum sheets together, the shearing strength was 3.1 MPa. The emulsion had added silane compound content of 15 wt%, and could be placed as stable in room temperature over half a year, and could be diluted with water in use.

Example 4:

Formula 4 of aqueous silylated polymer emulsion (scheme A)

Ingredients	Amount, gram
30 wt% nano silica hydrosol	10.0
vinyl triethoxy silane	2.0
methyldimethoxysilyl terminated polyoxypropylene ether	50.0
disodium dodecyl polyoxyethylene (1-4) ether sulfosuccinate	0.2
sodium hexadecyl sulphonate	0.2
lauryl polyoxyethylene (2) ether	0.1
nonyl phenol polyoxyethylene (30) ether	0.2
water	37.0
2wt% nitric acid	to pH = 6

10.0 g 30 wt% nano silica hydrosol (Nyacol® 2040 having an average particle size of 20 nm, manufactured by EKA Chemical Co., Germany), 2.0 g vinyl triethoxy silane and 37.0 g water were homogeneously mixed in a mixer at room temperature. The obtained mixture was ready for use in a dropping pipette. 50.0 g methyldimethoxysilyl terminated polyoxypropylene ether (having a viscosity of 12 Pa.s at 25°C, see U.S. Patent No. 3,971,751), 0.2 g disodium dodecyl polyoxyethylene (1-4) ether sulfosuccinate, 0.2 g sodium hexadecyl sulphonate, 0.1 g lauryl polyoxyethylene (2) ether, and 0.2g nonyl phenol polyoxyethylene (30) ether were added to a high speed mixer. The system was homogeneously mixed with stirring at 3,000 rpm at 60-80°C for 10 minutes. While controlling the temperature at 60-80°C, the mixture of nano silica hydrosol, silane compound and water obtained as above was evenly dropped to the system within 2 hours with stirring at 4,000 rpm. After finishing the dropping, the system was continually stirred for 1 hour at 3,000 rpm while keeping the temperature at 60-80°C. Then, 2 wt% nitric acid was added till pH = 6, thereby resulting in an aqueous silylated polymer emulsion.

The prepared silylated polymer emulsion had a solid content of 55 wt%, an average latex particle diameter of 900 nm. The emulsion had added silane compound content of 2 wt% and nano silica content of 3 wt%. The emulsion could be placed as stable in room temperature for over one month and could be diluted with water in use.

Example 5:

Formula 5 of aqueous silylated polymer emulsion (scheme B)

Ingredients	Amount, gram
γ-glycidyloxypropyl trimethoxy silane	5.0
fumed nano silica	1.0
vinyldiethoxysilyl terminated polyester	30.0
Triton™ X-305 (70 wt%)	0.2
Triton X-100	0.3
water	64.0

1.0 g fumed nano silica (CAB-O-SIL® M-5, having a particle size of 200-300 nm, manufactured by Cabot Corporation, Massachusetts, U.S.A.) and 64.0 g water were mixed in a mixer with stirring at 3,000 rpm at 80-95°C for 15 minutes, and then ultrasonic dispersing for 10 minutes to obtain a nano silica aqueous dispersion. The dispersion was ready for use in a dropping pipette. 5.0 g γ-glycidyloxypropyl trimethoxy silane, 30.0 g vinyldiethoxysilyl terminated polyester (polycondensate of neopentyl glycol, adipic acid, and *o*-phthalic anhydride, having a viscosity of 23 Pa.s at 25°C and a molecular weight (Mw) 4,000,see U.S. Patent No. 6,803,412), 0.2 g Triton^{TM} X-305 (70 wt%) (nonionic surfactant, having a HLB value of 17.3, and being nonylphenol ethoxylate, manufactured by Dow Chemical Co.), and 0.3 g Triton X-100 (nonionic surfactant, having a HLB value of 13.4, and being nonylphenol ethoxylate, manufactured by Dow Chemical Co.) were added to a high speed mixer. The system was homogeneously mixed with stirring at 2,000 rpm at 80-95°C for 30 minutes. While controlling the temperature at 80-95°C, the nano silica aqueous dispersion obtained as above was evenly dropped to the system within 1 hour with stirring at 2,500 rpm. After finishing the dropping, the system was continually stirred for 0.5 hour at 3,000 rpm while keeping the temperature at 80-95°C, thereby resulting in an aqueous silylated polymer emulsion.

The prepared silylated polymer emulsion had a solid content of 35 wt%, an average latex particle diameter of 1900 nm, added silane compound content of 5 wt% and nano silica content of 1 wt%. The emulsion could be placed as stable in room temperature for over one month, and could be diluted with water in use.

Example 6:

Formula 6 of aqueous silylated polymer emulsion (scheme A)

Ingredients	Amount, gram
dimethyl diethoxy silane	10.0
vinyl tri(β-methoxyethoxy) silane	10.0
ethyl dimethoxysilyl terminated polymethylphenylsiloxane	50.0

sodium lauryl benzenesulphonate	0.3
polyvinyl pyrrolidone	1.0
water	29.0

At room temperature, 10.0 g dimethyl diethoxy silane, 10.0 g vinyl tri(β-methoxyethoxy) silane and 29 g water were mixed in a mixer to form a homogeneous mixture and ready for use in a dropping pipette. 50.0 g ethyl dimethoxysilyl terminated polymethylphenylsiloxane [having a viscosity of 90000 mm^2/s at 25°C and molecular weight (Mw) 100000, see U.S. Patent No. 5,300,608], 0.3 g sodium lauryl benzenesulphonate, 1.0 g polyvinyl pyrrolidone (Tradename: K30, 98 wt%, homopolymer of vinyl pyrrolidone, M_w 44000-54000) were added to a high speed mixer. At room temperature, the system was homogeneously mixed with stirring at 3,000 rpm for 30 minutes. The silane-containing mixed liquid obtained as above was evenly dropped to the system at room temperature within 2 hours with stirring at a 4,000 rpm. After finishing the dropping, the system was continually stirred for 1 hour at 3,000 rpm at room temperature, thereby resulting in an aqueous silylated polymer emulsion.

The prepared aqueous silylated polymer emulsion had a solid content of 61 wt%, an average latex particle diameter of 400 nm. The emulsion had added silane compound content of 20 wt%, and could be placed as stable in room temperature over half a year, and could be diluted with water in use.

