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(54) Title: SURFACTANT MODIFIED SILICA (57) Abstract A novel and improved surfactant modified silica and method for making the same. The surfactant modified silica is characterized as a fumed silica having a surfactant material treated therewith. Also disclosed is a process of thickening aqueous systems which includes the addition of an effective amount of a fumed silica having a surfactant material treated therewith.		

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- 1 -

TITLE**SURFACTANT MODIFIED SILICA**BACKGROUND OF THE INVENTION1. Field of the Invention.

5 The present invention relates to surface modified silicas and in particular, a surfactant modified fumed silica.

2. Description of the Prior Art.

Both hydrophilic and hydrophobic fumed silicas are widely used in the coating industry to improve rheology, for flow control and storage stability, as well as serve as an anti-settling agent for pigments and fillers. The production of hydrophilic fumed silica is a well known process. Grades vary in particle and aggregate size. Hydrophobic silica can be produced by treating a fumed silica with a suitable agent which will vary depending on the desired degree of hydrophobicity and other characteristics. Typical treating agents include dimethyldichlorosilane, trimethoxyoctylsilane, hexamethyldi-silazane, and polymethylsiloxane. See, for example, *CAB-O-SIL® Treated Fumed Silica Technical Data Sheets* for TS-720, TS-610 and TS-530, Cabot Corporation (1991).

20 In aqueous systems, which include both emulsions and water reducible vehicles, untreated silicas are typically not effective because of the large concentrations of silica that are necessary to realize the desired thickening. However, methods exist for increasing the thickening capability of a given concentration of silica by using certain substances as additives to modify the nature of the system. For example, in systems that are not readily responsive to fumed silica because of inherent chemical properties, the correct additive

- 2 -

can often facilitate efficient viscosity and thixotropic control. See, for example, *CAB-O-SIL® Fumed Silica Properties and Functions*, p.22-27 (1987). See also, *Additives for CAB-O-SIL® Fumed Silica*, (1987). Such systems teach the separate
5 addition of certain additives to untreated silica dispersions.

As environmental awareness increases, coating manufacturers face increased pressure to replace conventional solvent based systems. As a result, aqueous systems are increasingly used in such applications. While hydrophilic and
10 hydrophobic silicas have both been used in solvent-based coating formulations on a commercial scale, their use in aqueous formulations have been plagued with disadvantages. For example, in aqueous systems, either the silica additive must be increased to unacceptable levels or the formulation
15 does not attain the desired level of performance. A demand therefore exists for aqueous systems which perform comparably to solvent based systems and, accordingly, for improved agents to accomplish such results.

SUMMARY OF THE INVENTION

20 It is therefore an object of the present invention to provide a novel silica that is a versatile and efficient rheological additive for aqueous coatings and other industrial applications. A further objective is to provide an agent that fosters stability in aqueous compositions. A still further
25 objective is to provide a novel silica which is an effective anti-settling agent.

According to the present invention, a novel and improved silica is disclosed which includes a fumed silica having a surfactant attached thereto. In one embodiment, the silica
30 is typically characterized as having a BET surface area of between about 50 m²/g and 400 m²/g and a bulk density of 10 lbs/ft³ or less and the surfactant is selected from the group consisting of nonionic surfactants, cationic surfactants, and amphoteric surfactants.

- 3 -

In a preferred embodiment, for example, the silica has a surface area of 200 m²/g and is treated with 1% by weight of polyoxyalkylene derivatives of ethylenediamine.

Other details, objects and advantages of the invention
5 and methods for making and using the same will be apparent from the following detailed description.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides an improved fumed silica having a surfactant attached to its surface which is useful
10 in coating compositions by enhancing rheology control and thixotropy.

Fumed silicas useful in this invention are those commercially available and generally characterized by a chain-like particulate structure having a high surface area per unit
15 weight.

Typically, fumed silica used in accordance with the present invention has the following characteristics:

	Surface Area (m ² /g)	50 - 400
	Bulk Density (lbs./ft ³)	2.3 - 10.0
20	Loss on Ignition (Max % at 1000°C)	0.5 - 2.5
	Silica Content (% SiO ₂ dry basis)	> 99.8

* Determined from BET surface area assuming a
25 spherical particle.

The production of fumed silica is a well-documented process which involves the hydrolysis of silicon tetrachloride vapor in a flame of hydrogen and oxygen. Molten spheres of silica are formed in the combustion process, the diameters of
30 the spheres being varied through process parameters and averaging about 7 to 40 millimicrons. These molten spheres

- 4 -

of fumed silica, sometimes referred to as primary particles, fuse with one another to form three dimensional branched, chain-like aggregates of approximately 0.1 to 0.5 micron in length. Cooling takes place very quickly, limiting the growth and ensuring that the fumed silica is amorphous. These aggregates in turn form agglomerates ranging in size from 0.5 to 44 microns (325 Mesh).

In general, the fumed silicas of the present invention will have a surface area between 50 m²/g and 400 m²/g (as measured by the nitrogen adsorption method of S. Brunauer, P.H. Emmet and I. Teller, *J. Am. Chemical Society*, vol. 60, page 309 (1938)). Although many commercially available fumed silicas are suitable, a most preferred fumed silica is that available under the name of CAB-O-SIL® and having a surface area of about 200 m²/g. (CAB-O-SIL® is a registered trademark of Cabot Corporation.) Such a silica has been found to be of high quality and readily dispersable.

