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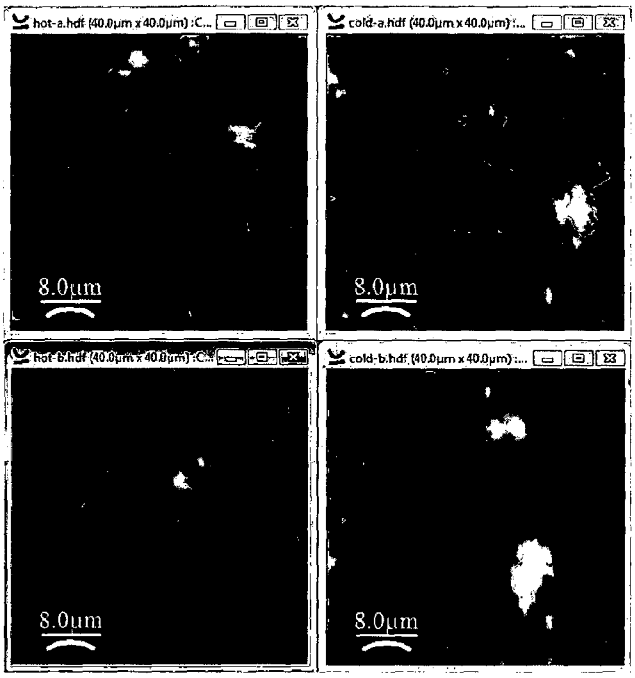
(54) Title: STIMULI RESPONSIVE SELF CLEANING COATING



(57) **Abstract**: Stimuli responsive self-cleaning aqueous coating compositions for masonry and other substrates involving coatings that are durable, storage stable, ambient curing and recoatable comprising of smart polymers, which said coatings exhibits reversible super-hydrophobic and super-hydrophilic behaviour in response to external stimuli based variable environmental conditions such as variations in at least one temperature, pH, humidity and light; also exhibiting low contact angle hysteresis of < 25 degrees which reversibly switches to a contact angle hysteresis of > 25 degrees with external stimuli. Said aqueous coating composition comprising a polymeric dispersion of either acrylic, fluorinated and amine backbone or acrylic, fluorinated and acid backbone in combination with hydrophobic and hydrophilic silicones and at least partially surface treated particles also including particulate mixture of micro and nano particles having balance of hydrophobicity and hydrophilicity, advantageously facilitates the attainment of contact angle hysteresis of < 25 degrees by the said self cleaning coating composition.

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TITLE: STIMULI RESPONSIVE SELF CLEANING COATING

FIELD OF THE INVENTION

The present invention particularly relates to stimuli responsive self-cleaning aqueous coating compositions for masonry and other substrates involving coatings that are durable, storage stable, ambient curing and recoatable comprising of smart polymers, and more particularly, relates to said coatings exhibiting reversible super-hydrophobic and super-hydrophilic behaviour in response to external stimuli based variable environmental conditions such as variations in at least one temperature, pH, humidity and light; also exhibiting low contact angle hysteresis of < 25 degrees which reversibly switches to a contact angle hysteresis of > 25 degrees with external stimuli. More specifically said aqueous coating composition comprising a polymeric dispersion of either acrylic, fluorinated and amine backbone or acrylic, fluorinated and acid backbone in combination with hydrophobic and hydrophilic silicones and at least partially surface treated particles also including particulate mixture of micro and nano particles having balance of hydrophobicity and hydrophilicity, advantageously facilitates the attainment of contact angle hysteresis of < 25 degrees by the said self cleaning coating composition. Advantageously, said attainment of such low contact angle hysteresis (< 25 degrees) and its subsequent reversible wettability switching by the aqueous coating composition/ stimuli responsive self-cleaning coatings enables the flow of rain water or forced air/ wind to clean the dirt from said coating surface wherein said coating can be formed by simple mixing of the components and applied by simple techniques such as brush, spray and dip coating application. More advantageously, the coating exhibits good dirt pickup resistance and resistance to dirt lines, streaks and water spots and also exhibits good anti microbial resistance to microorganisms, particularly algae. Additionally the coating displays enhanced photocatalytic activity under diffused sunlight with reduced chalking and shows good resistance to organic dirt and deposits such as bird droppings and oily stains. The coating also has a reduced tendency for spreading of water containing rust.

BACKGROUND ART

The surface of exterior coatings on exposure to outdoor environments is contaminated by organic and inorganic dust, clay particles, smoke, exhausts gas, rust, bird droppings and discoloured by ultraviolet rays.

The wetting of surfaces with water results in the retention of water droplets on the surface and their evaporation, with the solids suspended or dissolved in the water remaining as unsightly residues (water marks, smears or spots) on the surface.

The wetting of a surface with water is frequently also a trigger for its degradation or for infestation with microorganisms and the growth of algae, fungi, lichen, mosses, bacteria etc.

Therefore, it is particularly required for such outdoor coatings to show physical properties such as self-cleaning, weather resistance and anti microbial properties with long-term reliability.

Tremendous research efforts are being directed towards self-cleaning and stimuli responsive coatings. The field of self-cleaning coatings is divided into two types:
-hydrophilic
-and hydrophobic
Wettability of the surface can be measured by the contact angle which depends on the surface material and the surface texture. Alternatively, the wettability of a surface can be represented by the roll-off angle or Contact angle hysteresis. A hydrophobic surface in general exists if the roll-off angle is less than 25°.

Definition of terms:
Contact angle: The *contact angle* θ is the *angle* at which a liquid/vapor interface meets the solid surface wherein Fig 1 reveals contact angle measurement showing a hydrophobic and hydrophilic drop.
Hydrophobic: When the contact angle is >90° the surface is said to be hydrophobic.
Superhydrophobic: When the contact angle is >150° the surface is said to be superhydrophobic.
Hydrophilic: When the contact angle is <90° the surface is said to be hydrophilic.
Superhydrophilic: When the contact angle is <30° the surface is said to be superhydrophilic
Oleophobic: When the contact angle is >90° with oil/ oil like substance, the surface is said to be Oleophobic.

Contact angle hysteresis (CAH): Measure of the ease with which a drop of water rolls off a surface. It is the difference between the **advancing angle** and the **receding angle.**
Figure 2 reveals contact angle measurement showing the advancing and the receding angle wherein the **Advancing angle:** The contact angle which is a result of increasing volume of water on a surface is called the advancing angle and wherein the **Receding angle:** When

water with a syringe is removed from a surface the contact angle is called the receding angle.

It is known that the wettability of a surface by hydrophilic liquids may be reduced by a hydrophobic coating of the surface. Furthermore, it has proven favorable to structure hydrophobic surfaces. The structuring reduces the adhesion of the surface for polar liquids such as water and leads to reduced adhesion of solid deposits such as dirt particles on the surface. Given appropriate structuring, the dirt particles are flushed from the surface by moving water. The particulate solids may also be removed very easily by means of forced air or wind.

U.S. 2002/0048679 describes surfaces having a smooth, extremely hydrophobic polymer (for example, polytetrafluoroethylene) film and surfaces having a smooth extremely hydrophilic polymer film as examples of surfaces on which water and dirt can run off without forming droplets. U.S. 2002/0048679 further describes how a long-term hydrophobic coating may be formed by applying certain silane derivatives underneath a hydrophobic coating on a surface. Other self-cleaning surfaces are described in U.S. Patent Application numbers US 2002/0150723, US 2002/0150724, US 2002/0150725, US 2002/0150726, US 2003/0013795 and US 2003/0147932.

Oil and water repellent compositions based on fluoropolymers are described by Linert, et al, in WO 199700230, describe a composition comprising a fluoroaliphatic groups, carboxyl containing groups, oxyalkene groups and optionally silyl groups which provide repellency to oil- and water-based stains for porous substrates.

Ueda et al, in US20070197717, describe a masonry treating agent comprising fluoromonomer, a monomer having at least one acid group, and a non-fluorinated monomer having a hydrophobic group. A high content of fluorine containing monomer (35 to 90%) is being used.

Random fluorinated copolymers prepared by radical copolymerisation of monomers in solution in a water-miscible organic solvent using peroxides or azo compounds as initiators have been described (see, for example, EP 542598, EP 1106630 and US 2004026053), together with their hydrophobic and oleophobic properties on various substrates.

US 7781027 teaches durable, weatherable and scratch-resistant hydrophobic coatings comprising a fluorinated component and an adhesion promoter compound. The adhesion promoter compound is said to include an alkoxy group, a furfuryl-containing ring structure, and a reactive group.

US 4859754 teaches a water and oil repellent polymer having desoiling properties composed of a polyfluorinated group-containing copolymer obtained by copolymerizing high levels (65-95%) of a polyfluorinated group-containing monomer and an amphipathic monomer (5-35%) having a hydrophilic moiety and a lipophilic moiety.

A further development of these surfaces consists in structuring the surfaces in the µm to nm range wherein U.S. Pat. No. 5,599,489 discloses a process in which a surface can be rendered repellent by bombardment with particles of an appropriate size, followed by perfluorination.

US3,354,022 and WO 96/04123 describe other processes for reducing the wettability of articles by topological alterations in the surfaces wherein artificial elevations or depressions with a height of from about 5 to 1000 µm and with a separation of from about 5 to 500 µm are applied to materials which are hydrophobic or are hydrophobized after the structuring process. Unfortunately, such coatings have a disadvantage in that they possess a low abrasion resistance and only a moderate self-cleaning effect.

US 20110111659 teaches a method of providing oil repellency, water repellency, and dynamic water repellency to a substrate by coating with a polymer composition comprising hydrophobized nanoparticles and one or more monomers of C_1 to C_18, straight, branched, or cyclic alkyl (meth)acrylate, one or more monomers selected from the group consisting of N-methylol (meth)acrylamide and a second polymer comprising high quantities of fluorinated monomer.

EP2210921 teaches a hydrophobic composite coating which comprises a plurality of carbon nanotubes dispersed in a hydrophobic polymer resulting in a coating which has a water contact angle of least about 120°.

Super-hydrophobicity is frequently also referred to as the "lotus effect" because it was first observed on the leaves of the lotus plant. Super-hydrophobicity of a surface results in particularly easy dripping or rolling off of water from the surface, which supports fast drying of the surface and hampers the adhesion of dirt to the surface.

In this context, two states are known, namely the Wenzel state and the Cassie-Baxter state. In the Wenzel state, the drop of fluid completely covers the surface. As roughness increases, the hydrophobicity of a hydrophobic surface rises. Vice versa, the contact angle of a hydrophilic surface decreases with increasing roughness. In this way, a hydrophobic surface can be turned into a super-hydrophobic surface, and a hydrophilic surface can be turned into a super-hydrophilic surface by increasing the surface roughness. The Cassie-Baxter state furthermore considers that air bubbles are trapped between the drop and the rough surface.

The leaves of the lotus plant have elevations made from a wax, and these elevations lower the contact area with water. WO 00/58410 describes these structures and claims the formation of the same by spray-application of hydrophobic alcohols, such as 10-nonacosanol, or of alkanediols, such as 5, 10-nonacosanediol. The separations of the elevations in the structures are in the range from 0.1 to 200 μm and the heights of the elevations are from 0.1 to 100 μm.

US 7544411 teaches a self-cleaning paint coating that exhibits the "Lotus Effect". The paint coating comprises a paint base coat and a topcoat. The topcoat includes structure-forming particles and is at least partially hydrophobic. The structure-forming particles have an average particle diameter of less than 100 nanometers (nm) and form elevations in the topcoat surface that are interspaced at a distance of less than 50 nm. The topcoat of the paint coating is formed from the agent which contains a liquid medium, a hydrophobating agent dissolved in the liquid medium, and structure-forming particles suspended in the medium.

US7196043 targets a composition for producing a self-cleaning coating on a surface, the composition comprising: an aqueous mixture comprising water, metal oxide nanoparticles present at between 0.001 percent to 10 percent by weight of the mixture and having a particle size of less than 300 nanometers and a fluorinated water-soluble hydrophobic surface modifier of between 0.001 percent and 10 percent by weight of the mixture wherein the surface modifier can produce an unstructured surface having a surface energy below 30 dynes per centimeter, which fluorinated water-soluble hydrophobic surface includes fluorinated acrylic polymers.

CH-PS-26 82 58 describes water-repellent surfaces which exhibit a contact angle with water of more than 120°. They are obtained by applying powders, such as china clay, talc, clay or silica gel, on a substrate, the powder being first hydrophobized by organic silicon compounds. The application is performed together with curable resins or from solutions in organic solvents.

US3227675 and US4297145 teaches the hydrophobizaton of fillers such as kaolin, clay, chalk, siliceous chalk or diatomaceous earth with silane for use in vulcanisable rubber moulding compositions. US4715986, US6605351, EP0156270A2 and German Offenlegungsschrift No. 2107082 teaches particles modified by hydrophilic and hydrophobic groups wherein the hydrophilic and hydrophobic groups are distributed anisotropically on the surface of the modified particles and the use of such particles as surface active products.

US 4061503 teaches a composition comprising titanium dioxide particles containing on their surfaces a silane, in an amount sufficient to improve the dispersibility of said particles in a resin or plastic medium.

US8187707 teaches hydrophobic film or coating, comprising primary particles covalently bonded with secondary particles, adhering to the surface of the primary particles and having an average diameter that is smaller than the average diameter of the primary particles, and a hydrophobic layer covering at least partly the surface of the secondary particles and adhering to that surface.

US8202614 discloses an additive particle comprising a carrier microparticle, a plurality of nanoparticles adhered to and substantially covering a surface of the microparticle, and a hydrophobic surface treatment material in contact with exposed surfaces of the carrier microparticle and/or the nanoparticles sufficient to impart a superhydrophobic contact angle to the additive particle of greater than 150°; wherein the hydrophobic surface treatment material comprises a perfluorinated alkyl silane.

US8147607, US7964244 and US20050118433 relates to a hydrophobic coating composition for forming a coating on a substrate, consisting of hydrophobic particles, a solvent and water. The hydrophobic particles comprise one or more metal oxides that are treated with an organosilane, alkylsilane, fluorinated silane, and/or disilazane.

US6683126 provides a coating composition for producing difficult-to-wet surfaces, comprising at least one finely divided powder whose particles have a hydrophobic surface and a porous structure characterized by a BET surface area of at least 1 m^2 /g, and at least one film-forming binder characterized by a surface tension <50 mN/m, the weight ratio of powder to binder being at least 1:4.

On the other hand a hydrophilic surface may also produce good dirt shedding. The hydrophilic coating resists dirt pickup since water can wet the surface and flow off more easily allowing dirt to be easily washed off by rainwater.

US20060058490 claims a hydrophilic coating (contact angle <30°) formed using a hydrophilic silane and mixture of hydrophilic particles. They mention that if an organic binder is used, it may undergo degradation if photo catalytic particles are present in their system. Solgel network formation leads to a coating film with a hydrophilic surface where dirt streak marks can be avoided.

US20040082494 teaches hydrophobic-hydrophilic block copolymers to increase the water affinity of low energy surfaces using high contents of hydrophilic monomers (0 to 95%).

Waterborne fluoropolymers for paint use by Asakawa et al. in Journal of Fluorine Chemistry, Volume 104, Issue 1, June 2000, Pages 47–51 describes the synthesis of fluoropolymer emulsion having a hydroxy functionality, which could be cross-linked with water dispersible polyisocyanate resulting in a hydrophilic film-surface modifier which can prevent the dirt line on an outer wall.

Under UV irradiation TiO_2 (Titanium dioxide) is photocatalytically active and can produce super-wetting effects as a result of water hydrolysis effects. US6048910 teaches a coating composition comprising of an emulsion of a silicone resin, typically a water-insoluble, silanol group-bearing silicone resin dispersed in water, and contains photocatalyst particles, typically titanium oxide which forms a hydrophilic film having a water-drop contact angle of no more than 60° when irradiated with UV-containing light. Films obtained by applying this coating composition to the surface of substrates have excellent weathering resistance and antifouling properties due to a self-cleaning effect arising from the photocatalytic action of the particles.

The crystalline forms of titanium dioxide exhibit photocatalytic activity, of which, only anatase and rutile have potential commercial applicability as photocatalysts. Rutile titanium dioxide has band gap energy of 3.05 eV, which corresponds to approximately 420 nm wavelength of light, and anatase titanium dioxide has a band gap of 3.2 eV (approximately 385 nm). Within the field of photocatalysis, anatase titanium dioxide has established a reputation as generally superior to rutile titanium dioxide.

When a titanium dioxide crystal absorbs a photon of sufficient energy (from natural radiation, sun or from an artificial radiation exposure, lamp), an electron is promoted to the conduction band, and a positive hole (h+) is generated in the valence band. This "electron-hole pair" generates highly oxidizing hydroxyl and superoxide radicals at the crystal surface that are capable of oxidizing practically all organic matter to CO_2 and H_2O.

Photocatalytic oxides are known to have antifouling, antimicrobial, soil-degrading, deodorizing, air-cleaning, antifouling, antimicrobial, water-cleaning, superhydrophilicizing and/or antifogging effects. Due to photocatalysis the organic dirt even when deposited on the surface of the coating, are unstable and hence easily removed, permitting the surface to be kept clean.

US6337129 teaches an antifouling coating composition with both a hydrophobic portion, and a hydrophilic portion induced by a photocatalyst, both portions being present in a microscopically dispersed and exposed state on the surface. The content of the photocatalytic oxide in the surface layer is also not particularly limited. For example, the content of the photocatalytic oxide in the surface layer is preferably about 10 to 80% by weight, more preferably about 20 to 50% by weight. Thus high contents of photocatalysts are being used.

US7521039 describe photocatalytically active rutile titanium dioxide which demonstrates enhanced activity in the visible light spectrum. It is produced by neutralizing the rutile seed to a high pH prior to washing and thermally treating the seed.

US7955430 teaches a coating material comprising a binding agent and at least one filler including particles having a size and/or surface roughness of about 100 microns or less, and a photocatalytically active agent about 2 to about 15 weight percent of the coating material. The binding agent may be at least partially decomposed by a photocatalytic action, and a microstructured, self-cleaning surface may be formed. The photocatalytically active agent used is an oxide of titanium, zinc, iron, manganese, molybdenum and/or tungsten, which comprises at least one additive selected from C, N, S and/or from a transition metal oxide and/or transition metal halide. The selected additive(s) may enable the stimulation of the catalytic property even with wave lengths e.g. in the visible range of the solar spectrum. The desired self-cleaning properties may advantageously be achieved if the coating material is formulated using an excess of binding agent.

In WO00/06633, coating materials for plastics based on inorganic binding agents and fillers are described. The coating materials set forth in the known publication may additionally contain photocatalytically active agents for self-cleaning by means of decomposition of organic soiling and superhydrophilics, while the binding agents used in the manufacture of the known materials are stable to the photocatalytic effect of the photocatalytically active agents.

US20100311572 discloses a coating material comprising at least one binder and at least one photocatalytically active particle comprising a core composed of at least one first substance having a diameter of 0.1 to 1 μm and at least one envelope at least partly surrounding the core and composed of at least one second substance having an average layer thickness of 0.1 to 10 nm. The active particles are generally present in the coating material in an amount ranging from 0.1% to 10% by weight.

Useful metals or semimetals whose oxides are present in the core of the photocatalytically active particles are generally selected from the group consisting of elements of groups I to XV of the periodic table (in accordance with IUPAC), lanthanides, actinides and mixtures thereof, more preferably from the group consisting of V, Ti, Zr, Ce, Mo, Bi, Zn, Mn, Si, Ba, Au, Ag, Pd, Pt, Ru, Rh, La and mixtures thereof.

Very particularly preferred metal or semimetal oxides present in the at least one envelope of the particles are SiO_2, ZnO, CeO_2, TiO_2, SnO or mixtures thereof.

It is thus possible to adjust the activity of the core-envelope particles such that soils adhering to the coating material of the present invention are catalytically degraded, while the binder present in the coating of the present invention is essentially not catalytically degraded.

JP 11 181339 A discloses a hydrophilic coating comprising photocatalytically active titanium dioxide particles. The titanium dioxide particles have a particle diameter of 1 to 100 nm, comprise particles of SnO_2 and are silica and/or silicone coated. The coating material prevents soiling of a surface coated with this material. A surface thus treated further has self-cleaning properties when rained upon.

JP 2006-233343 discloses a liquid photocatalyst composition for coating textiles which comprise photocatalyst particles having a preset particle diameter and a coating. The size of these photocatalyst particles is 0.5 to 10 μm. In a preferred embodiment, the core of the photocatalyst particle consists of titanium dioxide and the envelope consists of silica.

JP 11228873 A discloses a paint composition comprising titanium dioxide particles coated with porous silica and having photocatalytic properties. The composition further comprises titanium dioxide pigment and an organic resin binder and does not teach any particle size of said photocatalytically active particles.

US20110129204 discloses a photocatalytic coating composition comprising a hydroxyapatite-coated photocatalyst, a silica-based binder, an acrylic emulsion, a thickener and water.

US 20110313095 relates to a mixture, comprising at least one thermoplastic polymer as component (A) and at least one photocatalytically active particle, comprising a non-porous core comprising at least one metal oxide or semimetal oxide with a diameter of from 0.1 nm to 1.mu.m, and, at least to some extent surrounding the core, at least one porous outer layer comprising at least one further metal oxide or further semimetal oxide with an average layer thickness of from 0.1 to 10 nm, as component (B), to a process for the production of this mixture, via mixing of components (A) and (B), to the use of the mixture as photocatalytically active surface, to moldings, comprising this mixture, and to the use of this mixture for the production of moldings.

EP1955767 A1 discloses a mixture comprising photocatalysts and organic polymers, such as polyacetals, polyethylene, polypropylene, polystyrene, polyvinyl chloride, nylon-type polymers, polycarbonates, etc. The photocatalysts used preferably comprise titanium dioxide particles, which have a coating composed of non-porous silicon dioxide.

JP2000-017096 discloses foamed foils composed of thermoplastic resins, which have titanium dioxide as antibacterial coating. Silanes have been applied as surface modifier on the surface of the titanium dioxide.

JP2000-204194 discloses a process for the production of polymer compositions which comprise titanium dioxide as photocatalyst. The titanium dioxide has, for example, a coating of silicon dioxide. The ratio of polymer to titanium dioxide is from 97:3 to 20:80.

JP 09/225321 A discloses a photocatalytically active body composed of titanium dioxide in the anatase form. The titanium dioxide used in that composition is present between two porous layers of another inorganic compound, such as silicon dioxide.

JP 2005-097608 A discloses a polyolefin film which comprises photocatalyst particles, where the photocatalyst particles are mixed crystalline oxides comprising titanium dioxide and silicon dioxide. Said JP patent does not disclose any core-outer layer photocatalysts or any use in thermoplastic polymers.

KJA Raj et al. in Indian Journal of Chemistry, July 2010, 49A(07), 867 have prepared a series of titania samples with different loadings of silica (0.5-10 wt.%) by wet impregnation method. High dispersion of silica in the Titania matrix and the bonding of Ti-O-Si in silica-titania samples are found to inhibit the transformation of amorphous to anatase Titania. Evaluation of photocatalytic activity of the samples shows greater activity for samples modified with silica with an optimal loading of 7.5 weight % silica calcined at 500 °C. Conversion of 90 % and 35 % of 4-chlorophenol for UV-visible and visible light respectively is observed.

US20110312065 A teaches a substrate or coating that includes a protease which is capable of enzymatically degrading of one or more components of the biological stain to facilitate biological stain removal from the substrate or said coating.

The early applications of titanium dioxide in photocatalysts used nearly exclusively ultraviolet light sources as is required by the band gap energies of anatase titania. Ultraviolet (UV) light refers to light of a wavelength below about 400 nm. By contrast, light from the visible spectrum refers to light of a wavelength from about 400 nm to about 800 nm.

Accordingly, when conventional photocatalytic products are applied to interior products, their performance is greatly reduced because UV light constitutes only a relatively small fraction of sunlight and in part because indoor lighting is typically very low in UV intensity. Thus, there is a need to develop a photocatalytic coating composition that is suitably applicable to interior products which work under diffused sunlight as well as exterior products. If a larger proportion of the electromagnetic spectrum could be used, then a more efficient catalytic performance could be achieved and a larger number of potential applications could be realized.

Conventionally high contents (>1% of formulation) of nano Titania are used in photocatalytic coatings required for interior paints. There is also a need to develop an economical formulation where a low content of nano Titania can be used to achieve enhanced photocatalytic activity even in diffused sunlight.

Most photocatalytic paints comprise silicone type mineral binders and not binders based on organic products, so as to prevent the binder itself from being photocatalytically degraded. There is also a need to develop an economical photocatalytic coating composition that can minimize degradation of the organic binder.

With conventional coating materials, resistance to weathering is achieved by subjecting coating components to which a photocatalytic action is attributed, such as titanium dioxide pigments, to a surface treatment in order to reduce the photocatalytic activity. In this way, highly stabilized pigments with excellent protective effect for coating materials are obtained with conventional coatings. Historically, when rutile titanium dioxide has been considered applicable as a photocatalyst, it has been in a state in which the rutile crystals are "metallized," that is, containing small islands of metals such as platinum, rhodium, gold and silver on the rutile crystals. Unfortunately, such catalysts are prohibitively costly and may be leached out in practical use. Thus, there is a need to develop an economical formulation where even rutile titanium dioxide photocatalyst can have enhanced photocatalytic activity and be activated by visible light.

Conventionally nano sized Titania (<100 nm, predominantly anatase) are used in photocatalytic coatings. There is also a need to develop an economical formulation where a variety of particle sizes of anatase or rutile TiO_2 from 1 nm to 1 micron can be used to achieve enhanced photocatalytic activity even in diffused sunlight.

US20030147932A1 claims an anti microbial coating with surface roughness. Amine functional monomer is used in combination with fluorinated monomers in US6521730, US5965659, US4147851 and US20110111659.

WO2007044784 teaches a self-decontaminating surface coating resistant to spores which when cured has a partially hydrophobic surface. The coating comprises a polymeric coating resin which, when cured, is hydrophilic. The coating also comprises a biocide, a germinating agent, and a hydrophobic micro/nano particulate material. The coating is suitable for application to ceramics, metals, and polymer substrates.

Polymers that have anti-microbial properties are disclosed by the following patent applications: DE10024270, DE10022406, PCT/EP 00/06501, DE10014726, and DE 10008177. The antimicrobial properties are attributable to the contact of bacteria with the surface. European patent application EP0862858 discloses that copolymers of tert-butylaminoethyl methacrylate, a methacrylate with a secondary amino function have microbicidal properties.

