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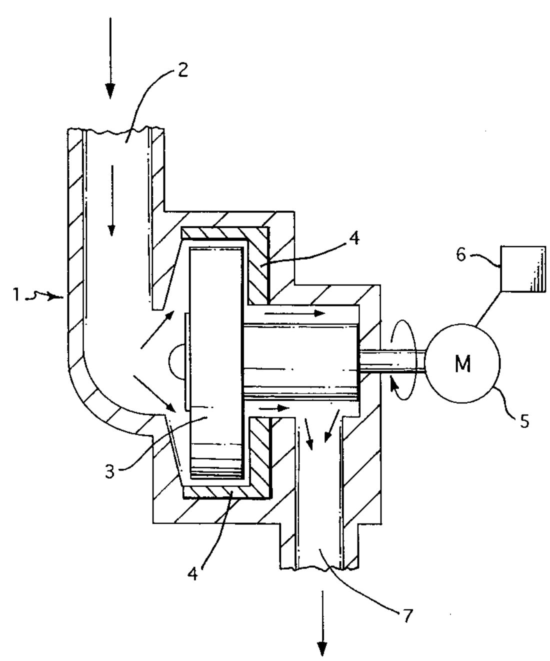
# (54) Emulsifier and method for manufacturing silicone oil emulsion or crosslinked silicone particle suspension

(57) An emulsifier in which the particle size of an emulsion or a suspension can be continuously adjusted, has a rotor (3) that is rotated by a motor (5) and a stator (4). It produces an emulsification action by shear force with said rotor, and the device is characterized by having an apparatus (6) for modulating the frequency of the input current to the motor in order to vary the rotational speed of the rotor. The corresponding methods for manufacturing either an emulsion of a silicone oil by emulsifying a silicone oil, an emulsifying agent, and water, or a suspension of crosslinked silicone particles by emulsifying a liquid crosslinkable silicone composition, an emulsifying agent, and water, are characterized by preparation of the emulsion or the suspension in an emulsifier in which the particle size of the emulsion or suspension is adjusted by varying the rotational speed of the rotor.




EP 1 093 843 A1

## Description

**[0001]** This invention is directed to an emulsifier and to a method for manufacturing a silicone oil emulsion or a crosslinked silicone particle suspension. More particularly, it relates to (i) an emulsifier with which the particle size of an emulsion or a suspension can be continuously adjusted, (ii) a method for manufacturing a silicone oil emulsion with which the particle size of the emulsion can be continuously adjusted, and (iii) a method for manufacturing a crosslinked silicone particle suspension with which the particle size of the suspension can be continuously adjusted.

**[0002]** Methods in which an emulsion or suspension is manufactured by using an emulsifier having a rotor that is rotated by a motor and a stator and produces an emulsification action by shear force with the rotor are known. Also known are (i) methods for manufacturing an emulsion of a silicone oil by emulsifying a silicone oil, an emulsifying agent, and water in this emulsifier, as well as (ii) methods for manufacturing a suspension of crosslinked silicone particles by emulsifying a liquid crosslinkable silicone composition, an emulsifying agent, and water in this emulsifier, to obtain an emulsion of a liquid crosslinkable silicone composition, and then crosslinking this composition that is emulsified in water.

**[0003]** According to such methods, the particle size of an emulsion or suspension is adjusted generally by (i) adjusting the clearance between the rotor and stator, (ii) changing the type of emulsifying agent, or (iii) increasing or decreasing the amount in which the emulsifying agent is employed.

**[0004]** However, in these methods for continuously adjusting the particle size of an emulsion or suspension, it was found to be difficult to suitably adjust the clearance between the rotor and stator, and it was also difficult to change the type of emulsifying agent. Furthermore, the problem with increasing or decreasing the emulsifying agent content was that it decreased the stability of the resulting emulsion or suspension.

**[0005]** It is therefore an object of the present invention to provide an emulsifier device in which the particle size of an emulsion or a suspension can be continuously adjusted. It is also an object of the present invention to provide (i) a method for manufacturing a silicone oil emulsion with which the particle size of the emulsion can be continuously adjusted, and (ii) a method for manufacturing a crosslinked silicone particle suspension with which the particle size of the suspension can be continuously adjusted.

**[0006]** The present invention is directed to an emulsifier having a rotor that is rotated by a motor and a stator that produces an emulsification action by shear force with the rotor, characterized by having an apparatus for modulating the frequency of the input current to the motor in order to vary the rotational speed of the rotor.

**[0007]** The present invention is also directed to a method for manufacturing an emulsion of a silicone oil by emulsifying a silicone oil, an emulsifying agent, and water, in an emulsifier having a rotor that is rotated by a motor and a stator, that produces an emulsification action by shear force with the rotor, characterized in that the particle size of the emulsion is adjusted by varying the rotational speed of the rotor.

**[0008]** The present invention is further directed to a method for manufacturing a suspension of crosslinked silicone particles by emulsifying a liquid crosslinkable silicone composition, an emulsifying agent, and water, in an emulsifier having a rotor that is rotated by a motor and a stator, that produces an emulsification action by shear force with the rotor, thereby obtaining an emulsion of a liquid crosslinkable silicone composition, and then crosslinking the composition that is emulsified in water, characterized in that the particle size of the suspension is adjusted by varying the rotational speed of the rotor.