Typically, the surfactant (also known as a surface active agent) is any water miscible structure containing both polar and non-polar sites. Preferably, the surfactant is an ethoxylated alkyl-phenol; heterocyclic, linear and linear ethoxylated alcohol; alkyl amine/amine salt; ethoxylated amine/amine salt; di-functional block copolymer; tetra-functional block copolymer, including polyether block polymer; sorbitan ester; ethoxylated decyn diol; monomeric and polymeric glycol and derivatives thereof; fatty acid and salts thereof; titanate; phospho-lipid ester; acid functional acrylic; and other equivalent surfactants.

Most preferred are high molecular weight surfactants such as di-functional EO-PO block copolymers (polyoxyalkylene derivatives of propylene glycol); tetra-functional EO-PO block copolymers (polyoxyalkylene derivatives of ethylenediamine); quaternary ammonium salts; polyethoxylated quaternary ammonium salts; ethoxylated linear alcohols; alkyl phenol ethoxylates; primary, secondary and tertiary alkylamines and salt derivatives thereof; alkyl alcohol ethoxylates; and

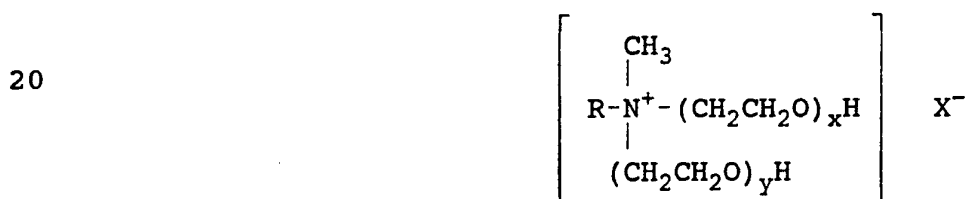
- 5 -

tertiary amines ethoxylates and salt derivatives thereof.

More particularly, quaternary ammonium salts suitable for use in the invention include dialkyl dimethyl ammonium salts represented by the formula:



wherein R is an alkyl group containing at least 6 carbon atoms; and X is an ionic species selected from halide, nitrate, carbonate, phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or aryl sulfonate, phosphate or phosphonate; polyethoxylated quaternary salts include monoalkyl monomethyl ammonium salts represented by the formula:



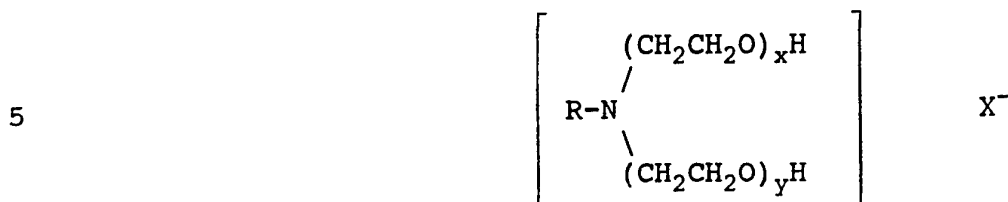
wherein R is an alkyl group containing at least 6 carbon atoms; the average (x + y) is between 2 and 15; and X is an ionic species selected from halide, nitrate, carbonate, phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or aryl sulfonate, phosphate or phosphonate; amine ethoxylates represented by the formula:



wherein R is an alkyl group containing at least 6 carbon atoms; the average (x + y) is between 2 and 50; amine

- 6 -

ethoxylates and salt derivatives represented by the formula:



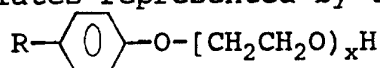
wherein R is an alkyl group containing at least 6 carbon
 10 atoms; the average (x + y) is between 2 and 50; and X is an
 ionic species selected from halide, nitrate, carbonate,
 phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or
 aryl sulfonate, phosphate or phosphonate; alkylamines, such
 as, monoalkyl, dimethylamines represented by the formula:



wherein R is an alkyl group containing at least 6 carbon
 atoms; alkylamine salts including monoalkyl dimethylamine
 salts represented by the formula:



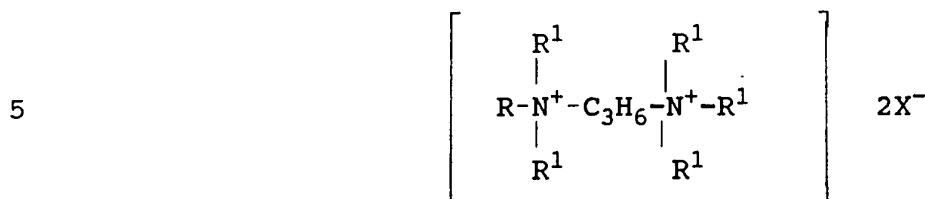
wherein R is an alkyl group containing at least 6 carbon
 atoms; and X is an ionic species selected from halide,
 nitrate, carbonate, phosphate, hydroxide, carboxylate, alkyl
 35 sulfate, alkyl or aryl sulfonate, phosphate or phosphonate;
 alkyl phenol ethoxylates represented by the formula:



wherein R is C₄ to C₂₂ alkyl and x is between 1 and 70; and
 ethoxylated quaternary salts including quaternary diamines

- 7 -

represented by the formula:



wherein R is an alkyl group containing at least 6 carbon
 10 atoms; R^1 is an alkyl, hydroxy alkyl or alkoxy alkyl; and X
 is an ionic species selected from halide, nitrate, carbonate,
 phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or
 aryl sulfonate, phosphate or phosphonate.