Peter Forbes dislcoses self cleaning materials in Scientific American 299, 88 - 95 (2008) wherein superhydrophilic titania has a contact angle of 0 degrees, hydrophilic standard window glass has a contact angle of 30 degrees, hydrophobic Teflon 100 degrees and superhydrophobic lotus leaves 160 degrees. The convergence of opposites is mentioned where researchers are exploring ways to get the same structure to switch from being superhydrophobic to superhydrophilic and vice versa. In the year 2000, titania pioneers Fujishima, Watanabe and Hashimoto in L. Jiang, R. Wang, B. Yang, T. Li, D. A. Tryk, A. Fujishima, K. Hashimoto, D. Zhu, Pure Appl. Chem. 2000, 72, 73, used small amounts of titania to prolong the life of lotus effect surfaces. In 2003, Rubner and Cohen used a LBL technique to stack up alternating layers of positively charged poly(allylamine hydrochloride) and negatively charged silica particles. This led to a transparent superhydrophilic coating that demonstrated anti fog behavior through a phenomenon called nanowicking. In earlier work they used silica particles to mimic the lotus's rough hydrophobic surface. Smart beetles in the Namib Desert harvest water from thick morning fogs. It squats with its head down and back up, facing the foggy wind. Water condenses on its back and trickles down its mouth. In 2001, Andrew R. Parker [*Nature* **414**, 33-34 (1 November 2001)], found that the back of the beetle has a bumpy, waxy, superhydrophobic surface. The tops of the bumps are free of wax and are hydrophilic. These hydrophilic spots capture water from the fog, forming droplets that quickly grow large enough for gravity and the surrounding superhydrophobic area to dislodge them. In 2006, Rubner and Cohen's team [*Nano Lett.*, 2006, 6 (6), pp 1213–1217] created superhydrophilic spots of silica on superhydrophobic multilayers. Thus textured surfaces can either be superhydrophobic or superhydrophilic depending on the surface chemistry of the elevated regions. In 2006, a team led by Kilwon Cho in H. S. Lim, J. T. Han, D. Kwak, M. Jin, K. Cho, J. Am. Chem. Soc. 2006, 128, 14458 achieved complete switchability by adding a compound based on the molecule azobenzene to the siliconized surface of a silica-polyelectrolyte multilayer. The surface is superhydrophobic, but under UV light the azobenzene compound changes configuration and changes to superhydrophilic.

Combinations of self-cleaning as well as stimuli responsive coatings with hydrophilicity and hydrophobicity as evident from the above discussions are thus reported in literature. To design such responsive surfaces, various methods such as self-assembled monolayers, layer-by-layer assembly, surface-initiated atom-transfer radical polymerization and electrochemical deposition have been proposed by X. Feng, L. Feng, M. Jin, J. Zhai, L. Jiang, D. Zhu, J. Am. Chem. Soc. 2004, 126, 62; H. S. Lim, J. T. Han, D. Kwak, M. Jin, K. Cho, J. Am. Chem. Soc. 2006, 128, 14458; X. Yu, Z. Wang, Y. Jiang, F. Shi, X. Zhang, Adv. Mater. 2005, 17, 1289; J. Lahann, S. Mitragotri, T. Tran, H. Kaido, J. Sundaram, I. S. Choi, S. Hoffer, G. A. Somorjai, R. Langer, Science 2003, 17, 371.

Most of these responsive materials designed by these methods are still limited to the laboratory as they involve use of complex polymers and application procedures.

Polymer systems that undergo a conformational change or phase transition in response to external stimuli such as temperature, pH, light and electric fields have opened up a number of opportunities for the development of new materials. Several environmentally responsive polymers are also described in WO2012075033.

Acid functional polymers are pH responsive with the polymer becoming hydrophilic with pH>7 and hydrophobic with pH<7. Polymers with sufficient hydrophilicity in their backbone can exhibit response to humidity with higher humidity conditions leading to water absorption and hence the surfaces behaving hydrophilic and vice versa. Of these, the most commonly utilised stimulus is temperature and polyacrylamide based copolymers are well known to create temperature-stimulus-sensitive surfaces as taught by Cheng, X.; Canavan, H. E.; Stein, M. J.; Hull, J. R.; Kweskin, S. J.; Wagner, M. S.; Somorjai, G. A.; Castner, D. G.; Ratner, B. D. Langmuir 2005, 21, 7833; Sun, T.; Wang, G.; Feng, L.; Liu, B.; Ma, Y.; Jiang, L.; Zhu, D. Angew. Chem., Int. Ed. 2004, 43, 357; Xia, F.; Feng, L.; Wang, S.; Sun, T.; Song, W.; Jiang, W.; Jiang, L. AdV. Mater. 2006, 18, 432.

Responses based on temperature stimulus are largely dependent on lower critical solution temperature (LCST). For example, poly-n-isopropylacrylamide (PNiPAm) exhibits a LCST of 32 °C in water. Below the LCST, PNiPAm expands and becomes hydrophilic (swollen coil conformation) while above the LCST it shrinks becoming hydrophobic (globular conformation) as disclosed in Benee, L. S.; Snowden, M. J., Chowdhry B. Z. Langmuir, 2002, 18, 6025. Copolymerization with hydrophobic monomers are known to decrease the LCST whereas with hydrophilic monomers increases the LCST.

Aqueous polymeric dispersions are taught in US5173523, using a two stage monomer addition process followed by stripping of the co-solvent. US6277953 teaches preparation of an aqueous polymeric dispersion which is substantially free of an emulsifier, having an acid value in the range of from about 10 to about 40 with a particle size of not more than about 300 nm and the aqueous dispersion has less than about 2 weight percent organic solvent, at least about 30 weight percent solids. US4616058, US5817370 also teach the preparation of polymeric dispersions. US5319019 teaches a process for making acrylic polymer ammonium salt/organic solvent/water mixture, the organic solvent and water being in amounts effective for forming an azeotrope; resulting in a polymer having less than 2 weight percent of organic solvent.

Responsive colloidal systems: Reversible aggregation and fabrication of superhydrophobic surfaces by Mikhail Motornov, Journal of Colloid and Interface Science 310 (2007) 481–488, reported a method of fabricating stimuli-responsive core–shell nanoparticles using block copolymers of poly(styrene-*b*-2-vinylpyridine-*b*-ethylene oxide) and poly(styrene-*b*-4-vinylpyridine) covalently bound to silica nanoparticles with two different diameters: colloidal silica 200 nm in diameter and fumed silica 15 nm in diameter.

The construction of a rough surface functionalized with carboxylic acid groups is capable of switching between superhydrophilic and superhydrophobic in response to pH. Wang and co-workers Wang, J.; Hu, J.; Wen, Y.; Song, Y. Jiang, L., Chem. Mater. 2006, 18, 4984-4986 produced a pH responsive surface from self assembled layers of polystyrene-poly(methyl methacrylate)/poly(acrylic acid) core-shell beads. The beads form the rough surface that is needed to obtain the extreme contact angles. Sodium dodecyl-benzenesulfonate (SDBS) was added as an emulsifier but is also part of the key to switching the behavior of the surface. The SO_3 groups of the SDBS hydrogen bonds with the COOH groups on the bead, creating a hydrophobic surface state. When the acid groups are deprotonated the COO- and the SO_3- groups repel each other and provide a hydrophilic surface state.

N Verplanck in Nanoscale Res Lett (2007) 2:577–596 teaches the use of self-organized TiO_2 nanotube layers grown on Ti by electrochemical anodization. The as-prepared TiO_2 nanotubes displayed a superhydrophilic wetting behavior. When modified with organic molecules, such as octadecylsilane or octadecylphosphonic acid layers, the surfaces showed a superhydrophobic behavior, wherein by combining said TiO_2 layer with an irreversible UV induced decomposition of the organic monolayers can be used to adjust the surface wetting properties to any desired degree from super-hydrophobic to superhydrophilic.

US7695814 and US7923106 are directed to a responsive coated substrate comprising at least one silicone-based, substantially hydrophobic polymer and at least one substantially hydrophilic polymer comprising polyethylenimine wherein said responsive coating substrate is in a first state; and methods of coating the same.

US6919398 teaches a hydrophobic coating with a contact angle of greater than 130° after 3 minutes equilibrium consisting of a hydrophobic polymer and a bimodal particle size distribution of particles more than 5 microns particle size and less than 3 microns. They also teach about their formulation containing an insufficient amount of hydrophilic components.

It is stated in DE2150736 that it is known to use vinyl chloride copolymers, chloro rubber, copolymers of acrylic esters, optionally with styrene and vinyl toluene, and siloxane resins as binders in modern pigment-containing facade paints; the publication suggests the use of a mixture of (a) siloxane resins and (b) copolymers or terpolymers of methylmethacrylate with acrylic acid esters, carboxylic acids or carboxylic acid esters, vinyl toluene or styrene. It is stated that such paint can penetrate into the outer layers of the surface to be painted, i.e. act to impregnate it and to be water-repellent. The kind of siloxane resins is not stated.

A paint described in DE2352242, particularly for protecting facades such as concrete facades, which paint contains pigment and as a binder copolymerisates of methacrylic acid esters has in the binder, in order to increase the water-repellent properties, a content of lower molecular weight methyl, phenyl or methylphenyl siloxanes in an amount of 10-50% by weight of the copolymerisate, and preferably also a catalyst for the siloxanes, e.g. an organotin compound. The siloxanes are stated to polymerise to form higher molecular weight compounds, which improves the water-repellency.

From DE2307422 there is known a water-repellent coating composition consisting of an inert carrier liquid, a resin-like binder and one or more metal or metalloid oxides the surface of which has been rendered hydrophobic with an organic silicon compound. A coating formed by such a composition must be expected to be surface-hydrophobic and hence give a good water-repellency.

US5584921 discloses coatings for building materials, in the form of an aqueous dispersion comprising: (a) 10 to 60 wt % of at least one polysiloxane (an aqueous emulsion of a hydroxyl-functional methyl silicone resin); (b) 5 to 65 wt % of at least one colloidal silica in the form of silica sol; (c) 5 to 80 wt % of at least one pigment or unreactive filler; and (d) 0 to 30 wt % of at least one further varnish or paint additive.

US6013724 teaches a raindrop fouling-resistant paint film comprising a tetramethoxysilane partial hydrolyzed condensate having a silanol (SiOH)-methoxysilyl (SiOMe) group molar ratio of not more than (SiOH)/(SiOMe)=1/10, a dimer through octamer content of 0-30 weight %, and a weight average molecular weight of 1500-5000 as available upon hydrolysis at a hydrolysis degree of less than 100% and condensation of tetramethoxysilane and at least one film-forming resin and/or at least one inorganic binder having alkoxysilyl as a reactive curing group as selected from the group consisting of an alkoxysilane compound, a partial hydrolyzed condensate of said alkoxysilane compound, and a siloxane polymer.

Coatings containing silicates have been shown to provide superior stain resistance. Such coatings are described, for example in EP0942052, JP2002294154, and JP01172389. Organosilicates have also been used with fluoropolymer resins to produce desirable coating compositions as described in JP02003775, JP2003020450, U.S. Pat. No. 6,635,341 and EP1035184. An organosilicate works by a mechanism of stratification first, and then hydrolysis with rain water in the surface increasing the hydrophilicity.

The book "Silicone resins and their combinations" Wernfried Heilen, Vincentz Network, 2005 teaches the use of silicone containing binders to enhance durability of architectural paints. The binder in silicone resin emulsion paints comprises 50 % mineral-based silicone resin and 50 % polymer emulsion. On mineral building surfaces and in coatings, silicone resin binders build up stable three-dimensional silicone resin networks which are chemically bound to the mineral substrate. The water repellency arises from the organic group on the silicone resin while the inorganic portion of the silicone resin bonds with the filler and the pigment together, creating permanently water-repellent capillaries and pores.

There are several published articles which address the elimination of water marks. In one example, US5759980 teaches a composition, which comprises a surfactant package consisting of a silicone-based surfactant and a polymer which is capable of bonding to a surface to make a hydrophilic film which eliminates the problem of water marks. However, this hydrophilic coating may tend to be removed from the surface by a single water rinse. German publication DE-A2161591 also describes a composition for cleaning cars wherein the surface is again made hydrophilic by using amino functional polymers. This coating also tends to be rinsed off from a single rinse. There are number of waxes and other products available in the market for attempting to retain this spot free finish. However, certain wax containing hydrophobic surfaces result in water marks when the water dries giving an unaesthetic appearance.

Therefore, there is a need to develop a process and coating for protecting various surfaces from the appearance of water marks, corrosion streaks, and dirt streaks while maintaining the water repellency even after several water rinses.

US20060110542 discloses a composition for forming a detachable and renewable protective coating produced by making a highly concentrated dispersion of hydrophobically modified silica particles in the presence of a disilazane derivative under high shear conditions.

Examples of commercially available materials which attempt to produce this "Lotus" cleaning effect are products sold under the trade name of MINCOR available from BASF, and TEGTOP available from Degussa. As stated in US20090018249 these products, when tested for their ability to protect various surfaces from the appearance of water marks, corrosion, and dirt repellency and while maintaining the water repellency, were deemed unsuitable. The coating is initially super hydrophobic and may remain so for long periods indoors; however, when exposed to outdoor UV light, rubbed even slightly, or in general exposed to weather, the coating loses super hydrophobicity and becomes less hydrophobic within days or even hydrophilic and hence less useful for the object of the present invention. Examination under the microscope after a week of exposure on a panel in a UV cabinet reveals that a coating made from fumed silica and at least one film forming binder as taught in US6683126 disintegrates.

US20030013795 teaches a self-regenerating, self-cleaning hydrophobic surface formed when particles are secured on a carrier, resulting in a long lasting self cleaning action.

WO2008071957 relates to novel block copolymers for use in coating surfaces to provide self-cleaning surfaces and capture/release materials wherein the copolymers comprises a first hydrophobic block and a second hydrophilic block comprising a non-fluorinated acrylate or methacrylate monomer.

Although some of the above-mentioned surfaces may have excellent self-cleaning properties, the attachment or colonisation of microorganisms can impair these properties.

For instance, micro-organisms (fungi, algae, bacteria) may colonise a self-cleaning surface which may impair, or may entirely remove, the self-cleaning properties of the surface. Further, organic dirt and deposits such as bird droppings and oily stains further mar the surface of these self cleaning coatings. Coatings containing photocatalytic particles use high contents of nano Titania or are doped with expensive materials to enhance activity under visible light which is not a feasible proposition.

As apparent from the above, most of the responsive materials discussed above and methods to reach to the said materials are either still limited to the laboratory as they involve use of complex polymers and application procedures or are not sufficiently durable, permanent or mechanically robust. Additionally, there is often a need for high contents of organofluorine compounds or fluoropolymers which are very expensive. With the ever-increasing practical needs of such smart surfaces, it is of particular importance and a long-felt need in the art to explore achievement of new water-borne pigmented coating exhibiting reversible hydrophilic-hydrophobic character with variation in temperature/ pH/ humidity/ light which would also possess the desired contact angle hysteresis of < 25 degrees which switches reversibly to > 25 degrees and would be obtained of a simple process with lower production cost to be thus economically and industrially facile thereby being attractive to the end users.

A further requirement of new generation smart surfaces in addition to the abovesaid, is the ability to dispose off the dirt deposited on the surface by a combination of hydrophobic and hydrophilic cleaning, to eventually not only prevent the deposition of the dirt but also prevent the infestation and growth of unwanted organisms, such as microorganisms, algae, lichen, and mosses.

There is, therefore, a need for ambient curing, storage stable and recoatable water-based coating composition, the composition which even when applied on a surface restores a balance between hydrophobicity and hydrophilicity such that it prevents the appearance of water marks and prevents attachment of dirt and the like, and above all would maintain its most important attribute of reversible switching between hydrophobicity and hydrophilicity even after long exposures to the environment, which in addition would also exhibit good resistance to bird droppings and oily stains and enhanced photocatalytic activity even under diffused sunlight with negligible chalking.

Hence there is a longfelt need for such a substrate comprising substantially hydrophobic coating as abovesaid which when exposed to at least one external stimulus such as UV, pH, humidity or temperature would cause the substrate to switch from the first substantially hydrophobic state to a second substantially hydrophilic state, with a provision to produce such smart coatings by facile, economical and simple techniques for manufacturing on a large scale and applied by conventional techniques such as brush and spray application that would thus exhibit superhydrophobicity under certain environmental conditions of high temperature/ low pH/ low humidity/ low intensity of light and superhydrophilicity at low temperature/ high pH/ high humidity/ high intensity of light.

OBJECTS OF THE INVENTION

It is thus a primary object of the present invention to provide for a stimuli responsive self-cleaning aqueous paint/ coating composition involving coatings that are durable, recoatable and storage stable and comprises of smart polymers in combination with at least partially surface treated particles including a particulate mixture that would be responsive to external stimuli related to certain environmental conditions such as variations in temperature, pH, light and humidity to thus exhibit super-hydrophobic and super-hydrophilic behaviour, and processes for manufacturing the same.

Another object of the present invention is to provide for a stimuli responsive self-cleaning aqueous paint/ coating compositions and self-cleanable surfaces which would be oleophobic and exhibit the desired reversible hydrophilic-hydrophobic switching to provide for a water contact angle hysteresis of <25° under certain environmental conditions with variations in at least one or more of temperature, humidity, pH, light that would be switchable to a water contact angle hysteresis of >25° under said environmental conditions offering benefits of both superhydrophobic and superhydrophilic cleaning, water marks, good organic and inorganic dirt pickup resistance, resistance to dirt streaks, dirt lines, water spotting, good cleanability with water and forced air or wind, reduced chalking, good resistance to organic dirt and deposits such as bird droppings and oily stains, and reduced tendency for spreading of water containing rust.

It is another object of the present invention to provide for stimuli responsive self-cleaning aqueous coating composition involving polymers that would be recoatable with low coating surface energy preferably in the range of < 40 mN/m, more preferably < 20 mN/m and most preferably < 10 mN/m.

It is yet another object of the present invention to provide for said stimuli responsive self-cleaning coating composition with low contact angle hysteresis (<25 degrees, preferably <10 degrees and more preferably<5 degrees) that would enable the flow of rain water or forced air to thereby clean the dirt from the coating surface and would also display good resistance to water containing rust i.e. corrosion marks, bird droppings.

It is yet another object of the present invention to provide for said stimuli responsive self-cleaning coating composition having high durability and negligible chalking of organic binders involved in the composition with photocatalytic particles and yet maintaining the stimuli responsive behaviour.

It is another object of the present invention to provide enhanced photocatalytic activity of the said composition even in the presence of very low contents of photocatalytically active particles in the said particulate mixture that would be photocatalytically active even in diffused sunlight thus facilitating use in both interior and exterior.

It is yet another object of the present invention to provide for said stimuli responsive self-cleaning coating composition with enhanced photocatalytical activity based on the presence of either nano anatase titania or even micronized rutile grades of TiO_2.

Still another object of the present invention is to provide a super hydrophobic coating, which would be so hydrophobic that water and even muddy water will bounce off the surface of nominally horizontal coated plates, and which would also be preferably styrene free to give a coating with reduced chalking behavior and high durability.

It is yet another object of the present invention to provide for said coating composition involving low contents of fluorine monomer, thus offering economic benefits and yet possessing said stimuli responsive self-cleaning coating composition with enhanced photocatalytical activity together with reduced chalking behavior, high durability and oleophobicity along with good dirt pickup resistance.

Another object of the present invention is to provide said coatings that are practical in use, that do not degrade rapidly in sunlight and have enough resistance to abrasion to survive for a practical length of time, preferably for several months or even several years depending upon environmental conditions to which the coating is exposed, which would not lose said hydrophobic-hydrophilic switching properties even over a period of time.

It is another object of the present invention to provide for said self-cleaning coating composition that cures by evaporation of the water and does not require any special treatment, such as heating or exposing to IR or UV light to cure.

It is yet another object of the present invention to provide a hydrophobic self-cleaning composition which upon application to a surface forms a uniform coating by drying and evaporation of water forming a coating or film at ambient temperature within 5 to 20 minutes.

It is another object of the present invention to provide for said self-cleaning hydrophobic coating which is easy to apply in the form of a liquid or paste which can be diluted with water or suitable solvent.

It is another object of the present invention to provide for a process to reach to said stimuli responsive self-cleaning paint/ coating composition that would be based on simple mixing of components applicable through simple techniques such as brush, roller, spray applications or dip coating, which process would be simple, industrially and economically facile to thereby lower the production cost to be thus attractive to the end users.

SUMMARY OF THE INVENTION

It is thus the basic aspect of the present invention to provide for an aqueous coating composition exhibiting reversible hydrophilic-hydrophobic switching with the variations in temperature, humidity, pH and or light comprising:

a) One or more oligomeric or polymeric dispersion/binder comprising acrylic, fluorinated and hydrophilic (acid/amine/ionic/non-ionic) backbone; and

b) One or more hydrophobic organosilicone or silane (monomeric, oligomeric or polymeric)

c) One or more hydrophilic organosilicone or silane (monomeric, oligomeric or polymeric) and

d) a particulate mixture comprising a plurality of particles at least partially surface treated (with a balance of hydrophobicity and hydrophilicity) with a particle size less than or equal to 100 microns, preferably less than or equal to 325 mesh (44 microns)

e) Wetting and dispersing agents,

f) At least one fungicide, algaecide and in-can preservative

g) Optionally contains one or more nano particles exhibiting photocatalytic properties, less than 1% and preferably less than 0.5% of total formulation especially for coatings containing particles equal to and over 325 mesh to selectively provide a balance of hydrophobicity and hydrophilicity such as to provide the desired reversible hydrophilic-hydrophobic switching.

Preferbaly, said aqueous coating composition is oleophobic and has a water contact angle hysteresis of < 25° under certain environmental conditions with variations in at least one or more of temperature, humidity, pH, light which is reversibly switchable to a water contact angle hysteresis of >25° under said environmental conditions offering benefits of both superhydrophobic and superhydrophilic cleaning, good organic and inorganic dirt pickup resistance, resistance to dirt streaks, dirt lines, water spotting, water marks, good cleanability with water and forced air or wind, reduced chalking, good resistance to organic dirt and deposits such as bird droppings and oily stains, and reduced tendency for spreading of water containing rust.

Said coating has excellent resistance to microbial growth, particularly algae and also exhibits enhanced photocatalytic activity for even rutile grades of Titania, even under diffused sunlight.

It is thus unexpectedly found by way of the present invention that when one or more oligomeric or polymeric dispersion/binder comprising acrylic, fluorinated and hydrophilic (acid/amine/ionic/non-ionic) backbone is selectively present in combination with at least partially surface treated particles, , hydrophobic and hydrophilic silanes, an aqueous coating composition exhibiting reversible hydrophilic-hydrophobic switching under variable environmental conditions including variations in at least one or more of temperature, pH, humidity or other external stimuli including light can be thus achieved with low contact angle hysteresis of < 25 degrees that is reversibly switchable to a contact angle hysteresis of >25°. The method of preparation of said aqueous coating composition is simple and industrially facile which coating composition in being adapted for both brush or spray type applications is also thus attractive to the consumers.

Surprisingly, said silicones both hydrophobic and hydrophilic when combined with the abovesaid ingredients including the particles with a balance of hydrophobicity and hydrophilicity, leads to a surface similar to desert beetle with the protrusions which arise from a plurality of particles being either hydrophobic or hydrophilic. Said silicones in the composition while advantageously facilitates to retain the stimuli responsive behavior and reversible wettability switching upon long exposures to environmental conditions, also provides for better weather durability and improved water resistance of the dried film. The effect of the silicone crosslinking further enables the coating to maintain a high contact angle conducive for self cleaning even after weathering of the coating over a period of time.

The coating composition of the present invention thus also exhibits good resistance to organic dirt and deposits such as bird droppings and oily stains even with low contents of fluoromonomers (<5%), wherein enhancement in photocatalytic activity are also exhibited even under diffused sunlight with low contents of nano anatase titania or even micronized rutile grades of TiO_2 with negligible degradation of the organic binder, subject to the selectively high particle to binder ratio with better dispersion of the photocatalytic particles due to the involvement of hydrophobic and hydrophilic silicones in a selective polymeric dispersion.

According to another preferred aspect of the present invention said aqueous coating composition reversibly switches from superhydrophobic (contact angle hysteresis <25° and water droplet rolling effect) to superhydrophilic (contact angle hysteresis >25° and complete wetting) for at least 2000 hours of accelerated exterior exposure (Atlas and QUV testing), preferably the contact angle hysteresis values are <20°, more preferably <10° and most preferably <5° in one state and higher in the switched state for a deposited 0.02 mL water droplet, wherein preferably the contact angle exhibited in one state is >100° with water, more preferably >120°, even more preferably superhydrophobic having contact angle >150° and contact angle <90° in the switched state for a deposited 0.02 mL droplet; and wherein said switching takes place within a varying period of time from a few seconds to several minutes dependent on a particular stimuli.

Preferably, said aqueous coating composition has low surface energy of <40 mN/m and preferably <20 mN/m and most preferably <10 mN/m even with the second coat and hence recoatable to enhance film build-up to attain desired opacity/ translucency/ hiding/ whiteness.

According to a preferred aspect of the present invention there is provided said aqueous coating composition comprising at least one or more wetting and dispersing agents, encapsulated or free antimicrobial agents selected from fungicide, algaecide, in-can preservative and optionally involving, one or more nanoparticles exhibiting photocatalytic activity.

Preferably, said aqueous coating composition especially favours photocatalytic activity even under diffused sunlight even with cost effective grades of micronized particles such as Titania while maintaining its durability together also exhibiting antimicrobial properties towards microorganisms such as algae, fungi and bacteria.

According to yet another preferred aspect of the present invention there is provided said aqueous coating composition wherein said polymeric dispersion comprises dispersion polymers involving primary or secondary dispersion in water or in a water/ co-solvent mixture with or without emulsion/latex polymers.

Preferably said polymeric dispersion comprises dispersion polymers with or without emulsion/ latex polymers that is preferably styrene free and is a free radical polymerization or controlled radical polymerization product of hydrophobic monomers C1-C8 straight, branched or cyclic esters of methacrylic acid/ acrylic acid selected from methyl methacrylate, ethyl methacrylate, butyl Methacrylate, isobutyl Methacrylate, tertiary butyl methacrylate, isobornyl methacrylate, 2-ethylhexyl methacrylate and various isomers and their corresponding acrylates also involving >C8 esters of methacrylic acid/ acrylic acid selected from lauryl acrylate, stearyl acrylate.

More preferably, said polymeric dispersion comprises dispersion polymers with or without emulsion/ latex polymers and has monomers selected such that the resulting polymer has an average octanol-water partition coefficient (log Kow) greater than 0.6, preferably greater than 1.5 and more preferably greater than 2.

