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(54) Title: FORMULATIONS FOR APPLYING A HYDROPHOBIC FILM TO A SUBSTRATE

(57) Abstract: A composition is provided that includes a universal hydrophobic active ingredient of modified silicone polymer forming a microemulsion in water, and a water miscible organic solvent to produce a clear and transparent solution that cleans and leaves a hydrophobic film on a glass substrate when dried. A process of applying the same is also provided.

FORMULATIONS FOR APPLYING A HYDROPHOBIC FILM TO A SUBSTRATE

FIELD OF THE INVENTION

[0001] The present invention in general relates to a composition for cleaning glass surface and rendering the surfaces hydrophobic and a process for the use thereof and in particular, to such a composition amenable to application to a variety of substrates in field operation with minimal re-formulation yet still able to impart the desired cleaning and hydrophobicity to the treated substrates.

BACKGROUND OF THE INVENTION

[0002] Automotive glass is exposed to everyday environmental and various traveling conditions. Fallout of dirt particulates, rain, snow, and bug impact, all contribute to soiling the automotive glass. These conditions affect both visual appearance and driving visibility.

[0003] Traditionally, to clean glass a surfactant with good wetting property is used. There is no hydrophobic effect on the surface which could improve visibility during driving and enhance driving safety by creating a hydrophobic surface that repels water droplets. Currently, there are cleaning products with hydrophobic coatings in the market. However, the coating hydrophobic effect is either not effective or not cost-effective. Most importantly, the active ingredients that provide the hydrophobic effect are not readily to be used in different areas of applications without substantially changing the formulations or needed to use different active ingredients.

[0004] Thus, there exists a need for a universal hydrophobic active ingredient that is readily used in a variety of formulations and for a process for the use thereof that is readily applied in the field to a substrate through resort added to the windshield washer reservoir which later the fluid be sprayed on the windshield, to the conventional trigger spray application, or propellant aerosol, or a sponge or cloth for wipe application onto the substrate

desired to clean and produce a hydrophobic film By creating a hydrophobic surface that repels water droplets as well as by cleaning auto glass without streaking will improve visibility during driving and enhance driving safety.

SUMMARY OF THE INVENTION

[0005] A composition is provided that includes a universal hydrophobic active ingredient of a modified silicone polymer forming a micro emulsion in water, and a water miscible organic solvent to produce a clear and transparent solution that cleans and leaves a hydrophobic film on a glass substrate when dried. A process of applying the same is also provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIG. 1 is a bar graph of contact angle in degrees for an inventive glass cleaner with repellent properties fluid (GCRPF) and comparative non-inventive products before wash;

[0007] FIG. 2 is a plot of contact angle as a function of abrasion cycles for GCRPF of FIG. 1;

[0008] FIG. 3 is a bar graph of ice adhesion for an inventive GCRPF and a comparative of untreated glass;

[0009] FIG. 4A is a bar graph of contact angle for an inventive composition (WWFA) and comparative non-inventive Windshield Washer Fluid Additive;

[0010] FIG. 4B is another bar graph of contact angle bar graph of contact angle for an inventive composition (WWFA) in water and comparatives of the same in Windshield Washer Fluid; and

[0011] FIG. 5 is a bar graph of slide angle for an inventive composition (WWFA) in water and comparative in Windshield Washer Fluid).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] The present invention has utility as glass cleaner with repellent properties fluid (GCRPF) that forms a film on a substrate to render the underlying substrate hydrophobic. The present invention has the attribute of being amenable to application as a wipe-on or spray applied composition that forms a film without resort to the complex deposition processes that characterized prior art systems. As a result of the durability of the hydrophobic film imparted to a substrate by the inventive composition, the substrate needs to be cleaned less often. An inventive composition is also amenable to formulation independent of, and therefore devoid of volatile organic compounds (VOCs).

[0013] While the present invention is further detailed with respect to application to a glass substrate such as a vehicle window, or building window, it is appreciated that an inventive composition is readily applied to numerous other substrates to impart hydrophobic films thereto. To the extent that an inventive composition is described herein with respect to total weight percentage of various components, these amounts are provided independent of propellants that are used in pressurized aerosol packages.

[0014] It is to be understood that in instances where a range of values are provided that the range is intended to encompass not only the end point values of the range but also intermediate values of the range as explicitly being included within the range and varying by the last significant figure of the range. By way of example, a recited range of from 1 to 4 is intended to include 1-2, 1-3, 2-4, 3-4, and 1-4.