Such surfactants are commercially available under various
 15 well-known trademarks, such as the PLURONIC® series (BASF
 Corporation, Parsippany, NJ), the TETRONIC® series (BASF
 Corporation, Parsippany, NJ), the ARQUAD® series (Akzo
 Chemical Inc., Chicago, IL), the TRITON® series (Union Carbide
 Corp., Danbury, CT), the SURFONIC® series (Texaco Chemical
 20 Company, Houston, TX), the ETHOQUAD® series (Akzo Chemical
 Inc., Chicago, IL), the ARMEEN® series (Akzo Chemical Inc.,
 Chicago, IL), the ICONOL® series (BASF Corporation,
 Parsippany, NJ), the SURFYNOL® series (Air Products and
 Chemicals, Inc. Allertown, PA), and the ETHOMEEN® series (Akzo
 25 Chemical Inc, Chicago, IL), to name a few.

Other suitable surfactants for use in the present
 invention are disclosed in, for example, Kirk-Othmer,
Encyclopedia of Chemical Technology, 3rd edition, Vol. 22
 pages 332-386 and available manufacturing literature,
 30 including for example McCutcheon's *Emulsifiers & Detergents*,
North American and International Edition (McCutcheon Division,
 The MC Publishing Co., 1991); Ash, *The Condensed Encyclopedia*
of Surfactants (Chemical Publishing Co., Inc. 1989); and, Ash,
What Every Chemical Technologist Wants to Know About ...
 35 *Emulsifiers and Wetting Agents, Volume I* (Chemical Publishing
 Co., Inc. 1988), all of which are incorporated herein by
 reference. The surfactants should be adequately stable and

- 8 -

inert to environmental conditions prevailing in end product applications incorporating the surfactant modified silica of the present invention.

5 In general, the amounts of silica to surfactant used in the present invention may vary provided that the amounts are sufficient to modify the properties of the silica to be treated therewith. By modify is meant that the surfactant modified silica will provide enhanced rheological performance and/or chemical stability to a particular aqueous system than
10 that achieved if the silica and surfactant were separately incorporated into the system.

In a preferred embodiment, the silica is treated with an amount of surfactant sufficient to provide a 0.01% to 30% treatment level based on the weight of the unmodified silica.
15 Especially preferred is an amount of surfactant sufficient to produce 0.5% to 10% treatment level based on the weight of the unmodified silica.

In accordance with the present invention, the modification of the silica surface may be accomplished by
20 suitable techniques known to those skilled in the art which will provide distribution of the surfactant on the silica. The mixture is then heated at a temperature and for a period of time sufficient to modify the properties of the silica. Typically, a temperature ranging from about 60°C to 300°C for
25 a period ranging from about 15 minutes to about 2 hours has been found suitable. A temperature range from about 80°C to 240°C for a time period between 30 and 60 minutes is preferred because such a range has been found to effectively modify the properties of the silica. During the modification, it is
30 theorized that the surfactant will associate with the silica by adsorption or reaction.

A process for modifying the silica with the surfactant includes a batch bulk mixing step followed by a heating cycle similar to that described above.

35 A preferred method of obtaining uniform surfactant distribution on the silica surface includes pumping the silica

- 9 -

from a holding reservoir by known means through a chamber where it is sprayed with surfactant. The surfactant delivery rate can be regulated with a flow meter to achieve the desired level of concentration. This method, having been found to
5 achieve uniform distribution of the surfactant material, is disclosed in further detail in U. S. Patent No. 5,153,030, the disclosure of which is incorporated herein by reference.

Other ways to enhance above mentioned processes will be appreciated by those skilled in the art and is within the
10 scope of the invention.

The surfactant modified silica of the present invention may be useful in aqueous systems to provide effective rheological control, especially in coating, adhesives, and inks applications.

15 A non-limiting illustration of the surfactant modified silica of the present invention follows.

EXAMPLE 1

In accordance with the present invention, a suitable cylindrical pressure vessel was equipped with means for
20 addition and removal of heat, temperature recording means, means for introducing the surfactant treating material, means for introducing the fumed silica, and means for the removal and collection of the surfactant modified silica. The vessel was charged at room temperature with 200 grams of CAB-O-SIL®
25 PTG fumed silica. CAB-O-SIL® PTG fumed silica is a pyrogenically produced silica (manufactured and sold by Cabot Corporation) having a BET surface area of about 200 m²/g, a particle size of about 0.014 microns, a density of about 2.5 lbs/ft³, an ignition loss at 1000°C of about 2% and a pH value
30 of from 3.7 to 4.3. Compressed air was piped through the bottom distributor plate of the vessel to fluidize the silica. Approximately 6 grams of TETRONIC® 701 block polymer (a registered trademark of BASF Corporation, Parsippany, NJ) was injected into the vessel of fluidized fumed silica. The top
35 of the vessel was attached and the vessel was then allowed to

- 10 -

fluidize with N₂ for approximately 10 minutes before heating at 230°C for approximately 30 minutes. The vessel was then placed into a cooling bath for approximately 20 minutes and collected with suitable means. The product was a fumed silica having approximately 3% surfactant by weight treated therewith.