According to another preferred aspect of the present invention there is provided said aqueous coating composition wherein said polymeric dispersion including dispersion polymers with or without emulsion/ latex polymers in being styrene free involves styrene or alkylstyrene group as part of the polymer or as a part of additives including opacifiers in less than 15% of the film forming composition favouring reduced chalking of said composition on UV exposure.

Preferably in said aqueous coating composition said polymeric dispersion comprising dispersion polymers and emulsion/ latex polymers is in the ratio range of dispersion to emulsion polymers of 95:5 to 5:95.

More preferably, in said aqueous coating composition said polymeric dispersion comprising dispersion polymers and emulsion/ latex polymers is preferably in the ratio range of 30:70.

According to yet another preferred aspect of the present invention there is provided said aqueous coating composition wherein said polymeric dispersion comprising dispersion polymers includes primary or secondary dispersion in water or in a water/ co-solvent mixture involves co-solvent that is VOC exempt under Green Seal standard GS-11 with resulting coating VOC's in the range of 1 to 100 grams/liter.

In said aqueous coating composition said polymeric dispersion comprising dispersion polymers with or without emulsion/ latex polymers includes polymers selected from natural polymer, a neoprene polymer, a nitrile polymer, a vinyl acrylic polymer, acrylic polymer; styrene acrylic polymer, styrene butadiene polymer, copolymer of vinyl acetate and butyl acrylate or veova monomers or ethylene/ propylene/ butylene, butadiene, isoprene involving crosslinkers selected from diacrylates, triacrylates, multifunctional acrylates, silane functional monomers, acetoacetate functional monomers, monomers with aziridine, hydrazine, carbodiimide or allylic functionality.

According to yet another aspect of the present invention there is provided said aqueous coating composition wherein said polymeric dispersion comprising dispersion polymers with or without emulsion/ latex polymers includes polymers of fluorinated monomers comprising 2 to 20 carbon atoms and polymeric fluorine content in the range of 0.1 to 50% on monomer solids and preferably in the range of less than 5% on monomer solids resulting in economic benefits and a surface energy of <50 mN/m ,preferably <30 mN/m and more preferably <20 mN/m

Preferably, in said aqueous coating composition said polymeric dispersion comprising fluorinated backbone comprises fluorinated monomers including esters of acrylic or methacrylic acid with a linear or branched perfluoroalkyl functional group preferably involving 1-6 fluorinated carbons selected from trifluoroethyl meth(acrylate), pentafluoropropyl meth(acrylate), heptafluorobutyl meth(acrylate).

More preferably, said aqueous coating composition comprises said ionic or ionizable or non-ionic hydrophilic monomers selected from acrylic acid, methacrylic acid and their aklali metal or quaternary ammonium ion salts; monoolefinic sulphonic acid compounds and their alkali metal salts including 2-acrylamido-2-methylpropanesulphonic acid; acrylates or methacrylates of aminoalcohols, acrylamides selected from N,N-dimethylaminopropylacrylamide or N, N-Dimethylaminoethylmethacrylate, polyalkylene oxide group containing monomers or a polymeric chain prepared by polymerizing a polyalkylene glycol (meth)acrylate, hydroxyl alkyl (ethyl, propyl or butyl) (meth)acrylates, wherein the hydrophilic component comprises at least one oxygen, sulfur, phosphorus and/or nitrogen atom.

According to another preferred aspect of the present invention there is provided said aqueous coating composition wherein said acrylic, fluorinated and amine backbone or acrylic, fluorinated and acid backbone of the primary or secondary polymeric dispersion comprises sufficient content of acid or amine monomer including ionic or non-ionic external surfactants adapted for acid or amine value in the range 5 to 100 mg KOH/g.

According to yet another preferred aspect of the present invention there is provided said aqueous coating composition wherein said particles comprising either micron sized particles or including particulate mixture of both micron sized and nano sized particles (mixture of micron sized and nano sized particles) and polymeric dispersion are present in selective ratios of 0.9 to 2.5 wherein higher ratios closer to 2 is preferred for a two coat application.

Said aqueous coating composition including said particles comprises either micron sized particles or includes particulate mixture of both micron sized and nano sized particles, and includes particulate pigments wherein the pigment volume concentration (PVC) is in the range of about 40 to 90 % and preferably in the range of 60 to 80% for the coating and preferably the coating PVC is lower than the practical critical pigment volume concentration (CPVC).

Preferably, in said aqueous coating composition said particles comprising either micron sized particles or including particulate mixture of both micron sized and nano sized particles comprises micronized and nanosized particles present in selective ratios of 3.5 to 8 with ratios closer to 8 being preferred for a two coat application.

More preferably, in said aqueous coating composition said at least partially surface treated particles involve organic and/or inorganic particles having size ranging from 1 nm-100 microns includes surface treated nanometer sized organic and/or inorganic particles have size ranging from about 1 nm to 300 nm, and wherein said particles preferably has mean particle size less than 325 mesh (44 microns) and even more preferably less than 40 microns.

In another preferred aspect of the present invention there is provided said aqueous coating composition wherein the mass ratio of said hydrophobic organosilicone to hydrophilic organosilicone is in the range 10/90 to 60/40.

Preferably, in said aqueous coating composition said hydrophilic organosilicone/silane having a contact angle hysteresis of >10 degrees based on the average of readings for 10 and 20 µL of water when applied on an aerated cement block is present in the range of 10% to 90% by weight of dispersion solids in said composition.

More preferably, in said aqueous coating composition said hydrophobic organosilicone/silane having a contact angle hysteresis of <10 degrees based on the average of readings for 10 and 20 µL of water when applied on an aerated cement block is present in the range of 5% to 80% by weight of dispersion solids in said composition.

Preferably, in said aqueous coating composition said hydrophobic and hydrophilic organosilicone content present as a part of the continuous phase in said composition is 10-90 % of the weight of the dispersion/binder.

In yet another aspect of the present invention there is provided said aqueous coating composition wherein said wetting agent and dispersing agent is balanced by having said dispersing agent upto 1% and preferably in the range of 0.1 to 0.5% and the wetting agent upto 2% and preferably in the range of 0.2 to 1% by weight in said composition favouring accelerated storage stability for atleast 30 days at 55°C and a composition that passes at least 5 cycles of freeze thaw stability test (-15°C to 30°C).

Aqueous coating composition as claimed in anyone of the preceding claims including photocatalytically active agents comprising one or more nano particles exhibiting photocatalytic properties in amounts less than 1% and preferably less than 0.5% of total formulation especially for coatings containing particles more than or equal to 325 mesh, preferably comprise nano titania of the anatase or rutile grade in the range of 0.1 to 1% of the formulation with a particle size of 1 to 300 nm and more preferably comprise titania in anatase form adapted for enhancement of photocatalytic activity of said composition (while maintaining its durability) against organic pollutants of atleast >5%, more preferably >20% and most preferably >80% of the activity of the control. Enhanced photocatalytic activity of coating with good durability is also demonstrated by even micron sized particles (>300 nm) such as Titania (anatase or rutile).

Said aqueous coating composition including photocatalytically active agents comprising one or more nano particles exhibiting photocatalytic properties in amounts less than 1% and preferably less than 0.5% of total formulation especially for coatings containing particles more than or equal to 325 mesh, preferably comprise nano titania of the anatase or rutile grade in the range of 0.1 to 1% of the formulation with a particle size of 1 to 300 nm and more preferably comprise titania in anatase form adapted for enhancement of photocatalytic activity of said composition while maintaining its durability by even micron sized particles (>300 nm) of Titania (anatase or rutile) against organic pollutants of atleast >5%, more preferably >20% and most preferably >80% of the activity of the control.

Preferably in said aqueous coating composition said at least partially surface treated particles are selected from substantially spherical particles, nodular particles, platy particles, cubical paraticles, various irregularly shaped particles, and mixtures thereof.

According to yet another preferred aspect of the present invention there is provided said aqueous coating composition wherein said at least partially surface treated particles comprise at least one material selected from the group of silicates, doped silicates, minerals, metal oxides, silicas and metal powders and are selected from the group of aluminum oxides (alumina), titanium oxide, zirconium oxide, silver, nickel, nickel oxide, iron oxide, and alloys, polystyrene particles, (meth)acrylate particles, PTFE particles, silica particles, polyolefin particles, polycarbonate particles, polysiloxane particles, silicone particles, polyester particles, polyamide particles, polyurethane particles, ethylenically unsaturated polymer particles, polyanhydride particles, biodegradable particles, polycaprolactone, nanofibers, nanotubes, nanowires, or combinations thereof that are preferably insoluble in organic solvents and water; and preferably comprise particles other than respirable crystalline silica wherein said silica is amorphous.

According to another preferred aspect of the present invention there is provided said aqueous coating composition wherein said at least partially surface treated particles comprise particles that are surface treated with compounds selected from silanes (alkylsilanes, perfluoroalkylsilanes, and alkyldisilazanes), silicones and fluorinated compounds or fluorinated acrylics or other organic/ inorganic treatments to achieve a balance between hydrophobicity and hydrophilicity.

Preferably, in said aqueous coating composition said at least partially surface treated particles comprise preferably externally surface treated particles with selective hydrophobic and hydrophilic balance and are obtained of sol-gel treatment to prevent any colour change or graying of white particles present in said coating composition, especially where fluorosilanes or fluorosilicones are used for treatment or is alternatively in-situ treated while preparation of the coating with said mixture of hydrophobic and hydrophilic silicones/silanes.

More preferably, said aqueous coating composition is flowable comprising at least one organic diluent or solvent, wherein the solvent is selected from the group comprising of water, an alcohol, an ether, a ketone, an ester, a glycol, a glycol ether, an alkylene carbonate, a C_5 - C_{18} aliphatic hydrocarbon, a C_6 - C_{18} aromatic hydrocarbon, various polar/non-polar solvents and mixtures thereof.

In said aqueous coating composition said polymeric dispersion comprises thermoplastic or thermosetting polymers including a single polymer or a blend of more than one polymer or self crosslinking polymers selected from acrylics, polyesters, polyurethanes, polycarbonates, polyolefins, alkyds, epoxies, polyamides, fluoropolymers, silicone polymers and their hybrids, wherein said fluoropolymers include polyperfluoropolyethers, and a polymer having one or more monomer repeat units selected from the group consisting of ethylene, propylene, styrene, tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene, perfluoro(methyl vinyl ether), perfluoro(ethyl vinyl ether), and perfluoro(propyl vinyl ether) and/ or includes a colloid, a latex, or a suspension of a fluoropolymer selected from a group comprising of polytetrafluoroethylene; perfluoroalkoxy polymer resin; copolymer of tetrafluoroethylene and hexafluoropropylene; copolymers of hexafluoropropylene and vinylidene fluoride; terpolymers of tetrafluoroethylene, vinylidene fluoride, and hexafluoropropylene.

Preferably, in said aqueous coating composition said polymeric dispersion comprising polymers have a Tg of -30 to 100 deg C or preferably Tg in the range of 0 to 50°C.

More preferably, said aqueous coating composition wherein said polymeric dispersion comprising polymers have surface energy of <50 mN/m and preferably less than 30 mN/m and more preferably <20 mN/m.

Said aqueous coating composition comprise components that are multifunctional or having individual functions selected from thickeners, biocides, wetting and dispersing agents, fluorosurfactants, defoamers, opacifying polymers, cosolvents, coalescents, plasticizers, pigments, special effect pigments, extenders, colorants, freeze thaw stabilizers, buffers, fire retardants, uv absorbers, organic fiber material, and inorganic fiber materials, flow and levelling agents, adhesion promoters, oil and water repellents and other components known to be provided in paint formulations.

According to another preferred aspect of the present invention said aqueous coating composition is ambient curing including air curing, infra-red curing and thermal curing.

According to yet another preferred aspect of the present invention there is provided said aqueous coating composition wherein a dry film of said coating has a dry film thickness of 1 to 200 microns and preferably 40 to 120 microns and withstands at least 30 to 1000 cycles and preferably 100 to 3000 cycles in a wet scrub resistance test with a scrub brush and a 0.45 kg load.

Said aqueous coating composition is adapted for applications comprising self cleaning, easy cleaning, anti-graffiti, stain resistant, soil-degrading, deodorizing, air-cleaning, antifouling, antimicrobial, water-cleaning, superhydrophobicizing, superhydrophilicizing and/or antifogging effects.

According to another aspect of the present invention there is provided a process for the preparation of said aqueous coating composition comprising the steps of:
a) providing at least partially surface treated organic or inorganic particles to selectively provide a balance of hydrophobicity and hydrophilicity that is either micron sized or includes a particulate mixture of micron sized and nanometer sized particles;
b) providing for one or more oligomeric or polymeric dispersion/binder comprising acrylic, fluorinated and hydrophilic (acid/amine/ionic/non-ionic) backbone;
c) providing for one or more hydrophobic organosilicone or silane (monomeric, oligomeric or polymeric) and one or more hydrophilic organosilicone or silane (monomeric, oligomeric or polymeric);
d) mixing said particles with said polymeric dispersion and silane; to obtain said aqueous coating composition therefrom having desired reversible hydrophilic-hydrophobic switching adapted for coating various types of substrates by brush, spray or roller type applications and also dipping, padding, doctor blade, wipe, wet-on-wet procedure or spin coating type applications.

According to yet another preferred aspect of the process for the preparation of said aqueous coating composition said at least partially surface treated organic or inorganic particles is provided by subjecting the particles to sol-gel treatment with compounds selected from silicones, fluorinated compounds to prevent color change of the particles.

According to another preferred aspect of the process for the preparation said step (a) of providing treated organic or inorganic particles that is either micron sized has a mean particle size of less than or equal to 100 microns, preferably less than or equal to 325 mesh (44 microns) or providing a particulate mixture of micron and nanometer sized particles involves providing micro and nanosized particles in selective ratios of 3.5 to 8, and are externally or in-situ treated particles with a balance of hydrophobicity and hydrophilicity;

wherein said step (d) comprising mixing said particles preferably in a slurry form in a water miscible co-solvent to the polymer dispersion including organosilicone or silane is mixed in selective ratios of 0.9 to 2.5.

According to yet another preferred aspect of the said process of preparation of aqueous coating composition that is adapted for substrates selected from masonary, concrete, cementitious, plaster, baked clay tiles, cellulosic, wood, one or more polymer, dry or damp surfaces, brick, tile, stone, grout, mortar, composite materials, gypsum board, , porous and non porous surfaces, interior surfaces or surfaces exposed to weathering on at least one surface of the substrate, which surface is preferably pretreated for better adhesion of the aqueous coating composition with various types of surface treatments.

According to another aspect of the present invention there is provided a commercial or industrial material, a structure or building or a substrate comprising said aqueous coating reversible switchable composition exhibiting reversible hydrophilic-hydrophobic switching under variable environmental conditions including variations in at least one or more of temperature, pH, humidity or other external stimuli including light.

According to yet another aspect of the present invention there is provided a method of producing reversible switchable coated commercial or industrial material, structure or building or substrate comprising

selectively applying the aqueous coating of said reversible switchable composition to atleast a portion of commercial or industrial material, a structure or building or a substrate requiring said reversible coating characteristic such as to exhibit reversible hydrophilic-hydrophobic switching under variable environmental conditions including variations in at least one or more of temperature, pH, humidity or other external stimuli including light.

BRIEF DESCRIPTION OF FIGURES:

Fig 1: reveals contact angle measurement showing a hydrophobic and hydrophilic drop;

Fig 2: reveals contact angle measurement showing the advancing and the receding angle;

Fig 3: reveals the image of untreated TiO2;

Fig 4: reveals the image of treated TiO2;

Fig 5: reveals Consecutive images of 5 µL incrementing volumes of water droplet from the syringe of the contact angle meter, with 45 µL forming a droplet having a contact angle of 143°;

Fig 6: reveals rheogram (temperature sweep at constant shear rate) for the water based pigmented coating system;

Fig 7: reveals differential scanning calorimetry thermogram for the dried pigmented coating;

Fig 8: reveals scanning electron micrograph of the paint surface showing 2 levels of topography;

Fig 9: reveals an AFM picture of the paint composition;

Fig 10: reveals an AFM picture showing the thermoresponsive behaviour of the paint (left: hot condition, right: cold condition)

Fig 11: reveals a photograph of the paint exposed outdoors for a period of 6 months showing its resistance to dirt streaks and water marks; (left side: paint according to present invention, right side: commercially available self cleaning paint).

DETAILED DESCRIPTION OF THE INVENTION

As discussed hereinbefore, the present invention provides for stimuli responsive self-cleaning water-borne pigmented aqueous coating composition responsive to at least one or more variations of temperature, pH, humidity or other external stimuli including light under variable environmental conditions that exhibits reversible switchable super hydrophilic-super hydrophobic characteristics. The said coating in comprising one or more oligomeric or polymeric dispersion/binder comprising acrylic, fluorinated and hydrophilic (acid/amine/ionic/non-ionic) backbone selectively present in combination with at least partially surface treated particles, hydrophobic and hydrophilic silanes is thus adapted for a stimuli responsive self-cleaning aqueous paint/ coating compositions and self-cleanable surfaces, which is oleophobic and exhibit the desired reversible hydrophilic-hydrophobic switching to provide for a water contact angle hysteresis of <25° under certain environmental conditions with variations in at least one or more of temperature, humidity, pH, light that is switchable to a water contact angle hysteresis of >25° under said environmental conditions offering benefits of both superhydrophobic and superhydrophilic cleaning, good organic and inorganic dirt pickup resistance, resistance to dirt streaks, dirt lines, water spotting, water marks, good cleanability with water and forced air or wind, reduced chalking, good resistance to organic dirt and deposits such as bird droppings and oily stains, and reduced tendency for spreading of water containing rust.

Said particles comprising at least partially surface treated particles are functionalized pigments or extenders present in selective sizes and ratios involving particulate mixture in selective ratios of micro and nano sized particles in said polymeric dispersion. More specifically, said pigments are surface treated/ functionalized either in-situ or prior to incorporation in the coatings and are present in said polymeric dispersion under a selective binder to pigment/ filler ratio such as to favour the desired contact angle hysteresis of < 25 degrees.

Advantageously, said attainment of low contact angle hysteresis (<25 degrees) and subsequent reversible wettability switching by the aqueous coating composition/ stimuli responsive self-cleaning coatings of the present invention enables the flow of rain water or forced air to clean the dirt from said coating/ paint surface wherein said coating can be formed by simple mixing of the components and applied by simple techniques such as brush and spray application.

The present invention in providing for at least partially surface treated particles including particles based on a mixture of micro and nanosized particles with a balance of hydrophobicity and hydrophilicity, a combination of silicones both hydrophobic and hydrophilic in combination with a suitable dispersion polymer leads to a surface similar to the desert beetle, with the protrusions which arise from a plurality of particles being either hydrophobic or hydrophilic.

Within the scope of the present invention, the hydrophobic or hydrophilic polymer coating shall be understood as a polymer coating which can change reversibly from a hydrophobic state into a hydrophilic state. The surface is therefore "switchable" and reversibly changed from one state to the other as a result of the influence of an external parameter. This external stimulus includes temperature change or humidity change or change in the intensity of UV light or change in the pH value.

Preferably, at a pH value of less than approximately 7.0, the polymer coating is hydrophobic and at a pH value of greater than approximately 7.0 it is hydrophilic. The coating, however, changes from a hydrophobic state into a hydrophilic state and vice versa at another suitable pH value, which preferably ranges between 3.0 and 10.0.

Preferably, the coating is hydrophobic at a temperature greater than ambient temperature (approximately 30° C) and is hydrophilic at a temperature of less than approximately 30° C. The coating, however, also changes from a hydrophobic state to a hydrophilic state at another suitable temperature, which preferably ranges between 5° C and 60° C.

Preferably, at a humidity of less than approximately 50%, the polymer coating is hydrophobic and at a humidity value of greater than approximately 50% it is hydrophilic. The coating, however, also changes from a hydrophobic state into a hydrophilic state and vice versa at another suitable humidity value, which preferably ranges between 5 to 100%.

Preferably for coatings containing particles with photocatalytic activity, under high intensity light, the polymer coating is hydrophilic and under low intensity light the polymer coating is hydrophobic. The coating, however, can also change from a hydrophobic state into a hydrophilic state and vice versa under a range of light between 200 to 800 nm.

As a result of this the stimuli responsive switchability of the coating of the present invention even when applied on a substrate, thus produce a masonary coating which displays benefits of both hydrophobic and hydrophilic cleaning, washing off the lightly deposited surface dirt at the beginning of the rains or with wind and on a rainy day, enables thorough cleaning of the surface. In addition to the abovesaid, said coating also exhibits enhanced photocatalytic activity even under diffused sunlight with negligible degradation of the organic polymer due to the presence of a combination of hydrophilic and hydrophobic organosilicones and titania, thereby showing improved resistance to organic dirt and deposits such as bird droppings and oily stains allowing them to degrade with UV exposure and finally get cleaned from the surface with rain or wind. In the present invention, under normal conditions the perfluorinated groups and silicone groups cover the surface of the coating. At the time of the rains, however, the hydrophilic moiety contained in the copolymer and the silicone appears on the surface of the coating to provide wettability and thereby to improve the desoiling properties. This is believed to be the reason why the water repellency and desoiling properties can be obtained simultaneously that is further assisted by the selectively high particle to polymer ratio.

The applied switchable hydrophobic or hydrophilic coating comprises at least one oligomer or polymer and a plurality of treated particles (with a balance of hydrophobicity and hydrophilicity) which is suited to reversibly switch the coating from a hydrophobic state to a hydrophilic state as a result of the influence of an external parameters.

Particles treated with a balance of hydrophobicity and hydrophilicity imply that the surface of the particles are functionalized with a combination of hydrophobic and hydrophilic groups.

The formulation of the present invention is thus economical in involving cost effective photocatalysts wherein even micron sized rutile or anatase titanium dioxide photocatalyst in the selective polymeric dispersion involving silicones exhibits enhanced photocatalytic activity to be activated by visible light and even diffused sunlight.

The deposited dirt on the rough surface of the smart paint of the present invention is able to get cleaned by this combination of hydrophobic and hydrophilic cleaning. Thus the coating, not only prevents the deposition of dirt from the water but also prevents the infestation and growth of unwanted organisms, such as microorganisms, algae, lichen, and mosses.

The silicone containing components (both hydrophobic and hydrophilic) are present in a concentration of 10 to 90% of the organic binder while maintaining the stimuli responsive behavior and also maintaining a clean surface that is free from dirt lines, streaks, water spots and algae, wherein said coating composition of the present invention displays enhanced photocatalytic activity under diffused sunlight with reduced chalking and also exhibits good resistance to organic dirt and deposits such as bird droppings and oily stains. Further said coating also has a reduced tendency for spreading of water containing rust.

Preferably, the coated substrate loses the hydrophobic property over the course of approximately one second to approximately one day, preferably over the course of approximately one minute to approximately 10 minutes. The switching may happen within a varying period of time from a few seconds to several minutes which are stimuli dependent.

Polymer

By binders are meant, polymers, oligomers and low molecular mass substances which form a solid film on a surface. The binders serve, for example, to fix the particles on the surface of the substrate to be coated. The binder should be stable when exposed outdoors to strong UV light, rain, wind, etc. for a minimum time of one month to several years. Preferred binders used in the invention have a surface energy <50 mN/m, preferably <30 mN/m and in particular <20 mN/m. The binders generally comprise thermoplastic polymers or organic prepolymers which undergo crosslinking by a thermal, oxidative or photochemical curing process.

The fluoropolymer could be any polymer having fluorine functionality. Examples of such polymers include, but are not limited to fluoroolefins, vinylidene difluoride-based polymers, fluoroethylene vinyl ethers. The fluoropolymer may be a thermoplastic or thermoset polymer. Fluoropolymers are available under the trade name Kynar and lumiflon and may be blended with the preferred binder.

Further, to the polyfluorinated copolymer, other polymer blends may be incorporated. Further self crosslinking polymers can also be used. The polymers can be acrylics, polyesters, polyurethanes, alkyds, epoxies, urethane acrylates, homopolymers and copolymers of ethylenically unsaturated monomers, and acrylic acid/maleic anhydride copolymers known in the art.

Also suitable as co-binders are natural waxes such as beeswax, carnauba wax, wool wax, candelilla wax, and also synthetic waxes such as montanic acid waxes, montanic ester waxes, amide waxes, and also waxlike polymers of ethylene and of propylene (polyethylene wax, polypropylene wax).

As the polymerization initiating source, various polymerization initiators such as an organic peroxide, an azo compound and a persulfate may be employed. As an emulsifier for emulsion polymerization, almost all emulsifiers including anionic, cationic and non-ionic emulsifiers may be used. Catalyst concentration can be about 0.1 to 2 percent based on the weight of total monomers.

Conventional chain transfer agents, such as dodecyl mercaptan, and crosslinking agents, such as ethylene dimethacrylate, can be used in amounts of 0.1 to 2 percent by weight of the monomers to control the molecular weight of the polymer.

The number average molecular weight of the binder polymers may vary over a wide range and is generally in the range from 1000 to 1 million g/mol and preferably in the range from 2500 to 0.5 million g/mol, in particular 10,000 to 0.5 million, g/mol (determined by GPC). The polymer has a Tg of -30 to 100 deg C. Alternatively a blend of polymers having different Tg's can be used. Most preferably the Tg is in the range of 0 to 50°C.

The aqueous polymer dispersions have a solid content of 25% to 70% by weight, preferably 40% to 65% by weight.

The polymer can be made by Free radical polymerization or controlled radical polymerization (CRP). CRP / living polymerization can be used to achieve a desired molecular weight and a narrow weight distribution or polydispersity. CRP provides a maximum degree of control for the synthesis of polymers with predictable and well-defined structures. Atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), reversible addition fragmentation transfer polymerization (RAFT), activated regenerated by electron transfer (ARGET) are some of the techniques of CRP.

To obtain the copolymer of the present invention, various systems and conditions for the polymerization reaction may be employed, and any of various polymerization systems such as bulk, solution, suspension or emulsion polymerization may be used.

Examples of preferred hydrophobic monomers are C_2 -C_{24} olefins, such as ethylene, propylene, n-butene, isobutene, n-hexene, n-octene, isooctene, n-decene, isotridecene, C_5 -C_8 cycloolefins such as cyclopentene, cyclopentadiene, cyclooctene, vinyl aromatic monomers, such as styrene and alpha-methylstyrene, and also fluoroolefins and fluorochloroolefins such as vinylidene fluoride, chlorotrifluoroethylene, tetrafluoroethylene, vinyl esters of linear or branched alkane carboxylic acids having 2 to 36 carbon atoms, e.g., vinyl acetate, vinyl propionate, vinyl n-butyrate, vinyl isobutyrate, vinyl hexanoate, vinyl octanoate, vinyl laurate and vinyl stearate, and also esters of acrylic acid and of methacrylic acid with linear or branched C.sub.2 -C.sub.36 alkanols, e.g., ethyl (meth)acrylate, n-butyl (meth)acrylate, tert-butyl (meth)acrylate, n-hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-propylheptyl (meth)acrylate, lauryl (meth)acrylate and stearyl (meth)acrylate and also vinyl ethers and allyl ethers of C.sub.2 -C.sub.36 alkanols, such as n-butyl vinyl ether and octadecyl vinyl ether, fluorinated monomers and also monomers containing polysiloxane groups.