**[0009]** These and other features, objects, and advantages of the invention will become apparent from a consideration of the detailed description.

**[0010]** The accompanying Figure is a pictorial representation shown partly in cross section, and a schematic diagram of the emulsifier device of the present invention. In the single figure, 1 represents the emulsifier device generally, 2 is the raw material supply port, 3 is a rotor, 4 is the stator, 5 is the motor, 6 is an inverter, and 7 is the finished product discharge port.

**[0011]** The emulsifier device of the present invention has a rotor that is rotated by a motor and a stator that produces an emulsification action by shear force with the rotor. The device is characterized by having an apparatus for modulating the frequency of the input current to the motor, in order to vary the rotational speed of the rotor.

**[0012]** Examples of the device include a colloid mill, homomixer, and an inline mixer, with the colloid mill being preferred. The rotor may supported on the rotary shaft of the motor such that it transmits the rotation of the motor, or the rotation of the motor may be transmitted by gears, a belt, and a chain. An apparatus termed an inverter is used as a mechanism for modulating the frequency of the input current to the motor, in order to vary the rotational speed of the rotor.

**[0013]** The inverter is able to vary the rotational speed of the motor directly by modulating the frequency of the input current to the motor, which allows the emulsifier to be more compact. With the emulsifier of the present invention, the particle size of an emulsion or suspension can be adjusted continuously, so it is possible to continuously prepare an emulsion or suspension with a large particle size to an emulsion or suspension with a small particle size. In specific terms, it is preferred for the emulsion or suspension particle diameter to be adjusted within a range of 0.1 to 500 μm, and for the volume average diameter of the particles to be within a range of 1 to 100 μm.

**[0014]** In the accompanying Figure, the emulsifier device 1 of the present invention includes a raw mate supply port 2 through which the raw material is supplied; a rotor 3 and a stator 4 for emulsifying the raw material; a motor 5 for rotating the rotor 3; an inverter 6 that functions as the apparatus for modulating the frequency of the input current to the motor 5, in order to vary the rotational speed of the motor 5; and a finished product discharge port 7 from which the emulsified finished product is removed.

**[0015]** While the rotor 3 in the accompanying Figure is shown supported on the rotary shaft of the motor 5, the rotation of the motor 5 may be transmitted to the rotor 3 by other means as noted above. An emulsifying action is produced by the shear force in the clearance between the rotor 3 and stator 4, and it is preferred that this clearance be between 1 and 1000 μm. It is also preferred that the rotational speed of the rotor be between 1000 and 20,000 rpm. If the viscosity of the raw material to be emulsified is over 5000 mPa·s at 25 °C, it is preferred that the rotational speed of the rotor be between 10,000 and 20,000 rpm. If the viscosity of the raw material is no more than 5000 mPa·s at 25 °C, however, there are no limitations on the rotational speed of the rotor, and in this case, allows for adjustment to a broader range of particle size.

**[0016]** In another aspect of the invention, there is provided a method for manufacturing an emulsion or suspension of a silicone oil by emulsifying a silicone oil, an emulsifying agent, and water, in an emulsifier having a rotor that is rotated by a motor and a stator, and which produces an emulsification action by shear force with the rotor. The method is characterized in that the particle size of the emulsion is adjusted by varying the rotational speed of the rotor. It is preferred that the emulsion or suspension particle diameter be adjusted to be within a range of 0.1 to 500 μm, for example, and in particular, for the volume average diameter of these particles to be within a range of 1 to 100 μm. Some examples of means for varying the rotational speed of the rotor in the manufacturing method of the invention include (i) methods involving modulating the frequency of the input current to the motor, in order to vary the rotational speed of the rotor, and (ii) methods involving using a transmission to vary the speed at which the rotation of the motor is transmitted, however, the former method (i) is preferred. An inverter can be used as the mechanism for modulating the frequency of the input current to the motor. The inverter is able to vary the rotational speed of the motor directly by modulating the frequency of the input current to the motor, and this feature allows the emulsifier to be more compact.

**[0017]** There are no particular limitations on the silicone oil used in the manufacturing method of the present invention. Some examples include silicone oils with a molecular structure that is cyclic, straight chain, partially branched straight chain, and branched chain. Particular examples of silicone oils include dimethylpolysiloxanes capped at both ends of the molecular chain with trimethylsiloxy groups, dimethylpolysiloxanes capped at both ends of the molecular chain with silanol groups, and cyclic dimethylsiloxanes.

**[0018]** In these silicone oils, some of the methyl groups may be substituted with phenyl groups, vinyl groups, 3,3,3-trifluoropropyl groups, 3-aminoaryl groups, and 3-glycidoxypropyl groups. There are no particular limitations on the viscosity of the silicone oil, but a range of 5 to 1,000,000 mPa·s at 25 °C is preferred, with a range of 5 to 5000 mPa·s being most preferred.

**[0019]** There are no particular limitations on the type of emulsifying agent used in the manufacturing method of the present invention. Examples of cationic surfactants which can be used include primary to tertiary aliphatic amine salts, alkyltrimethyl ammonium salts, dialkyldimethyl ammonium salts, tetraalkyl ammonium salts, trialkylbenzyl ammonium salts, alkyl pyridinium salts, and polyethylene polyamine fatty acid amide salts.