Example 7:

Formula 7 of aqueous silylated polymer emulsion (scheme B)

Ingredients	Amount, gram
precipitated nano silica	15.0
n-octyl triethoxy silane	2.0
propyl triethoxy silane	3.0
methyl diethoxysilyl terminated polyacrylate	40.0
sodium divalerate sulfosuccinate	0.2
nonyl phenol polyoxyethylene (9) ether	0.8
water	39.0
1 wt% ammonia water	to pH = 8

15.0 g precipitated nano silica (Ultrasil® 360, specific surface area 50m^2/g, bulky density 220g/l, Degussa Corporation), and 39.0 g water were mixed in a mixer with stirring at 3,000 rpm at a temperature of 90-95°C for 20 minutes, and further ultrasonic dispersing for 5 minutes to form a dispersion of nano silica and water, and ready for use in a dropping pipette. 40.0 g methyl diethoxysilyl terminated polyacrylate (molecular weight (Mw) 110000, see U.S. Patent Nos. 5,986,014 and 6,420,492), 2.0 g n-octyl triethoxy silane, 3.0 g propyl triethoxy silane, 0.2 g sodium divalerate sulfosuccinate, and 0.8 g nonyl phenol polyoxyethylene (9) ether were added to a high speed mixer. At room temperature, the system was homogeneously mixed with stirring at 3,000 rpm for 30 minutes. The dispersion obtained as above was evenly dropped to the system at 90-95°C temperature within 1 hour with stirring at a 4,000 rpm. After finishing the dropping, the system was continually stirred for 1 hour at 3,000 rpm while keeping the temperature of 90-95°C. Then, 1 wt% ammonia water was added till pH = 8, thereby resulting in an aqueous silylated polymer emulsion.

The prepared silylated polymer emulsion had a solid content of 59 wt%, an average latex particle diameter of 2670 nm. The emulsion had added silane compound content of 5 wt% and nano silica content of 15 wt%, and could be placed as stable in room temperature over three months, and could be diluted with water in use.

Example 8:

Formula 8 of aqueous silylated polymer emulsion (scheme A)

Ingredients	Amount, gram
chloropropyl methyl diethoxy silane	1.0
n-hexyl trimethoxy silane	1.0
vinyl dimethoxysilyl terminated polydimethylsiloxane	40.0
active clay thickening agent	2.0
water	55.0

1.0 g chloropropyl methyl diethoxy silane, 1.0 g n-hexyl trimethoxy silane and 55.0 g water were added into a mixer and ultrasonic dispersed at 50-65°C for 10 minutes and ready for use in a dropping pipette. 40.0 g vinyl dimethoxysilyl terminated polydimethylsiloxane (molecular weight (Mw) 12000, provided by Henkel KGaA, Duesseldorf, Germany, see U.S. Patent No. 5,300,608), and 2.0 g active clay thickening agent were added to a high speed mixer. At room temperature, the system was homogeneously mixed with stirring at 3,000 rpm for 30 minutes. The silane/water mixture obtained as above was evenly dropped to the system at 50-65°C temperature within 2 hours with stirring at a 4,000 rpm. After finishing the dropping, the system was continually stirred for 0.5 hour at 3,000 rpm at 50-65°C temperature, thereby resulting in an aqueous silylated polymer emulsion.

The prepared aqueous silylated polymer emulsion had a solid content of 44 wt%, an average latex particle diameter of 2570 nm. The emulsion had added silane compound content of 2 wt%, and could be placed as stable in room temperature over half a year, and could be diluted with water in use.

Example 9:

Formula 9 of aqueous silylated polymer emulsion (scheme C)

Ingredients	Amount, gram
methyl dimethoxysilyl terminated polyoxypropylene ether	47.2
Rhodia CO436	1.1
Rhodia CA 897	1.0
fumed nano silica	4.1
ethylene glycol	2.0
γ-(β-aminoethyl)-aminopropylmethydimethoxysilane	5.2
demineralised Water	40.0

40.0 g demineralised water was weighted in a 250 ml beaker, and 4.1 g fumed nano silica (Cabot® H-5, without surface treatment, specific surface area 300±25 m^2/g, provide by Fuxiang Chemical Inc., Shanghai) was added into the beaker, and ultrasonic dispersed at 40-50°C for 15 minutes and ready for use in a dropping pipette. 47.2 g methyl dimethoxysilyl terminated polyoxypropylene ether (dynamic viscosity at 25°C: 8000mPa.s, provided by Henkel KGaA, Duesseldorf, Germany), 1.1 g Rhodia CO436 (anionic surfactant, a polyethylene oxide (4) alkylphenol ether sulfate, manufactured by Rhodia Co.), and 1.0 g Rhodia CA897 (nonionic surfactant, a polyethylene oxide (40) nonyl phenol ether, manufactured by Rhodia Co.) and 2.0 g ethylene glycol (AR, Lingfeng

Chemical Agents Ltd., Shanghai) were added to a 250 ml beaker. At room temperature, the system was homogeneously mixed with stirring at 1500 rpm for 10-20 minutes. The dispersion obtained as above by ultrasonic dispersion was evenly dropped to the system at not more than 90°C temperature within 30 minutes to 1 hour with stirring at a 3,000 rpm. After finishing the dropping, the system was continually stirred for 0.5 hour at 3,000 rpm at not more than 90°C temperature. 5.2 g γ-(β-aminoethyl)-aminopropylmethydimethoxysilane (Shuguang Chemical Inc., Nanjing, China) was added into the system, and the system was mixed three times (3000 rpm × 10s) by high speed shearing mixer Speedmixer ™ (Flacktek Inc.), thereby resulting in an aqueous silylated polymer emulsion.

The prepared silylated polymer emulsion had a solid content of 60 wt%. The emulsion had a silylated polymer content of 47 wt% , added silane compound content of 5 wt% and nano silica content of 4 wt%. The emulsion could be placed as stable under following conditions: over 3 months at room temperature, over five days at 60°C, centrifugalled by centifugal machine at 3000 rpm for 30 minutes, returned to the ambient temperature(25°C) after kept in -30°C for one day. After the emulsion was cured in air for 17 days, its shearing strength for bonding aluminum substrate was 0.75 MPa. The emulsion could be diluted with water in use.