Typical binder polymers of this type are polyethylene, polypropylene, polyisobutene, polychlorotrifluoroethylene, polytetrafluoroethylene, polyvinyl acetate, polyethyl methacrylate, poly-n-butyl methacrylate, polyisobutyl methacrylate, poly-tert-butyl methacrylate, polyhexyl methacrylate, poly(2-ethylhexyl methacrylate), polyethyl acrylate, poly-n-butyl acrylate, polyisobutyl acrylate, poly-tert-butyl acrylate, poly(2-ethylhexyl acrylate), and copolymers of maleic acid with at least one hydrophobic monomer selected from C.sub.3 -C.sub.6 olefins, C.sub.1 -C.sub.36 alkyl vinyl ethers, the vinyl esters of aliphatic C.sub.1 -C.sub.36 carboxylic acids.

Further suitable binders are poly-C.sub.1 -C.sub.4 -alkylene oxides, such as polyoxymethylene, polypropylene oxide and polybutylene oxide, polytetrahydrofuran and also polycaprolactone, polycarbonates, polyvinylbutyral, polyvinylformal, and also linear or branched polydialkylsiloxanes such as polydimethylsiloxane (silicones).

The polymer contains fluorinated monomers (comprising from 2 to 20 carbon atoms). Further the polymer contains fluorine content in the range of 0.1 to 50% on monomer solids and preferably in the range of less than 5% on monomer solids thus offering economic benefits. The fluorinated monomers can be esters of acrylic or methacrylic acid with a linear or branched perfluoroalkyl functional group.

Preferably the fluoromonomer or fluoromonomers contain up to six fluorinated carbons such as trifluoroethyl meth(acrylate), pentafluoropropyl meth(acrylate), heptafluorobutyl meth(acrylate) among others.

In the present invention, the hydrophilic moiety, a non-ionic group such as a polyoxyethylene chain, a polyoxypropylene chain, a polyoxybutylene chain, an anionic group such as a sulfonic acid group or a carboxylic acid group, or a cationic group such as an ammonium salt or an amine salt. Usually, an amphipathic monomer having a hydrophilic-lipophilic balance (HLB) of hydrophilic moiety/lipophilic moiety being from 5 to 15 is selected.

The polymer wherein the ionic or ionizable hydrophilic monomer or monomers are selected from: acrylic acid, methacrylic acid, maleic acid and their alkali metal or quaternary ammonium ions salts; monoolefinic sulphonic acid compounds and their alkali metal salts including 2-acrylamido-2-methylpropanesulphonic acid; acrylates or methacrylates of aminoalcohols, acrylamides such as N,N-dimethylaminopropylacrylamide or N,N-Dimethylaminoethylmethacrylate, polyalkylene oxide group containing monomers or a polymeric chain prepared by polymerizing a polyalkylene glycol (meth)acrylate, hydroxyl alkyl (ethyl, propyl or butyl) (meth)acrylates. Preferably the hydrophilic component comprises at least one oxygen, sulfur, phosphorus and/or nitrogen atom.

A monomer containing at least one acid group selected from the group comprising of a carboxylic acid group, a phosphoric acid group, a phosphonic acid group, a phosphinic acid group, a sulfuric acid group, a sulfonic acid group and a sulfinic acid group.

The polymeric dispersion comprises acid or amine monomer (in the range 5 to 100 mg KOH/g acid or amine value) and may contain external surfactants;

The amount of hydrophilic monomer is in the range of 2 to 20%. If the hydrophilic monomer content is high (>20%), the coating will have very poor water resistance, exhibit yellowing (where hydrophilic monomer is amine) and hence poor durability. Further, it will not be of any commercial importance as a coating.

In the present invention, in addition to the above-mentioned components, one or more additional monomers such as a monomer having a cross-linking group or a chelating group to the substrate, a high Tg monomer for improving the film-forming property, or a low Tg monomer for improving the flexibility of the coating film, may be incorporated without any particular restriction.

The polymer (dispersion or latex) is preferably styrene free with the preferred hydrophobic monomers being C1 to C8 straight, branched or cyclic esters of methacrylic acid/ acrylic acid such as methyl methacrylate, ethyl methacrylate, butyl Methacrylate, isobutyl Methacrylate, tertiary butyl methacrylate, isobornyl methacrylate, 2-ethylhexyl methacrylate and various isomers and their corresponding acrylates. Styrene or alkylstyrene may be used as part of the polymer or through additives such as opacifiers such that it is under 15% of the film forming composition to reduce chalking tendency on UV exposure. Other long chain monomers, >C8 esters of methacrylic acid/ acrylic acid such as lauryl acrylate, stearyl acrylate etc. can also be used.

The polymer is selected from the group consisting of a natural polymer; a neoprene polymer; a nitrile polymer; a vinyl acrylic polymer; a acrylic polymer; a styrene acrylic polymer; a styrene butadiene polymer; a copolymer of vinyl acetate and butyl acrylate or veova monomers or ethylene/ propylene/ butylenes, butadiene, isoprene etc. Crosslinkers such as diacrylates, triacrylates, multifunctional acrylates, silane functional monomers, acetoacetate functional monomers, monomers with aziridine, hydrazine, carbodiimide, allylic functionality, divinyl benzene, divinylsulfone, thallyl phosphate, zinc diacrylate, zinc dimethacrylate, diallyphthalate, diallylacrylamide, polyethylene glycol dimethacrylate, polypropylene glycol dimethacrylate, pentaerythritol tetramethacrylate, pentaerythritol trimethacrylate, pentaerythritol dimethacrylate, trimethylolpropane -trimethacrylate, dipentaerythritol hexamethacrylate, dipentaerythritol pentamethacrylate, glycerol trimethacrylate or a mixture thereof can also be used.

The monomers are selected such that the resulting polymer has an octanol-water partition coefficient (log Kow) greater than 0.6, preferably greater than 1.5 and more preferably

greater than 2 (calculated as a weighted average of the monomers used to prepare the polymer). The octanol/water partition coefficient is defined as the ratio of a chemical's concentration in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system and can be calculated by methods known in the art such as UV/visible absorbance, use of separatory funnels, high performance liquid chromatography etc.
An aqueous coating composition wherein said polymeric dispersion comprises dispersion polymers with or without emulsion/latex polymers wherein the ratio of dispersion to emulsion polymers is preferably in the range of 95: 5 to 5:95.

Neutralizing agents

Various amines can be used as the neutralizing agents for the anionic polymers such as liquor ammonia, morpholine, triethyl amine, vantex T, AMP-95, Advantex etc. Various acids can be used such as acetic acid etc. for the neutralization of the cationic polymers.

Particles type, sizes and contents
As used herein, the term "particle" is intended to include any discrete particle, primary particle, aggregate and/or aggregated collection of primary particles, agglomerate and/or agglomerated collection of aggregates, colloidally dispersed particles, loose assemblies of particulate materials, and combinations thereof.

The particles that may be used include organic or inorganic particles currently used and known to one skilled in the art. The particles preferably have an average particle diameter of between 1 nm to 44 microns, preferably being of inorganic nature. Depending on the size and material of the particles used, it is possible to obtain translucent or opaque self-cleaning surfaces.

Surface treated micron sized particles involve organic or inorganic particles lower than 44 microns and wherein said surface treated nanometer sized organic or inorganic particles in the size range of about 1 nm to 300 nm.

Only micron sized particles can be used or a combination of micron and nano sized particles can be used to prepare the aqueous coating composition. Only nano sized particles may be used, however they increase the cost of the coating. The surface of particles should preferably have a high oil absorption value or an irregular structure. Examples of such materials include clays from Hoffmann (Silitin and Aktisil grades), high oil absorption value titanium dioxide from DuPont e.g. TiO2 R931, calcium carbonate grades from Omya and Jorcal grades form Jordan carbonate Co. Several such materials are available such as extenders prepared using the ground process which leads to rougher surfaces as compared to the precipitation process. Cristobalite and respirable crystalline silica are not desired due to their carcinogenicity. Preferred fillers include gypsum, magnesium silicate, magnesium or calcium carbonate, pyrophyllite, mica, pumice, silica, diatomite, barium sulphate, alumina or mixtures thereof.

The filler also serves to improve the film durability, abrasion resistance, and lower cost. The filler may be present in the aqueous composition in a range of from about 2.0 percent by weight to about 50.0 percent by weight, preferably from about 5.0 percent by weight to about 40.0 percent by weight based on the total weight of the composition.

The combination of said micronized to nanosized particles is in selective ratios of 3.5 to 8 with ratios closer to 8 being preferred for a two coat application.

The particulate mixture (micron and nano meter sized) and polymeric dispersion is in selective ratios of 0.9 to 2.5 wherein higher ratios closer to 2 being preferred for a two coat application.

The micron sized and nano sized particles may be of the same chemistry or different chemistries. The nano sized particle maybe for example silicon dioxide, calcium carbonate or Teflon and the micron sized particle maybe silicon dioxide, calcium carbonate or titanium oxide.

Nanoparticles that can be used to make the coatings of this invention are generally from the class of fumed silica's, titania's, zinc oxides, aluminium oxides, zirconium dioxide and tin dioxide. The average particle size may be from about 1 nm to 300 nm.

Among the inorganic substances there may be mentioned by way of example: metal oxides, mixed oxides, silicates, sulfates, phosphates, borates, metal sulfides, oxosulfides, selenides and sulfoselenides, metal nitrides and oxide-nitrides and metal powders. Among the organic structure-forming particles there may be mentioned by way of example carbon blacks and nanoscale organic polymeric particles, and among these fluorine-containing polymers. Examples of finely divided organic powders with a hydrophobic surface are finely divided polymer powders, e.g., polytetrafluoroethylene powders or C2-C4 polyolefin powders, examples being the polyethylene powders and polypropylene powders.

The structure-forming particles used are preferably those which comprise at least one material selected from silicates, doped silicates, minerals, metal oxides, silicas, and polymers. The structure-forming particles are particularly preferably naturally occurring, precipitated or pyrogenically prepared metal oxides. Pyrogenic silicas are commercially obtainable with an average primary particle size in the range from about 5 to 40 nm. In some embodiments of the invention, the silicon dioxide utilized is a colloidal silicon dioxide. Such products are commercially available from a number of sources, including Cabot Corporation, (under the trade name CAB-O-SIL) and Degussa, Inc., (under the trade name AEROSIL).

A plurality of particles of different particle sizes can be used for the coating composition with different hydrophobic and hydrophilic silicone treatments provided they are incorporated with the polymer in certain ratios which are discussed below.

Hydrophobic Titanium dioxide e.g. R101, R102, R103, R104 and R105 grade (0.31 microns average particle size) is available from companies such as DuPont, which are recommended for use in plastics products. These grades being hydrophobic are difficult to disperse into waterborne systems. Even if dispersed with high quantity of surfactants, they lead to poor hydrophobicity (low water contact angles because of high quantity of surfactants). Other hydrophobic micron sized particles are available from Hoffman Minerals under the trade name Aktisil PF777 (d50 particle size = 2.2 microns). These are a mixture of silica and kaolinite. Other Aktisil grades are also available with different silane treatments Aktisil EM (epoxysilane), AM (aminosilane) etc. Micronized PTFE is available from Micro Powders, Inc. Some examples are Fluo 300 (mean particle size 5 to 6 microns), Fluo 625F-H (13 to 21 microns), Fluo HT-LS (2 to 3 microns).
Several hydrophilic Rutile grades of titanium dioxide are available R902, R902 plus, R 900, R931 etc that can be treated. The photocatalytically active agent comprises titanium dioxide in a form selected from the group consisting of amorphous form, partially crystalline form, and anatase form.

The photocatalyst may be selected from titanium dioxide (anatase and rutile form), zinc oxide, zirconium oxide, tin oxide, vanadium trioxide, ferric oxide, dibismuth trioxide, tungsten trioxide, and-strontium titanate and combinations thereof. Titanium dioxide is preferred because of its high photocatalytic activity. It is known that the photocatalytic activity of the photocatalysts changes in the order: titanium dioxide>zinc oxide>zirconium oxide>tin oxide>vanadium oxide.

A suitable source of light is from sunlight, diffused sunlight, a room lamp, a fluorescent lamp, a mercury lamp, an incandescent lamp, a xenon lamp, a high pressure sodium lamp, a metal halide lamp, a BLB lamp and light sources known to the person skilled in the art. In one preferred embodiment, the photocatalytically active particles present in the mixture according to the invention develop their activity on irradiation by sunlight.

The preferred photocatalysts are p25 (21 nm, BET surface area 50 m^2/g, mixed anatase and rutile) from Evonik, VP Aeroperl P25/ 20 (20 μm) and LPX 21530 (30 nm) from BYK. Alternately rutile grade nanosized or micron sized TiO_2 may also be used alone or in combination with nano Titania.

Hydrophobic nanometer sized silica available from Evonik under the trade name Aerosil R972 (primary particle size 16 nm), Aeroxide LE1 (primary particle size 20 nm), LE2 (primary particle size 7 nm) and LE3 from Evonik. can be used.
Alternate hydrophilic grades are available such as Cabosil M5 (200 nm – 300 nm aggregates with a primary particle size of 14 nm in diameter) from Cabot or Aerosil R200 (average particle size of 12 nm) from Evonik that can be either heat treated or treated by sol-gel process.

Particles and treatment (external or internal)
It is important that the particle be treated to exhibit a balance of hydrophobicity and hydrophilicity. The hydrophilic or hydrophobic behavior of a solid is determined essentially by the groups at its surface. For example, particles which have hydroxyl groups at their surface are usually hydrophilic. However, if there are hydrocarbon groups, such as, alkyl groups, and especially longer chain alkyl groups, at the surface of the particle, then the particles have hydrophobic properties.

It has long been known that it is possible to influence the hydrophilic or hydrophobic character of inorganic or organic particles. This can be accomplished by adsorption of substances on the surface of a particle, especially by chemical reactions with reactive groups, which are at the surface of the particle.

This balance of hydrophobicity and hydrophilicity may be obtained by using a mixture of hydrophobic and hydrophilic particles which are available commercially, using particles treated with hydrophobic and hydrophilic surface modifiers (organosilanes etc.) by the sol-gel, heat treatment process or other process known in the art, using particles treated with hydrophobic and hydrophilic organosilicones during the paint making process.

It is possible that the nano sized particles are treated with hydrophobic surface groups and the micron sized particles are treated with hydrophilic surface groups or vice versa. Preferably both the particles are treated with functional groups such that they exhibit a balance of hydrophobicity and hydrophilicity.

Alternately, if the modifying agent is used in an amount less than equivalent, so that not all of the reactive groups at the surface of the particles can be modified, it may be assumed that the distribution of the modified groups on the surface follows statistical laws so that the modified particle behaves equally hydrophilic or hydrophobic at any position on its surface.

The solids with modified surface properties known from the state of the art, have hydrophobic or hydrophilic groups, which are located at the surface of the particles in a uniform random distribution. Therefore, it is only possible to hydrophobize a hydrophilic particle more or less pronouncedly. This is shown for by example dispersing treated TiO2 in water and the particles partly float on water and partly disperse in water.

During different types of treatment the surface of the particle may be modified by physisorption, chemisorption or covalent bonding with organic molecules with a variety of hydrophobic and hydrophilic functional groups.

The hydrophobic properties are a result of a suitable hydrophobizing treatment, e.g., treatment with at least one compound from the group of the silsesquioxanes, perfluoroacrylic resins, organosilanes, alkylsilanes, fluorinated silanes, disilazanes, waxes, paraffins, fatty esters, fluorinated and/or functionalized alkanes.

Suitable organosilanes include, but are not limited to: alkylchlorosilanes; alkoxysilanes, e.g., ethyltrimethoxysilane, ethyltriethoxysilane, n-propyltrimethoxysilane, n-propyltriethoxysilane, i-propyltrimethoxysilane, i-propyltriethoxysilane, butyltrimethoxysilane, butyltriethoxysilane, hexyltrimethoxysilane, octyltrimethoxysilane, 3-

mercaptopropyltrimethoxysilane, n-octyltriethoxysilane, phenyltriethoxysilane, polytriethoxysilane; trialkoxyarylsilanes; isooctyltrimethoxy-silane; N-(3-triethoxysilylpropyl) methoxyethoxyethoxy ethyl carbamate; N-(3-triethoxysilylpropyl) methoxyethoxyethoxyethyl carbamate; polydialkylsiloxanes including, e.g., polydimethylsiloxane; arylsilanes including, e.g., substituted and unsubstituted arylsilanes; alkylsilanes including, e.g., substituted and unsubstituted alkyl silanes including, e. g., methoxy and hydroxy substituted alkyl silanes; and combinations thereof. Some suitable alkylchlorosilanes include, for example, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, octylmethyldichlorosilane, octyltrichlorosilane, octadecylmethyldichlorosilane and octadecyltrichlorosilane. Other suitable materials include, for example, methylmethoxysilanes such as methyltrimethoxysilane, dimethyldimethoxysilane and trimethylmethoxysilane; methylethoxysilanes such as methyltriethoxysilane, dimethyldiethoxysilane and trimethylethoxysilane; methylacetoxysilanes such as methyltriacetoxysilane, dimethyldiacetoxysilane and trimethylacetoxysilane; vinylsilanes such as vinyltrichlorosilane, vinylmethyldichlorosilane, vinyldimethylchlorosilane, vinyltrimethoxysilane, vinylmethyldimethoxysilane, vinyldimethylmethoxysilane, vinyltriethoxysilane, vinylmethyldiethoxysilane and vinyldimethylethoxysilane.

Suitable disilazanes include for example, but are not limited to: hexamethyldisilazane, divinyltetramethyldisilazane and bis(3,3-trifluoropropyl)tetramethyldisilazane. Cyclosilazanes are also suitable, and include, for example, octamethylcyclotetrasilazane. Suitable fluorinated silanes include the fluorinated alkyl-, alkoxy-, aryl- and/or alkylaryl-silanes, and fully perfluorinated alkyl-, alkoxy-, aryl- and/or alkylaryl-si lanes. Examples of fluoroalkyl silanes include, but are not limited to: those marketed by Degussa under the trade name of Dynasylan F8261, F8815 etc. An example of a suitable fluorinated alkoxy-silane is perfluorooctyl trimethoxysilane.

Alternately oligomeric silicones may also be used for the treatment such as DC 3074 and DC 3037 from Dow Corning, Silres SY 231 from Wacker etc. Oligomers have the benefit of having a very low vapour pressure whereas monomeric corresponding compounds have a comparatively high vapour pressure.

Hydrophilic organosilanes that may be used include tetraalkoxysilane or silanes having hydrophilic functional groups other than hydroxy groups after hydrolysis. It is preferable to use a silane having one or two hydrophilic functional groups. Particular examples thereof include a glycidoxyalkyl group, aminoalkyl group, isocyanatoalkyl group, etc. Additionally, the hydrophilic functional group may include a thiol group, amine oxide group, sulfoxide group, phosphate group, sulfate group or salts thereof; or hydrophilic groups of polyoxyethyelne or polyoxypropylene.

More particularly, non-limiting examples of the hydrophilic silane include N-aminoethyl gamma-aminopropyl trimethoxysilane, N-aminoethyl gamma-aminopropyl triethyoxysilane, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-glycidoxypropyl trimethoxysilane, gamma-glycidoxypropyl triethoxysilane, gamma-isocyanopropyl triethoxysilane, gamma-isocyanopropyl trimethoxysilane or mixtures thereof.

The organosilane is used to treat the particles to prepare particles with a balance of hydrophobicity and hydrophilicity. They can be used suitably in an amount of 1-50 wt % based on 100 wt % of the particle content. This content varies with the chemistry and surface area of the particles to be treated. Nano sized particles may require higher quantities of silanes while micron sized particles may require lower quantities. Where fluorosilanes are used the slurry or sol-gel treatment may be preferred as compared to the heat treatment to avoid discoloration/ graying of the white particles such as titanium dioxide.

Further though external surface treatment of the particles can be performed, insitu surface treatment can also be performed. For hydrophobic surface treatment, organosilicones/ silanes such as Dow Corning 3074, Silres SY 231 from Wacker, Protectosil SC concentrate, Dynasylan F8261, Tegophobe 1500, 1401, 1505 etc from Evonik Degussa can be used to impart hydrophobicity to the pigments and extenders and subsequently to the paint film. Further one or more of the hydrophobic organosilicones/silanes can be used which are described above. For hydrophilic surface treatment, organosilicones such as Dow Corning QP8 5314, Tegophobe 1650, Wacker BS 45 etc. can be used. Further one or more of the hydrophilic organosilicones/silanes can be used which are described above. These silicones are added during the paint making process to functionalize the particles in-situ.

The hydrophobic agent may be present in the aqueous composition in a range of from about 5 to 80% by weight of polymeric dispersion. The hydrophilic agent may be present in the aqueous composition in a range of from about 10 to about 90% percent by weight of the polymeric dispersion. It is preferred to have a combination of both types of silicones (hydrophilic and hydrophobic) to get a balance of hydrophobicity and hydrophilicity and attain a coating that exhibits good resistance to dirt lines, streaks and water spots.

The hydrophobic organosilicone/silane has a contact angle hysteresis of <10 degrees (average of 2 readings for 10 and 20 μL of water) when applied on an aerated cement block. The hydrophilic organosilicone/silane has a contact angle hysteresis of >10 degrees when applied on an aerated cement block (average of 2 readings for 10 and 20 μL of water). When a continuous stream of water is poured on a hydrophilic organosilicone coated aerated cement block it completely wets the surface. On the other hand the aerated cement block coated with the hydrophobic organosilicone is completely water repellent even under a continuous stream of water. One or more organosiloxanes are present as part of said continuous phase, the total organosiloxane being present in an amount of 10 to 90% of the weight of binder. The mass ratio of the hydrophobic silicone to the hydrophilic silicone is in the range 10/90 to 60/40.

PVC

The ratio of the various components may vary rather much and in many cases they may be characterized by various key figures. One of these is the pigment-volume concentration (PVC), which represents the percentage of the total volume of particles (pigments, extenders etc.) relative to the volume of non-volatile binder plus volume of particles.
If the concentration of particles in the paint is low even in the dry paint film each particle will be entirely enclosed by binder. This will also be the case with increasing particle concentration up to a certain limit at which the amount of binder is just sufficient to enclose all of the particles. The point where the amount of binder is exactly sufficient for such enclosure is called the critical pigment-volume concentration, CPVC. At values above CPVC the dry paint film may contain voids and become porous and generally permeability, strength and gloss may hereby be influenced unfavourably; in case of outdoor paints the durability may become unsatisfactory.

Prior art uses organic silicon compounds in combination with the binder to render paints watertight or hydrophobic. However, paints with only hydrophobicity or superhydrophobicity lead to inefficient and uneven cleaning of dirt form the surface of coatings with rain water. This leads to dirt lines and dirt patches which eventually leads to microbial growth. Hence it is important according to the current invention, to use a combination of hydrophobic and hydrophilic silicones in a certain ratio with a specific binder, particular PVC and specific particle size which lead to surfaces with very high durability and good aesthetic appearance benefitting from combined superhydrophobic and superhydrophilic cleaning effects.

The composition has a pigment volume concentration (PVC) in a range of from about 40 to 90 % and preferably in the range of 60 to 80%. Said concentration is under the practical CPVC as tested by the curling test or other suitable tests known in the art, wherein the benefit of operating below the practical CPVC (practical pigment volume concentration) could be derived by careful formulation aided by the use of dispersion polymers as compared to latex polymers in combination with functionalized particles that eventually generates coatings also having high durability and good antimicrobial properties at reduce dosages of biocides.

Solid contents

The aqueous composition has a solid content in a range of from about 25 to about 65 percent, preferably in a range of from about 35 to about 55 percent. Solids content greater than about 65 percent may be less desirable in that there would be a difficulty in application and a loss of storage stability.

pH

The aqueous composition has a pH in a range of from about 5 to about 10, preferably in a range of from about 6 to about 9.0.

VOC

The water-based compositions are preferably free of volatile organic compounds. The water-based compositions have a calculated volatile organic content of < 100 g/liter and more preferably < 50 g/liter as per Green Seal standard GS-11. The term volatile organic chemical as described herein is defined as an organic compound having a boiling point less than 280 °C at ambient pressure.

Solvents

In order to disperse treated particles into water, the particles must be wetted by one or more non-aqueous liquids such as ketones, glycol ethers, glycol ether acetates, alcohols, aliphatic hydrocarbon solvents, polydimethylsiloxane, cyclic polydimethylsiloxane, aromatic hydrocarbon solvents, tetrahydrofuran, acetic acid, acetates, and glycols. The preferred solvents are acetone and isopropyl alcohol. A non-VOC material may be selected or a VOC exempt material may be selected to produce non-VOC hydrophobic particle dispersion in water. Example of non VOC solvents are Ecosoft PB form Dow, dimethyl carbonate, tertiary butyl acetate, Optifilm enhancer 300 from Eastman, Triethylene glycol etc.

The solvent is present at a level of less than 50 percent by weight based on the total weight of the composition, and preferably in an effective amount of between 0.001 to 50 percent by weight, more preferably between 1 to 5 percent by weight based on the weight of the total composition.

Suitable examples of less volatile organic solvents are those with lower vapor pressures, for example those having a low vapor pressure which include, but are not limited to: dipropylene glycol n-propyl ether, dipropylene glycol t-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol methyl ether, tripropylene glycol n-butyl ether, diethylene glycol propyl ether, diethylene glycol butyl ether, dipropylene glycol methyl ether acetate, diethylene glycol ethyl ether acetate, and diethylene glycol butyl ether acetate.
The composition may also comprises one or more organic solvents which are capable of dissolving the dispersion polymer. Suitable solvents are, for example, monohydric alcohols having 1 to 4 C atoms and mono-, di- and trialkylene glycol monoalkyl ethers, wherein the alkylene group usually contains 2 or 3 C atoms and the alkyl group 1 to 4 C atoms.