**[0020]** Examples of anionic surfactants which can be used include fatty acid salts, alkylbenzene sulfonates, alkyl sulfonates, alkyl naphthalene sulfonates, α-olefin sulfonates, dialkyl sulfosuccinates, α-sulfonated fatty acid salts, N-acyl-N-methyllaurate, alkylsulfates, sulfated lipids, polyoxyethylene alkyl ether sulfates, polyoxyethylene alkylphenyl ether sulfates, polyoxyethylene styrenated phenyl ether sulfates, alkylphosphates, polyoxyethylene alkyl ether phosphates, polyoxyethylene alkylphenyl ether phosphates, and naphthalene sulfonate formaldehyde condensates.

**[0021]** Examples of amphoteric surfactants which can be used include

N,N-dimethyl-N-alkyl-N-carboxymethyl ammonium betaines,
N,N-dialkylaminoalkylene carboxylates,
N,N,N-trialkyl-N-sulfoalkylene ammonium betaines,
N,N-dialkyl-N,N-bispolyoxyethylene ammonium sulfate ester betaines, and 2-alkyl-1-carboxymethyl-1-hydroxyethyl imidizolinium betaines.

**[0022]** Examples of nonionic surfactants which can be used include polyoxyethylene alkyl ethers, polyoxyethylene alkenyl ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene polystyrylphenyl ethers, polyoxyethylene polyoxypropylene glycols, polyoxyethylene polyoxypropylene alkyl ethers, sorbitan fatty acid esters, glycerol fatty acid esters, deca-glycerol fatty acid esters, polyglycerol fatty acid esters, propylene glycol pentaerythritol fatty acid esters, polyhydric alcohol fatty acid partial esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene glycerol fatty acid esters, polyoxyethylene polyhydric alcohol fatty acid partial esters, polyoxyethylene fatty acid esters, polyglycerol fatty acid esters, polyoxyethylenated castor oil, fatty acid diethanolamides, polyoxyethylene alkylamines, triethanolamine fatty acid partial esters, trialkylamine oxides, and polyoxyalkylene group containing organopolysiloxanes.

**[0023]** Mixtures of two or more types of these surfactants can also be employed.

**[0024]** The water used in the manufacturing method of the present invention can be any of a variety of types of water including ion exchanged water.

**[0025]** In the manufacturing method of the present invention, the silicone oil, the emulsifying agent, and water can each be put into the emulsifier individually, or they can first be mixed and then put into the emulsifier. In emulsifying these components, the particle size of a continuously obtained emulsion can be adjusted by varying the rotational speed of the rotor. As stated above, the preferred method of varying the rotational speed of the rotor is to modulate the frequency of the input current to the motor.

**[0026]** There are no particular limitations on the composition of the silicone oil emulsion obtained by the manufacturing method of the present invention. However, it is preferred that the emulsifying agent be used in an amount of 0.05 to 100 weight parts, and that the water be used in an amount of 20 to 1000 weight parts, each based on 100 weight parts of silicone oil. In these proportions, the stability of the emulsion will be better,

More preferably, the amount of the emulsifying agent to be used should be in an amount of 0.1 to 50 weight parts, and the water in an amount of 20 to 1000 weight parts, again each being based on 100 weight parts of silicone oil. This is for the reason that the stability of the emulsion will be poor if the emulsifying agent content is below the above range, and applications of the emulsion will be limited if the above range is exceeded. Also, preparation of a uniform emulsion will be difficult if the water content is below the above range, and the stability of the emulsion will decrease if the above range is exceeded.

**[0027]** An emulsion with a particle size ranging from large to extremely small can be continuously prepared by the manufacturing method of the present invention. The silicone oil emulsion can be used as a raw material for matting agents, defoaming agents, fiber treatment agents, and in cosmetics.

**[0028]** In another embodiment, the present invention includes a method for manufacturing a suspension of crosslinked silicone particles by (i) emulsifying a liquid crosslinkable silicone composition, an emulsifying agent, and water, in an emulsifier having a rotor that is rotated by a motor and a stator; (ii) producing an emulsification action by shear force with the rotor; (iii) obtaining an emulsion of a liquid crosslinkable silicone composition; and (iv) crosslinking the composition that is emulsified in water. This embodiment is also characterized in that the particle size of the suspension is adjusted by varying the rotational speed of the rotor.

**[0029]** In this alternate embodiment, it is preferred that the suspension particle diameter be adjusted to within a range of 0.1 to 500 μm, and that the volume average diameter of the particles be within a range of 1 to 100 μm. Two examples of the means of varying the rotational speed of the rotor include (i) modulating the frequency of the input current to the motor to vary the rotational speed of the rotor, and (ii) using a transmission to vary the speed at which the rotation of the motor is transmitted. The former means (i) is preferred. An inverter can be used as the mechanism for modulating the frequency of the input current to the motor. The inverter is able to vary the rotational speed of the motor directly by modulating the frequency of the input current to the motor, and this feature allows the emulsifier to be more compact.

**[0030]** There are no particular limitations on the liquid crosslinkable silicone composition used in the manufacturing method of this embodiment of the present invention. Some examples include liquid crosslinkable silicone compositions crosslinked by a hydrosilylation reaction, liquid crosslinkable silicone compositions crosslinked by a condensation reaction, liquid crosslinkable silicone compositions crosslinked by ultraviolet irradiation, and liquid crosslinkable silicone compositions crosslinked by an organic peroxide. Liquid crosslinkable silicone compositions crosslinked by a hydrosilylation reaction or by a condensation reaction are most preferred. While there are no particular limitations on the viscosity of the liquid crosslinkable silicone composition, it is preferred it be in the range of 5 to 1,000,000 mPa·s at 25 °C , most preferably in the range of 5 to 5000 mPa·s.