Example 10:

Formula 10 of aqueous silylated polymer emulsion (scheme C)

Ingredients	Amount, gram
methyl dimethoxysilyl terminated polyoxypropylene ether	44.2

Rhodia CO436	2.1
Rhodia CA 897	1.0
fumed nano silica	4.0
ethylene glycol	1.0
polyethylene glycol 10000	2.0
epoxypropyloxypropyl trimethoxy silane	4.6
demineralised Water	40.2

40.2 g demineralised water was weighted in a 250 ml beaker, and 4.0 g fumed nano silica (Cabot® H-5, without surface treatment, specific surface area 300±25 m^2/g, provide by Fuxiang Chemical Inc., Shanghai) was added into the beaker, and ultrasonic dispersed at 40-50°C for 15 minutes and ready for use in a dropping pipette. 44.2 g methyl dimethoxysilyl terminated polyoxypropylene ether (dynamic viscosity at 25°C: 8000mPa.s, provided by Henkel KGaA, Duesseldorf, Germany), 2.1 g Rhodia CO436 (anionic surfactant, a polyethylene oxide (4) alkylphenol ether sulfate, manufactured by Rhodia Co.), and 1.0 g Rhodia CA897 (nonionic surfactant, a polyethylene oxide (40) nonyl phenol ether, manufactured by Rhodia Co.), 1.0 g ethylene glycol (AR, Lingfeng Chemical Agents Ltd., Shanghai) and 2.0 polyethylene glycol 10000 (China (Medical) Shanghai Chemical Agent Ltd.) were added to a 250 ml beaker. At room temperature, the system was homogeneously mixed with stirring at 1500 rpm for 10-20 minutes. The dispersion obtained as above by ultrasonic dispersion was evenly dropped to the system at not more than 90°C temperature within 30 minutes to 1 hour with stirring at a 3,000 rpm. After finishing the dropping, the system was continually stirred for 0.5 hour at 3,000 rpm at not more than 90°C temperature. 4.6 g epoxypropyloxypropyl trimethoxy silane (Guibao Chemical Ltd., Hangzhou, China) was added into the system, and the system was mixed three times (3000 rpm × 10s) by high speed shearing mixer Speedmixer ™ (Flacktek Inc.), thereby resulting in an aqueous silylated polymer emulsion.

The prepared silylated polymer emulsion had a solid content of 59 wt%. The emulsion had a silylated polymer content of 44 wt%, added silane compound content of 5 wt% and nano silica content of 4 wt%. The emulsion had average latex particle size of 439 nm. The emulsion could be placed as stable under following conditions: over 3 months at room temperature, over five days at 60°C, centrifugalled by centifugal machine at 3000 rpm for 30 minutes, returned to the ambient temperature (25°C) after kept in -30°C for one day. The emulsion could be diluted with water in use.

Example 11:

Formula 11 of aqueous silylated polymer emulsion (scheme C)

Ingredients	Amount, gram
vinyl dimethoxysilyl terminated polydimethylsiloxane	45.1
Rhodia CO436	1.0
Rhodia CA 897	1.0
fumed nano silica	4.2
ethylene glycol	1.1
polyethylene glycol 10000	1.0
methyl triethoxy silane	4.3
demineralised Water	40.2

40.2 g demineralised water was weighted in a 250 ml beaker, and 4.2 g fumed nano silica (Cabot® H-5, without surface treatment, specific surface area 300±25 m^2/g, provide by Fuxiang Chemical Inc., Shanghai) was added into the beaker, and ultrasonic dispersed at 40-50°C for 15 minutes and ready for use in a dropping pipette. 45.1 g vinyl dimethoxysilyl terminated polydimethylsiloxane (Mw: 60000, provided by Henkel KGaA, Duesseldorf, Germany), 1.0 g Rhodia CO436 (anionic surfactant, a polyethylene oxide (4) alkylphenol ether sulfate, manufactured by Rhodia Co.), 1.0 g Rhodia CA897 (nonionic surfactant, a polyethylene oxide (40) nonyl phenol ether, manufactured by Rhodia Co.), 1.1 g ethylene glycol (AR, Lingfeng Chemical Agents Ltd., Shanghai), and 1.0 polyethylene glycol 10000 (China (Medical) Shanghai Chemical Agent Ltd.) were added to a 250 ml beaker. At room temperature, the system was homogeneously mixed with stirring at 1500 rpm for 10-20 minutes. The dispersion obtained as above by ultrasonic dispersion was evenly dropped to the system at not more than 90°C temperature within 30 minutes to 1 hour with stirring at a 3,000 rpm. After finishing the dropping, the system was continually stirred for 0.5 hour at 3,000 rpm at not more than 90°C temperature. 4.3 g methyl triethoxy silane (Guotai Huarong Chemical New Materials Ltd., Zhangjiagang City, China) was added into the system, and the system was mixed three times (3000 rpm × 10s) by high speed shearing mixer Speedmixer ™ (Flacktek Inc.), thereby resulting in an aqueous silylated polymer emulsion.

The prepared silylated polymer emulsion had a solid content of 57 wt%. The emulsion had a silylated polymer content of 45 wt%, added silane compound content of 4 wt% and nano silica content of 4 wt%. The emulsion could be placed as stable under following conditions: over 3 months at room temperature, over five days at 60°C, centrifugalled by centifugal machine at 3000 rpm for 30 minutes. After the emulsion was placed at room temperature for 14 days, its average latex particle size was

927 nm. The emulsion could be diluted with water in use.

Example 12:

Formula 12 of aqueous silylated polymer emulsion (scheme A)

Ingredients	Amount, gram
vinyl dimethoxysilyl terminated polydimethylsiloxane	41.0
Rhodia CO436	1.0
Rhodia CA 897	1.0
γ-(β-aminoethyl)-aminopropylmethydimethoxysilane	4.1
tetraethoxy silane	1.1
demineralised Water	50.0

50.0 g demineralised water was weighted in a 250 ml beaker, and 4.1 g γ-(β-aminoethyl)-aminopropylmethydimethoxysilane (Shuguang Chemical Ltd., Nanjing city, China) and 1.1 g tetraethoxy silane (WD-932, Wuhai University, Wuhai city, China) was added into the beaker, and the system was mixed three times (3000 rpm × 30s) by high speed shearing mixer Speedmixer ™ (Flacktek Inc.) and ready for use in a dropping pipette. 41.0 g vinyl dimethoxysilyl terminated polydimethylsiloxane (Mw: 12000, provided by Henkel KGaA, Duesseldorf, Germany), 1.0 g Rhodia CO436 (anionic surfactant, a polyethylene oxide (4) alkylphenol ether sulfate, manufactured by Rhodia Co.), and 1.0 g Rhodia CA897 (nonionic surfactant, a polyethylene oxide (40) nonyl phenol ether, manufactured by Rhodia Co.) were added to a 250 ml beaker. At room temperature, the system was homogeneously mixed with stirring at 1500 rpm for 10-20 minutes. The aqueous mixed silane solution obtained as above was evenly dropped to the system at not more than 90°C temperature within 30 minutes to 1 hour with stirring at a 3,000 rpm. After finishing the dropping, the system was continually stirred for 0.5 hour at 3,000 rpm at not more than 90°C temperature, thereby resulting in an aqueous silylated polymer emulsion.