The aqueous composition may contain at least one co-solvent. When present in the composition, the co-solvent is a means to improve film coalescence at low temperatures of below 10°C, and improve sprayability and substrate wetting. Useful cosolvents include Dowanol DPnB, PnP and PPH from Dow Chemical, Texanol from Eastman Chemical, Glycol Ether PB, EB, and DPM from Ashland Chemical. Examples of preferred cosolvents include Dowanol DPnB from Dow Chemical and Texanol from Eastman Chemical. The co-solvent may be present in the aqueous composition in a range of from about 0.20 percent by weight to about 4.0 percent by weight, preferably from about 0.40 percent by weight to about 2.0 percent by weight based on the total weight of the composition. Alternatively, co-solvent content less than about 0.20 percent by weight may be less desirable in that it would be insufficient for insuring good film formation at low temperatures.

UV Protection

The aqueous composition may contain at least one UV absorbing component. The UV absorbing component is used as a means to provide weather protection for the film forming polymer and antimicrobials used in the product by protecting them against degradation caused by UV radiation. Useful UV absorbers include conventional zinc oxide, nano zinc oxide, titanium dioxide etc. The nanometer sized zinc oxide particles are broad spectrum UV absorbers (UV-A and UV-B) which is not the case for micro fine TiO2 and organic UV absorbers. It also has anti-bacterial properties and is mildew resistant. The UV absorbing component may be present in the aqueous composition in a range of from about 0.1 percent by weight to about 50 percent by weight of the dry composition. Other UV absorbing components useful include Tinuvin 292 1130, and 5151 from Ciba Specialty Chemical, These UV absorbing components may be present in the aqueous composition in a range of from about 0.10 percent by weight to about 5.0 percent by weight of the composition.

Preservatives (Algaecide, Fungicide, Incan preservative)

It is essential that the formulation contains at least one or more biocides which can be in liquid or solid form. Suitable types of incan preservatives, antifungal agents and anti algal agents and their contents can be decided by carrying out tests to determine a level required for long term protection depending upon the degree of exposure. Some biocides which can perform a multifunctional role of antifungal and antialgal can also be used. Antibacterial film properties can be conferred by suitable antibacterial agents such as silver etc. Further, encapsulated biocides can also be used.

The aqueous composition contains at least one algaecide. Useful algaecides include Terbutrin, Rocima 344, Rocima 350, Rozone 2000, etc. The algaecide (active content) is present in the aqueous composition in a range of from about 0.05 percent by weight to about 3.0 percent by weight, preferably from about 0.10 percent by weight to about 2.0 percent by weight based on the total weight of the composition.

The aqueous composition contains at least one fungicide. Useful fungicides include Zinc and Sodium Omadine from Arch Chemical, Rozone 2000, Rocima 200, Rocima 63, and Skane M-8 from Rohm & Haas, Mergal S-90, Polyphase 678, and Mergal S-89 from Troy Chemical, and Fungitrol 720 from ISP Corp. The fungicide (active content) is present in the aqueous composition in a range of from about 0.05 percent by weight to about 3.0 percent by weight, preferably from about 0.10 percent by weight to about 2.0 percent by weight based on the total weight of the composition.

A biocide, such as DANTOGARD, TROYSAN 395, Nipacide CFX, Thor MBS etc. can be used as a preservative in the product. The preservative provides a useful shelf life to the product. The biocide preservative is added in an effective amount to preserve the composition product and ranges from 0.01 to 1.0 percent by weight, and more preferably in a range of from 0.05 to 0.9 percent by weight.

In situations where multiple types or species of organisms are likely to be found, two or more biocides may be required in other to inhibit the growth of all of them. Preferably, the biocides have low water solubility (less than about 50 parts per million), excellent resistance against hydrolysis, be resistant to degradation by UV where exposed to sunlight (unless sufficient UV absorbers are used) and should be free from formaldehyde.

Wetting and dispersing agents

Surfactants may also be used to help wet the surface in order to form a uniform coating. Surfactants can be nonionic, cationic, amphoteric, or anionic in nature.

The aqueous composition contains at least one dispersant. The dispersant is a means to disperse the pigments and prevent agglomeration on product aging. Useful dispersants include BYK 190, 191, 194 from BYK Chemie, AMP-95, Orotan 850, Orotan 731 etc from Dow Chemical Company. The dispersant is present in the aqueous composition in a range of from about 0.10 percent by weight to about 1.0 percent by weight, preferably from about 0.20 percent by weight to about 0.5 percent by weight based on the total weight of the composition. Dispersant content greater than about 1.0 percent by weight may be less desirable in that it could adversely affect viscosity stability and water resistance of the dried film. Alternatively, a dispersant content less than about 0.10 percent by weight may be less desirable in that the product would show poor viscosity stability on aging, pigment agglomeration.

The aqueous composition contains at least one surfactant. The surfactant is a means to lower surface tension for improved surface wetting, pigment dispersion and polymer stability. Useful surfactants include Triton X-100 and Triton X-405 from Dow Chemical, Surfynol series from Air Products, Cresmer series from Croda. The surfactant is present in the composition in a range of from about 0.10 percent by weight to about 2.0 percent by weight, preferably from about 0.20 percent by weight to about 1.0 percent by weight based on the total weight of the composition. Surfactant content greater than about 2.0 percent by weight may be less desirable in that it would hamper the dried film's water resistance and durability. Alternatively, a surfactant content less than about 0.10 percent by weight may be less desirable in that it would not sufficiently lower the surface tension for adequate surface wetting and aiding in pigment dispersion.

Other suitable surfactants include non-ionic surfactants having an HLB value of from between 9-13, branched ethoxylated alcohols, linear ethoxylated alcohols, and silicone surfactants. These surfactants are sold under the trade names of Tomah, Triton, Surfonic, Igepal, Alfonic, Rhodasurf, Synperonic etc.

It is preferred to have certain ratios of the non-ionic wetting agent as compared to the ionic dispersing agent in the composition as shown in example number 56 to achieve a good accelerated storage stability (studied at 55°C for 30 days).

In addition, other polymer and surfactant materials known in the art may also be suitably employed in the inventive treatment compositions provided that they do not negatively impact the performance of the coatings.

Further the composition passes at least 5 cycles of freeze thaw stability (-15 deg C to 30 deg C).

Fluorosurfactants

The aqueous composition may contain at least one fluorosurfactant. These are available from DuPont and 3M. It is preferred that the fluorosurfactant contain less than 6 carbon atoms and can be either ionic or non-ionic.

Rheological agents

The aqueous composition may contain at least one rheological agent. Useful thickeners include Rheolate 278, Rheolate 244, Rheolate 300 from Elementis Specialties, Acrysol DR-1, Acrysol DR-72, Acrysol DR-73, Acrysol ASE-60, Acrysol TT-615, Acrysol TT-935, Acrysol RM-5, Acrysol RM-6000, Acrysol RM-5000, Acrysol RM-2020NPR, Acrysol RM-8W, Acrysol STC-275, Acrysol RM-825 from Dow, Coapur 6050 form Coatex. Inorganic thickeners such as bentone Lt, Laponite SD, laponite RD can also be used.

The thickener may be present in the aqueous composition in a range of from about 0.10 percent by weight to about 3.0 percent by weight, preferably from about 0.20 percent by weight to about 1.0 percent by weight based on the total weight of the composition. The aqueous composition has a viscosity in a range of from about 100 to 1000 grams on the stormer viscometer. A viscosity greater than about 1000 grams may be less desirable in that it would not be easy to handle. Alternatively, a viscosity less than about 100 grams may be less desirable in that it would run down on vertical surfaces providing reduced coat weight and would tend to show separation in the container on standing before it could be applied.

Suspending agents may optionally be included in the inventive treatment compositions to improve the suspension and/or dispersion properties of the inventive compositions. Polymer type suspending agents include anionic, cationic and nonionic polymers. Examples include, but are not limited to: vinyl polymers such as, cross linked acrylic acid polymers, cellulose derivatives and modified cellulose polymers such as, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl methyl cellulose, nitro cellulose, sodium cellulose sulfate, sodium carboxymethyl cellulose, crystalline cellulose, cellulose powder, polyvinylpyrrolidone, polyvinyl alcohol, guar gum, hydroxypropyl guar gum, xanthan gum, arabia gum, tragacanth, galactan, carob gum, karaya gum, carrageen, pectin, agar, starch (rice, corn, potato, wheat), microbiological polymers such as, dextran, succinoglucan, pulleran, starch-based polymers such as, carboxymethyl starch, methylhydroxypropyl starch, alginic acid-based polymers such as, sodium alginate, alginic acid propylene glycol esters, acrylate polymers such as, sodium polyacrylate, polyethylacrylate, polyacrylamide, and polyethyleneimine.

Defoamer

The aqueous composition may contain at least one defoamer. Useful defoamers include mineral oil, silicone defoamers, etc. Examples of preferred defoamers include BYK -012, BYK-020, BYK-022, Dapro-4164, Dapro 7005, Dapro-7010. The defoamer may be present in the composition in a range of from about 0.05 percent by weight to about 1.0 percent by weight, preferably from about 0.1 percent by weight to about 0.50 percent by weight based on the total weight of the composition.

Freeze thaw stabilizer

The aqueous composition may contain at least one freeze/thaw stabilizer. Useful freeze/thaw stabilizers include ethylene glycol, propylene glycol and triethylene glycol. The freeze/thaw stabilizer may be present in the aqueous composition in a range of from about 0.50 percent by weight to about 4.0 percent by weight, preferably from about 1.0 percent by weight to about 3.0 percent by weight based on the total weight of the composition. Freeze/thaw stabilizer content greater than about 4.0 percent by weight may be less desirable in that it would make the composition too water sensitive and the drying time too long and increase the volatile organic content of the aqueous composition.

Colorants

Organic or inorganic colorants can be used. Some examples of colorants suitable for use include naphthol, pyrazalones, quinacridones, phthalocyanines, pigments including titanium nickel yellow, limonites, haematites, magnetites, micaceous oxides of iron, iron ferrites and Prussian blue. Further effect pigments may also be used to create special effect finishes with wettability switching properties e.g. Sumica Pearl (Bright gold) available from Sudarshan Chemical Industries Ltd.

Coating thickness

Although there is no limitation in thickness of the coating layer having self-cleaning property formed on the substrate surface, the coating can have a dry film thickness of 1 to 200 microns and preferably from 40 to 120 microns. If the thickness is less than 1 micron, the film hardness is poor. If the thickness is greater than 200 microns, the coating layer has poor flexibility, resulting in generation of cracking in the coating film.

Method of making formulation

The aqueous composition can be formed using conventional blending and mixing techniques. Preferably, water is added first, then the thickeners, surfactants, dispersants, and defoamer, followed by the particles, silicones, then the polymer and other additives using mechanical agitation.

Application

In the method of the present invention, the water-based composition can be either spray, brushed, or paint roller applied on the construction site to the construction surfaces, or supplied as an article to the construction site by pre-application to construction panels, such as oriented strand board, plywood, gypsum based sheeting, and other sheeting materials. It can also be applied by dip coating and spin coating.

If desired, the wet-coated substrate formed in the method of the present invention may be dried using conventional techniques including ambient environmental drying, forced air drying, and forced air/ thermal drying. Preferably, the composition is dried under ambient conditions.

The coating compositions may be processed both at room temperature and at temperatures above or below room temperature, for example, at temperatures in the range from 0 °C to 55 °C.

Substrates

When applied to a surface, the coating has good adhesion to masonry surfaces, painted and many other surfaces such as concrete, cementitious, plaster, cellulosic, wood, one or more polymer, dry or wet surfaces, surfaces exposed to weathering on at least one surface of the substrate. The adhesion of the coating to the substrate may be produced by chemical bonding, or else by physical forces.

Contact angle and surface energy

The contact angle can be measured using a goniometer and the CAH can be measured using the dynamic sessile drop method. 20 µL drop of water is taken, 10 µL of diiodomethane and 15 µL of hexadecane is taken for surface energy measurements by the Owens-Wendt equation.

The contact angle of water on the coated surface made according to the present invention may be difficult to measure with conventional means because the water droplet bounces or runs off the surface when applied. As illustrated in Example 27 the surface energy for one embodiment of the coating is < 10 mN/m. The self-cleaning surfaces of the invention have a roll-off angle of less than 20 degrees, preferably less than 10 degree, even more preferably less than < 5 degrees in one state. The water contact angles are preferably above 100 degrees, more preferably over 120 degrees, even more preferably superhydrophobic i.e. difficult to measure by conventional techniques.

The coating has a surface energy of <40 mN/m, preferably <20 mN/m and most preferably < 10 mN/m and is recoatable favouring application of a second coat to enhance film build-up to attain desired opacity/ hiding/ whiteness.

Durability

A coating formed from the coating composition of the present invention, has good durability when exposed outdoors to extreme weather for a time period of a few months to several years. Stability is determined by observing that the unwettability, by measuring the contact angle of a droplet on the surface, has not diminished over the course time being exposed to the environment in addition to the colour difference after exposure to Atlas and QUV testing after 2000 hours as illustrated in example 41.

Test methods

The following test methods were used to quantify the properties of the inventive water-based compositions.

Accelerated storage stability

To assess the stability of the paint on storage at elevated temperature conditions (55 +- 1 °C) for 30 days. The initial stormer viscosity of the paint was checked at 30 °C and the paint was kept in a 250 ml lacquered tin container in a forced air circulated oven maintained at 55 + 1 °C with an open vent. The container was removed after 30 days and allowed to reach ambient temperature. The contents were mixed well and the stormer viscosity was determined at 30 °C.

Wet Scrubs testing

To assess the wet scrub resistance of the paint under accelerated conditions to determine the resistance of paints to erosion caused by scrubbing in presence of scrub medium using paint washability apparatus (Erichsen or equivalent). A pig bristle brush (DIN specification) [Hog hair brush], (Brush holder, brush, packing mat.) Total weight: 430 +/- 20 gms.

A film of WFT (wet film thickness) 6 mil was applied on a Leneta P-121 ION dull black plastic panels (165 x 432 x 0.25 mm). The panels are air dried in horizontal position for seven days in a dust free open room.

Scrub medium consisting of water, thickener, Liquor ammonia, surfactant, Silica 400 mesh and preservative.

The panel was placed and clamped in the tray of washability apparatus. The brush was soaked with 1% solution of SLS. The brush was removed and shaken vigorously to remove any excess SLS solution. The brush was mounted in the holder. The scrub medium was stirred with a stainless steel spatula and 10g was spead evenly on the panel.

The brush was placed at one end of the path and attached to the guide cables. The panel was wet with 5 ml of distilled water in the path of the brush.

After each 400 cycles before failure; 10 g of stirred scrub medium and 5 ml of water was added on the panel. The number of cycles was recorded to remove the paint film fully in one continuous line across the 1/2 inch wide of the shim. The panel was washed under tap water and allowed to stand vertically for 2 hrs. The panel was inspected for signs of integrity failure (colour change, gloss change & rate of loss of film).

Anti algal chamber testing

To assess the anti-algal performance of the paints under accelerated conditions over a period of 30 days.

Algae inoculum preparation: Two species of algae, *Chlorella and Oscillatoria*, were cultured separately. Aerated Cement Blocks (ACBs) of similar surface profile were used for a set of paints under study. The ACBs were sanded with emery paper (No. 180). Two coats of paint were applied on the ACBs with the help of a brush, on the cut surface barring 1 cm area on the top portion of the side. Also paint was applied on the bottom side of the ACBs. During first coat, 3 ± 0.1 gm was deposited by wet wt. and during 2^{nd} coat, 1.2 ± 0.1 gm was deposited by wet wt. on the top portion. Overnight curing was allowed between two coats and 7 days curing was allowed after 2^{nd} coat. ACBs were prepared in triplicate for every sample. The cured painted panels were leached under running tap water for 3 hours, keeping the panel in inverted position [painted surface down] in a tray. The bottom tank of the Algae Test Chamber was filled with tap water. Mixed algal inoculum was charged and algae culture broth was added. Performance rating was given as 10 for No growth and 0 for complete growth.

Freeze thaw stability

To determine the freeze thaw stability of the water based paint to determine the extent to which water borne paints retain their original properties free of detrimental changes in consistency, resist coagulation or the formation of the lumps and deterioration of dried film properties such as appearance, gloss and film integrity, when subjected to freezing & subsequent thawing. The stormer viscosity of the paint was measured at 30 °C and the paint was kept in a 250 ml lacquered tin container in a deep freezer maintained at -15 °C (+-2 °C) for 18 hrs and then removed and allowed to come to thermal equilibrium undisturbed at 30 +- 2 °C or room temperature for 6 hrs. This constitutes one cycle. The test was repeated for 5 cycles. Before stirring, the specimen condition in the can was examined for settling, gelation, coagulation, lumpiness. The paint specimens were stirred and the consistency on stormer viscometer at 30 + 1 °C was determined. The paint was applied to a cement concrete block of 6"x6" by brushing. The performance of the test specimen with the control was compared in terms of dried film properties, such as gloss and film integrity. The paint will be considered to have passed this test if no significant difference in performance/ behaviour is observed between control and test samples.

The present invention is illustrated hereunder in greater details in reference to the non-limiting exemplary illustrations and figures.

Example 1: Surface treatment/ Functionalization of TiO_2 with Dynasylan F8261 by heat treatment/ sol-gel treatment
In a typical experiment 100 g of TiO_2 R902 (0.32 microns average particle size) from DuPont was treated with 10 g of Dynasylan F8261 (tridecafluroocty1 triethoxysilane) from Degussa, Evonik at 80 °C for 30 minutes after which it was subjected to the process of heat treatment (upto 150°C) for 2 hours. Subsequently, soxhlet extraction was carried out with boiling acetone for 3 hrs to measure the permanency of the treatment and to test whether the particles still remain hydrophobic following the soxhlet wash.

The thus treated TiO_2 was both hydrophobic as well as oleophobic as it floats on water and a bed of the TiO2 powder spread on a glass panel is able to repel both water and oil. Heating the pigment with Dynasylan F8261 caused greying of TiO_2 which was not desired as TiO_2 is added to paint and coatings for its whiteness and hence the greying is undesirable.

Therefore, a sol-gel process under ambient conditions was followed for surface treatment and modification of TiO_2 with Dynasylan F8261 to prevent the undesired greying of TiO_2 using isopropanol as the solvent and liquor ammonia as the catalyst. The resulting TiO2 was white in colour by visual observation and also showed both hydrophobicity and oleophobicity.

Example 2: Surface treatment/ Functionalization of TiO_2 with VTMO by heat treatment/ sol-gel treatment

Further in another typical experiment, the functionalization of TiO_2 R902 pigment (20 g) was carried out with VTMO (vinyl trimethoxy silane, 10 g) in 20 g of isopropanol and in 1 g of 25% solution of liquor ammonia. However, to avoid greying of TiO_2 the functionalization was carried out at room temperature (for 4 hours) using a sol-gel process instead of employing high temperatures as discussed above. The results reveal that the treated TiO_2 pigment showed good hydrophobicity (floating on water) which may be used in the coating composition.

It was found by way of the present invention that even when heat treatment process was followed (upto 150 °C, 2 hours) for functionalization of TiO_2 pigment (100 grams) with VTMO (10 grams), no discoloration of the TiO_2 pigments was observed when functionalized with VTMO as was observed with the fluorosilane shown in example 1.

Example 3: Surface treatment/ Functionalization of amorphous nanosilica with VTMO and Dynasylan F8261 by sol-gel treatment
Cabosil M5 amorphous nanosilica (200 nm – 300 nm aggregates with a primary particle size of 14 nm in diameter) (5g) was treated with VTMO (2.5 g) in isopropanol (1.8 g) and 25% liquor ammonia solution (0.7g) using a sol-gel method at room temperature (30°C) for 5 hours and 30 minutes.

The results revealed that the same process of functionalization with Dynasylan F8261 instead of VTMO resulted in both hydrophobic and oleophobic nanosilica as compared to only the hydrophobic nanosilica obtained by treatment with VTMO by following the same said method.

Example 4: Selection of the treatment process of the pigments present in the aqueous coating composition of the present invention, and selection of the material for functionalization to achieve a balance of hydrophobicity and hydrophilicity.

It was therefore found by way of the present invention that discolouration or greying of TiO_2 pigments was observed only when heat treatment (upto 150°C) was applied while functionalizing with Dynasylan F8261, whereas the same TiO_2 pigments did not change colour when heat treatment was given while functionalizing with VTMO.

However functionalization with Dynasylan F8261 is preferred over functionalization with VTMO as VTMO imparts only hydrophobicity whereas Dynasylan F8261 imparts both hydrophobicity and oleophobicity.

Table 1 below reveals the surface treatments carried out with monomeric and oligomeric silicones for Titanium dioxide and other fillers. These were carried out by heat treatment/ sol gel method. Further they also represent some of the particles and their sizes that may be used in the present invention.

Table 1

Pigment/Filler/particle type	%Treatment & Treating material (on particle weight basis)
TiO2 R902, 0.32µ	10% Silicone oligomer (Silres SY 231 from Wacker)
Silica 10µ	10% Silicone oligomer
CaCO3 LH 2300,	10% Silicone oligomer
TiO2 R900, 0.41 µ	10% Silicone oligomer
Steatite 10µ	10% Silicone oligomer
Sumica Pearl (Bright gold), effect pigments, 10-40 microns	10% Silicone oligomer
Cabosil M5, 14 nm	10% Silicone oligomer
TiO2 R902	2% Silicone oligomer
Silica 10µ	2% Silicone oligomer
CaCO3 LH 2300 4µ	2% Silicone oligomer
Steatite10µ	2% Silicone oligomer
Cristobalite 14µ	2% Silicone oligomer
TiO2 R902	0.5% Silicone oligomer (no hydrophobicity observed) even after 15 days
TiO2 R902 0.32µ	2% Monomeric silane (VTMO) vinyltrimethoxysilane
Silica 10µ	2% Monomeric silane
Steatite10µ	2% Monomeric silane
China clay BCK	2% Monomeric silane
Cristobalite 14µ	2% Monomeric silane
TiO2 R900, 0.41 µ	10% 3-glycidoxypropyltrimethoxysilane (hydrophilic treatment)
Cabosil M5, 14 nm	25% 3-methacryloxypropyltrimethoxysilane
TiO2 R902 0.32µ	2% 3-methacryloxypropyltrimethoxysilane
Cabosil M5, 14 nm	2% 3-methacryloxypropyltrimethoxysilane

Also, Fig 3 and 4 clearly shows the image of untreated and treated TiO_2 with silicone Silres SY231, wherein it is clearly seen in Fig 4 that a fine 27 nm layer of silicone is bonded to the pigment. All of the above treated pigments and extenders as per Table 1 were found to be either hydrophilic (disperses in water) or hydrophobic (floating on water) or partly floating and partly dispersing in water.

As an example, the TiO2 treated with 10% 3-glycidoxypropyltrimethoxysilane showed a lower degree of hydrophobicity (the treated materials are getting dispersed in water and not floating on it) as compared to treatment with Silres SY231 and may be considered as a hydrophilic treatment of silicone. Other such hydrophilic silanes are those with the amine or isocyanate group.

Further, it was noticed that the treatment of nano particles such as nanosilica even up to higher temperatures 290-300°C was showing partial settling in water (vigorous shaking of a test tube containing water) indicating complete hydrophobization was not taking place. This was also observed for the micron sized particles treated with a lower dosage (2%) of VTMO (vinyltrimethoxy silane) and Silres Sy231. This is advantageous since we want a balance of hydrophobicity and hydrophilicity in the polymer as well as the particles to get a surface that is free of dirt streak marks, dirt lines and water spots. Hence, particles showing a balance of hydrophobicity and hydrophilicity are preferred. Further, treatment of TiO2 with 0.5% of Silres Sy231 did not result in hydrophobic particles.

In the case of nano silica treated with 25% 3-methacryloxypropyltrimethoxysilane, the treated silica was not having hydrophobic character (treated for 5h 30 minutes at upto 80°C. However, when checked after a period of 1 month, the particles showed good hydrophobicity (floating on water). Treatment of nanosilica with 2% 3-methacryloxypropyltrimethoxysilane did not lead to hydrophobicity. However, the TiO2 treated with 2% 3-methacryloxypropyltrimethoxysilane, showed good hydrophobicity immediately after heat treatment. Hence it is possible to achieve particles with varying levels of hydrophobicity and hydrophilicity, a balance being preferred to achieve the desired coating composition.

In the case of formation of any lumps during treatment, a mortar and pestle can be used for crushing the lumps and the particles can be passed through a suitably sized sieve. Also, the extent of hydrophobization varied with the particle being treated, the quantity of treating agent and the time and temperature of the treatment reaction. Higher temperatures were used for treatment with oligomeric silicones (silres sy 231) as compared to the monomeric silanes.

A plurality of particles of different particle sizes can be used for the coating composition with different hydrophobic and hydrophilic silicone treatments provided they are incorporated with the polymer in certain ratios which are discussed below.

Several rutile and anatase grades of titanium dioxide are available such as R902, R902 plus, R 900, R931 etc that can be treated as per the process discussed above.

Hydrophilic grades of nano silica are available such as Cabosil M5 from Cabot or Aerosil R200 (average particle size of 12 nm) from Evonik that can be either heat treated or treated by sol-gel process as discussed above.

Further though external surface treatment of the particles can be used in order to ensure uniform treatment of the particles, in-situ treatment can also be used with a combination of hydrophobic and hydrophilic organosilicones/ silanes which are shown in latter examples.

Example 5: Preparation of a solvent borne resin

In a typical experiment, a solvent borne resin was prepared using hydrophobic monomers wherein 38 pbw of styrene, 40 pbw of n-BMA (n-butyl Methacrylate), 20 pbw of MPTMS (3-methacryloxypropyl trimethoxy silane were copolymerized in the presence of 2 pbw of Zonyl TM from DuPont (perfluorinated monomer), 66 pbw of o-xylene, 1.2 pbw of tbpb (tertiary butyl perbenzoate) initiator and 4 pbw of triethylorthoformate (moisture scavenger) at 135°C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Nitrogen gas was passed during the reaction. The resin cast on a glass panel showed good water repellency/beading. However, the Contact angle hysteresis values for water were more than 25 ° i.e. complete roll off of water was not observed.

Example 6: Preparation of a modified solvent borne resin

In another typical experiment for the preparation of a hydrophobic solvent borne resin, the preparation of the resin of example 5 was repeated with tertiary butyl methacrylate as a substitute for styrene, wherein the said resin was prepared by reacting 20 pbw of tertiary butyl methacrylate, 18 pbw styrene, 40 pbw n-BMA (n-butyl Methacrylate), 20 pbw MPTMS (3-methacryloxypropyl trimethoxy silane) in the presence of 2 pbw Zonyl TM (perfluorinated monomer), 66 pbw o-xylene, 1.2 pbw tbpb (tertiary butyl perbenzoate) initiator and 4 pbw triethylorthoformate.

The resin cast on a glass panel showed similar water repellency/ beading as that of a solvent borne resin of Example 5, wherein the similar repellency to water droplets was also observed on the coating. Another batch with 4 pbw Zonyl TM showed similar results. The Contact angle hysteresis values for water were more than 25° i.e. complete roll off of water was not observed.