Surfactant modified fumed silica was then dispersed directly into water at 3% silica weight using a commercial Waring Blender controlled by a rheostat. The surfactant modified fumed silica was integrated at low speed and then dispersed at high speed for 5 minutes. Aqueous dispersions were de-aired under vacuum followed by a gentle agitation to reduce foam. Brookfield LVT viscosity measurements were taken at 1, 7 and 28 days using Nos. 2 or 3 spindle at 6 and 60 rpms. For comparative purposes, equivalent ratios of fumed silica and TETRONIC 701 block polymer were separately dispersed ("separate additions") into water at 3% silica weight using a commercial Waring Blender controlled by a rheostat. The silica and surfactant were integrated into the water at low speed and then dispersed at high speed for 5 minutes. The aqueous dispersions was similarly de-aired and gently agitated to reduce foam. Finally, the viscosity of fumed silica in water without any surfactant (referred to as "base silica") was also measured and compared. The aqueous dispersions had the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
30	Day 7	5	1670	14,000
	Day 14+	8	3400	68,000

- 11 -

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
5	Day 7	6	236	962
	Day 14+	7	244	396

As illustrated by Example 1, the surfactant modified silica of the present invention had greater than thickening effect than the conventional addition of silica and
10 surfactant.

EXAMPLE 2

The process of Example 1 was repeated except that 6 grams of TETRONIC® 901 block polymer were injected into the vessel of 200 grams of fluidized fumed silica. The aqueous
15 dispersions had the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
20	Day 7	5	+	10,200
	Day 14+	8	+	4100

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
25	Day 7	6	+	748
	Day 14+	7	+	160

The plus (+) sign indicates that the dispersion formed by the separate addition of fumed silica and surfactant phase
30 separated into distinct layers of foam, liquid and precipitate.

- 12 -

EXAMPLE 3

The process of Example 1 was repeated except that 6 grams of TETRONIC® 908 block polymer were injected into the vessel of 200 grams of fluidized fumed silica. The aqueous
 5 dispersions had the following characteristics.

VISCOSITY (centipoise)
 Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
10	Day 7	5	+	3320
	Day 14+	8	+	4840

VISCOSITY (centipoise)
 Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
15	Day 7	6	+	450
	Day 14+	7	+	504

EXAMPLE 4

The process of Example 1 was repeated except that 3 grams of PLURONIC® F88 (a registered trademark of BASF Corporation, Parsippany, NJ) surfactant were injected into the vessel of
 20 200 grams of fluidized fumed silica. The aqueous dispersions had the following characteristics.

25 VISCOSITY (centipoise)
 Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
	Day 7	5	+	4620
	Day 14+	8	+	5560

- 13 -

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
5	Day 7	6	+	698
	Day 14+	7	+	720

EXAMPLE 5

The process of Example 1 except that 6 grams of PLURONIC® P85 surfactant were injected into the vessel of 200 grams of fluidized fumed silica. The aqueous dispersions had the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
15	Day 7	5	+	1840
	Day 14+	8	+	3400

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
20	Day 7	6	+	284
	Day 14+	7	+	394

EXAMPLE 6

The process of Example 1 was repeated except that 6 grams of PLURONIC® L31 surfactant were injected into the vessel of 200 grams of fluidized fumed silica. The aqueous dispersions had the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
30	Day 7	5	+	360
	Day 14+	8	+	1030

- 14 -

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
5	Day 7	6	+	67
	Day 14+	7	+	155

EXAMPLE 7

The process of Example 1 was repeated except that 6 grams of ETHOMEEN S-12 surfactant (Available from Akzo Chemicals, Inc., Chicago, Illinois) were injected into the vessel of 194 grams of fluidized fumed silica. The aqueous dispersions had the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
15	Day 7	5	5240	4100
	Day 14+	8	2060	17300

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
20	Day 7	6	280	520
	Day 14+	7	293	2400

EXAMPLE 8

25

The process of Example 1 was repeated except that 6 grams of ETHOMEEN S-15 surfactant were injected into the vessel of 194 grams of fluidized fumed silica. The aqueous dispersions had the following characteristics.

- 15 -

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
5	Day 7	5	+	16,800
	Day 14+	8	+	11,800

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
10	Day 7	6	+	1100
	Day 14+	7	+	1660

EXAMPLE 9

The process of Example 1 was repeated except that 6 grams
15 of ETHOMEEN S-25 surfactant were injected into the vessel of
194 grams of fluidized fumed silica. The aqueous dispersions
had the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
20	Day 7	5	+	17,400
	Day 14+	8	+	35,000

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
25	Day 7	6	+	1610
	Day 14+	7	+	3110

30

EXAMPLE 10

The process of Example 1 was repeated except that 7.5
grams of ETHOMEEN S-12 salt surfactant (a quaternary

- 16 -

derivative of ETHOMEEN S-12, available from Akzo Chemicals, Inc., Chicago, Illinois) were injected into the vessel of 194 grams of fluidized fumed silica. The aqueous dispersions had the following characteristics.

5

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
	Day 7	5	+	58,700
10	Day 14+	8	+	70,300

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
	Day 7	6	+	5450
15	Day 14+	7	+	6770

EXAMPLE 11

The process of Example 1 was repeated except that 7.5 grams of ETHOMEEN S-15 salt surfactant (a quaternary derivative of ETHOMEEN S-15) were injected into the vessel of 194 grams of fluidized fumed silica. The aqueous dispersions had the following characteristics.

25

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
	Day 7	5	+	17,100
	Day 14+	8	+	19,200

- 17 -

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
5	Day 7	6	+	1850
	Day 14+	7	+	2100

EXAMPLE 12

The process of Example 1 except that 7.7 grams of
ETHOMEEN S-25 salt surfactant were injected into the vessel
of 194 grams of fluidized fumed silica. The aqueous
dispersions had the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
15	Day 7	5	+	27,300
	Day 14+	8	+	36,200

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
20	Day 7	6	+	2090
	Day 14+	7	+	3040

EXAMPLE 13

The process of Example 1 except that 6 grams of TRITON®
X-100 surfactant (Available from Union Carbide, Chicago,
Illinois) were injected into the vessel of 200 grams of
fluidized fumed silica. The aqueous dispersions had the
following characteristics.