The prepared silylated polymer emulsion had a solid content of 48 wt%. The emulsion had a silylated polymer content of 40 wt%, and added silane compound content of 5 wt%. The emulsion could be placed as stable under following conditions: over 3 months at room temperature, over five days at 60°C.

Example 13:

Formula 13 of aqueous silylated polymer emulsion (scheme C)

Ingredients	Amount, gram
hydroxyl terminated polydimethylsiloxane	39.5
Rhodia CO436	0.4
Rhodia CA 897	0.4
fumed nano silica	5.8
polyethylene glycol 10000	1.0
methyl triethoxy silane	10.0
demineralised Water	65.6

65.6 g demineralised water was weighted in a 250 ml beaker, and 5.8 g fumed nano silica (Cabot® H-5, without surface treatment, specific surface area 300±25 m^2/g, provide by Fuxiang Chemical Inc., Shanghai) was added into the beaker, and ultrasonic dispersed at 40-50°C for 15 minutes and ready for use in a dropping pipette. 39.5 g hydroxyl terminated polydimethylsiloxane (dynamic viscosity at 25°C: 2000 cst, DC 3-0136, provided by Dow Corning), 0.4 g Rhodia CO436 (anionic surfactant, a polyethylene oxide (4) alkylphenol ether sulfate, manufactured by Rhodia Co.), 0.4 g Rhodia CA897 (nonionic surfactant, a polyethylene oxide (40) nonyl phenol ether, manufactured by Rhodia Co.) and 1.0 g polyethylene glycol 10000 (AR, China (Medical) Shanghai Chemical Agent Ltd.) were added to a 250 ml beaker. At room temperature, the system was homogeneously mixed with stirring at 1500 rpm for 10-20 minutes. The dispersion obtained as above by ultrasonic dispersion was evenly dropped to the system at not more than 90°C temperature within 30 minutes to 1 hour with stirring at a 3,000 rpm. After finishing the dropping, the system was continually stirred for 0.5 hour at 3,000 rpm at not more than 90°C temperature. 10.0 g methyl triethoxy silane (Guotai Huarong Chemical New Materials Ltd., Zhangjiagang City, China) was added into the system, and the system was mixed three times (3000 rpm × 10s) by high speed shearing mixer Speedmixer ™ (Flacktek Inc.), thereby resulting in an aqueous silylated polymer emulsion.

The prepared silylated polymer emulsion had a solid content of 43 wt%. The emulsion had a silylated polymer content of 32 wt%, added silane compound content of 8 wt% and nano silica content of 5 wt%. The emulsion could be placed as stable under following conditions: over 3 months at room temperature, over five days at 60°C. The emulsion could be diluted with water in use.

Example 14:

Formula 14 of aqueous silylated polymer emulsion (scheme B)

Ingredients	Amount, gram
vinyl dimethoxysilyl terminated polydimethylsiloxane	10.1

Rhodia CO436	1.0
Rhodia CA 897	1.1
ethylene glycol	2.0
methyl trimethoxy silane	6.0
demineralised water	80.4

80.4 g demineralised water was weighted in a 250 ml beaker and ready for use in a dropping pipette. 10.1 g vinyl dimethoxysilyl terminated polydimethylsiloxane (Mw being 12000, provided by Henkel KGaA, Duesseldorf, Germany), 1.0 g Rhodia CO436 (anionic surfactant, a polyethylene oxide (4) alkylphenol ether sulfate, manufactured by Rhodia Co.), and 1.1 g Rhodia CA897 (nonionic surfactant, a polyethylene oxide (40) nonyl phenol ether, manufactured by Rhodia Co.),2.0 g ethylene glycol (AR, the Chemical Agents Ltd. Of Guoyao Group Corporation, China) and 6.0 g methyl trimethoxy silane (Guibao Chemical Ltd., Hangzhou, China) were added to a 250 ml beaker. At room temperature, the system was homogeneously mixed with stirring at 1,500 rpm for 10-20 minutes. The demineralised water as above was evenly dropped to the system at a temperature not higher than 90°C within 30 minutes to 1 hour with stirring at a 3,000 rpm. After finishing the dropping, the system was continually stirred for 0.5 hour at 3,000 rpm while keeping the temperature of not more than 90°C, thereby resulting in an aqueous silylated polymer emulsion.

The prepared emulsion had a solid content of 18 wt%, a silylated polymer content of 10 wt%, and an added silane compound content of 6 wt%. The emulsion could be placed as stable in room temperature over three months, and could be diluted with water in use.

WHAT IS CLAIMED IS:

1. A silylated polymer emulsion, which comprises:
   (1) silylated polymer;
   (2) water;
   (3) hydrolysable silane compound;
   (4) optional nano silica; and
   (5) optional emulsifying agent.

2. An emulsion according to claim 1, wherein said silylated polymer is functionalized with at least one hydrocarbyloxysilyl group(s).

3. An emulsion according to claim 2, wherein said silylated polymer is selected from the group consisting of hydrocarbyloxysilyl polyether, hydrocarbyloxysilyl polyester, hydrocarbyloxysilyl polysiloxane, hydrocarbyloxysilyl polyacrylate, hydrocarbyloxysilyl polycarbonate, hydrocarbyloxysilyl polyurethane, hydrocarbyloxysilyl polyamide, hydrocarbyloxysilyl polyimide, hydrocarbyloxysilyl polyolefins and any combinations thereof.

4. An emulsion according to claim 1, wherein said silylated polymer has a viscosity of 0.01 to 10,000 Pa.s at 25°C.

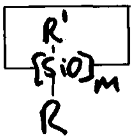
5. An emulsion according to claim 1, wherein said silylated polymer has a weight average molecular weight of 1000-200000, and molecular weight distribution of 1-3, determined by GPC method.