**[0031]** An example of a silicone composition that can be crosslinked by a hydrosilylation reaction and used in the manufacturing method of the present invention is one composed of at least one (i) organopolysiloxane having two or more alkenyl groups per molecule, an (ii) organopolysiloxane having two or more silicon atom bonded hydrogen atoms per molecule, and (iii) a hydrosilylation reaction catalyst. Alkenyl groups in organopolysiloxane (i) include the vinyl group, allyl group, pentenyl group, and hexenyl group, with the vinyl group being preferred. Organopolysiloxane (i) may contain groups bonded to silicon atoms other than the alkenyl groups such as the methyl group, ethyl group, propyl group, butyl group, or other alkyl group; the cyclopentyl group, cyclohexyl group, or other cycloalkyl group; the phenyl group, tolyl group, xylyl group, or other aryl group; the benzyl group, phenethyl group, 3-phenylpropyl group, or other aralkyl group; the 3-chloropropyl group, 3,3,3-trifluoropropyl group, or other halogen substituted hydrocarbon group; and other monovalent hydrocarbon groups. Its molecular structure includes linear, cyclic, reticulated, and partially branched linear structures, but to form elastomeric crosslinked silicone particles, the linear or partially branched linear structure is preferred. There are no particular limitations on the viscosity of organopolysiloxane (i) provided it allows the crosslinkable silicone composition to be dispersed in water. A range of 20 to 100,000 mPa·s at 25 °C is preferred, with a range of 20 to 10,000 mPa·s being most preferred.

**[0032]** Examples of groups bonded to silicon atoms other than hydrogen in organopolysiloxane (ii) include the same monovalent hydrocarbon groups as listed above. Examples of the molecular structure of organopolysiloxane (ii) include linear, cyclic, reticulated, and partially branched linear structures. There are no particular limitations on the viscosity of organopolysiloxane (ii) provided it allows the crosslinkable silicone composition to be dispersed in water. A range of 1 to 10,000 mPa·s at 25 °C is preferred however.

**[0033]** The amount of organopolysiloxane (ii) used to prepare the crosslinkable silicone composition should be sufficient to crosslink the composition, and is preferably between 0.3 and 200 weight parts per 100 weight parts of organopolysiloxane (i).

**[0034]** A catalyst is required in the hydrosilylation reaction, and the catalyst serves to promote the crosslinking reaction of the crosslinkable silicone composition. Preferably, the catalyst is platinum-based, and some examples include chloroplatinic acid, an alcohol solution of chloroplatinic acid, an olefin complex of platinum, an alkenylsiloxane complex of platinum, platinum black, and platinum carried on silica. In the manufacturing method of the invention, the crosslinkable silicone composition into which the hdrosilylation reaction catalyst has been added can be dispersed in water, or the crosslinkable silicone composition excluding the catalyst may be dispersed in water and then added to the water, which in either case allows the crosslinkable silicone composition containing the catalyst to be prepared in water.

**[0035]** In this regard, it is preferred to use an aqueous dispersion containing the hydrosilylation reaction catalyst with an average particle diameter of 1 μm or less. The amount of catalyst used in the crosslinkable silicone composition should be sufficient to promote the crosslinking reaction of the crosslinkable silicone composition. For a platinum-based catalyst, the amount of platinum metal in the catalyst should be between $1 \times 10^{-7}$ and $1 \times 10^{-3}$ weight parts per 100 weight parts of organopolysiloxane (i).

**[0036]** It is also possible to employ silicone compositions that can be crosslinked by a condensation reaction, and a suitable composition that can be used in the manufacturing method of the invention is one composed of (i) at least one organopolysiloxane having two or more hydroxyl groups, alkoxy groups, oxime groups, acetoxy groups, aminooxy groups, or other such hydrolyzable groups, which are bonded to silicon atoms in the molecule, (ii) a silane based crosslinking agent having three or more alkoxy groups, oxime groups, acetoxy groups, aminooxy groups, or other such hydrolyzable groups, bonded to silicon atoms in the molecule, and (iii) a condensation reaction catalyst such as an organotin or organotitanium compound.

**[0037]** Examples of alkoxy groups in organopolysiloxane (i) include the methoxy group, ethoxy group, and methoxyethoxy group. Examples of oxime groups include the dimethyl ketoxime group and the methyl ethyl ketoxime group. Examples of some other types of groups which can be bonded to silicon atoms in organopolysiloxane (i) include the methyl group, ethyl group, propyl group, butyl group, and other alkyl groups; the cyclopentyl group, cyclohexyl group, and other cycloalkyl groups; the vinyl group, allyl group, butenyl group, pentenyl group, and hexenyl group; the phenyl group, tolyl group, xylyl group, and other aryl groups; the benzyl group, phenethyl group, 3-phenylpropyl group, and other aralkyl groups; the 3-chloropropyl group, 3,3,3-trifluoropropyl group, and other halogen substituted hydrocarbon groups.