Example 7: Preparation of amine functional water borne/ water reducible resin in absence of a fluoro monomer with a high content of amine monomer

In a typical experiment a cationic water borne resin was prepared by reacting methyl methacrylate 60 pbw, butyl acrylate (25 pbw), N,N-dimethylaminopropylmethacrylamide (15 pbw), cellosolve (43 pbw), tert-butyl perbenzoate (1.2 pbw), water (100 pbw), acetic acid (6 pbw). The reaction was carried out at 130 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and acetic acid was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an amine value of 99 mg KOH/g.

Since this resin has an amine backbone, the same is responsive to stimuli of change of temperature as well as humidity.

Example 8: Preparation of cationic water borne/ water reducible resin by incorporation of a fluoro monomer and with high content of amine monomer

Since fluoro monomer imparts hydrophobicity and oleophobicity, and does not undergo hydrolysis and condensation reaction with water like MPTMS (3-methacryloxypropyltrimethoxysilane), in a typical experiment a cationic water borne resin was prepared by reacting tertiary butyl methacrylate 60 pbw, Zonyl TAN (perfluorinated monomer, 25 pbw), DMAPMA (N,N-dimethyl aminopropyl methacrylamide, 15 pbw), cellosolve (43 pbw), tert-butyl perbenzoate (1.2 pbw), water (100 pbw), glacial acetic acid (6 pbw). The reaction was carried out at 130 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and acetic acid was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an amine value of 99 mg KOH/g.

Even though a high quantity of fluoro monomer was used along with the tertiary butyl Methacrylate contact angle hysteresis < 25 ° could not be achieved by the resin film alone.

Moreover, since this resin has an amine backbone, the same is responsive to stimuli of change of temperature which is demonstrated in the example 27. In addition it is responsive to the stimulus of humidity.

Example 9: Preparation of acid functional water borne/ water reducible resin in the absence of fluoro monomer but with a high content of acid monomer

In a typical experiment the anionic water reducible resin was prepared by the reaction of MMA (methyl methacrylate, 65 pbw), BA (butyl acrylate, 29.5 pbw), MAA (glacial methacrylic acid, 5.5 pbw), cellosolve (43 pbw), tert-butyl perbenzoate (1.2 pbw), water (100 pbw), triethylamine (4.5 pbw). The reaction was carried out at 130 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and triethylamine was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an acid value of 36 mg KOH/g.

Since this resin is acid functional, the same is responsive to stimuli of change of pH and humidity.

Example 10: Preparation of acid functional water borne/ water reducible resin by incorporation of a fluoro monomer with a high content of acid monomer.

In a typical experiment an anionic water borne resin was prepared by reacting tertiary butyl methacrylate 64.5 pbw, Zonyl TAN (perfluorinated monomer, 30 pbw), MAA (glacial methacrylic acid, 5.5 pbw), cellosolve (43 pbw), tert-butyl perbenzoate (1.2 pbw), water (100 pbw), triethylamine (4.5 pbw). The reaction was carried out at 130 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and triethylamine was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an acid value of 36 mg KOH/g.

Even though a high quantity of fluoro monomer was used along with the tertiary butyl methacrylate, contact angle hysteresis < 25° could not be achieved by the resin film alone.

Since this resin is devoid of amine backbone and is acid functional instead, the same is responsive to stimuli of change of pH and humidity.

Example 11: Selection of type of resin in the aqueous coating composition of the present invention

The treated hydrophobic and oleophobic TiO_2 obtained by the sol-gel process as discussed under Example 1 when mixed with a solvent borne resin of Example 5 and 6 in 50:50 or even in 80:20 ratios, the same resulted in a coating that did not exhibit the desired superhydrophobicity (Contact angle hysteresis < 25°). This may be due to the excellent pigment wetting and binding characteristics of solvent borne resins of Examples 5 and 6 which may be responsible for non-migration of the treated TiO_2 particles to the surface. There is a continuous layer of polymer film at the surface with insufficient protrusions which is responsible for Contact angle hysteresis >25°. Thus the surface structure is not conducive towards obtaining superhydrophobicity.

Moreover, the solvent borne polymers are less preferred over water borne coatings especially in decorative applications as environmental regulations are driving the use of low VOC (volatile organic content) coatings which contain minimum level of solvents. Further, water can be used to clean the brushes used by the painters for application thereby being relatively easier to apply in addition to being environmentally friendly.

Example 12: Evaluation of incorporation of only one kind of functionalized particle in making paint/ coating composition with water borne resin

In an experiment, either the treated TiO_2 of Example 1 or Example 2 or TiO_2 treated with SY231 under Table 1 were used in high doses (50:50 or 80:20, particles : binder) in combination with either the resin of Example 8 or the resin of example 10 to prepare the paint/ coating composition.
In yet another experiment, treated silica of Example 3 was used in high doses (50:50 particles: binder) in combination with either the resin of Example 8 or the resin of example 10 to prepare the paint/ coating composition.

It was found by way of the present invention that paint/ coating composition obtained from the above experiments though showed thermoresponsive and pH responsive character none of the paint/ coating compositions obtained of the above experiments imparted complete water rolling property, even when the above particles are specifically present in combination with the resins of examples 8 and 10.

Example 13: Evaluation of one and two kinds of functionalized particles in making paint/ coating composition with water borne resin

Blends of treated TiO2 (micron sized treated with silres sy231) and treated Cabosil M5 fumed silica (nano sized treated with VTMO) have been evaluated with different resins of experiments 7, 8, 9 and 10. Slurry of treated TiO2 in isopropanol and the slurry of sol-gel treated fumed silica in isopropanol is added individually and a mixture is made with resins 7, 8, 9 and 10.

Treated TiO2 slurry = 70% R902 in isopropanol
Fumed silica slurry = 15% in isopropanol
Resin =10 grams (at 40% solids)
TiO2 slurry = 5.4 grams
Silica slurry = 5.6 grams
Ratio of Micron to nano sized particles = 4.5
Ratio of particles to polymer = 1.155

Table 2

Resin	Pigment (treated TiO2 slurry)	Treated silica slurry	Contact angle hysteresis at 30 deg C < 10° (complete water rolling)
9	Yes	No	No
9	No	Yes	No
9	Yes	Yes	No
7	Yes	No	No
7	No	Yes	No
7	Yes	Yes	No
10	Yes	No	No

10	No	Yes	No
10	Yes	Yes	Yes
8	Yes	No	No
8	No	Yes	No
8	Yes	Yes	Yes
Blend of 9 and 10 (50:50)	Yes	Yes	Yes
Blend of 7 and 8 (50:50)	Yes	Yes	Yes

The coatings were made by simple mixing, diluted with water and applied by brush on fiber cement board panels coated with Asian Paints water based exterior primer (Asian paints exterior primer is based on a modified acrylic emulsion polymer with titanium dioxide along with fillers like calcium carbonate, clays, silicates with a PVC in the range 50 to 80%. It contains additives such as rheology modifiers, pigment dispersing and wetting agents, film and in can stabilizers.), and allowed to dry under ambient conditions for 7 days. It was observed that a combination of treated TiO2 and treated silica when mixed in water reducible resins 8 and 10 gave contact angle hysteresis <10°. Charcoal powder when deposited on the coating gets cleaned with a stream of water giving the benefit of superhydrophobic cleaning. The coating subsequently gets completely wet offering the benefits of superhydrophilic cleaning. The balance of hydrophilicity and hydrophobicity of the polymer, pigments and extenders with a high content of particles/ binder may be responsible for this behavior. The coating was also oleophobic due to the presence of fluorine based monomer. The pigmented coating of resin 8 when placed under a continuous stream of water shows complete wettability. However, as the coating was dried overnight at ambient conditions it regained its superhydrophobicity (CAH < 10°).

These low values of Contact angle hysteresis (<10°) were not observed for resins 7 and 9 indicating the importance of the presence of hydrophobic monomers such as tertiary butyl Methacrylate and fluorine based monomer.

Use of only a high quantity of treated TiO2 in a very high quantity leads to chalking of the paint film with resin 8 and 10, while the use of a very high quantity of only treated fumed silica leads to cracking of the paint film due to its high oil absorption value.

Example 14: Further evaluation of two kinds of commercially available functionalized particles in making paint/ coating composition with water borne resin

The following slurries were prepared, 54.54% of Hoffmann PF 777 clay in isopropanol and 14.28% of Aerosil R972 in isopropanol.

In an experiment, 6.7 grams of Hoffmann PF777 clay slurry, 7 grams of Aerosil R972 slurry and the resin of example 8 (12.8 g) were used to prepare an aqueous paint composition.

Ratio of Micron to nano sized particles = 3.654

Ratio of particles to polymer = 0.9089

The coating showed a CAH<10° and also a stimuli responsive behaviour.

Example 15: Further evaluation of two kinds of functionalized particles in making paint/ coating composition with water borne resin

The following slurries were prepared, 60% of treated R902 TiO2 in isopropanol and 15% of Aerosil R972 in isopropanol.

In an experiment, 7 grams of TiO2 slurry, 7 grams of Aerosil R972 slurry and the resin of example 8 (12 g) were used to prepare an aqueous paint composition.

Ratio of Micron to nano sized particles = 4

Ratio of particles to polymer = 1.094

The coating showed a CAH<10° and also a stimuli responsive behaviour.

Example 16: Preparation of amine functional water borne/ water reducible resin using styrene and 2-ethyl hexyl acrylate in place of MMA and BA in absence of a fluoro monomer with a high content of amine monomer

In a typical experiment a water borne resin was prepared by reacting styrene 60 pbw, 2-ethyl hexyl acrylate (25 pbw), N,N-dimethylaminopropylmethacrylamide, (15 pbw), cellosolve (43 pbw), tert-butyl perbenzoate (1.2 pbw), water (100 pbw), acetic acid (6 pbw). The reaction was carried out at 130 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and acetic acid was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an amine value of 99 mg KOH/g and a pH of 6.

The following slurries were prepared, 60% of treated R902 TiO2 in isopropanol and 15% of Aerosil R972 in isopropanol.

In an experiment, 7 grams of TiO2 slurry, 7 grams of Aerosil R972 slurry and the resin of example 8 (12 g) were used to prepare an aqueous paint composition.

Ratio of Micron to nano sized particles = 4

Ratio of particles to polymer = 1.094

The coating did not show rolling of water and showed a CAH>20°

Example 17: Preparation of amine functional water borne/ water reducible resin using isobutyl Methacrylate, t-butyl Methacrylate and fluoro monomer with a high content of amine monomer

In a typical experiment a water borne resin was prepared by reacting t-butyl Methacrylate (30 pbw), isobutyl Methacrylate (30 pbw), N,N-dimethylaminopropylmethacrylamide, (15 pbw), zonyl TAN (25 pbw), cellosolve (43 pbw), tert-butyl perbenzoate (1.2 pbw), water (100 pbw), acetic acid (6 pbw). The reaction was carried out at 130 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and acetic acid was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an amine value of 99 mg KOH/g and a pH of 6.

The following slurries were prepared, 60% of treated R902 TiO2 in isopropanol and 15% of Aerosil R972 in isopropanol.

In an experiment, 7 grams of TiO2 slurry, 7 grams of Aerosil R972 slurry and the resin of example 8 (12 g) were used to prepare an aqueous paint composition.

Ratio of Micron to nano sized particles = 4

Ratio of particles to polymer = 1.094

The coating showed a CAH<10° and also a stimuli responsive behaviour indicating the importance of selective monomers (in this example isobutyl Methacrylate, t-butyl methacrylate and perfluorinated monomer) in the composition.

Example 18: Preparation of acid functional water borne/ water reducible resin in the presence of fluoro monomer but with a high content of acid monomer

In a typical experiment the anionic water reducible resin was prepared by the reaction of tert-butyl acrylate (67.4 pbw), zonyl TAN (25 pbw), MAA (glacial methacrylic acid, 7.6 pbw), cellosolve (43 pbw), tert-butyl perbenzoate (1.2 pbw), water (98.4 pbw), triethylamine (7.6 pbw). The reaction was carried out at 130 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and triethylamine was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an acid value of 50 mg KOH/g.

Example 19: Preparation of acid functional water borne/ water reducible resin in the absence of fluoro monomer but with a high content of acid monomer

In a typical experiment the anionic water reducible resin was prepared by the reaction of tert-butyl acrylate (58.5 pbw), 2-ethyl hexyl acrylate (35.5 pbw), MAA (glacial methacrylic acid, 6 pbw), cellosolve (43 pbw), tert-butyl perbenzoate (1.2 pbw), water (98.95 pbw), triethylamine (7.05 pbw). The reaction was carried out at 130 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and triethylamine was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an acid value of 40 mg KOH/g.

Example 20: Preparation of acid functional solvent borne (unneutralized) resin in the presence of fluoro monomer but with a high content of acid monomer

In a typical experiment solvent borne (unneutralized) resin was prepared by the reaction of tert-butyl acrylate (53.3 pbw), 2-ethyl hexyl acrylate (17 pbw), MAA (glacial methacrylic acid, 4.7 pbw), Zonyl TM (25 pbw), butyl cellosolve (43 pbw), tert-butyl perbenzoate (0.9 pbw). The reaction was carried out at 130 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. The resin was discharged without neutralization at 70% solids in cellosolve for subsequent use for the preparation of a stimuli responsive coating with reversible wettability switching and CAH < 25°.

Example 21: Further evaluation of two kinds of functionalized particles in making paint/ coating composition with water borne resin

A. In an experiment, treated TiO_2 of Example 1 (4 g), treated amorphous silica of Example 3 (1 g) and the resin of example 8 (10g) were used to prepare an aqueous paint composition.

B. In yet another experiment, treated TiO_2 of Example 2 (4 g), treated Silica of Example 3 (1 g) and the resin of example 8 (10g) were used to prepare an aqueous paint composition.

C. In yet another experiment, treated TiO_2 of Example 2 (4 g), treated Silica of Example 3 (1 g) and the resin of example 10 (10g) were used to prepare an aqueous paint composition.

It was found by way of the present invention that in case of all the above experiments under A and B above a thermoresponsive aqueous coating/ paint composition was achieved due to the amine backbone in the resin exhibiting superhydrophobicity and superhydrophilicity with a low contact angle hysteresis of <10 degrees having self cleaning behaviour as it helps the dirt get cleaned from its surface with the flow of rain water on the paint surface without leaving behind water spots, dirt lines or streaks only when the resin having a specific backbone of acrylic, fluorinated and amine/ acid is present in combination with both kinds of surface treated particles with a balance of hydrophobicity and hydrophilicity. However, in case of experiment C above the only difference was that a pH and humidity responsive aqueous coating/ paint composition was achieved with other characteristics of the coating composition remaining the same. The coating can be brush applied on a cement/ concrete panel. The coating is recoatable and 2 coats can be applied on a waterborne primer. Alternately a self priming system can be used. Charcoal powder when deposited on the coating is cleaned with a stream of water giving the benefit of superhydrophobic cleaning. The coating subsequently gets completely wet offering the benefits of superhydrophilic cleaning. The balance of hydrophilicity and hydrophobicity of the polymer, pigments and extenders with a high ratio of particles/binder may be responsible for this behaviour.

Example 22: Evaluation of stimuli responsive resin having the specific acrylic and amine/ acid backbone in combination with both functionalized TiO2 and nanosilica based pigments to achieve the desired contact angle hysteresis vis-à-vis the resin beyond the scope of the present invention

D. In an experiment the resin of Example 9 (10g) devoid of the fluoro and tertiary butyl Methacrylate backbone in combination with the treated TiO2 of Example 1 (4 g), and silica of Example 3 (1 g) were used to prepare an aqueous paint composition.

E. In yet another experiment the resin of Example 9 (10g) devoid of the fluoro and tertiary butyl methacrylate backbone in combination with the treated TiO2 of Example 2 (4 g), treated Silica of Example 3 (1 g) were used to prepare an aqueous paint composition.

It was thus found by way of the present invention that the aqueous coating composition under 22 D and E above failed to exhibit the desired superhydrophobicity (low contact angle hysteresis < 10 °) as compared to the aqueous coating compositions under Examples 21 A, B and C above, and hence it was thus found by way of the present invention that the backbone of the resin plays an equally important role to impart the desired superhydrophobicity and superhydrophilicity having self cleaning behaviour and low contact angle hysteresis of < 10 degrees when present in combination with two types of functionalized pigments as discussed above.

Thus it can be seen that superhydrophobic coatings can be prepared using externally treated combination of micron and nano sized particles in combination with a polymer; in this example an acrylic polymer with suitably selected monomers.

Example 23: Evaluation of the ratio of functionalized particles of two different sizes present in combination with resin involving the selective acrylic fluorinated amine/acid backbone to attain very low contact angle hysteresis of <10 degrees

This study reveals the importance of functionalized particles with a balance of hydrophobicity and hydrophilicity present in the resin of the aqueous coating/ paint composition of the present invention under a certain binder to particle (pigment/ filler) ratio. Single coat of the composition was brush applied over Asian Paints exterior primer applied on a fiber cement board panel (6 inch x 3 inch). The coating was dried under ambient conditions for 7 days.

Table 3

Single waterborne resin Resin 8	10	40% solids in water and cellosolve
treated TiO_2	4	
treated silica	1	

ttl particles	5
ratio of micron to nano particles	4
ratio of total particles to resin	1.25
Contact angle hysteresis attained	<10°

Blend of resins

A

	PBW	actual solids
Resin blend of 18 and 19	12.8	5.12 (40% in water and cellosolve)
TiO2 slurry in cellosolve	6.7	4.69
silica slurry in cellsolve	7	0.994
ratio of micron to nano particles		4.718309859
ttl particles		5.684
ratio of total particles to resin		1.11015625
Contact angle hysteresis attained		<10°

B

	PBW	actual solids
Resin blend of 18 and 19	12.8	5.12
tio2 slurry	7	4.9 (70% solids in cellosolve)
silica slurry	7.2	1.0224
ratio of micron to nano particles		4.792644757
ttl particles		5.9224
ratio of total particles to resin		1.15671875

Contact angle hysteresis attained		<10°

C	PBW	actual solids
Resin blend of 18 and 19	12.8	5.12
tio2 slurry	7.4	5.18
silica slurry	7.6	1.0792
ratio of micron to nano particles		4.799851742
ttl particles		6.2592
ratio of total particles to resin		1.2225
Contact angle hysteresis attained		<10°

The ratios are as follows: micronized to nano sized particles = 3.5 to 8 (higher ratios being preferred for 2 coat application).

Ratio of particulate mixture (micron sized and nano sized particles) to polymer = 0.9 to 2.5 (higher ratios being preferred for 2 coat application)"

The CAH of <25°, preferably<20°, more preferably<10° and more preferably <5° is desired in one state and higher than 25° in the other switched state. The selective combination of hydrophobic and hydrophilic silicones with suitable acrylic, fluorinated and hydrophilic backbone gives the desired durability and water resistance to the coating composition along with reversible hydrophilic-hydrophobic switching under variable environmental conditions including variations in at least one or more of temperature, pH, humidity or other external stimuli including light .

Example 24: Preparation of acid functional water borne/ water reducible resin using tertiary butyl Methacrylate and fluoro monomer with a high content of acid monomer by dispersion polymerization

In a typical experiment the anionic water reducible resin was prepared by the reaction of t-BMA (t-butyl methacrylate, 42.4 pbw), Zonyl TM (50 pbw), MAA (glacial methacrylic acid, 7.6 pbw), butyl cellosolve (43 pbw), t-butyl perbenzoate (2.2 pbw), water (98.4 pbw), triethylamine (7.6 pbw). The reaction was carried out at 140 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and triethylamine was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an acid value of 50 mg KOH/g and pH=8.5.

Since this resin is acid functional, the same is responsive to stimuli of change of pH.

Example 25: Details of acrylic latex prepared using emulsion polymerization

Standard acrylic emulsion was used as co-binder in the present invention. It is a pure anionic acrylic emulsion with a solid content of 45% NVM (Non volatile matter), pH = 9 with a particle size of 0.05 to 0.25 µm. The emulsion film has a water contact angle of 74°, hexadecane contact angle of 2.9° and a surface energy of 36.9 mN/m.

The blend of example 24 with the emulsion of example 25 shows the following surface energies. Thus a low surface energy was obtained even for a blend of the 2 polymers (emulsion and dispersion).

Table 4

Emulsion 25: Dispersion 24	**Water contact angle (°)**	**Hexadecane contact angle (°)**	**Surface energy (mN/m)**
60:40	108.1	68.6	14.2
70:30	106.9	63.3	15.7
80:20	105.4	60	16.8
90:10	90	59.8	21.9

Example 26: Evaluation of the ratio of dispersion to emulsion polymer involving the selective acrylic fluorinated amine/acid backbone in combination with the specific ratios of micronized to nano sized particles to attain desired low contact angle hysteresis of <10 degrees

Single and two coats of the blend of dispersion and emulsion polymer with the particle mixture composition was brush applied over Asian Paints exterior primer that is based on a modified acrylic emulsion polymer with titanium dioxide along with fillers like calcium carbonate, clays, silicates with a PVC in the range 50 to 80%. It contains additives such as rheology modifiers, pigment dispersing and wetting agents, film and in can stabilizers, applied on a fiber cement board panel (6 inch x 3 inch). The coating was dried under ambient conditions for 7 days.

Table 5: Study on the ratio of emulsion to dispersion

Here a blend of dispersion polymer and emulsion polymer has been used in 40/60 ratio

	PBW	actual solids	
dispersion 24	5.12	2.048	40% in water and cellosolve
emulsion 25	7.68	3.456	45% in water
tio2 slurry	10	7	
silica slurry	10	1.42	
ratio of micron to nano particles		4.929577465	
ttl particles		8.42	
ttl resin		5.504	
ratio of total particles to resin		1.529796512	
Contact angle hysteresis attained		<10° in only first coat	

The above 2 ratios was unable to exhibit low contact angle hysteresis in 2 coats

A; Different ratio was studied

	PBW	actual solids	
dispersion 24	5.12	2.048	40% in water and cellosolve
emulsion 25	7.68	3.456	45% in water
tio2 slurry	10	7	
silica slurry	8	1.136	
ratio of micron to nano particles		6.161971831	

ttl particles	8.136
ttl resin	5.504
ratio of total partilces to resin	1.478197674
Contact angle hysteresis attained	<10°in only first coat

Above 2 ratios remained unable again to exhibit low contact angle hysteresis in 2 coats.

B; Different ratio was studied

	PBW	actual solids	
dispersion 24	5.12	2.048	40% in water and cellosolve
emulsion 25	7.68	3.456	45% in water
tio2 slurry	10	7	
silica slurry	12	1.704	
ratio of micron to nano particles		4.107981221	
ttl particles		8.704	
ttl resin		5.504	
ratio of total particles to resin		1.581395349	
Contact angle hysteresis attained		<10°in only first coat	

C, Different ratio was studied

	PBW	actual solids	
dispersion 24	5.12	2.048	40% in water and cellosolve

emulsion 25	7.68	3.456	45% in water
tio2 slurry	10	7	
silica slurry	15	2.13	
ratio of micron to nano particles		3.286384977	
ttl particles		9.13	
ttl resin		5.504	
ratio of total partilces to resin		1.658793605	
Contact angle hysteresis attained		<10°in only first coat	

Above ratios again remained unable to exhibit low contact angle hysteresis in 2 coats.

D; different ratio tried

	PBW	actual solids	
dispersion 24	5.12	2.048	40% in water and cellosolve
emulsion 25	7.68	3.456	45% in water
tio2 slurry	8	5.6	
silica slurry	10	1.42	
ratio of micron to nano particles		3.943661972	
ttl particles		7.02	
ttl resin		5.504	
ratio of total particles to resin		1.275436047	
Contact angle hysteresis attained		<10°in only first coat	

Above ratio also remained unable to exhibit low contact angle hysteresis in 2 coats.

E	PBW	actual solids	
dispersion 24	5.12	2.048	40% in water and cellosolve
emulsion 25	7.68	3.456	45% in water
tio2 slurry	12	8.4	
silica slurry	10	1.42	
ratio of micron to nano particles		5.915492958	
ttl particles		9.82	
ttl resin		5.504	
ratio of total partilces to resin		1.784156977	
Contact angle hysteresis attained		<10°in first and second coat	

Above ratio was **preferred** to impart low contact angle hysteresis for 2 coat application

F	PBW	actual solids	
dispersion 24	5.12	2.048	40% in water and cellosolve
emulsion 25	7.68	3.456	45% in water
tio2 slurry	15	10.5	
silica slurry	10	1.42	
ratio of micron to nano particles		7.394366197	
ttl particles		11.92	
ttl resin		13.956	

ratio of total partilces to resin	2.165698
Contact angle hysteresis attained	<10°in first and second coat

The emulsion is described in Example 25 above and the dispersion polymer is prepared in accordance to the present invention as per example 24 above.

Dispersion polymerization is known to a person skilled in the art wherein the polymer with acid or amine functionality is prepared in water compatible cosolvent such as cellosolve, carbitol or any other water compatible co solvent or other suitable solvent. After preparation of the polymer, amine such as liquor ammonia etc. or acid such as acetic acid etc. is added to neutralize the polymer (anionic or cationic) and water is added to disperse the polymer into water at a high speed (500 rpm using a stirrer). The dispersion polymers are typically free from surfactants. Although polymerizable or free surfactants maybe added for improving stability, ease of processing, adjusting viscosity, etc. The remaining cosolvent can be stripped out under vacuum resulting in a low VOC resin or alternately VOC exempt solvents can be used for the preparation leading to a reduction in the cycle time involved with stripping of the solvent. Such examples of low VOC solvents are Ecosoft PB, dimethyl carbonate etc.

The low contact angle hysteresis <10° was obtained above for 1 coat application in accordance with the invention, however for 2 coat applications higher ratios of total particles to binder and micron to nanometer particles were required to achieve contact angle hysteresis < 10 degrees since the surface profile of the topcoat may change depending on the surface profile of the substrate/ undercoat.

Experiment E under Table 5 above provided for the preferred low contact angle hysteresis of <10 degrees wherein the ratio of emulsion (25) to dispersion polymer (24) was in 60/40 ratio. However, several ratios of emulsion to dispersion polymers of 70/30, 80/20 and 90/10 revealed that 70/30 and 80/20 showed the desired low contact angle hysteresis of <10 degrees, whereas 90/10 showed high contact angle hysteresis of >10 degrees, and hence a sufficient high quantity of dispersion polymer is preferred to be present in the paint/coating composition of the present invention.