6. An emulsion according to claim 1, wherein said silylated polymer is present in the emulsion in an amount of 20 to 84 wt%, based on the total

weight of the emulsion, and in case that the silylated polymer is polysiloxane, the silylated polymer is present in the emulsion in an amount of preferably 20 to 74 wt%.

7. An emulsion according to claim 1, wherein said water is present in the emulsion in an amount 15 to 78 wt%, based on the total weight of the emulsion, and in case that the silylated polymer is polysiloxane, the water is present in the emulsion in an amount of preferably 25 to 78 wt%.

8. An emulsion according to claim 1, wherein said hydrolysable silane compound is represented by the general formula: Y_nSiX_{4-n} or



$$\left[\overset{R'}{\underset{R}{Si}}O\right]_m$$

, wherein R and R' are the same or different, and are hydrogen or C1-C10 hydrocarbyls, and m is an integer from 3-10, wherein X is selected from: C1-C16 hydrocarbyloxy, C1-C16 acyloxy, C3-C16 ketoximino, and any of their combinations; Y is selected from: hydrogen, hydroxyl, C1-C16 hydrocarbyl, amino, C1-C16 hydrocarbylamino, C1-C16 halohydrocarbyl, C1-C16 mercaptohydrocarbyl, C1-C16 hydroxyhydrocarbyl, C1-C16 aminohydrocarbyl, C3-C16 epoxyhydrocarbyl, C4-C16 acryloxyhydrocarbyl, C3-C16 (hydrocarbyl)phosphatohydrocarbyl, and any of their combinations; and n is an integer from 0-3.

9. An emulsion according to claim 8, wherein said hydrolysable silane compound is hydroxyl silane, hydrocarbyl hydrocarbyloxy silane, hydrocarbyl epoxy silane, amino hydrocarbyloxy silane, halohydrocarbyl hydrocarbyloxy silane, mercaptohydrocarbyl

hydrocarbyloxy silane, hydroxyhydrocarbyl hydrocarbyloxy silane, aminohydrocarbyl hydrocarbyloxy silane, epoxyhydrocarbyl hydrocarbyloxy silane, (meth)acryloxyhydrocarbyl hydrocarbyloxy silane, hydrocarbyl acyloxy silane, hydrocarbyl ketoximino silane, (hydrocarbyl)phosphatohydrocarbyl silane, hydrocarbyl cyclosiloxane and any of their combinations.

10. An emulsion according to claim 8, wherein said hydrolysable silane compound is present in the emulsion in an amount of 1-20 wt% of the total weight of the emulsion.

11. An emulsion according to claim 1, wherein said emulsifying agent is selected from the group consisting of anionic surfactant, nonionic surfactant, and any combinations thereof.

12. An emulsion according to claim 11, wherein said emulsifying agent is selected from anionic surfactant having a HLB value of 3 to 50, nonionic surfactant having a HLB value of 3 to 50, and any combinations thereof.

13. An emulsion according to claim 11, wherein said emulsifying agent is selected from the group consisting of C8-C22 alkyl sulfonates, C8-C22 alkyl benzene sulfonates, C8-C22 alkyl sulfates, phosphates, polyether-type surfactants, C8-C22 fatty amide-polyethylene oxide, hydrophilic block polymer containing emulsified silylated polymer segment, and any combinations thereof.

14. An emulsion according to claim 1, wherein said emulsifying agent is present in the emulsion in an amount of 0 to 4 wt%, based on the total weight of the emulsion.

15. An emulsion according to claim 1, wherein said nano silica is present and has a particle size of 10 to 300 nm.

16. An emulsion according to claim 1, wherein said nano silica is present and has a BET specific surface area of 30 m^2/g to 400m^2/g.

17. An emulsion according to claim 1, wherein said nano silica is present in the emulsion in an amount of 0 to 20 wt%, based on the total weight of the emulsion.

18. An emulsion according to claim 1, wherein said emulsion has a pH of 4-10.

19. An emulsion according to claim 1, wherein said emulsion has a solids content of 20-85 wt%, and in case that the silylated polymer is polysiloxane, its solid content is preferably 20- 75 wt%.

20. An emulsion according to claim 1, wherein said emulsion has average latex particle size of less than 3 μm.

21. An emulsion according to anyone of claims 1-20, wherein said emulsion is an oil-in-water type emulsion.

22. An emulsion according to anyone of claims 1-20, wherein said emulsion is a water-in-oil type emulsion.

23. A method for preparing a silylated polymer emulsion according to any one of claims 1 to 22, which comprises the following steps:

(1) blending silylated polymer, optional emulsifying agent and optional emulsifying aid together, to form Component AI;

(2) optionally mixing silane compound, water and optional nano silica together, to form Component AII;

(3) with stirring, adding the Component AII obtained in step (2) to the Component AI obtained in step (1), or simultaneously adding silane compound, water and optional nano silica separately, to carry out post-emulsification; and

(4) optionally, after finishing the post-emulsification, regulating the pH of the resultant emulsion to 4-10.

24. A method for preparing a silylated polymer emulsion according to any one of claims 1 to 22, which comprises the following steps:

(1) blending silylated polymer, silane compound, optional emulsifying agent and optional emulsifying aid together, to form Component BI;

(2) mixing water and optional nano silica together, to form Component BII;

(3) with stirring, adding the Component BII obtained in step (2) to the Component BI obtained in step (1), to carry out post-emulsification; and

(4) optionally, after finishing the post-emulsification, regulating the pH of the resultant emulsion to 4-10.

25. A method for preparing a silylated polymer emulsion according to any one of claims 1 to 22, which comprises the following steps:

(1) blending silylated polymer, optional emulsifying agent and optional emulsifying aid together, to form Component CI;

(2) with stirring, adding water and optional nano silica together to Component CI obtained in step (1), to form Component CII;

(3) with stirring, adding silane compound to the Component CII obtained in step (2), to carry out post-emulsification; and

(4) optionally, after finishing the post-emulsification, regulating the pH of the resultant emulsion to 4-10, thereby preparing the present silylated polymer emulsion.

26. Use of a silylated polymer emulsion according to any one of claims 1 to 22 as a raw material for coatings, adhesives, sealants, inks, release agents, skin care products and detergents.