**[0038]** The molecular structure of organopolysiloxane (i) can be linear, cyclic, reticulated, or it can be partially branched linear. However, to form elastomeric crosslinked silicone particles, a linear or partially branched linear structure is preferred. There are no particular limitations on the viscosity of organopolysiloxane (i) provided it allows the crosslinkable silicone composition to be dispersed in water. A range of 20 to 100,000 mPa·s at 25 °C is preferred, while a range of 20 to 10,000 mPa·s is most preferred.

**[0039]** The alkoxy groups and the oxime groups in the silane based crosslinking agent (ii) are the same as the groups noted above. Some examples of suitable silane based crosslinking agents (ii) are methyltrimethoxysilane, vinyltrimethoxysilane, methyltrioximesilane, and vinyltrioximesilane. The amount of silane based crosslinking agent (ii) in the crosslinkable silicone composition should be sufficient to crosslink the composition, and is preferably between 0.3 and 200 weight parts per 100 weight parts of organopolysiloxane (i).

**[0040]** The condensation reaction catalyst, i.e., the organotin or organotitanium compound, promotes the crosslinking reaction of the crosslinkable silicone composition, and some representative examples include dibutyltin dilaurate, dibutyltin diacetate, tin octenoate, dibutyltin dioctoate, tin laurate, tetrabutyl titanate, tetrapropyl titanate, and dibutoxybisethyl acetate. The amount of condensation reaction catalyst used in the crosslinkable silicone composition should be sufficient to crosslink the composition, and is preferably between 0.01 and 5 weight parts per 100 weight parts of organopolysiloxane (i), with a range of 0.05 to 2 weight parts being most preferred.

**[0041]** A filler may be included in the crosslinkable silicone composition as an optional component for adjusting the fluidity of the composition or for increasing the mechanical strength of the crosslinked silicone particles obtained. Some examples of fillers include precipitated silica, fumed silica, baked silica, fumed titanium oxide, and other such reinforcing fillers; pulverized quartz, diatomaceous earth, aluminosilicic acid, iron oxide, zinc oxide, calcium carbonate, and other such non-reinforcing fillers. If desired, the filler can be one which has been surface treated with hexamethylsilazane, trimethylchlorosilane, polydimethylsiloxane, polymethylhydrogensiloxane, or other organosilicon compound.

**[0042]** There are no particular limitations on the emulsifying agent used in the manufacturing method provided it does not hinder the crosslinking reaction of the liquid crosslinkable silicone composition. Nonionic surfactants which can be used include polyoxyethylene alkyl ethers, polyoxyethylene polyoxypropylene alkyl ethers, polyoxyethylene alkylphenyl ethers, polyethylene glycol fatty acid esters, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene sorbitol fatty acid esters, glycerol fatty acid esters, polyoxyethylene glycerol fatty acid esters, polyglycerol fatty acid esters, propylene glycol fatty acid esters, polyethylene glycol, polypropylene glycol, and ethylene oxide adducts of diethylene glycol trimethylnonanol.

**[0043]** Some examples of anionic surfactants which can be used are hexylbenzene sulfonic acid, octylbenzene sulfonic acid, decylbenzene sulfonic acid, dodecylbenzene sulfonic acid, cetylbenzene sulfonic acid, myristylbenzene sulfonic acid, and the sodium salts of such anionic surfactants. Suitable cationic surfactants include octyltrimethyl ammonium hydroxide, dodecyltrimethyl ammonium hydroxide, hexadecyltrimethyl ammonium hydroxide, octyldimethylbenzyl ammonium hydroxide, decyldimethylbenzyl ammonium hydroxide, dioctadecyldimethyl ammonium hydroxide, tallow trimethyl ammonium hydroxide, and palm oil trimethyl ammonium hydroxide. Mixtures of two or more of these types of surfactants can also be employed. Nonionic surfactants are the most preferred.

**[0044]** Again, the water used can be any of a variety of types of water including ion exchanged water.

**[0045]** According to this embodiment of the invention, the liquid crosslinkable silicone composition, the emulsifying agent, and water can each be placed in the emulsifier individually, or the components can first be mixed and then placed in the device. It is preferred that the liquid crosslinkable silicone composition first be cooled to 5 °C or less to suppress the crosslinking reaction until the composition is emulsified. More preferred ranges are between -60 °C and +5 °C or between -30 °C and 0 °C.

**[0046]** If the silicone composition is crosslinked by a hydrosilylation reaction, the crosslinkable silicone composition excluding the hydrosilylation reaction catalyst may be emulsified, and the hydrosilylation reaction catalyst can then be added to the emulsion, in which case, the hydrosilylation reaction catalyst should be added as a dispersion with an average particle size of 1 μm or less.

**[0047]** In emulsifying these components, the particle size of the emulsion of the liquid crosslinkable silicone composition can continuously be adjusted by varying the rotational speed of the rotor, and this in turn allows the particle size of a suspension of crosslinked silicone particles to be adjusted. As explained above, modulating the frequency of the input current to the motor is the preferred method of varying the rotational speed of the rotor. A suspension of crosslinked silicone particles can then be prepared by simply leaving the resulting emulsion of liquid crosslinkable silicone composition at room temperature, heating the suspension, or placing it in a hot water bath, to crosslink the liquid crosslinkable silicone composition emulsified in water. The resulting crosslinked silicone particles should have an elastomeric form such as rubber or gel.