- 18 -

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
5	Day 7	5	+	2780
	Day 14+	8	+	2120

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
10	Day 7	6	+	374
	Day 14+	7	+	230

EXAMPLE 14

The process of Example 1 was repeated except that 6 grams
15 of TRITON X-45 surfactant were injected into the vessel of 200
grams of fluidized fumed silica. The aqueous dispersions had
the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
20	Day 7	5	+	1980
	Day 14+	8	+	5640

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
25	Day 7	6	+	286
	Day 14+	7	+	370

30

EXAMPLE 15

The process of Example 1 except that 6 grams of SURFONIC®
N-100 (a trademark of Texaco Chemical Company, Houston, Texas)

- 19 -

surfactant were injected into the vessel of 200 grams of fluidized fumed silica. The aqueous dispersions had the following characteristics.

5

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
Day 7	5	+	13,300
Day 14+	8	+	3360

10

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
Day 7	6	+	1990
15 Day 14+	7	+	226

EXAMPLE 16

The process of Example 1 except that 7 grams of ARQUAD® HTL8 MS-85 quaternary salt (Available from Akzo Chemicals, Inc., Chicago, Illinois) were injected into the vessel of 200 grams of fluidized fumed silica. The aqueous dispersions had the following characteristics.

25

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
Day 7	5	849	33,400
Day 14+	8	+	42,100

30

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
Day 7	6	461	3820
Day 14+	7	+	3120

- 20 -

EXAMPLE 17

The process of Example 1 except that 10 grams of ARQUAD HTL8 CL-85 quaternary salt were injected into the vessel of 200 grams of fluidized fumed silica. The aqueous dispersions
5 had the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
10	Day 7	5	48	18,000
	Day 14+	8	136	22,300

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
15	Day 7	6	5	1400
	Day 14+	7	3	1820

EXAMPLE 18

The process of Example 1 except that 7 grams of ARQUAD 2T-75 quaternary salt were injected into the vessel of 200
20 grams of fluidized fumed silica. The aqueous dispersions had the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
25	Day 7	5	3040	3100
	Day 14+	8	7040	9720

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
30	Day 7	6	332	850
	Day 14+	7	257	986

- 21 -

EXAMPLE 19

The process of Example 1 except that 10 grams of ARMEEN® Z (a registered trademark of Akzo Chemicals Inc., Chicago, Illinois) were injected into the vessel of 200 grams of fluidized fumed silica. The aqueous dispersions had the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

10	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
	Day 7	5	+	21,100
	Day 14+	8	+	20,400

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

15	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
	Day 7	6	+	1650
	Day 14+	7	+	1670

EXAMPLE 20

The process of Example 1 except that 6 grams of ETHOQUAD® 18/25 quaternary salt (a registered trademark of Akzo Chemicals Inc., Chicago, Illinois) were injected into the vessel of 200 grams of fluidized fumed silica. The aqueous dispersions had the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

25	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
	Day 7	5	295	6700
30	Day 14+	8	500	10,800

- 22 -

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
5	Day 7	6	23	840
	Day 14+	7	56	930

EXAMPLE 21

The process of Example 1 except that 6 grams of ETHOQUAD® T/13 quaternary salt were injected into the vessel of 194 grams of fluidized fumed silica. The aqueous dispersions had the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
15	Day 7	5	+	15,400
	Day 14+	8	+	20,600

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
20	Day 7	6	+	1600
	Day 14+	7	+	2450

EXAMPLE 22

Similar to Example 1, a suitable cylindrical pressure vessel is equipped with means for addition and removal of heat, temperature recording means, means for introducing the surfactant treating material, means for introducing the fumed silica, and means for the removal and collection of the surfactant modified silica. CAB-O-SIL® PTG fumed silica was pumped from a holding reservoir through a chamber where it was sprayed with TETRONIC® 701 block polymer in accordance with the process of U. S. Patent No. 5,153,030. The delivery rate

- 23 -

of the TETRONIC surfactant was regulated with a flow meter to achieve approximately 3% treatment level. After being contacted with the surfactant, the silica flowed into the vessel was then heated at approximately 93°C for 30 minutes.

- 5 The vessel was then placed into a cooling bath for approximately 20 minutes and collected with suitable means. The product was a fumed silica having approximately 3% surfactant by weight treated therewith.

Surfactant modified fumed silica was then dispersed
 10 directly into water at 3% silica weight using a commercial Waring Blender controlled by a rheostat. The surfactant modified fumed silica was integrated at low speed and then dispersed at high speed for 5 minutes. Aqueous dispersions were de-aired under vacuum followed by a gentle agitation to
 15 reduce foam. Brookfield LVT viscosity measurements were taken at day 7 using Nos. 2 or 3 spindle at 6 and 60 rpms. For comparative purposes, equivalent ratios of fumed silica and TETRONIC 701 block polymer were separately dispersed ("separate additions") into water at 3% silica weight using
 20 a commercial Waring Blender controlled by a rheostat. The silica and surfactant were integrated into the water at low speed and then dispersed at high speed for 5 minutes. The aqueous dispersions was similarly de-aired and gently agitated to reduce foam. As in the previous examples, the viscosity
 25 of base silica in water was also measured. The aqueous dispersions had the following characteristics.