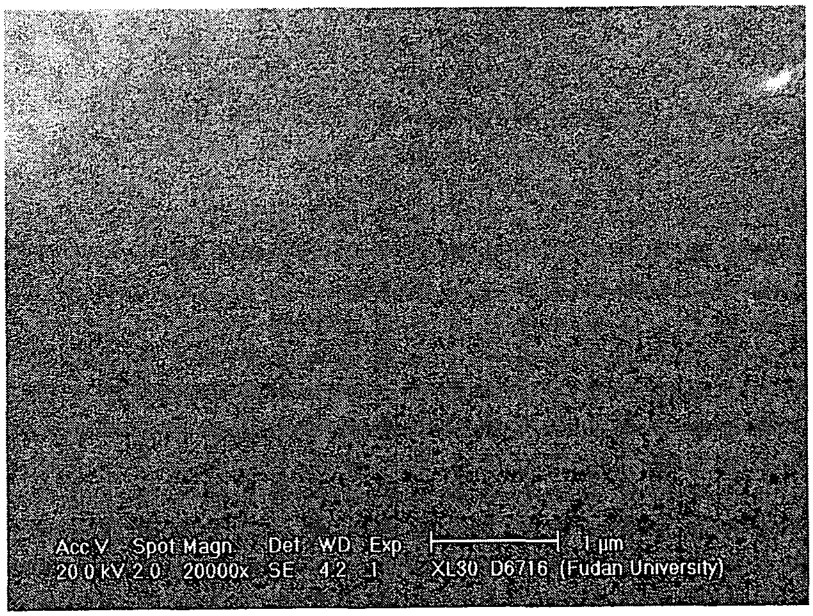

Acc.V Spot Magn Det WD Exp
1 µm
20.0 kV 2.0 20000x SE 4.2 1
XL30 D6716 (Fudan University)

Fig.1

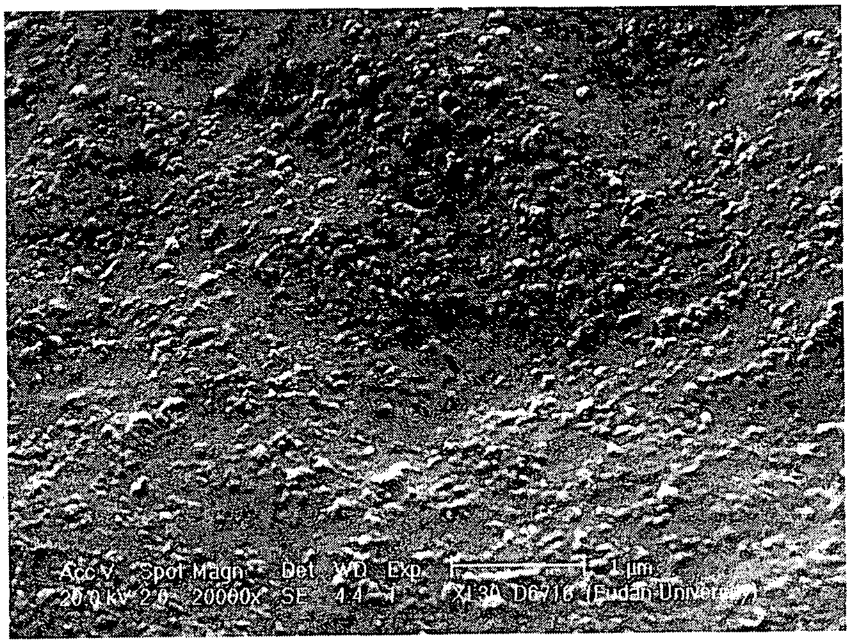

Acc.V Spot Magn Det WD Exp
1 µm
20.0 kV 2.0 20000x SE 4.4 1
XL30 D6716 (Fudan University)