**[0048]** There are no particular limitations on the composition of the crosslinked silicone particle suspension, but because the stability of the emulsion is better, it is preferred that the emulsifying agent be used in an amount of 0.05 to 100 weight parts, and water in an amount of 20 to 1000 weight parts, each per 100 weight parts of silicone oil. More preferred ranges are 0.1 to 50 weight parts and 20 to 1000 weight parts, respectively. These ranges should be employed because the stability of the suspension will be poor if the emulsifying agent content is below these ranges, and the use of the suspension will be limited if the ranges are exceeded. In addition, preparation of a uniform suspension is difficult if the water content is below the ranges, and the stability of the suspension decreases if the ranges are exceeded.

**[0049]** An emulsion with particle size ranging from large to extremely small can be continuously prepared by the method according to this invention. It can be used as a raw material for matting agents, defoaming agents, fiber treating agents, and in cosmetic applications.

*WORKING EXAMPLES*

**[0050]** The following working examples are set forth to illustrate the emulsifier device and method of manufacturing a silicone oil emulsions or crosslinked silicone particle suspensions according to this invention. In the examples, viscosity is the value determined at 25 °C, and the emulsifier device was a type 2F Colloid Mill manufactured by Manton Gaulin in which an inverter, i.e., current frequency modulator, was added to the motor. The rotational speed in revolutions per minute (rpm) of the rotor of the Colloid Mill is the equivalent of about 330 times the frequency of the input current to the motor. The clearance between the rotor and the stator was in graduations of 25.4 μm (0.001 inch).

*Volume Average Particle Size of Emulsion or Suspension*

**[0051]** The particle size of the silicone oil emulsion and the particle size of the crosslinked silicone particle suspension were measured using a laser diffraction particle size distribution meter Model LA-500 manufactured by Horiba. A median diameter was obtained which was is a particle diameter corresponding to 50 % of the cumulative distribution, and this value was used as the volume average particle size.

*Gel Proportion of Aqueous Dispersion*

**[0052]** 200 g of the crosslinked silicone particle suspension was passed through a 200 mesh screen, and the proportion of crosslinked silicone particles remaining on the screen with respect to the total crosslinked silicone particles was used as the weight percentage.

*Working Example 1*

**[0053]** 96 weight parts of a dimethylvinylsiloxy terminated polydimethylsiloxane with a viscosity of 400 mPa·s, 4 weight parts of a trimethylsiloxy terminated polydimethylhydrogen siloxane with a silicon atom bonded hydrogen atom content of 1.5 weight percent and viscosity of 20 mPa·s, and 7 weight parts of a trimethylsiloxy terminated polydimethylsiloxane with a viscosity of 20 mPa·s, were mixed and cooled to -5 °C. A liquid silicone rubber composition with a viscosity of 300 mPa·s. was prepared by uniformly mixing into this mixture an isopropyl alcohol solution of chloroplatinic acid. It was added in an amount such that platinum metal atoms in the alcohol solution accounted for 20 ppm weight units with respect to the dimethylvinylsiloxy terminated polydimethylsiloxane.

**[0054]** The liquid silicone rubber composition was allowed to stand at room temperature for 1 day. The Type A Durometer Hardness of the silicone rubber was measured according to Japanese Industrial Standard JIS K 6253 and determined to be 29.

**[0055]** The total amount of the liquid silicone rubber composition was then mixed with 60 weight parts of an aqueous solution of 1.5 weight percent of polyoxyethylene nonylphenyl ether with an HLB of 13.1. The mixture was emulsified in a colloid mill using three graduations of clearance, in which the frequency of the input current to the motor was 20 Hz, 30 Hz, 40 Hz, and 50 Hz, respectively. Accordingly, four different liquid silicone rubber composition emulsions were prepared. Their characteristics are set forth in Table 1. The emulsions were allowed to stand for 1 day at room temperature to cure the liquid silicone rubber composition and prepare silicone rubber particle suspensions. Their characteristics are also set forth in Table 1.

*Comparative Example*

**[0056]** Working Example 1 was repeated in all respects, except that a Colloid Mill without an inverter was used in which the frequency of input current to the motor remained at 50 Hz. The clearance graduations were also changed to 10. Characteristics of the emulsion are set forth in Table 1. The emulsion was allowed to stand for 1 day at room temperature to cure the liquid silicone rubber composition and prepare a silicone rubber particle suspension. Its characteristics are also set forth in Table 1.

TABLE 1

| | Working Examples | | | | Comparative Example |
|---|---|---|---|---|---|
| Rotational speed of rotor, rpm | 6600 | 9900 | 13,200 | 16,500 | 16,500 |
| Volume average particle size, µm<br>Emulsion<br>Suspension | 12.3<br>12.7 | 10.5<br>11.1 | 7.8<br>8.0 | 3.4<br>3.6 | 4.1<br>4.3 |
| 200 mesh remainder, wt % | 0.3 | 0.2 | 0.2 | 0.2 | 0.3 |

**[0057]** In Table 1, it can be seen that by using the emulsifier device according to this invention, that the particle size of an emulsion or a suspension can be adjusted continuously, and that anything from an emulsion or a suspension with a large particle size to an emulsion or a suspension with an extremely small particle size can be manufactured continuously.

## Claims

1. An emulsifying device for producing an emulsification action including a rotor (3) rotated by a motor (5) and a stator (4) for producing the emulsification action by shear force with the rotor, characterised in that the device comprises means (6) for modulating the frequency of input current to the motor for varying the rotational speed of the rotor.