VISCOSITY (centipoise)
 Spindle Speed - 6 rpm

30	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
	Day 7	5	1670	3470

- 24 -

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
5	Day 7	6	236	331

EXAMPLE 23

The process of Example 22 was repeated except that TETRONIC® 901 block polymer was sprayed in accordance with the process of U. S. Patent No. 5,153,030. The delivery rate of the TETRONIC surfactant was again regulated with a flow meter to achieve approximately 3% treatment level. The aqueous dispersions had the following characteristics.

VISCOSITY (centipoise)
Spindle Speed - 6 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
15	Day 7	5	+	3280

VISCOSITY (centipoise)
Spindle Speed - 60 rpm

	<u>Time</u>	<u>Base Silica</u>	<u>Separate Addition Silica & Surfactant</u>	<u>Surfactant Modified Silica</u>
20	Day 7	6	+	316

As illustrated by the above examples, the surfactant modified silica of the present invention had greater thickening effect than the conventional addition of silica and surfactant. Furthermore, some of the cationic and nonionic surfactant treated silica provided three to five orders of magnitude greater thickening than untreated base silica. In addition, dispersion stability was provided in aqueous systems employing the surfactant modified silica of the present invention, whereas the conventional addition of silica and

- 25 -

surfactant resulted in, for many of the examples, immediate phase separation. The present invention provides a versatile and efficient rheological additive for aqueous coatings and other industrial applications.

- 5 It is understood that the present invention is not limited to the particular embodiments shown and described herein, but that various changes and modifications may be made without departing from the scope and spirit of the invention.

What is claimed is:

- 26 -

CLAIMS

1. A surfactant modified silica comprising fumed silica having a surfactant material treated therewith.
2. The surfactant modified silica according to claim 1
5 wherein said silica is a fumed silica having a BET surface area of between about 50 m²/g and 400 m²/g and a bulk density of 10 lbs/ft³ or less.
3. The surfactant modified silica according to claim 1
10 wherein said surfactant material is selected from the group consisting of nonionic surfactants, cationic surfactants, and amphoteric surfactants.
4. The surfactant modified silica according to claim 1
15 wherein said fumed silica has a BET surface area of between about 50 m²/g and 400 m²/g and a bulk density of 10 lbs/ft³ or less and said surfactant material is selected from the group consisting of nonionic surfactants, cationic surfactants, and amphoteric surfactants.
5. The surfactant modified silica according to claim 3
20 wherein said surfactant is a high molecular weight surfactant selected from the group consisting of: di-functional EO-PO block copolymers; tetra-functional EO-PO block copolymers; quaternary ammonium salts; ethoxylated quaternary ammonium salts; ethoxylated linear alcohols; alkyl phenol ethoxylates; primary, secondary and tertiary alkylamines and salt
25 derivatives thereof; or amine ethoxylates and salt derivatives thereof.

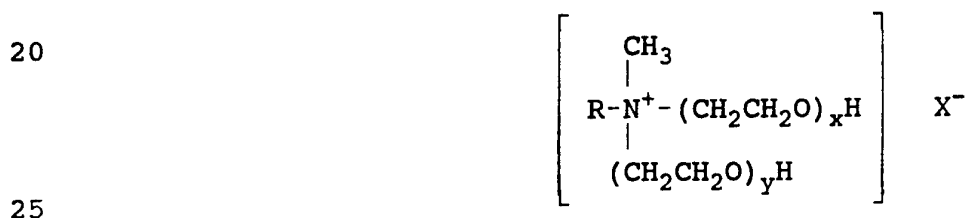
- 27 -

6. The surfactant modified silica according to claim 5 wherein said quaternary salt is a dialkyl dimethyl ammonium salt represented by the formula:



wherein R is an alkyl group containing at least 6 carbon atoms and X is an ionic species selected from halide, nitrate, carbonate, phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or aryl sulfonate, phosphate or phosphonate.

7. The surfactant modified silica according to claim 5 wherein said polyethoxylated quaternary salt is a monoalkyl monomethyl diethoxylated ammonium salt represented by the formula:



wherein R is an alkyl group containing at least 6 carbon atoms; the average (x + y) is between 2 and 15; and X is an ionic species selected from halide, nitrate, carbonate, phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or aryl sulfonate, phosphate or phosphonate.

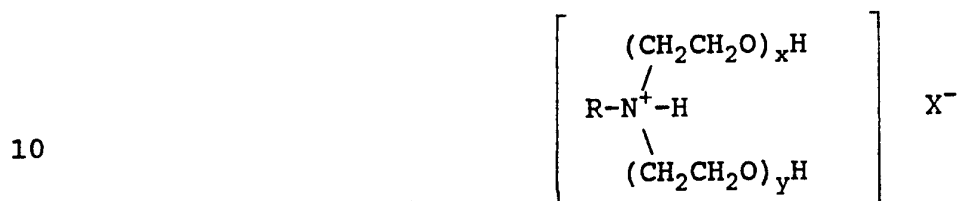
8. The surfactant modified silica according to claim 5 wherein said amine ethoxylates are represented by the formula:



- 28 -

wherein R is an alkyl group containing at least 6 carbon atoms and the average (x + y) is between 2 and 50.

9. The surfactant modified silica according to claim 5 wherein said amine ethoxylates are salt derivatives represented by the formula:



wherein R is an alkyl group containing at least 6 carbon atoms; the average (x + y) is between 2 and 50; and X is an ionic species selected from halide, nitrate, carbonate, phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or aryl sulfonate, phosphate or phosphonate.