[0015] An inventive composition is provided based on a silicone microemulsion system in water with a minor quantity of organic solvent to product a clear and transparent

solution. In some embodiments of the present invention, a wetting agent is also present. In still other embodiments, the inventive composition includes a propellant to afford a pressurized aerosol container for dispensing onto a target substrate.

[0016] In other embodiments, the silicone microemulsion system based on amino functional silicones that emulsify in a solvent that is more than 5 total weight percent water and in other instances up to 99 total weight percent water to form a stable silicone microemulsion system. An inventive composition in some embodiments also contains a fluorocarbon or hydrocarbon propellant when aerosol delivery is desired. In other embodiments, inventive compositions are applied by consumers by a simple trigger spray or simply by sponging or wiping onto a target substrate.

[0017] An inventive composition includes a silicone microemulsion which is capable of forming a hydrophobic film on a glass substrate, as measured by a water droplet contact angle of greater than 90 degrees and typically between 95 and 105 degrees. An inventive composition includes a silicone microemulsion that is a storage stable (thermodynamically stable) dispersion, with the dispersed phase having small droplets ranging in size of less than a micron. In certain inventive embodiments, and for ease of formulation silicone compounds are selected that self-emulsify in water. The loadings of the microemulsion are limited to maintain clear and transparent solutions that follow from the small size of the dispersed phase. Transparency is an aesthetic aspect that enhances consumer acceptance of an inventive composition.

[0018] Silicone compounds suitable for the preparation of the silicone microemulsions of the present invention illustratively include amino functional silicone fluids having a viscosity range from 40 centistokes (cSt) to 500,000 cSt at room temperature, as well as blends of emulsifiable silicone-based polymers. The structures and properties of silicone-based polymers able to form microemulsions in an inventive composition

illustratively include those detailed in U.S. Pat. Nos. 4,600,436; 4,880,557; and 5,378,271. The amino modified silicone compounds of the invention are present in the range of 0.05 to 20 total weight percent. It is appreciated that innovative glass cleaner formulations imparting hydrophobic properties are comprised of previously manufactured microemulsion, more specifically from amino modified, mildly cationic silicone fluids with 30% solid content and pH ranging from 6.5 to 7.5. In addition wetting and/or cleaning agents, and media to control stability and/or product environmental depending performance requirements.

[0019] In certain embodiments of the invention, a wetting agent is present in an amount to reduce the surface tension of the composition to the extent that the composition is able to wet a glass target surface. A wetting agent is chosen that is compatible with the silicone microemulsion system. Wetting agents operative herein illustratively include various classes of wetting surfactants for reducing interfacial tension at the substrate-water and/or oil/water interfaces for easy removal of soils or solvents such as glycol ethers, alcohols and ketones, Anionic, such as linear alkylbenzene sulfonates, alcohol sulfates, alcohol ether sulfates, alcohol ethoxylated sulfates, alpha olefin sulfonates, alphasulfomethyl ester; and nonionic, such as alcohol ethoxylates, alkyl phenol ethoxylates. Alkanolamides, alkylglucosides; surfactants are used as wetting agents. It should be appreciated that each of the above wetting agents is commercially available in at least one form. A wetting agent, if present, in an inventive composition is present from 0.05 to 5 total weight percent.

[0020] The silicone polymer based microemulsion, wetting agent (if present) and additives (if present) are dissolved or suspended in a solvent system that includes water and a miscible organic solvent. The organic solvent is at least one of acetone, isopropanol, methanol, ethylene glycol monobutyl ether, propylene glycol, dipropylene glycol methyl ether, propylene glycol n-butyl ether typically present from 5 to 35 total weight percent, with the proviso that a de-icer fluid has methanol present in lieu of water where water represents

the minor phase by weight. Organic solvents operative herein illustratively including C₁-C₄ alcohols, acetone, (C₁-C₄)-O-(C₁-C₄), ethylene glycol butyl ether, dipropylene glycol methyl ether, and combinations thereof. Preferably, the solvent system is 5-90 percent by weight of an inventive composition. Preferably, the organic solvent is VOC exempt. As used herein, "VOC" is defined as a compound listed on the United States Environmental Protection Agency Master List of Volatile Organic Compounds.

[0021] An inventive composition optionally includes a halocarbon or hydrocarbon propellant in instances when an aerosol delivery system of an inventive composition is desired. Aerosol propellants operative herein illustratively include difluoroethane, trifluoroethane; alkanes such as butane, pentane, isobutane; propane; ethers such as dimethyl ether and diethyl ether; nitrogen; carbon dioxide; and combinations thereof. The resultant formulation inclusive of a propellant is sealed within a conventional metal aerosol canister and applied by spray application as is conventional to the art.