However, presence of emulsion polymer having surfactants may still give low hysteresis provided a dispersion polymer is present in the system. Ratio of dispersion polymer to emulsion polymer (5/95 to 100% dispersion polymer is preferred). Emulsion polymers are not preferred in the composition of the present invention as the film formation mechanism coupled with the presence of surfactants increases the contact angle hysteresis values possibly due to a non-continuous film covering the pigment and extender particles.

Only emulsion polymers may be used, however, the CAH values will be higher, more than 20 degrees for emulsions of example 25 and 44 (shown in example 55) and further the time of switching from hydrophobicity to hydrophilicity will be decreased to under few minutes. Also if the emulsion has a high contents of external surfactants, water marks may appear on the paint. Polymerizable surfactants may be used to prepare emulsions (shown in example 44), however the CAH value will be higher for a given composition when compared with dispersion. Thus dispersion polymers are preferred.

Other components to prepare a coating formulation can be present in the paint formulation and low hysteresis can be obtained. Other components include but not limited to thickeners, biocides, dispersing agents, defoamers, buffers etc. These components are known to those skilled in the art. This is shown in example number 34.

It is thus apparent form the tables above that apart from the surface chemistry, the surface morphology of the particles comprising of micro- to nano structures, or even micro structures alone, the ratios between said micro to nano structures as well as the ratios between the particulate mixtures to polymer all contribute to lowering the contact angle hysteresis of the composition to < 10 degrees. These ratios are valid where a combination of micron sized and nano sized particles are used. It is also possible to achieve low hysteresis values using only micron sized particles of a variety of sizes (preferably less than 325 mesh) or irregularly shaped particles as shown in latter examples. It is also possible to achieve low hysteresis using only nano particles; however the formulation will be comparatively more expensive. Moreover, the ratio of dispersion to emulsion polymers in the aqueous coating composition of the present invention also plays a role in determining the contact angle hysteresis. The adhesion of dirt particles to these surfaces is minimal because they touch only the tips of the structure leading to the dirt particles being only lightly deposited on the coating surface. The particles are easily washed away by water droplets, which roll off.

Example 27: Characterization and study of the water-borne acrylic random copolymer dispersions in combination with the functionalized pigments in accordance with the present invention

A series of water-borne acrylic random copolymer dispersions comprising specialty monomers; tertiary butyl Methacrylate (TBMA) for hydrophobicity and perfluorinated monomer (Zonyl TAN/ Zonyl TM) for oleophobicity and improved dirt pickup resistance of coating were synthesized by conventional free radical polymerization as per examples 8 and 10.

They can be acid or amine functional. These copolymers were processed with several functionalized pigments to give stimuli responsive (pH/ temperature/ humidity) water-borne coatings as shown above.

One of these coatings (cationic) was taken up for the study that was prepared by dispersing the treated pigments in the amino functional acrylic dispersions to get weight solids of about 40 % in water. The resulting coating composition was free flowing liquid that could be applied as such or with little dilution using the conventional brush, roller or airless spray application techniques.
Here for the purpose of characterization and to minimize the errors in dry film thickness (DFT), coatings were applied on glass panels of dimensions 6 x 4 square inches using a 100-µm SHEEN draw-down applicator to form uniform films of about 50-µm DFT. The coated panels were matured for 7 days and tested for contact angle measurements using a Digidrop Contact Angle Meter of GBX Surface Science Technologies make. The contact angle values were measured using the static sessile drop method after a time period of 60 seconds. An average of 5 readings taken at different parts of the coating is reported.
The contact angle measurements were first carried out at ambient temperature of about 30°C. It was an interesting observation to note that the coating surface behaved superhydrophobic with contact angle hysteresis $\theta_A - \theta_R < 10$ degrees. When a 5 µL water droplet is pumped through a syringe needle, it touches the surface and becomes non-coaxial with the needle as soon as it begins to advance. The droplet then moves to the right and around to the back of the needle. As the water droplet is removed with the syringe, it remains stationary until it spontaneously dewets the surface and rises into the needle.

However, to quantify the contact angle of our pigmented coating in this study, the syringe was further pumped to elute water droplet at increasing intervals of 5 µL as per Figure 5. It was thus observed that water droplet is released from the syringes only after it reaches a volume of 45 µL. The contact angle of this droplet was found to be 143°.

The study of contact angle was also carried out using hexadecane as a probe. The minimum volume eluting from the syringe needle to form a droplet was 15 µL in the case of hexadecane due to its low surface tension. The contact angle value for hexadecane was found to be 98° at ambient temperature. The value clearly indicates that the coating is not just hydrophobic but also oleophobic in nature.

Table 6: Surface energy of pigmented coating

Temperature (°C)	Polar component (mN/m)	Dispersive component (mN/ m)	Surface energy (mN/ m)
30	0.2	5.1	5.3

Table 6 above shows the surface energies of the coating. The surface energy was calculated by the Owens-Wendt equation utilizing the contact angles of distilled water and hexadecane using Windrop++ software. The surface energy obtained for the coating is 5.3 mN/m.

The switching behaviour from superhydrophobicity to superhydrophilicity is demonstrated from the following experiments. The coated glass panel was placed in a deep freezer at 0°C for 5 hours and then immediately subjected to contact angle measurement. It was possible to measure the contact angle with just a 5 µL water droplet with the angle reducing down to <90°. When the panel removed from the freezer is placed under a continuous flow of water, the pigmented coating exhibits superhydrophilicity as a thin sheet of water covers the surface. This complete wetting of the surface with water enables cleaning of the surface thereby preventing dirt streak marks, which is associated with non-responsive superhydrophobic coatings. When the same panel was allowed to attain ambient temperature, it regained superhydrophobicity indicating the thermoresponsive wettability switching of the coating. The experimental values were found to be reproducible for more than five times explaining that the phenomenon of switching from superhydrophobicity to superhydrophilicity is reversible.

The rheological behavior of the liquid pigmented system (50% non volatile content) was measured in a cup and bob assembly (CC27/ T200/ AL) using the Anton Paar Physica MCR 301 rheometer. The temperature sweep at shear rates 0.001, 0.01, 0.1 and 1 s^{-1} was carried out over a range of 0 to 75 °C at 5 °C/min.

The switching behavior from superhydrophilicity to superhydrophobicity with the temperature variation was further substantiated by carrying out rheological studies of the liquid pigmented system. As the polymer conformational change is a delicate molecular phenomenon the rheological measurements were performed at low shear rates 0.001, 0.01, 0.1 and 1 s^{-1}. The viscosity values are plotted as a function of temperature in Figure 6. The rheograms show an initial decrease in viscosity with temperature followed by an anomalous increase between 20-50°C. The viscosity passes through a maxima at a low shear rate (< 1 s^{-1}) while at a higher shear rate (1 s^{-1}) there is only a slight increase in viscosity before it again decreases. This indicates that at low shear rate the system shows some kind of interchain associations (probably driven by hydrophobic associations) in the temperature range of 20-50°C. This interchain association results into the observed temperature independent viscosity behaviour because there are two opposing tendencies, which apparently seem to balance each other. The usual Arrhenius-like decrease in viscosity with increase in temperature is balanced by association driven increase in viscosity with increase in temperature.

Thermal changes in the dried pigmented coating were studied using Differential Scanning Calorimetry (DSC). TA instruments Q10 apparatus was used to record DSC thermograms at a heating rate of 2°C/min over a temperature range of -40 °C to 90 °C, under nitrogen atmosphere.

The changes in polymer conformation with temperature for the dried pigmented coating were carried out by DSC studies. Figure 7 depicts an endotherm corresponding to the temperature region (30-55°C) where the coating is switching from hydrophilicity to hydrophobicity.

Both the rheology and thermal analysis data support our observation that the coating becomes hydrophobic with increase in temperature for the pigmented coating system.

A SEM (Scanning electron microscopy) micrograph of stimuli responsive paint as shown in Figure 8 also supports the fact that use of functionalized pigments helps in creating two levels of topography on the paint surfaces. This topography can increase receding contact angles and decrease contact angle hysteresis.

The topography of the paint surface is further substantiated by AFM (Atomic Force Microscopy) studies. The AFM picture as shown in Figure 9 depicts high surface heterogeneity having a root mean square surface roughness of 210 nm. The AFM image of Figure 10 shows the thermoresponsive behaviour of the paint, wherein the images on the left are under hot condition and the images on the right are under cold condition.

It is thus possible by the technically advanced stimuli responsive water based paint/ coating composition of the present invention exhibiting reversible hydrophilic-hydrophobic switching with variations in external stimuli to achieve a low contact hysteresis of < 10 degrees due to the involvement of the specific polymeric dispersion containing acrylic, fluorinated and amine/ acid backbone in combination with a particulate mixture comprising surface treated combination of micron and nano sized particles.

The stimuli responsive coating of the present invention can be thus used to make self-cleaning/ easy cleaning, anti-graffiti and stain resistant coatings wherein the said coatings are made by a simple, facile and economically viable process and can be applied by conventional techniques such as brush, roller and airless spray application.

Example 28: Preparation of acid functional water borne/ water reducible resin using tertiary butyl Methacrylate and fluoro monomer with a high content of acid monomer and a triacrylate crosslinker.

In a typical experiment the anionic water reducible resin was prepared by the reaction of t-BMA (t-butyl methacrylate, 42.4 pbw), Zonyl TM (perfluorinated monomer, 50 pbw), MAA (glacial methacrylic acid, 7.6 pbw), TMPTA (trimethylolpropane triacrylate, 0.5 pbw), butyl cellosolve (43 pbw), di-tert butyl peroxide (2.2 pbw), water (98.4 pbw), triethylamine (7.6 pbw). The reaction was carried out at 140 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and triethylamine was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an acid value of 50 mg KOH/g and pH=8.

Since this resin is acid functional, the same is responsive to stimuli of change of pH and humidity.

Example 29: Preparation of acid functional water borne/ water reducible resin using tertiary butyl Methacrylate and fluoro monomer with a high content of acid monomer and a triacrylate crosslinker using an alternate initiator

In a typical experiment the anionic water reducible resin was prepared by the reaction of t-BMA (t-butyl methacrylate, 42.4 pbw), Zonyl TM (perfluorinated monomer, 50 pbw), MAA (glacial methacrylic acid, 7.6 pbw), TMPTA (trimethylolpropane triacrylate, 0.5 pbw), butyl cellosolve (43 pbw), t-butyl perbenzoate (2.2 pbw), water (98.4 pbw), triethylamine (7.6 pbw). The reaction was carried out at 140 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and triethylamine was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an acid value of 50 mg KOH/g and pH=8.5.

Since this resin is acid functional, the same is responsive to stimuli of change of pH and humidity.

Example 30: Preparation of acid functional water borne/ water reducible resin using tertiary butyl acrylate and fluoro monomer with a high content of acid monomer

In a typical experiment the anionic water reducible resin was prepared by the reaction of t-BA (t-butyl acrylate, 42.4 pbw), zonyl TM (50 pbw), MAA (glacial methacrylic acid, 7.6 pbw), butyl cellosolve (43 pbw), t-butyl perbenzoate (1 pbw), water (98.4 pbw), triethylamine (7.6 pbw). The reaction was carried out at 130 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 4 hours. Subsequently water and triethylamine was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an acid value of 50 mg KOH/g and pH=8.5.

Since this resin is acid functional, the same is responsive to stimuli of change of pH and humidity.

Example 31: Preparation of acid functional water borne/ water reducible resin using tertiary butyl methacrylate and fluoro monomer with a high content of acid monomer and high initiator content.

In a typical experiment the anionic water reducible resin was prepared by the reaction of t-BMA (t-butyl methacrylate, 42.4 pbw), MAA (glacial methacrylic acid, 7.6 pbw), Zonyl TM (50 pbw), butyl cellosolve (43 pbw), ditertiarybutyl peroxide (2.2 pbw), water (98.4 pbw), triethylamine (7.6 pbw). The reaction was carried out at 140 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and triethylamine was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an acid value of 50 mg KOH/g and pH=8.5.

Since this resin is acid functional, the same is responsive to stimuli of change of pH and humidity.

Example 32: Preparation of acid functional water borne/ water reducible resin using tertiary butyl methacrylate and fluoro monomer with a high content of acid monomer, multifunctional acrylate and a silane monomer

In a typical experiment the anionic water reducible resin was prepared by the reaction of t-BMA (t-butyl methacrylate, 40.4 pbw), MAA (glacial methacrylic acid, 7.6 pbw), Zonyl TM (50 pbw), 3-methacryloxypropyltrimethoxysilane (0.5 pbw), Trimethylolpropanetriacrylate (0.5 pbw), butyl cellosolve (43 pbw), ditertiarybutyl peroxide (2.2 pbw), water (98.4 pbw), triethylamine (7.6 pbw). The reaction was carried out at 140 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and triethylamine was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an acid value of 50 mg KOH/g and pH=8.5.

Since this resin is acid functional, the same is responsive to stimuli of change of pH and humidity.

Example 33: Preparation of acid functional water borne/ water reducible resin using tertiary butyl methacrylate and fluoro monomer with a high content of acid monomer

In a typical experiment the anionic water reducible resin was prepared by the reaction of t-BA (t-butyl acrylate, 41.9 pbw), MAA (glacial methacrylic acid, 7.6 pbw), Zonyl TAN (50 pbw), Trimethylolpropanetriacrylate (0.5 pbw), butyl cellosolve (43 pbw), ditertiarybutyl peroxide (1 pbw), water (98.4 pbw), triethylamine (7.6 pbw). The reaction was carried out at 140 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 4 hours. Subsequently water and triethylamine was added to disperse the resin into water at 50°C resulting into a 40% solids resin with an acid value of 50 mg KOH/g and pH=8.5.

Since this resin is acid functional, the same is responsive to stimuli of change of pH and humidity.

Example 34: Sample Paints prepared using the water-borne acrylic random copolymer dispersions in combination with the functionalized particles (pigments and extenders) in accordance with the present invention

Table 7

Ingredient	**MB 1**	**MB 2**	**MB 3**	**MB 4**
Water	10.35	12.35	17.15	13.35
anionic dispersing agent from Dow Chemical	0.75	0	0	0
Dispersion polymer 30	0	1	1	0
Dispersion polymer 31	0	0	0	1
(non-ionic surfactant of HLB = 13)	1	0.3	0.2	0.2
Mineral oil defoamer	0.3	0.3	0.3	0.3
Glycol	2	0.2	0.2	2
In can preservative	0.1	0.1	0.1	0.1
Antifungal agent	0.2	0.2	0.2	0.2
Antialgal agent	3	6.22	1	0
Dipentene	0.5	1	0.5	0.5
Hydroxyethyl cellulose	0.1	0.1	0	0
Rheolate 278 (rheological additive)	0.5	0.5	0.5	0.5
pH adjustment	0.2	0.2	0	0
TiO2 R902, 0.32 microns	22	22	22	22
Calcium carbonate 4 microns	8	8	8	8
Coalescent	1	1	1	1
TOTAL	50	53.47	52.15	49.15

Using the above mill base, several different paints were prepared. Blends of dispersion and emulsion have been used in this example with a balance of hydrophobicity and hydrophilicity. Conventional paint ingredients have been used in this formula. These coatings exhibit good water repellency after application as shown in Table 8, 9 and 10.

The water, dispersion polymer, dispersing agent, wetting agent, defoamer, glycol, biocides, dipentene, rheological additive are mixed on a high speed disperser for 15 minutes at 500 rpm, after which the pigments and extenders are added. The grinding stage is carried out at 2000 rpm for 20 minutes after which speed is reduced to 800 rpm and coalescent is added followed by the binder. The examples show the contact angle hysteresis values after 1 coat application on fiber cement boards after 7 days air drying.

Table 8

a) MB1 = 3.2 grams
Resin 24= 3.2 grams
CAH> 25°

b) MB1 = 3.2 grams
Resin 24= 1.28 grams
Emulsion 25 = 1.92 grams
CAH> 25°

c) MB1 = 3.2 grams
Resin 24= 1.28 grams
Emulsion 25 = 1.92 grams
Aerosil R972 slurry (14.3%) = 1 gram
CAH< 25°

d) Resin 24= 3.2 grams
Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 (14.3%) = 2.5
CAH<20°

e) MB1 = 3.2 grams
Resin 24= 3.2 grams

Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 (14.3% slurry) = 2.5 grams
CAH< 25°

f) MB1 = 3.2 grams
Resin 30 = 3.2 grams
Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 (14.3% slurry) = 2.5 grams
CAH< 25°

g) MB1 = 3.2 grams
Resin 24 = 1.28 grams
Emulsion 25 = 1.92 grams
Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 slurry (14.3%) = 2.5 grams
CAH< 25°

h) MB2 = 3.2 grams
Resin 24= 3.2 grams
Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 (14.3% slurry) = 2.5 grams
CAH< 25°

i) MB2 = 3.2 grams
Resin 30 = 3.2 grams
Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 (14.3% slurry) = 2.5 grams
CAH< 25°

j) MB2 = 3.2 grams
Resin 24 = 1.28 grams
Emulsion 25 = 1.92 grams
Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 slurry (14.3%) = 2.5 grams
CAH< 25°

k) MB2 = 3.2 grams
Resin 30 = 1.28 grams
Emulsion 25 = 1.92 grams
Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 slurry (14.3%) = 2.5 grams
CAH< 25°

l) MB2 = 3.2 grams
Resin 32 = 1.28 grams
Emulsion 25 = 1.92 grams
Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 slurry (14.3%) = 2.5 grams
CAH< 25°

m) MB2 = 3.2 grams
Resin 29 = 3.2 grams
Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 slurry (14.3%) = 2.5 grams
CAH< 25°

n) MB2 = 3.2 grams
Resin 29 = 1.28 grams
Emulsion 25 = 1.92 grams
Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 slurry (14.3%) = 2.5 grams
CAH< 25°

o) MB3 = 3.2 grams
Resin 24 = 1.28 grams
Emulsion 25 = 1.92 grams
Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 slurry (14.3%) = 2.5 grams
CAH< 25°

p) MB3 = 3.2 grams
Resin 30 = 1.28 grams
Emulsion 25 = 1.92 grams
Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 slurry (14.3%) = 2.5 grams
CAH< 25°

q) MB3 = 3.2 grams
Resin 33 = 1.28 grams
Emulsion 25 = 1.92 grams
Hoffman Clay slurry (63.63% in butyl cellosolve) = 3.3 grams
Aerosil R972 slurry (14.3%) = 2.5 grams
CAH< 25°

The examples show the contact angle hysteresis values after 1 coat application in the presence of conventional paint ingredients.

A Sample PVC calculated for example d indicates the coating is 23.13% above the theoretical CPVC (critical Pigment Volume concentration).

Table 9

Mill base MB4	1.6	2	1.6	3.2
Emulsion 25 : Resin 31 (60:40)	3.2	3.2	3.2	3.2
Hoffman Clay slurry (63.63% in butyl cellosolve)	3.3	3	1.32	1.32
Aerosil R972 slurry (14.3%)	2.5	2	1	1
Contact angle hysteresis	< 25°	< 25°	> 25°	> 25°

Table 10

Mill base MB4	2	2.5	1.6	2

Emulsion 25 : Resin 34 (60:40)	3.2	3.2	3.2	3.2
Hoffman Clay slurry (63.63% in butyl cellosolve)	3.3	3	3.3	3
Aerosil R972 slurry (14.3%)	2.5	2	2.5	2
Contact angle hysteresis	< 25°	> 25°	< 25°	> 25°

Tables 9 and 10 above show that it is possible to attain low CAH values provided certain ratios of micron and nano sized particles (commercially available treated clay and treated silica) are present along with conventional paint ingredients and specific polymers.

Example 35: Sample Paints prepared using the water-borne acrylic random copolymer dispersions in combination with the functionalized particles in accordance with the present invention

Table 11

Emulsion 25 : Resin 31 (60:40)	3.2	3.2	3.2	3.2
TiO2 R105 slurry (80.35% in butyl cellosolve)	2.618	3	1.32	1.32
Aerosil R972 slurry (14.3%)	1.95	2	1	1
Contact angle hysteresis	< 25°	< 25°	> 25°	> 25°

Table 11 shows that it is possible to attain low CAH values provided certain ratios of micron and nano sized particles (commercially available treated Titanium dioxide and treated silica) are present along with conventional paint ingredients and specific polymers.

Example 36: Sample Paints prepared using the water-borne acrylic random copolymer dispersions in combination with the functionalized pigments in accordance with the present invention and their exterior exposure data

Blends of dispersion and emulsion have been used in this example with a balance of hydrophobicity and hydrophilicity. Conventional paint ingredients have been used in this formula. These coatings exhibit good water repellency after application.

Table 12

Paints	**SC-1**	**SC-2**	**SC-3**	**SC-4**
Dispersion: Emulsion	10/90	10/90	30/70	30/70
Resin of example 24	3.32	3.365	9.92	10.07
Emulsion of example 25	29.71	30.155	23.11	23.45
Aktisil PF777 Clay slurry	31.23	31.7	31.23	31.7
Aerosil R972 slurry	20.12	20.42	20.12	20.42
Millbase formula of table 13 below (with anti algal agent)	0	14.36	0	14.36
Millbase formula of table 13 below (without anti algal agent)	15.62	0	15.62	0
TOTAL	100	100	100	100

The paints pass the water immersion test over a period of 7 days without blistering. The wet scrub resistance of these coatings was 60 cycles. Accelerated anti-algal chamber testing for 30 days shows the paints 1 and 2 to have a rating of 7.5/10. 2 coats of paint were brush applied over 1 coat of Asian Paints exterior primer.

Table 13: Millbase formula

Ingredient	**Content**
Water	13.35
Dispersion polymer of example 18	1
(non-ionic surfactant of HLB = 13)	0.2
Dapro 7010 (defoamer)	0.3

Propylene glycol	2
In can preservative	0.1
anti fungal agent	0.2
Anti algal agent	6.22
Dipentene	0.5
Rheolate 278 (rheological additive)	0.5
TiO2 R902	22
Calcium carbonate 4 microns	8
Coalescent	1
TOTAL	55.37

The water, dispersion polymer, surfactant, defoamer, glycol, biocides, dipentene, rheological additive are mixed on a high speed disperser for 15 minutes at 500 rpm, after which the pigments and extenders are added. The grinding stage is carried out at 2000 rpm for 20 minutes after which speed is reduced to 800 rpm and coalescent is added followed by the binder.

Exterior exposure was studied for these paints on a vertical concrete wall over a period of 4 months during the rainy season. SC 4 was found to exhibit over all best performance including anti algal performance.

Table 14

Paints	**SC1**	**SC2**	**SC3**	**SC4**
Peel Off	No	No	No	No
Flaking	No	No	No	No
Water beading	Fair	Good	Not Good	Very good
Biocide present	no	yes	no	yes
RATINGS				

Fungal growth	No	No	No	No
Algal growth	No	No	Initiated	No
Performance rating	10	10	9	10

Performance rating [0=Poor & 10=Best]

These paints demonstrate the durability of the coating and paint SC4 demonstrates the good hydrophobicity achieved even after 4 months of exterior exposure. The paints had a good DPUR (dirt pickup resistance) and did not show dirt streaks, lines and water spots. In addition, all paints showed good antimicrobial properties. Algal growth was initiated for SC3 where no biocide was present.

Example 37: Durability study of paints according to this invention.

Table 15

Monomers	**A (pbw)**	**B (pbw)**	**C (pbw)**
MMA	56	54	54
2-EHA	36.4	33.4	33.4
MAA	7.6	7.6	7.6
Zonyl TAN	0	5	0
Zonyl TM	0	0	5
Tertiary butyl perbenzoate	1.2	1.2	1.2
Butyl cellosolve	43	43	43
Water	98.4	98.4	98.4
Triethylamine	7.6	7.6	7.6
% Solid content	41.8	41.4	40.01

MMA: methyl methacrylate, n-BMA: n-Butyl methacrylate, MAA: Glacial methacrylic acid, Zonyl TAN and Zonyl TM: Perfluorinated monomer, 2-EHA: 2-ethyl hexyl acrylate

Paints with 65, 70 and 75 PVC were prepared according to this invention and exposed to QUV B, 313 nm for 1100 hours.

Table 16

Paints	Δ E
PVC 65, Non-fluorinated binder A	1.894871
Binder B, Fluorinated binder based paint at 65 PVC	1.357983
Binder C, Fluorinated binder based paint at 65 PVC	1.385471
PVC 70, Non-fluorinated binder, A	1.235034
PVC 75, Non-fluorinated binder, A	0.84092

All paints showed excellent durability after 1100 hours of QUV exposure, with the fluorinated binder showing lower delta E values and hence better durability.

Example 38: Water-borne acrylic random copolymer dispersions prepared with a combination of different monomers

A series of different polymers (A to D) were prepared with different starting monomers. All the polymers have an acid value of 50 mg KOH/g and contain the perfluorinated monomer at a fixed content of 5% on monomer composition (except E which does not contain the fluorine based monomer). The resin E does not contain the perfluorinated monomer and is shown to compare the surface energies of the coatings with and without the perfluorinated monomer.

Table 17

Monomers	A (pbw)	B (pbw)	C (pbw)	D (pbw)	E (pbw)

MMA	22.5	22.5	46.4	45.9	49
Styrene	0	18.4	0	0	0
t-BMA	18.4	0	0	0	0
BA	46.5	46.5	0	0	0
2-EHA	0	0	41	40.5	43.4
MAA	7.6	7.6	7.6	7.6	7.6
MA 2000	0	0	0	1	0
Zonyl TM	5	5	5	5	0
Azo initiator	0.7	0.7	0.7	0.7	0.7
Glycol ether	33.33	33.33	33.33	33.33	43
% Solid content in water (neutralized with liquor ammonia)	27.75	25%	29.4%	27%	25
Water contact angle (°)	97	92.5	101	99	85
Hexadecane contact angle (°)	49	45	47	44	6
Surface energy (mN/m)	21.7	24.3	20.4	22	31.9

MMA: methyl methacrylate, n-BMA: n-Butyl methacrylate, MAA: Glacial methacrylic acid, t-BMA: Tertiary butyl methacrylate, MA 2000: Polyethylene glycol methacrylate with molecular weight 2000, Zonyl TM: Perfluorinated monomer, BA: Butyl acrylate, 2-EHA: 2-ethyl hexyl acrylate

The film cast from resin E which does not contain fluorinated monomer shows a surface energy of 31.9 mN/m while films of resins A to D which contain 5% fluorinated monomer on resin solids give a surface energy of <25 mN/m and is preferred for exhibiting dirt pickup resistance.

The reaction was carried out at 80 °C for 6 hours with drop wise monomer addition for 3 hours followed by digestion for 3 hours. Subsequently water and liquor ammonia was added to disperse the resin into water at 50°C resulting into a 25-30% solids resin with an acid value of 50 mg KOH/g and pH=8.5. Since this resin is acid functional, the same is responsive to stimuli of change of pH and humidity. The water absorption of the resin films varied between 5 to 20% after 96 hours in water for the different resins.