2. An emulsifying device according to Claim 1 which is a colloid mill.

**3.** A method for manufacturing emulsions of silicone oils comprising (i) emulsifying a silicone oil, an emulsifying agent and water, in an emulsifier device (1) having a rotor (3) rotated by a motor (5), and a stator (4) for producing an emulsification action by shear force with the rotor (3), and (ii) continuously adjusting the particle size of the silicone oil in the emulsion by varying the rotational speed of the rotor during manufacture of the silicone oil emulsion.

**4.** A method according to Claim 3 which comprises varying the rotational speed of the rotor by modulating the frequency of the input current to the motor.

**5.** A method according to Claim 3 or 4, in which the emulsion comprises 100 weight parts of the silicone oil, 0.05 to 100 weight parts of the emulsifying agent, and 20 to 1000 weight parts of water.

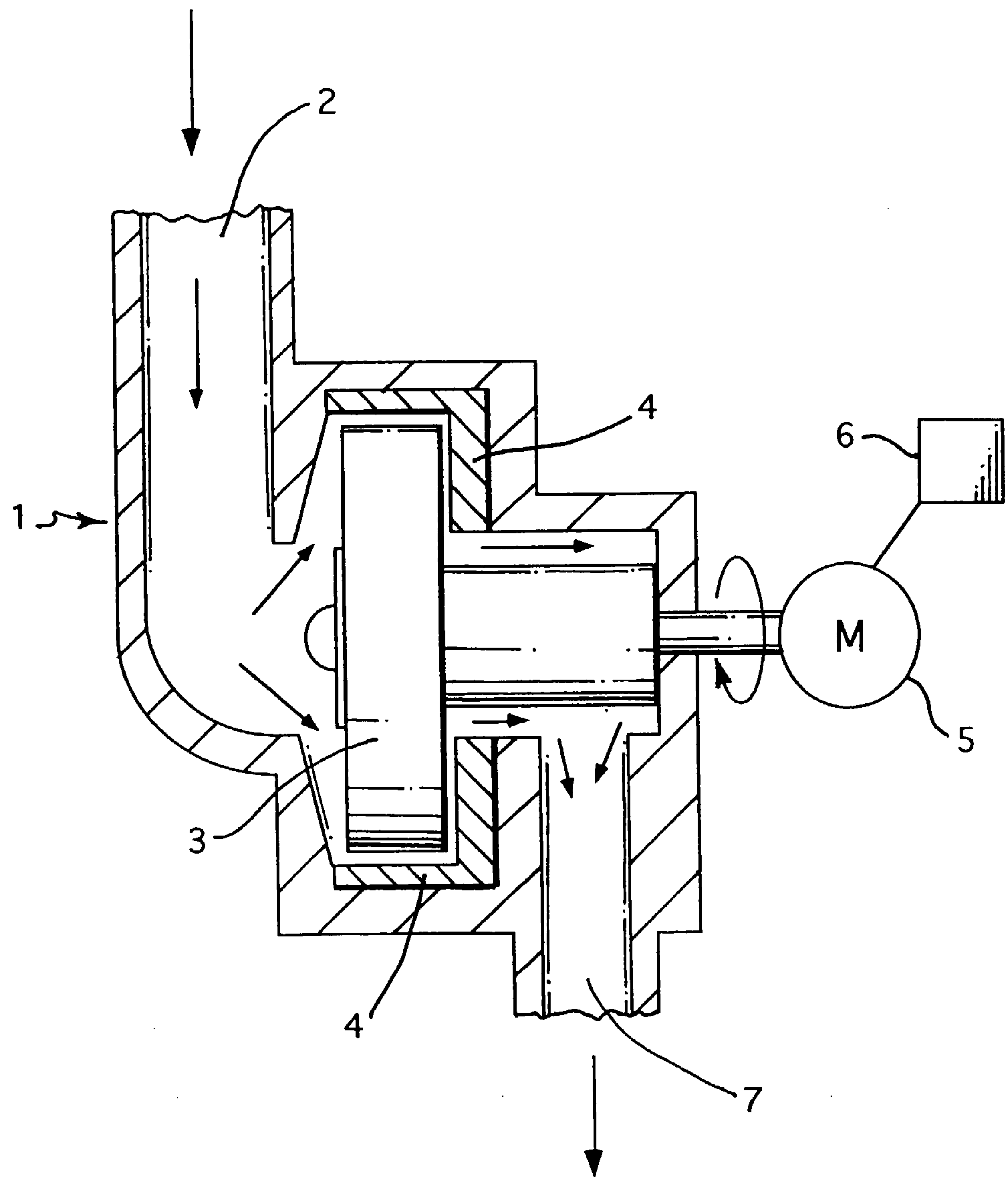
**6.** A method for manufacturing a suspension of crosslinked silicone particles comprising (i) emulsifying a liquid crosslinkable silicone composition, an emulsifying agent and water, in an emulsifier device (1) having a rotor (3) rotated by a motor (5), and a stator (4) for producing an emulsification action by shear force with the rotor (3), (ii) first forming an emulsion of the liquid crosslinkable silicone composition, (iii) crosslinking the liquid crosslinkable silicone composition to form crosslinked silicone particles, and then (iv) forming a suspension of the crosslinked silicone particles by continuously adjusting the particle size of the crosslinked silicone particles in the suspension by varying the rotational speed of the rotor (3).