10. The surfactant modified silica according to claim 5 wherein said tertiary alkylamines are monoalkyl, dimethylamines represented by the formula:



wherein R is an alkyl group containing at least 6 carbon atoms.

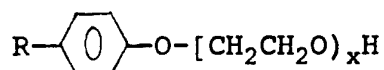
11. The surfactant modified silica according to claim 5 wherein said tertiary alkylamine salts are monoalkyl dimethylamine salts represented by the formula:



- 29 -

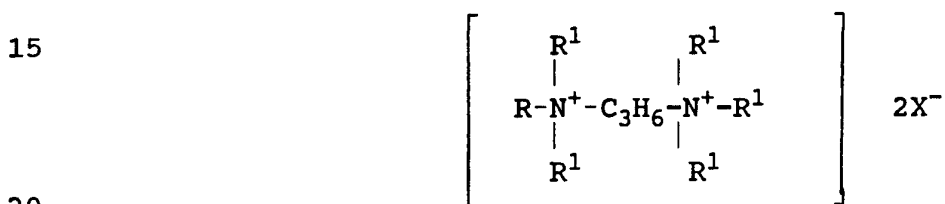
wherein R is an alkyl group containing 6 carbon atoms; and X is an ionic species selected from halide, nitrate, carbonate, phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or aryl sulfonate, phosphate or phosphonate.

- 5 12. The surfactant modified silica according to claim 5 wherein said alkyl phenol ethoxylates are represented by the formula:



- 10 wherein R is C₄ to C₂₂ alkyl and x is between 1 and 70.

13. The surfactant modified silica according to claim 5 wherein said ethoxylated quaternary salt is a diguaternary diamine represented by the formula:



wherein R is an alkyl group containing at least 6 carbon atoms; R¹ is alkyl, hydroxyl alkyl or alkoxy alkyl; and X is an ionic species selected from halide, nitrate, carbonate, phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or aryl sulfonate, phosphate or phosphonate.

14. The surfactant modified silica according to claim 1 wherein said treating is a heat treatment.

15. A method of making a surfactant modified silica material comprising the steps of:

- 30 mixing fumed silica with surfactant material; and
heating for a time and at a temperature sufficient to treat the surface of said fumed silica with said surfactant material.

- 30 -

16. The method according to claim 15 wherein said fumed silica has a BET surface area of between about 50 m²/g and 400 m²/g and a bulk density of 10 lbs/ft³ or less.

17. The method according to claim 15 wherein said surfactant material is selected from the group consisting of nonionic surfactants, cationic surfactants, and amphoteric surfactants.

18. The method according to claim 15 wherein said fumed silica has a BET surface area of between about 50 m²/g and 400 m²/g and a bulk density of 10 lbs/ft³ or less and said surfactant material is selected from the group consisting of nonionic surfactants, cationic surfactants, and amphoteric surfactants.

19. The method according to claim 15 wherein said surfactant is a high molecular weight surfactant selected from the group consisting of: di-functional EO-PO block copolymers; tetra-functional EO-PO block copolymers; quaternary ammonium salts; ethoxylated quaternary ammonium salts; ethoxylated linear alcohols; alkyl phenol ethoxylates; primary, secondary and tertiary alkylamines and salt derivatives thereof; or amine ethoxylates and salt derivatives thereof.

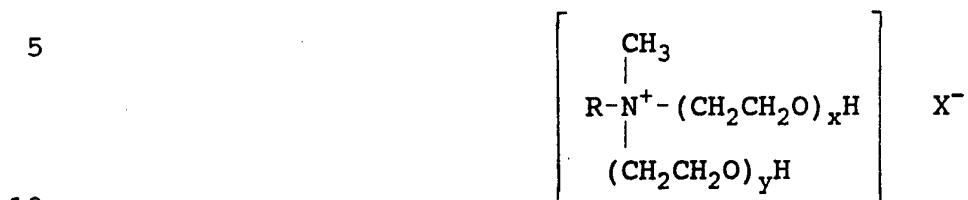
20. The method according to claim 19 wherein said quaternary salt is a dialkyl dimethyl ammonium salt represented by the formula:



wherein R is an alkyl group containing at least 6 carbon atoms and X is an ionic species selected from halide, nitrate, carbonate, phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or aryl sulfonate, phosphate or phosphonate.

- 31 -

21. The method according to claim 19 wherein said polyethoxylated quaternary salt is a monoalkyl monomethyl diethoxylated ammonium salt represented by the formula:



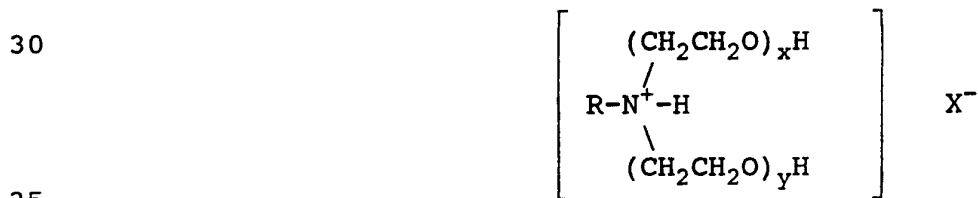
wherein R is an alkyl group containing at least 6 carbon atoms; the average (x + y) is between 2 and 15; and X is an ionic species selected from halide, nitrate, carbonate, phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or aryl sulfonate, phosphate or phosphonate.