Fig.2

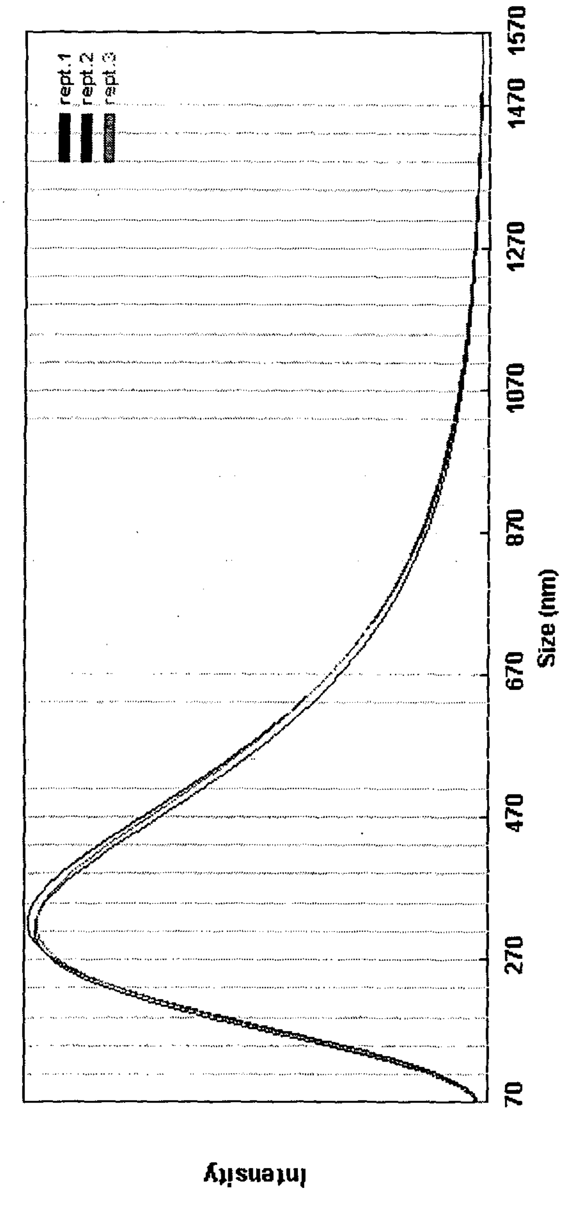

rept.1
rept.2
rept.3
Intensity
Size (nm)
70
270
470
670
870
1070
1270
1470
1570

Fig. 3

Scheme A:Simultaneoue-Addition of Silane

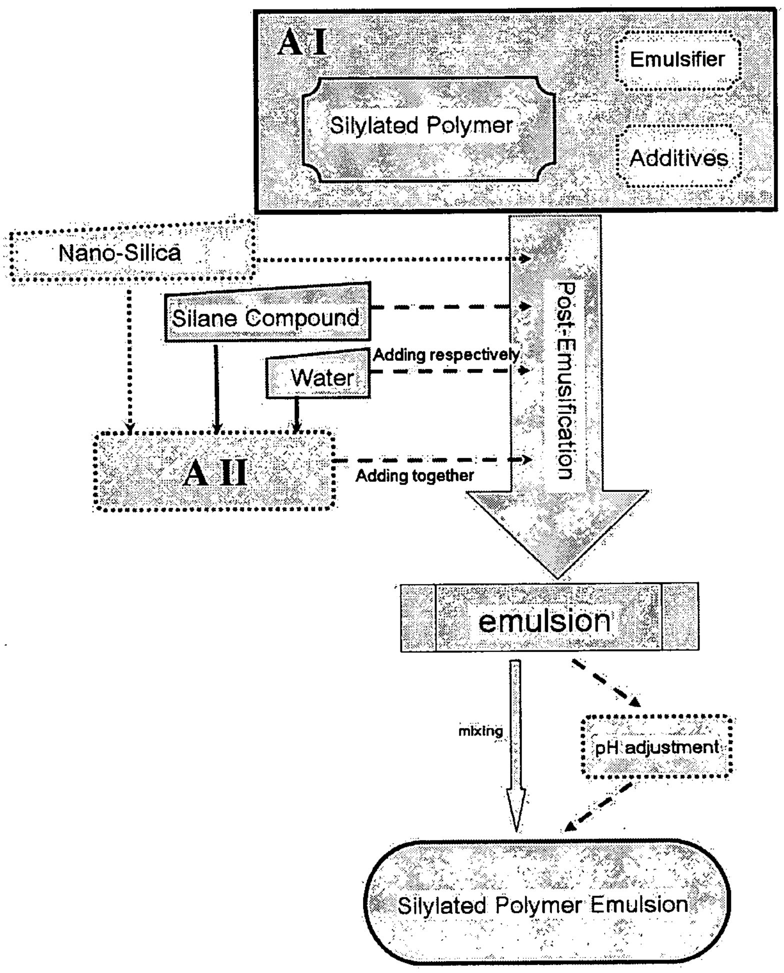


Fig. 4

Scheme B:Pre-Addition of Silane

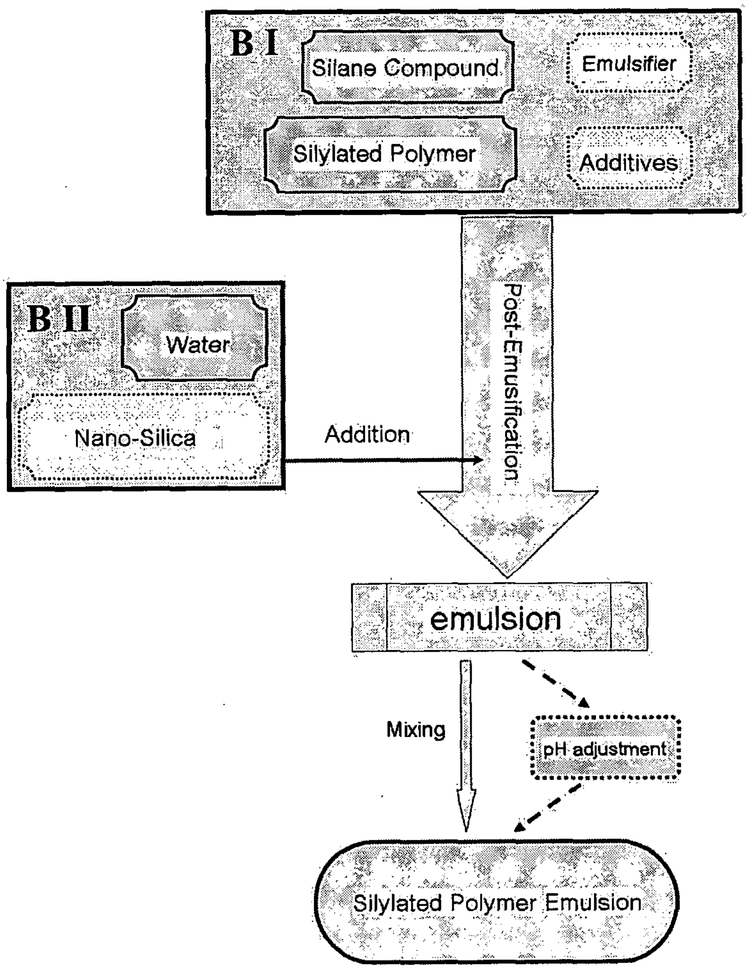


Fig.5

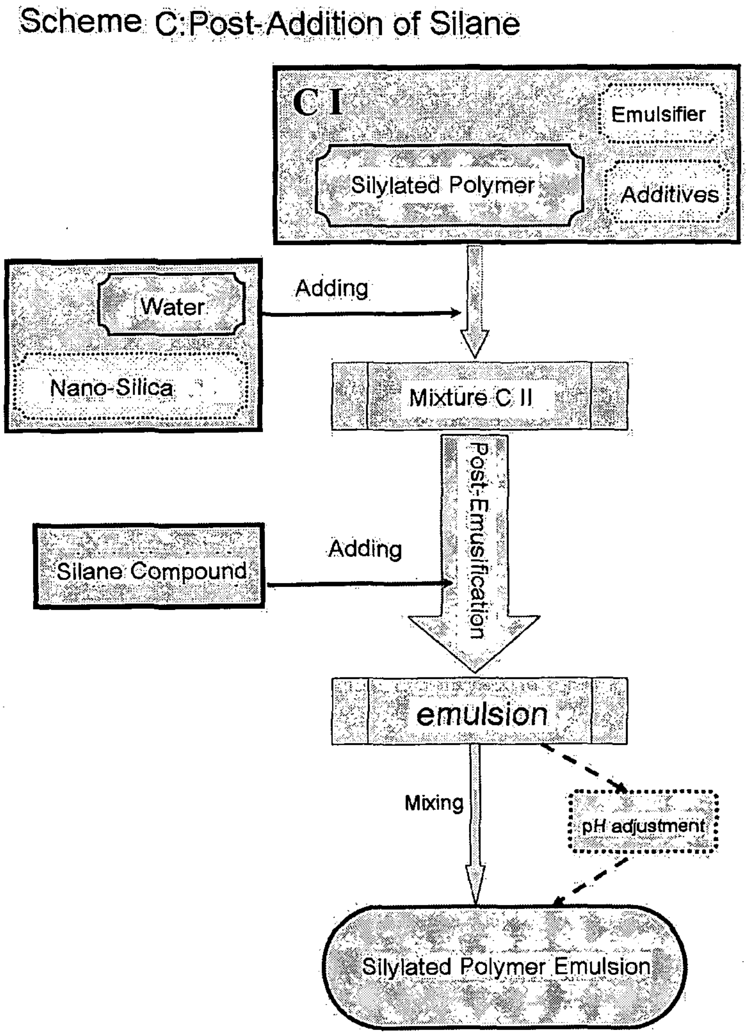

Scheme C:Post-Addition of Silane
C I
Emulsifier
Silylated Polymer
Additives
Water
Nano-Silica
Adding
Mixture C II
Post-Emusification
Silane Compound
Adding
emulsion
Mixing
pH adjustment
Silylated Polymer Emulsion

Fig.6

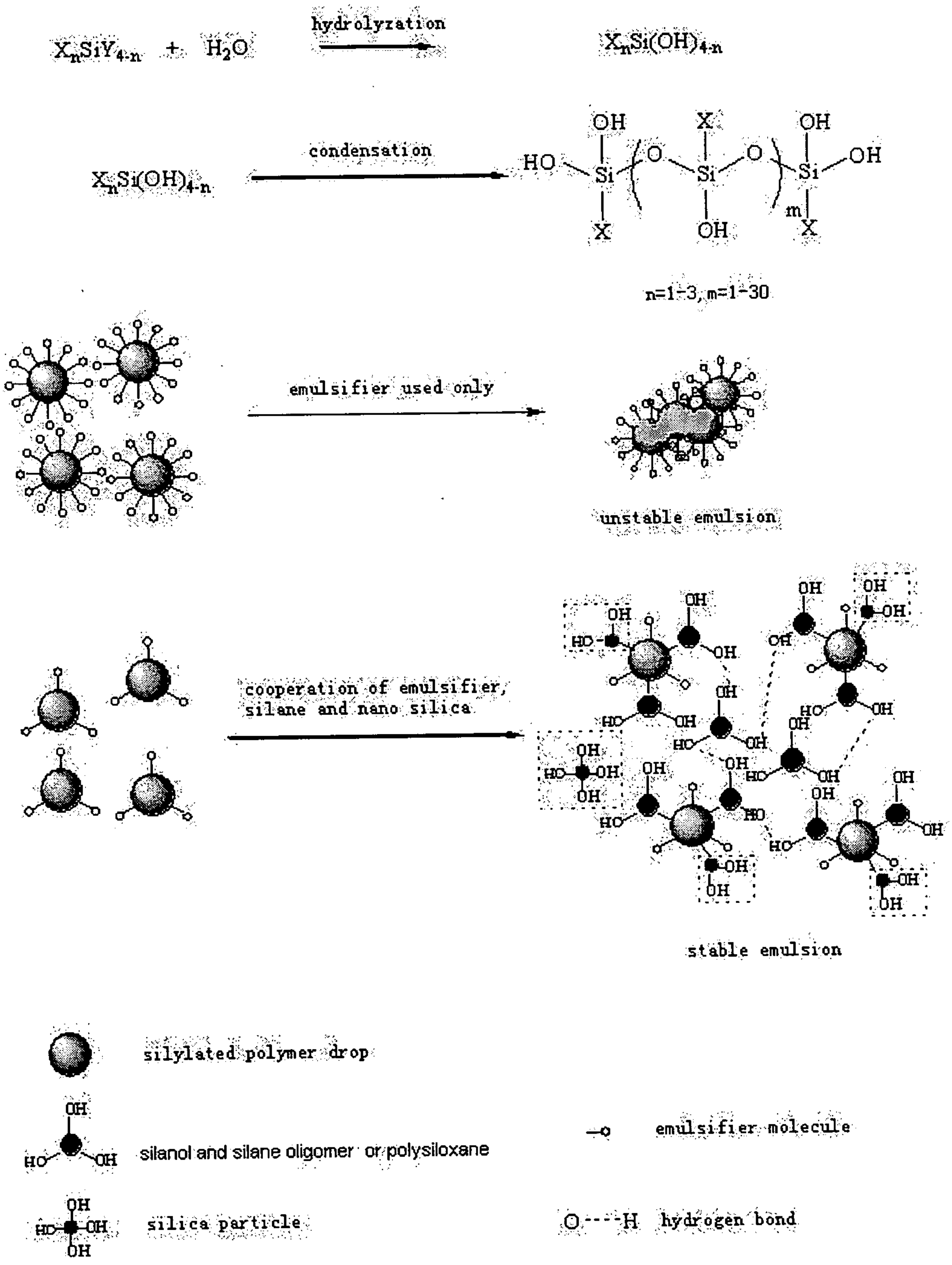

X_nSiY_4-n + H_2O
hydrolyzation
X_nSi(OH)_4-n
X_nSi(OH)_4-n
condensation
HO Si O Si O Si OH
OH X OH
X OH X
m
n=1-3, m=1-30
emulsifier used only
unstable emulsion
cooperation of emulsifier, silane and nano silica
stable emulsion
silylated polymer drop
silanol and silane oligomer or polysiloxane
emulsifier molecule
silica particle
O---H hydrogen bond
OH
HO

Fig.7

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2008/000167

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L83/00 C09J143/00

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 C09J

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	WO 97/12940 A (OSI SPECIALTIES INC [US]) 10 April 1997 (1997-04-10) page 3, line 29 - page 4, line 7 page 7, line 1 - line 5 page 9, line 21 page 13, line 6 page 15, line 24 page 17, line 20 - page 18, line 10 -----	1-23,26

☐ 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 document 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 11 June 2008	Date of mailing of the international search report 18/06/2008
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Trauner, H

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2008/000167

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9712940 A	10-04-1997	AT 264370 T	15-04-2004
		BR 9608437 A	09-03-1999
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		JP 2000512662 T	26-09-2000
		TW 397850 B	11-07-2000