**7.** A method according to Claim 6, which comprises varying the rotational speed of the rotor by modulating the frequency of the input current to the motor.

**8.** A method according to Claim 6 or 7, in which the emulsion comprises 100 weight parts of the liquid crosslinkable silicone composition, 0.05 to 100 weight parts of the emulsifying agent, and 20 to 1000 weight parts of water.

**9.** A method according to any of Claims 6 to 8, in which the crosslinked silicone particles are crosslinked by hydrosilylation or condensation reactions.

**10.** A method according to any of Claims 6 to 9, in which the crosslinked silicone particles are elastomeric particles.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# EUROPEAN SEARCH REPORT

Application Number
EP 00 30 9249

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.7) |
|---|---|---|---|
| Y | GB 2 120 565 A (JANKE AND KUNKEL GMBH) 7 December 1983 (1983-12-07) * abstract; claim 2; figure * | 1 | B01F15/00 B01F3/08 B02C7/14 B02C7/175 |
| Y | FR 2 454 094 A (SREDNEAZIATSKY NAUCHNO-ISSLEDOVATELSKY INSTITUT PRIRODNOGO GAZA) 7 November 1980 (1980-11-07) * claim 1; figure * | 1 | |
| X | US 4 963 778 A (N.D.JENSEN ET AL) 16 October 1990 (1990-10-16) * claim 1; figure 2 * | 1 | |
| A | DE 32 21 476 A (PROBST & CLASS GMBH & CO KG) 8 December 1983 (1983-12-08) * claims; figure 1 * | 2 | |
| Y | CH 683 322 A (GLATT MASCHINEN- UND APPARATEBAU AG) 28 February 1994 (1994-02-28) * claims; figure 1 * | 1-10 | TECHNICAL FIELDS SEARCHED (Int.Cl.7) |
| Y | US 4 380 503 A (G.KOERNER ET AL) 19 April 1983 (1983-04-19) * claim 1; example 1 * | 1-10 | B01F B02C |
| Y | US 4 589 598 A (J.M.ELLERY) 20 May 1986 (1986-05-20) * claims * | 1,2 | |
| Y | PATENT ABSTRACTS OF JAPAN vol. 017, no. 489, 6 September 1993 (1993-09-06) & JP 05 123592 A (TOPY IND LTD) * abstract * | 1,2 | |

-/--

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| BERLIN | 30 January 2001 | Cordero Alvarez, M |

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## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.7) |
|---|---|---|---|
| A | DE 27 42 229 A (ESCHER WYSS GMBH) 8 March 1979 (1979-03-08) * claims; figures * ----- | 1,2 | |

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| BERLIN | 30 January 2001 | Cordero Alvarez, M |

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## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 30 9249

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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30-01-2001

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| GB 2120565 A | 07-12-1983 | DE 3220453 A | 01-12-1983 |
| | | FR 2527476 A | 02-12-1983 |
| | | IT 1166520 B | 06-05-1987 |
| FR 2454094 A | 07-11-1980 | AU 5733580 A | 02-10-1980 |
| | | DE 2953616 T | 23-04-1981 |
| | | NL 8001806 A | 30-09-1980 |
| | | WO 8002039 A | 02-10-1980 |
| US 4963778 A | 16-10-1990 | DE 3642724 A | 23-06-1988 |
| | | FR 2608332 A | 17-06-1988 |
| | | GB 2201297 A,B | 24-08-1988 |
| | | IT 1223419 B | 19-09-1990 |
| | | JP 2865290 B | 08-03-1999 |
| | | JP 63161843 A | 05-07-1988 |
| DE 3221476 A | 08-12-1983 | NONE | |
| CH 683322 A | 28-02-1994 | NONE | |
| US 4380503 A | 19-04-1983 | DE 3024870 A | 21-01-1982 |
| | | AT 19596 T | 15-05-1986 |
| | | DE 3174551 D | 12-06-1986 |
| | | EP 0043091 A | 06-01-1982 |
| | | ES 502511 D | 01-04-1982 |
| | | ES 8203232 A | 01-07-1982 |
| US 4589598 A | 20-05-1986 | BR 8504894 A | 22-07-1986 |
| | | CA 1266714 A | 13-03-1990 |
| | | CN 85106484 A,B | 10-04-1986 |
| | | ES 547783 D | 16-03-1987 |
| | | ES 8704224 A | 01-06-1987 |
| | | ES 557139 D | 01-05-1987 |
| | | ES 8705547 A | 16-07-1987 |
| | | GB 2165673 A,B | 16-04-1986 |
| | | IN 163356 A | 10-09-1988 |
| | | IT 1200780 B | 27-01-1989 |
| | | JP 1037517 B | 08-08-1989 |
| | | JP 1553037 C | 04-04-1990 |
| | | JP 61108788 A | 27-05-1986 |
| | | KR 9002100 B | 02-04-1990 |
| | | PH 22268 A | 14-07-1988 |
| JP 05123592 A | 21-05-1993 | NONE | |
| DE 2742229 A | 08-03-1979 | CH 616507 A | 31-03-1980 |

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 30 9249

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

30-01-2001

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
| --- | --- | --- | --- |
| DE 2742229 A | | AT 358914 B | 10-10-1980 |
| | | AT 639077 A | 15-02-1980 |

EPO FORM P0459

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