[0022] In certain embodiments of the invention, various additives enhance a property of an inventive composition; the property illustratively including storage stability, film formation, film durability and cleaning properties. Additives are provided such as a dye to modify the color of an inventive composition, a bitterant such as a denatonium benzoate, a surfactant, light stabilizers, defoamer, corrosion inhibitors or combinations thereof. Each additive independently is typically in an inventive composition in an amount from 0 to 3 total weight percent, while in other specific embodiments, each is present from 0.01 to 0.5 total weight percent.

[0023] A defoaming agent is present in certain embodiment in an amount present to inhibit surfactant foaminess, if desired, and allow for smooth formation of a hydrophobic film produced from an inventive composition. Defoamer agents operative herein illustratively include silicone-based defoamers; mineral

oil-based defoamers, and mixtures of foam destroying polymers and hydrophobic solids such as polyurias, as are known to the art. Specific exemplary silicone-based defoamers illustratively include silica-filled polydimethyl siloxane and polyether-modified polysiloxanes.

[0024] A corrosion inhibitor operative herein illustratively includes sodium benzoate, triethanolamine dinonylnaphthalene, boric acid-triethanolamine salt, phosphoric acid-triethanolamine salt, ammonia, triethanolamine, capryloamphoprionate, and mixtures thereof.

[0025] An inventive composition is readily stored in glass, metal, or plastic containers made of plastics such as polyethylenes, polypropylenes, nylons, PVC, or PET, or aerosol cans or soaked wipe substrate.

[0026] While it should be appreciated that there is virtually no limit as to the nature of a substrate to which an inventive composition is applied to as to form a hydrophobic film, with the proviso that the substrate is not dissolved or otherwise damaged through exposure to an inventive composition, exemplary substrates that are exposed to environmental conditions in which water droplet nucleation can occur on the substrate and have optical transmission attributes in their usage illustratively include optically transparent or translucent substrates formed of polystyrene, polycarbonate, polymethyl methacrylate, quartz glasses, silicate glasses, and ceramics.

[0027] Typical and preferred compositions according to the present inventions are provided in Table 1.

Table 1. Inventive Composition (amounts in total weight percent exclusive of optional propellant)

Ingredient	Typical	Preferred
Silicone micromulsion	0.05-10	0.2-3
Wetting agent	0-5	0.1-10
Cleaning solvent	1-90	2-10 except for deicer or

		windshield wiper fluid
Light stabilizer	0-1	0-0.2
Defoamer	0-1	0.01-0.5
Corrosion inhibitor	0-2	0-1
Solvent system	to 100%	to 100%
Organic: water 0.01-0.8:1*		

* ratio for windshield wiper fluid and deicer inverted.

[0028] An inventive composition is readily provided as a kit in the form of a bottle, wipe or aerosol canister. The bottle optionally equipped with a pump- or spray-trigger. With the provision of an optional wipe remove excess composition, along with instructions for doing so, an inventive kit is operational. The instructions providing details as how to prepare a substrate, apply the inventive composition, removal of excess from the substrate and the time and properties of the film so applied. The instructions can also provide details as to how the composition is re-applied after an applied film is worn.

[0029] The present invention is further detailed with respect to the following non-limiting examples that are provided to further illustrate the preparation of specific inventive compositions and certain attributes associated with the resulting films on substrates.

EXAMPLE 1

[0030] Glass Cleaner with Repellant Properties Fluid (GCRPF):

[0031] A formulation for glass cleaner with repellant properties fluid (GCRPF) contains 1 total weight percent of a silicone microemulsion:

DI Water	94 wt%
Acetone	5 wt%
Silicone microemulsion	1 wt%

In water based GCRPF, acetone is used as cleaning agent and solvent. The silicone microemulsion which may be present from 0.1 to 10 % is microemulsion and hence forms a clear and transparent solution.

EXAMPLE 2

[0032] Windshield Washer Fluid Additive (WWFA):

General formula for WWFA is shown below from following table:

WWFA	(1) wt.%	(2) wt.%
DI Water	90.70	87.80
IPA 99% Anhydrous	1.20	1.20
Methanol		3.00
silicone microemulsion	6.80	6.80
Ethylene Glycol Monobutyl Ether	1.30	1.20

[0033] Water based Windshield Washer Fluid Additive formula contains glycol ether solvent as cleaning, wetting, and degreasing agent; isopropyl alcohol is added for surface cleaning and drying purposes as well as for reducing surface tension of glass. Some formulations may contain methanol for cleaning and freezing benefit; and universal ingredient amino modified silicone microemulsion, which may be present from 5 to 20 %.