22. The method according to claim 19 wherein said amine ethoxylates are represented by the formula:



wherein R is an alkyl group containing at least 6 carbon atoms and average (x + y) is between 2 and 50.

23. The method according to claim 19 wherein said amine ethoxylates are salt derivatives represented by the formula:



wherein R is an alkyl group containing at least 6 carbon atoms; the average (x + y) is between 2 and 50; and X is an ionic species selected from halide, nitrate, carbonate,

- 32 -

phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or aryl sulfonate, phosphate or phosphonate.

24. The method according to claim 19 wherein said tertiary alkylamines are monoalkyl, dimethylamines represented by the
5 formula:



wherein R is an alkyl group containing at least 6 carbon atoms.

25. The method according to claim 19 wherein said tertiary alkylamine salts are monoalkyl dimethylamine salts represented by the formula:



25 wherein R is an alkyl group containing at least 6 carbon atoms and X is an ionic species selected from halide, nitrate, carbonate, phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or aryl sulfonate, phosphate or phosphonate.

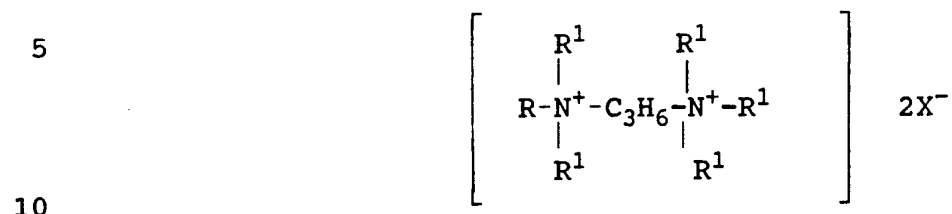
26. The method according to claim 19 wherein said alkyl phenol ethoxylates are represented by the formula:



wherein R is C₄ to C₂₂ alkyl and x is between 1 and 70.

- 33 -

27. The method according to claim 19 wherein said ethoxylated quaternary salt is a diguaternary diamine represented by the formula:



wherein R is an alkyl group containing 6 carbon atoms; R¹ is alkyl, hydroxy alkyl or alkoxy alkyl; and X is an ionic species selected from halide, nitrate, carbonate, phosphate, hydroxide, carboxylate, alkyl sulfate, alkyl or aryl sulfonate, phosphate or phosphonate.

28. The method according to claim 19 wherein said fumed silica and surfactant material are heated at a temperature between about 80°C and 240°C for a period of time between about 30 minutes and 60 minutes.

29. The method according to claim 15 wherein said heating is in a closed vessel under a non-oxidated environment.

30. A process of thickening aqueous systems comprising the addition thereto of an effective amount of fumed silica having surfactant material treated therewith.

31. The process according to claim 30 wherein said fumed silica has a BET surface area of between about 50 m²/g and 400 m²/g and a bulk density of 10 lbs/ft³ or less.

32. The process according to claim 30 wherein said surfactant material is selected from the group consisting of nonionic surfactants, cationic surfactants, and amphoteric surfactants.

- 34 -

33. The process according to claim 30 wherein said fumed silica has a BET surface area of between about 50 m²/g and 400 m²/g and a bulk density of 10 lbs/ft³ or less and said surfactant material is selected from the group consisting of
5 nonionic surfactants, cationic surfactants, and amphoteric surfactants.

34. The process according to claim 30 wherein said surfactant is a high molecular weight surfactant selected from the group consisting of: di-functional EO-PO block copolymers; tetra-
10 functional EO-PO block copolymers; quaternary ammonium salts; ethoxylated quaternary ammonium salts; ethoxylated linear alcohols; alkyl phenol ethoxylates; primary, secondary and tertiary alkylamines and salt derivatives thereof; or amine ethoxylates and salt derivatives thereof.

15

INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/US 94/01397

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C09C1/30

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)

IPC 5 C09C

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 9212, Derwent Publications Ltd., London, GB; AN 92-093649 & JP,A,04 037 603 (MIZUSAWA CHEMICAL IND.) 7 February 1992 see abstract	1, 2, 30, 31
A	---	4, 33
X	EP,A,0 399 442 (BASF) 28 November 1990 see page 2, line 48 - line 50; claims 1,2,4 --- -/--	1, 3, 30, 32

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

7 July 1994

Date of mailing of the international search report

22. 07. 94

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Van Bellingen, I

INTERNATIONAL SEARCH REPORT

Internal I Application No

PCT/US 94/01397

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 117, no. 4, 27 July 1992, Columbus, Ohio, US; abstract no. 29896s, page 201 ; see abstract & CN,A,1 057 818 (CHINESE ACADEMY OF SCIENCES, PHOTO-SENSITIVE CHEMISTRY RESEARCH INST.) ---	1
P,X	EP,A,0 558 045 (DOW CORNING TORAY SILICONE COMPANY) 1 September 1993 see page 2, line 53 - line 55 see page 3, line 55 - line 57; claim 2 ---	1,3,5, 15,17,19
X	EP,A,0 392 262 (DOW CORNING TORAY SILICONE COMPANY) 17 October 1990 see page 2, line 43 - page 3, line 11 -----	1,3,5, 15,17,19

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat Application No

PCT/US 94/01397

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0399442	28-11-90	NONE	
CN-A-1057818	15-01-92	NONE	
EP-A-0558045	01-09-93	NONE	
EP-A-0392262	17-10-90	JP-A- 2255769	16-10-90
		AU-B- 625466	09-07-92
		AU-A- 5232290	04-10-90
		CA-A- 2011194	29-09-90