EXAMPLE 3

Windshield Washer Fluid (WWF):

[0034] While ranges of ingredients may vary depending on type of WWF some general formulations are shown below.

WWF	All Season & Bug Removers WWF	Winter & De-Icer WWF
	wt. %	wt. %
DI Water	68.95	64.58
Methanol	30.00	35.00
Silicone microemulsion	0.40	0.40
Biterant (Bitrex PG)	0.02	0.02
Ethylene Glycol Monobutyl Ether	0.63	
Dye	0.001-0.29	

[0035] Water based Windshield Washer Fluids are designated as All Season, Bug Remover, Winter, De-Icer and combination thereof. WWF is water based and contains methanol to fight freezing, glycol ether solvent as cleaning, wetting, and degreasing agent; and amino-modified silicone microemulsion, which may be present from 0.1 to 10 %. Dye (Drimarine K3R CDG Orange; FD&C Yellow; Dayglo Orange ECX #15) is dispersed and added aesthetics.

EXAMPLE 4

De-Icer Fluid (DIF):

[0036] While ranges of ingredients may vary depending on application (trigger spray or aerosol) general formulation is shown below. Amino-modified silicone microemulsion, AP-0282, which may be present from 0.05 to 20 %

De-Icer Fluid	wt. %
DI Water	10.00
Propylene Glycol	5.00

Methanol	84.78
Silicone microemulsion	0.10
Bitterant (Bitrex PG)	0.02
Hydroxyl terminated nonionic surfactant	0.10

EXAMPLE 5

[0037] Contact angle instrument (Krüss Mobile Drop) was used to measure contact angle of water on a clean-untreated or a clean-treated glass surface. A higher contact angle value indicates better water droplet beading on the surface (hydrophobicity), and hence better repellency and better conditions for water removal from the surface under external force such as blowing wind or gravity.

[0038] The durability test was conducted using the Abrasion Tester (BYK) and abraded (with section of a wiper squeegee) for a prescribed interval of cycles with water dripping from the sprinklers.

[0039] An in-house built sliding angle instrument was used to measure the sliding angle of a water drop on a glass surface. The angle at which the water droplet starts sliding down the glass surface (due to gravity force) was recorded as the sliding angle. The lower the sliding angle value, the easier the water droplet rolls-off the glass surface.

[0040] ASTM D 1003 was used to quantitatively measure some optical properties of the glass. Specifically, the light transmittance (T), haze (H), and clarity (C) of the glass were measured. The difference, Δ , of T, H, or C between before and after product application is used as a measure of the cleaning effectiveness of the product:

$$\Delta = \chi_c - \chi_b$$

where χ_c represents T, H, or C after cleaning or applying product and χ_b is the corresponding parameter before cleaning or applying product. A clean glass will have a higher T and C and lower H than a dirty glass.

[0041] An in-house built Ice Adhesion test unit was used to measure the force required to detach an ice cube / ice block from the glass surface. To make an ice cube, water is poured into a cup and placed in the freezer, which is then adhered to a clean-untreated or a clean-treated glass panel. After at least an hour of settling an external force was used to pull the ice cube from the glass panel. Smaller the force necessary to detach the ice cube from the glass panel, the less adhesive is the ice cube to the glass surface.

EXAMPLE 6

[0042] To test if the glass surfaces cleaned and treated with Glass Cleaner with Repellant Properties Fluid (GCRPF) will improve the water droplet contact angle on the glass surface several glass panels were used to apply the formula and then contact angle (CA) measurements were taken. Before Wash (BW) = after product application, before rinse with water; After Wash (AW) = after rinse with water.

[0043] The innovative formula GCRPF has an average CA of 100.5° before wash (BW) and 101.8° after wash (AW) (FIG. 1). These values show desired improvement as compared to the m,c-GCRR, which have average CA of 76.9° BW and 81.5° AW. The contact angle improvements (23.6° BW and 20.2° AW) of the GCRPF over the m-GCRR are statistically significant with 95% confidence level.

[0044] In general, the higher the CA, the more spherical the rainwater droplets are, and hence better repellency and better conditions for easier rolling away from the surface under external

force such as blowing wind or gravity. This results in better visibility if one looks through the glass.

[0045] The durability test was conducted to see how the contact angle changes with the number of abrasion wipe cycles. The treated panels were abraded and after the prescribed wipe cycle, the panels were removed from the tester, air dried, and the water contact angle was measured. As expected, the results showed that the contact angle slowly decreased with number of abrasion wipe cycles, (FIG. 2).

EXAMPLE 7

[0046] To test if the glass surfaces cleaned and treated with Glass Cleaner with Repellant Properties Fluid (GCRPF) will improve the removal of sleet/snow/ice, ice adhesion test was conducted. Results showed that the average force required to detach the ice-cubes on the glass surfaces that were treated with innovative GCRPF formula was about 2.6 lb_f (Figure 3, Table 2). Contrary to treated glass, the force required to detach the ice cubes from the untreated glass surfaces was so great that the experiments were stopped before ice cubes could be removed from the panels. Hence, the actual force was much higher than the reported force of 22.4 lb_f (FIG. 3, Table 1). The test demonstrated with 95% confidence level that the ice cubes have extremely low adhesion to the glass treated with GCRPF.

[0047] **Table 1.** Results of the ice adhesion test. * = the experiments were stopped before ice cubes could be removed from the panels.

Panel No.	Average Force Required to Detach the Ice from Surface(lb _f)	
	GCRPF	Untreated*
1	1.9	> 19.25
2	2.8	> 27.35
3	3.1	> 20.6
Average	2.6	22.4

EXAMPLE 8

[0048] To test if the glass surface treated with Windshield Washer Fluid Additive (WWFA) repels rain and raindrops bead up, Contact Angle measurement was conducted. The innovative WWFA has higher Contact Angle (CA) of about 88° , in water which is superior to the current market product m-WWFA with CA of about 68° (FIG. 4A). The innovative WWFA has a CA reading of about 85° , in WWF-RX, and a CA reading of 75° , in another WWF-BC (FIG. 4B). In general, higher the CA, the more spherical the rainwater droplets are, and hence easier to roll away from the surface under external force such as blowing wind or gravity. This results in a better visibility through the treated glass.

EXAMPLE 9

[0049] To test if the glass surface treated with WWFA repels rain and raindrops bead up, Sliding Angle measurement was conducted. The innovative WWFA has Sliding angle (SA) of 35 degrees in water and the SA of 39 and 42 degrees in WWF-RX and WWF-BC, respectively (FIG. 5). The lower the sliding angle value, the easier the water droplet rolls-off the glass surface.

EXAMPLE 10

[0050] The composition of Example 1 is sealed in a conventional metal aerosol canister with gaseous nitrogen as a propellant. The canister mixture is applied by spray application to the same substrates as Example 1 with excess liquid being removed from the substrate surface. The resulting film coated substrates are tested and perform in a similar manner as to those in Example 1.

[0051] Patents and publications mention the specification are indicative of the levels of those skilled in the art to which the invention pertains. These patents and publications are incorporated herein by reference to the same extent as if each individual patent or publication was specifically and individually incorporated herein by reference.

[0052] The forgoing description is illustrative of particular embodiments of the invention, but is not meant to be a limitation upon the practice thereof. The following claims, including all equivalents thereof are intended to define the scope of the invention.

CLAIMS

1. A hydrophobic film forming composition comprising:
A universal hydrophobic active ingredient of a silicone based microemulsion;
water; and
an organic solvent miscible with water.
2. The composition of Claim 1 wherein said microemulsion is an amine modified silicone polymer that self emulsifies in water.
3. The composition of Claim 1 further comprising a wetting agent.
4. The composition of Claim 1 wherein said organic solvent is at least one of acetone, isopropanol, methanol, ethylene glycol monobutyl ether, or propylene glycol, Dipropylene glycol methyl ether, Propylene glycol n-butyl ether
5. The composition of Claim 1 wherein the water is present at between 5 and 99 total weight percent.
6. The composition of Claim 1 wherein the organic solvent is present at between 1 and 90 total weight percent.
7. The microemulsion of Claim 2 wherein the said microemulsion is present between 0.05 and 20 total weight percent.

8. The composition of Claim 1 wherein said microemulsion, and said organic solvent are devoid of volatile organic compounds (VOCs).
9. The composition of Claim 1 further comprising at least one additive of a dye, a biocide, a surfactant, a defoamer, a light stabilizer, and a corrosion inhibitor.
10. Hydrophobic film forming composition consisting essentially of:
A universal hydrophobic active ingredient of a amino silicone based microemulsion;
water; and
an organic solvent miscible with water; and
an optional additive of at least one of a dye, a bitterant, a surfactant, a defoamer, a light stabilizer, and a corrosion inhibitor.
11. A process for applying a hydrophobic film to a substrate consisting of:
applying the composition of Claim 1 to the substrate;
and removing excess from the surface to form the film.
12. The process of Claim 11 wherein applying is with a spray, soaked wipe.

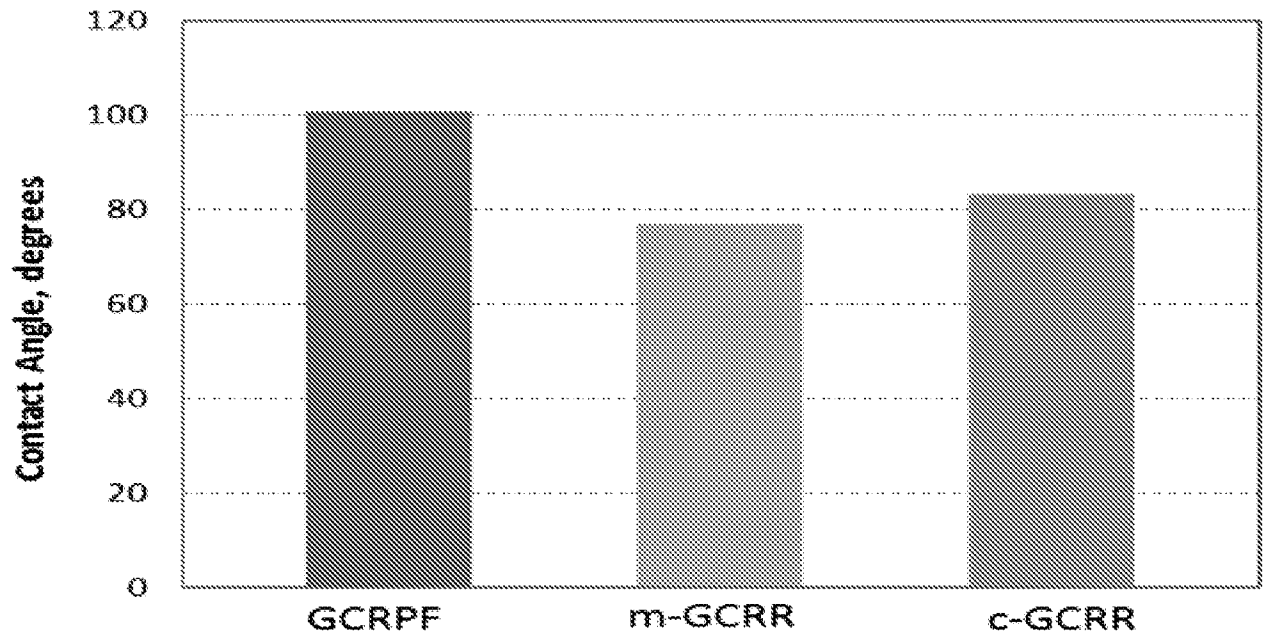


FIG. 1

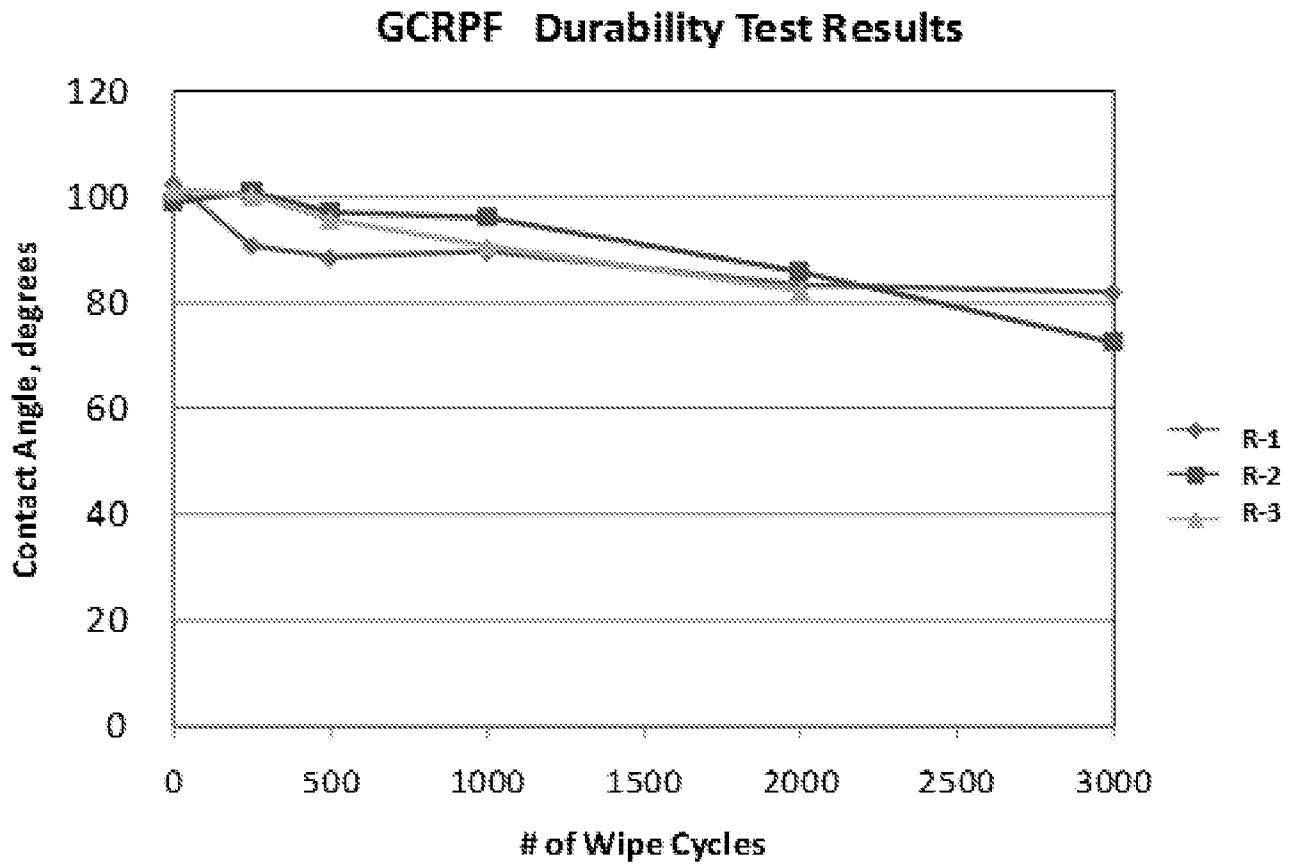


FIG. 2

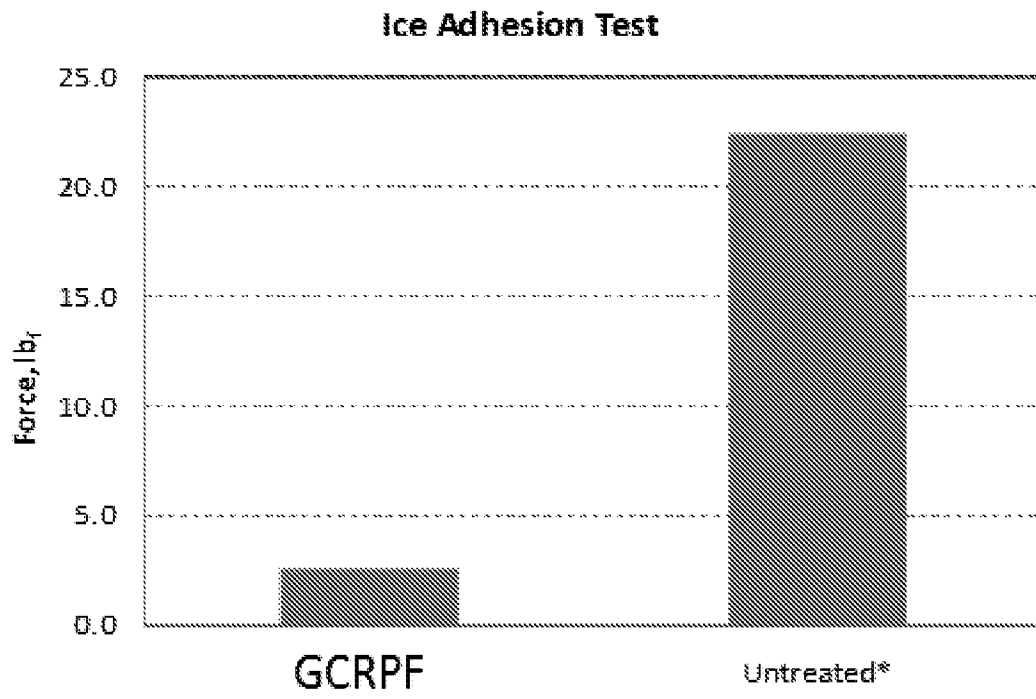


FIG.3

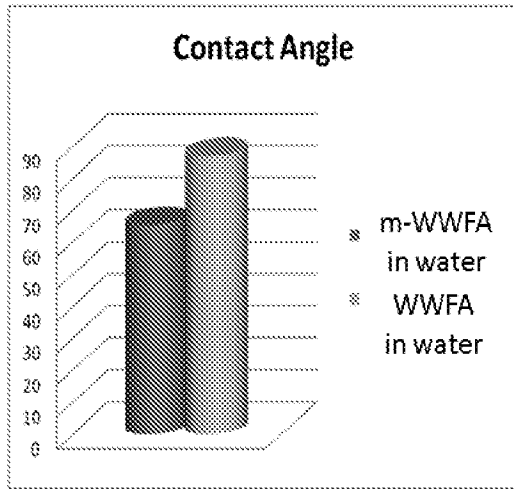


FIG. 4A

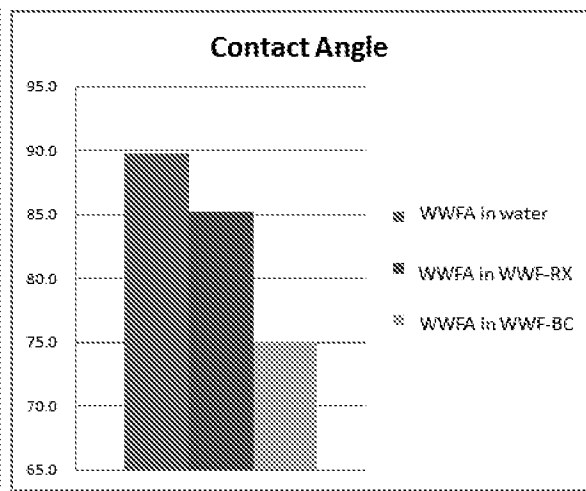


FIG. 4B

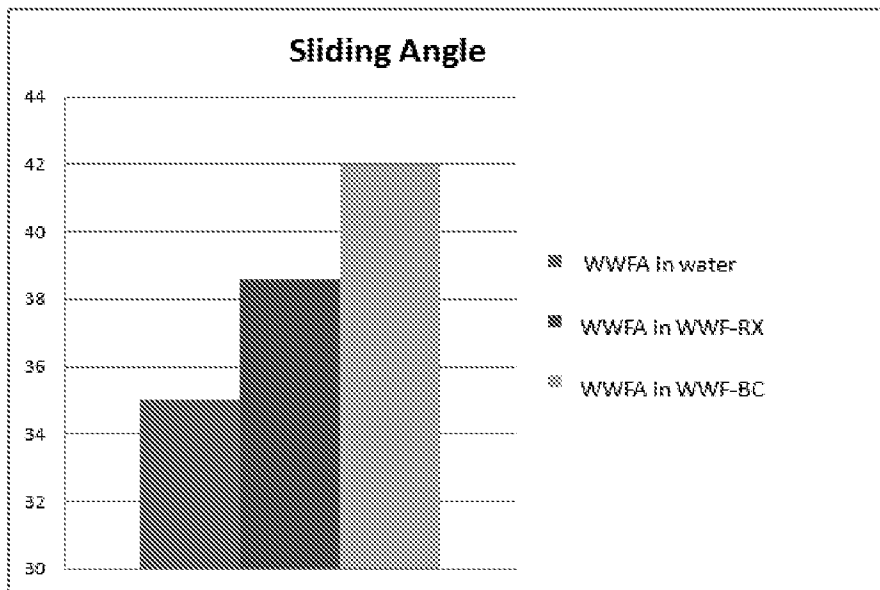


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/024655

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/37 C11D17/00 C09K3/18
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C07C C08G B01F C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/197465 A1 (BYRNE LUCIA JIENSUK [US] ET AL) 18 August 2011 (2011-08-18) paragraphs [0001], [0032], [0033], [0034], [0038], [0048]; claims -----	1-6,8-12
X	EP 2 514 405 A1 (SHINETSU CHEMICAL CO [JP]) 24 October 2012 (2012-10-24) paragraph [0002]; claims; examples; tables 1, 2 -----	1,3,5-9
X	EP 1 184 422 A1 (DOW CORNING [US]; DOW CORNING SA [BE]) 6 March 2002 (2002-03-06) paragraphs [0004], [0027] - [0028]; claims ----- -/--	1-9

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"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 17 July 2014	Date of mailing of the international search report 25/07/2014
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