Example 39: Paints prepared using the water-borne acrylic random copolymer dispersions of example 38 in combination with the functionalized pigments in accordance with the present invention and their exterior exposure data with only hydrophobic organosilicone resin which is hydrophobic.

Nine paints were prepared using the resins 39A, B, C and D. The paint formulation is given in Table below. In these paints micron sized pigments and extenders have been used to prepare the paints. The TiO2 used has an average particle size of 0.32 microns. The water, surfactants, defoamer, glycol, biocides, rheological additive are mixed on a high speed disperser for 15 minutes at 600 rpm, after which the pigments and extenders are added. Insitu treatment of the pigments and extenders was carried out during paint making using a hydrophobic organosilicone in the formulation. The grinding stage is carried out at 2000 rpm for 20 minutes after which speed is reduced to 800 rpm and the binder is added followed by thickener and coalescent.

Table 18 Paint Formula

Paints	**Sc1**	**Sc2**	**sc3**	**sc4**	**sc5**	**sc6**	**sc7**	**sc8**	**sc9**
Water	14.02	14.89	14.99	13.82	14.02	14.89	14.92	14.92	14.19
Glycol	0.934	0.875	0.999	0.92	0.934	0.876	0.878	0.878	0.945
Mineral oil defoamer	0.046	0.043	0.05	0.046	0.046	0.043	0.044	0.044	0.047
Wetting agent	0.186	0.175	0.199	0.184	0.186	0.175	0.176	0.176	0.189
Incan preservative	0.098	0.091	0.104	0.096	0.098	0.091	0.092	0.092	0.098
Antifungal agent	0.195	0.183	0.209	0.193	0.195	0.183	0.184	0.184	0.197

Dispersing agent	0.186	0.201	0.199	0.184	0.186	0.175	0.176	0.176	0.189
Cellulosic thickener	0	0	0	0	0	0	0	0	0.472
Clay thickener	0	0	0	0	0	0	0.439	0.439	0
PU thickener	0.186	0.175	0.199	0.184	0.186	0.175	0	0	0
pH adjustment	0.093	0.087	0.1	0.092	0.0934	0.087	0.088	0.088	0.094
TiO2 Rutile, 0.32 microns	18.679	17.515	19.99	18.41	18.679	17.519	17.55	17.55	18.91
Quartz (particle size 4 microns)	5.977	5.604	6.396	5.891	0	5.606	5.616	5.616	0
Quartz (particle size 14 microns)	23.91	22.419	25.587	23.56	29.8874	22.425	22.47	22.47	30.266
Antialgal agent	1.955	1.833	2.092	1.927	1.955	1.833	1.837	1.837	1.979
Acrylic binder	8.321 (C)	7.881 (A)	8.665 (C)	8.726 (D)	8.321 (C)	8.759 (B)	8.776 (C)	8.776 (C)	7.348 (D)
Hydrophobic organosilicone	4.669	4.378	4.997	4.602	4.669	4.379	4.388	4.388	4.729
Emulsion of example 25	0	0	13.213	0	0	0	0	0	0
Acrylic binder	18.679	21.893	0	19.33	18.679	21.023	21.06	19.06	18.916
Rheological additive	0.467	0.437	0.499	0.46	0.467	0.438	0	0	0
Polyurethane dispersion	0	0	0	0	0	0	0	2	0
Coalescent	1.401	1.313	1.499	1.381	1.401	1.313	1.316	1.316	1.418
TOTAL	100	100	100	100	100	100	100	100	100

Asian Paints exterior primer followed by 2 coats of these paints at 25% volume dilution was applied on a vertical wall with a horizontal ledge. The wet scrub resistance of these coatings was 500 cycles. As seen after the exposure all the samples except sc6 show good properties in terms of DPUR, whiteness, hydrophobicity and good antimicrobial properties. This demonstrates the importance of other acrylic monomers such as t-butyl methacrylate, n-butyl methacrylate as part of the resin composition, apart from the perfluorinated monomer and a high acid value (50 mg KOH/g) in this example. However, over a period of time (12 months) exterior exposure, the coatings show dirt streak marks indicating that only the hydrophobic organosilicones are not suitable to resist dirt streak marks. The styrene containing coating (sc6-involving Acrylic binder B illustrated in Table 17) shows inferior results in terms of DPUR, microbial growth and even exhibits chalking. Hence it is preferred to use a styrene free polymer. A study is carried out as shown in example 40 that highlights the importance of a combination of hydrophobic and hydrophilic organosilicones with monomers having a balance of hydrophobicity and hydrophilicity.

Example 40: Water-borne acrylic random copolymer dispersions prepared with a combination of different monomers and varying acid values

A series of different polymers were prepared with varying acid values from 25 to 50 mg KOH/g. 6 resins made with different hydrophobic monomers were made. All the resins had a pH of 8 to 9.

Table 19

Monomers	**A**	**B**	**C**	**D**	**E**	**F**
MMA	0	15	0	0	0	0
BA	10	0	19.4	20	43	38
2-EHA	0	16.4	0	0	0	0
n-BMA	77.4	56	53	52.4	143.5	152.5
Styrene	0	0	15	0	0	0
t-BMA	0	0	0	15	37.5	37.5
MAA	7.6	7.6	7.6	7.6	13.5	9.5
Zonyl TM	5	5	5	5	12.5	12.5
Glycol ether	38.8	38.8	38.8	38.8	95	95
Azo initiator	0.7	0.7	0.7	0.7	1.75	1.75
Acid value (mg KOH/g)	50	50	50	50	35	25

% Solid content in water (neutralized with liquor ammonia)	25.12	25.68	27.54	26.72	28.44	35.87

MMA: methyl methacrylate, n-BMA: n-Butyl methacrylate, MAA: Glacial methacrylic acid, t-BMA: Tertiary butyl methacrylate, Zonyl TM: Perfluorinated monomer, BA: Butyl acrylate, 2-EHA: 2-ethylhexyl acrylate

The above resins with a range of acid values can be used in the present invention in combination with hydrophobic and hydrophilic organosilicones and the particulate mixture to achieve the desired wettability switching.

Monomer water solubility of common monomers and octanol water coefficient values indicates that a combination of monomers is preferred with a balance of hydrophobicity and hydrophilicity to prepare polymers suited for the current invention.

Table 20: The values of octanol water coefficients for the monomers are taken from "Journal of Biomedical Materials Research" Volume 15, 787-793 (1981), S. Fujisawa and E. Masuhara (log Kow values for acrylic acid, methacrylic acid and t-butyl acrylate are from literature)

Monomer	**Water solubility (g/ 100 mL)**	**Octanol/ water coefficients at 20-25 °C (log Kow)**
t-BMA	0.05	2.01
MMA	1.72	0.73
BA	0.14	1.77
2-EHA	0.01	3.72
MAA	8.9	0.93
AA (Acrylic acid)	Miscible	0.46
n-BMA	0.3	2.29

t-BA	0.2	2.32
Styrene	0.03	2.76

Example 41: Paints prepared using the water-borne acrylic random copolymer dispersions of example 40 in combination with the functionalized pigments in accordance with the present invention and their exterior exposure data

Ten paints were prepared using the resins 40A, B, C, D, E and F to study permanency via showering, Atlas and QUV testing. The paint formulation is given in Table 21 below. The water, surfactants, defoamer, glycol, biocides, rheological additive are mixed on a high speed disperser for 15 minutes at 600 rpm, after which the pigments and extenders are added. Insitu treatment of the pigments and extenders was carried out during paint making using several different combinations of the hydrophobic and hydrophilic silicones. In these examples, only the hydrophobic organosilicone and a combination of a hydrophobic organosilicone at 2 levels and a hydrophilic organosilicone at 3 levels have been studied. The grinding stage is carried out at 2000 rpm for 20 minutes after which speed is reduced to 800 rpm and the binder is added followed by thickener and texanol. All paints showed a scrub resistance of > 500 cycles.

Paints were diluted at 20 to 40% by volume and 2 coats were brush applied over 1 coat of Asian Paints exterior primer after a gap of 4 hours.

Table 21

Paints	**A1**	**A2**	**A3**	**B2**	**C2**	**D2**	**E1**	**F1**	**F2**	**F3**
Water	19.28	15.68	17	16.265	18.04	17.19	22.52	27.23	23.23	18.23
Defoamer	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Thickener	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
pH adjustment	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Dispersing agent	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Wetting agent	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
In can preservative	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Rutile TiO2, 0.55 microns	18	18	18	18	18	18	18	18	18	18
Quartz (14 microns)	28.8	28.8	28.8	28.8	28.8	28.8	28.8	28.8	28.8	28.8
Hydrophilic organosilicone	0	4	9	4	4	4	0	0	4	9
Hydrophobic organosilicone	2.7	2.7	2.7	2.7	2.7	2.7	3	2.7	2.7	2.7
Polymer	26.87	26.87	26.87	26.285	24.51	25.26	23.734	18.82	18.82	18.82
Glycol	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Coalescent	1.5	1	1.5	1	1	1	1	1.5	1.5	1.5
Rozone 2000	1	1	1	1	1	1	1	1	1	1
Fluorosurfactant	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Acrysol sct 275	0.1	0.2	0.1	0.2	0.2	0.3	0.2	0.2	0.2	0.2
Total	100	100	106.72	100	100	100	100	100	100	100

After 6 months of exterior exposure, the Styrene acrylic based paints showed the maximum algal growth. Hence it is preferred to use a styrene free polymer. All the paints had a water contact angle of paint > 130° and the contact angle hysteresis for all the paints <10 degrees. (C2 is styrene based as is revealed from Table 19 above). Both the contact angle and CAH values were maintained even after QUV exposure of 2000 hours and the Atlas exposure. After continuous showering of 15 days and 24 hours drying period the contact angle of the paint when checked is maintained. The ΔE values of the coatings are < 2 even after 2000 hours indicating the coatings in accordance with this invention have excellent durability as well as retain the contact angle hysteresis values of < 10 degrees.

Table 22

Paint no.	Calculated average Octanol water partition coefficient of polymer (excluding perfluorinated monomer)	Water contact angle Initial	Water contact angle after 1100 hours QUV A (333 nm) exposure	**Contact angle after 2000 hours Atlas exposure**
A1	2.020	137.2	140.5	139.6
A2	2.020	132.9	140.5	138.33
A3	2.020	135.45	134.5	136.3
B2	2.072	134.76	135.6	142.13
C2	2.041	138.05	139.2	138.2
D2	1.926	133.56	137.5	139.4
E1	1.970	139.32	139.9	142.4
F1	2.002	140.5	136.4	135.2
F2	2.002	137.38	138.5	135.43
F3	2.002	134.6	136.5	139.36

Table 23

Paint set No.1	**QUVB 2000 hours exposure (313 nm)**				**Atlas 2000 hours exposure**				**Chalking after 2000 hours exposure**
	ΔE	YI	W I	C R	ΔE	YI	W I	C R	
A1	1.606	2.184	89.096	99.156	1.176	2.127	89.235	101.322	Low
A2	0.863	0.96	89.744	102.247	1.601	3.056	86.417	102.369	Low
A3	1.373	1.844	89.334	103.454	0.221	0.885	91.405	99.959	Low

B2	0.863	0.987	91.042	102.246	0.877	2.175	88.876	101.274	Medium
C2	1.562	3.455	88.188	103.719	1.009	3.354	88.87	101.832	Heavy
D2	1.101	1.475	89.921	102.76	0.538	1.682	90.03	100.643	Low
E1	1.495	1.653	89.315	103.932	0.684	1.699	89.915	101.317	Low
F1	1.818	2.102	88.89	104.755	0.854	2.26	90.082	101.448	Negligible
F2	1.317	1.538	89.865	103.494	1.718	2.953	87.737	103.752	Low
F3	1.499	2.606	88.024	103.593	0.652	1.753	89.827	101.106	Negligible

ΔE: Colour difference, YI: Yellowness index, WI: whiteness index, CR: Contrast ratio

The styrene based resin system C2 shows heavy chalking after Atlas, QUV exposure and the yellowness index is above 3 while for the styrene free systems, the yellowness index is below 3 and the extent of chalking was negligible.

Natural exterior exposure over a period of 6 months shows the following results:

Table 24

Paints	**Natural exposure Overall rating Microbial growth and DPUR out of 10**	**Red oxide cleaning test**	**Red oxide cleaning test (oven at 50 □)**
A1	Not checked	4	3
A2	8	5	7
A3	Not checked	7	8
B2	9	9	7.5
C2	7	3	3

D2	9	5	7.5
E1	10	4.5	3
F1	Not checked	4	4.5
F2	10	5	6.5
F3	Not checked	9	8

For the red oxide cleaning test, aqueous slurry of fine red oxide particles was applied onto the coatings and allowed to dry. a) After a period of 2 hours, the dried stain was washed off under running water. It is observed that the best cleanability and least residual stain are obtained for the systems containing a balance of both the silicones (hydrophobic and hydrophilic). For the styrene based system C2 above, poor cleanability was observed.

b) After application of the stain, the panels were kept in an air circulating oven at 50°C for a period of 4 hours. The stain was then washed off under running water. Similar observations were attained. With increasing hydrophilic silicone contents, lesser residual stains were attained. However when only the single hydrophobic silicone (A1, E1 and F1) was used, residual stains were more indicating an importance of the balance between the two. For the styrene based system, poor cleanability was observed.

Contact angles conducive to self cleaning and the wettability switching property have been shown to be maintained even after weathering with the present invention.

Example 42: Study of different contents of hydrophobic and hydrophilic organosilicones in paint formulation of example 41

Table 25

	A	**B**	**C**	**D**	**E**	**F**
Hydrophilic organosilicone (pbw in coating formulation)	5	4.5	4	3.5	3	2.5
Hydrophobic	1.5	2	2.5	3	3.5	4

organosilicone (pbw in coating formulation)						
Natural exposure rating (DPUR, whiteness) (higher the better)	9/10	5/10	5/10	4/10	2/10	2/10

According to the above data a balance of hydrophobic and hydrophilic organosilicones results in cleaner systems after a period of 90 days of exterior exposure emphasizing a balance of hydrophobicity and hydrophilicity.

Example 43: Paints prepared with different micron sized particles using the water-borne acrylic random copolymer dispersions with a low content of short chain fluorinated monomer in combination with the functionalized pigments and extenders in accordance with the present invention

Table 26

Monomers	1	2	3	4
MMA	47.5	41.25	11.5	42.25
BA	0	0	22	0
2-EHA	51.5	51.5	0	52
n-BMA	103.2	103.2	193.7	109.2
Styrene	0	0	0	0
t-BMA	25	31.25	0	31.25
MAA	10.3	10.3	10.3	10.3
Fluorinated monomer with 6 carbon atoms	12.5	12.5	12.5	5

Glycol ether	81.25	81.25	81.25	81.25
Azo initiator	1.49	1.49	1.49	1.49
Acid value (mg KOH/g)	27	27	27	27
% solid content in water (neutralized with Bisomer amine D700)	40	40.99	39.9	41.89

Low content of fluorinated monomers result into an economic benefit and short chain fluorinated monomers (up to C6 fluorinated carbons) are environmentally friendly. All the resins had a pH of 8 to 9.

MMA: methyl methacrylate, n-BMA: n-Butyl methacrylate, MAA: Glacial methacrylic acid, t-BMA: Tertiary butyl methacrylate, BA: Butyl acrylate, 2-EHA: 2-ethylhexyl acrylate, Bisomer amine D700 form Cognis

Table 27

Paints	**A**	**B**	**C**	**D**	**E**	**F**
Water	18.39	21.8	21.725	20.725	21.8	21.8
Defoamer	0.1	0.1	0.1	0.1	0.1	0.1
Thickener	0.4	0.3	0.3	0.3	0.3	0.3
pH adjustment	0.05	0.05	0.05	0.05	0.05	0.05
Dispersing agent	1	1	1	1	1	1
Wetting agent	0.2	0.2	0.2	0.2	0.2	0.2
Fungicide	0.2	0	0	0	0	0
Incan preservative	0.2	0.2	0.2	0.2	0.2	0.2
TiO2 Rutile, particle size 0.32 microns	25	0	23	24	0	0
TiO2 Rutile, particle size 0.55 microns	0	18	0	0	18	18

Quartz, 14 microns	0	28.8	26	26	0	28.8
Quartz, 40 microns	27	0	0	0	28.8	0
Hydrophilic organosilicone	4	4	4	4	4	4
Hydrophobic organosilicone	2.5	2.5	2.5	2.5	2.5	2.5
Dispersion polymer	16.91	19	16.875	16.875	19	19
Glycol	1	1	1	1	1	1
Coalescent	1	1	1	1	1	1
Algaecide	2	2	2	2	2	2
Fluorosurfactant	0.05	0.05	0.05	0.05	0.05	0.05
Results	5/10	9/10	9/10	7/10	5/10	8/10

Paint 43-A shows dirt streak marks after a 12 month exterior exposure while the others do not show any dirt streaks, lines or water spots. This shows the importance of the particle size of the fillers and extenders added. Quartz used in 43A has a d50 particles size of 40 microns (size range of 1 to 160 microns). Thus it is preferred to have a coating with plurality of particles with particles having a size less than d50 of 40 microns to avoid dirt streak lines.

Example 44: Emulsions/ latex polymers prepared using the preferred monomer backbone in accordance with the present invention and their paint data

Sample latex with the preferred monomers was prepared as shown in the following table. A combination of polymerizable surfactants (ADEKA SR10, Ether sulfate with 100% solids and ER40, nonionic, 60% solids) was used to prepare the latex. It was found that using the above latex the paints showed a CAH of >20 degrees (refer example 55) even though the paint formulas were same as that used above and the monomer combination of the latex was the same. Therefore the latex polymer of example 44 for a given coating formulation alone does not reduce the value of CAH below 20 degrees and it is preferred to have a dispersion polymer in the formulation either alone or in combination with the latex polymer.

Table 28

Kettle charge	Ingredients (pbw)
DMW (demineralized water)	60
Reasop SR-10	1.511
Reasoap ER-40	0.457
DMW	140
Reasop SR-10	3.976
Reasoap ER-40	1.579
MMA	36.47
2-EHA	35.31
n-BMA	88.65
t-BMA	19.4
MAA	4.46
Fluorinated monomer with 6 carbon atoms	9.7
Initial Potassium persulfate	0.033
DMW	8
Sodium bicarbonate	0.05
DMW	7.5
Continuous Potassium persulfate	0.303
DMW	80
	497.399

The properties of the latex prepared at 75 to 80. are as follows: 40% solids, Acid value = 15 mg KOH/g, pH=9.35, median particle size = 106.8 nm, surface energy = 29.9 mN/m

Example 45: Paints prepared with respirable crystalline silica free extenders using the water-borne acrylic random copolymer dispersions of example 43 (2) in combination with the functionalized pigments in accordance with the present invention and their exterior exposure data

Table 29

Ingredients	**1**	**2**	**3**	**4**	**5**
WATER	21.525	21.6	21.4	22.025	21.525
Defoamer	0.1	0.1	0.1	0.1	0.1
Thickener	0.3	0.3	0.3	0.3	0.3
pH Adjustment	0.05	0.05	0.05	0.05	0.05
Dispersing agent	0.5	0.5	0.5	0.5	0.5
Wetting agent	0.8	0.8	0.8	0.8	0.8
Glycol	0.5	0.5	0.5	0.5	0.5
In can preservative	0.1	0.1	0.1	0.1	0.1
Rocima 350	0	1	0	0	0
Encapsulated algaecide	0	0	1	0	0
Algaecide	2.5	1.5	1.5	1.5	2.5
TIO_2 Rutile, 0.32 microns	23	23	23	23	23
40% solid dispersion of nano Titania	0	0	0	0.5	0
Calcium carbonate, 20 microns	26	28	26	0	0
Calcium carbonate 325 mesh	0	0	0	26	26
Hydrophilic organosilicone	4	4	4	4	4
Hydrophobic organosilicone	2.5	2.5	2.5	2.5	2.5
Antifungal agent	0.2	0	0.2	0.2	0.2
Fluorosurfactant	0.05	0.05	0.05	0.05	0.05
Coalescent	1	1	1	1	1

Dispersion Polymer, example 43 (2)	16.875	15	16.875	16.875	16.875
Total	100	100	100	100	100
Rating after natural exposure of 180 days in terms of dirt pickup resistance, resistance to water marks, streak marks, and anti microbial performance (higher the better)	9/10	9/10	9/10	8/10	7/10

Two coats of the above paints with 25% dilution were brush applied over a concrete wall over which one coat of Asian Paints exterior primer was applied. The paints 1, 2 and 3 had excellent appearance over a period of 180 days of exterior exposure. According to the above formulas, the coatings where calcium carbonate 325 mesh (44 microns) is used the coating shows some streak marks. This is reduced where nano TiO2 is used in the coating of formula 4 as compared to the coating of formula 5. Further the coatings do not show any significant chalking. Conventionally, only inorganic polymers/ binders are used to prepare paints with photocatalytic activity since organic binders undergo degradation. However, we have observed over a period of 180 days in the field exposure that the patch does not show significant chalking (removal of surface layer due to degradation of binder). This may be occurring in our system due to the combined presence of organic and inorganic binders and also a high particles (non degradable) to binder ratio. Further the particles may be covered with/ treated with hydrophobic and hydrophilic organosilicones during paint making or film formation which may modify their photocatalytic activity. The paints 4 and 5 were subject to QUV B (313 nm) accelerated tests for a period of 45 days. Both the paints showed negligible chalking, CAH < 10° and the desired wettability switching property after 45 days exposure in QUV B. Further, the paint containing nano TiO_2 (paint 4), showed improved color retention and better durability than (paint 5).

As shown in Figure 11, the paint 1 given in Table 29 (1) when exposed outdoors for a period of 6 months on a vertical surface shows excellent resistance to dirt streaks and water marks (left side of figure: paint according to current invention, right side of figure: commercial self cleaning paint).

Example 46: Microbiology data of the paints prepared using the water-borne acrylic random copolymer dispersions in combination with the functionalized pigments in accordance with the present invention

Various encapsulated and free biocides were evaluated with paints according to the invention such as Rocima 344, Rocima 350, Rozone 2000 alone and in combination with different chemistries. Paints in accordance with the present invention, show excellent anti algal properties in accelerated algal chamber testing, showing a rating of at least 8 to 9 out of 10 after 30 days testing. Further the coatings also show excellent anti fungal and anti bacterial properties after accelerated testing.

Example 47: Photocatalytic activity of the paints 4 and 5 of example 45 prepared using the water-borne acrylic random copolymer dispersions in combination with the functionalized pigments in accordance with the present invention

The paints 4 and 5 were subject to the methylene blue discoloration test. They were brush applied on a fiber cement board panel (6 inch x 3 inch). The coating was dried under ambient conditions for 7 days.

The photoactivity of the paints was determined by determining the photocatalytic decolorization of a methylene blue solution by UV-vis measurements. The peak of methylene blue was monitored at 664 nm.

30% of the panels were dipped in a 100 μL aqueous solution of methylene blue in a 500 mL glass beaker. The entire setup was irradiated with UV light from 2 tubes of wavelength 254 nm and 365 nm. The decolourization of the methylene blue dye was quantified on a UV-2450, Shimadzu UV-vis spectrophotometer. The table below shows the concentration of methylene blue in the solution after 4 hours and 8 hours of exposure showing paint 4 with 0.2% nano titania having a higher photocatalytic activity than paint 5.

Table 30: showing the concentration of methylene blue in solution after 4 h and 8 h of UV exposure

	Paint 4	**Paint 5**
After 4 hours	0.706	0.773
After 8 hours	0.4699	0.5053

Bird droppings: Fresh liquid bird droppings were spread with a spatula on 6 inch x 3 inch panels of both the paints. These were kept under natural exterior exposure and monitored over a period of 30 days. It was observed that due to a combined effect of sunlight and rain, the paint 4 showed a lower residual stain of bird droppings as compared to paint 5. In addition the panel appeared cleaner and whiter. For comparison a non stimuli responsive paint (commercially available) which exhibits a contact angles <90 degrees and shows hydrophilicity when water is poured on its surface was also subject to the liquid bird droppings. This showed the highest residual stain of bird droppings, with the white paint becoming yellowish in the spot where the dropping was deposited. Thus paints according to this invention show improved resistance to organic deposits such as bird droppings.

Examples 48: Photocatalytic activity of the paints prepared using the water-borne acrylic random copolymer dispersions in combination with the functionalized pigments in accordance with the present invention

The coating was brush applied over Asian Paints exterior primer applied on a fibre cement board panel (6 inch x 3 inch). The coating was dried under ambient conditions for 7 days at room temperature (25 to 30 °C) and a relative humidity of 50 to 60%.

The photoactivity of the paints was determined by determining the photocatalytic decolorization of a methylene blue solution by UV-vis measurements. The peak of methylene blue was monitored at 664 nm.

30% of the panels were dipped in a 100 microliter aqueous solution of methylene blue in a 500 mL glass beaker. The entire setup was irradiated with UV light with a wavelength of 365 nm. The decolorization of the methylene blue dye was quantified on a UV-2450, Shimadzu UV-vis spectrophotometer.

Six paints containing 3 levels of nano TiO_2 (0, 0.5 and 1% Evonik P25) with (sc 1, 2, and 3) and without (sc 4, 5, 6) the hydrophilic and hydrophobic organosilicones were also exposed to accelerated QUV A (333 nm) chamber testing for a period of 450 hours.

Table 31

	SC-1	**SC-2**	**SC-3**	**SC-4**	**SC-5**	**SC-6**	**Sc 7**	**Sc 8**
Raw Material	**PBW**	**PBW**	**PBW**	**PBW**	**PBW**	**PBW**	**PBW**	**PBW**

Water	18.825	18.825	18.825	18.825	18.825	18.825	18.825	18.825
Defoamer	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Thickener	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
pH Adjustment	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Dispersing agent	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Wetting agent	1	1	1	1	1	1	1	1
Glycol	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
In can preservative	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Algaecide	1.5	1.5	1.5	1.5	1.5	1.5	0	0
TIO_2 Rutile, 0.405 microns	23	23	23	23	23	23	23	23
Calcium carbonate, 20 microns	26	26	26	26	26	26	26	26
Hydrophilic organosilicone	4	4	4	0	0	0	**8**	**8**
Hydrophobic organosilicone	2.5	2.5	2.5	0	0	0	**0**	**0**
Nano Titania	0	0.5	1	0	0.5	1	0	0
Antifungal agent	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Fluorosurfactant	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Coalescent	1	1	1	1	1	1	1	1
Dispersion Polymer, example 43 (2)	19.375	19.375	19.375	19.375	19.375	19.375	**19.375**	**16.25**
Total	99	99.5	100	92.5	93	93.5	98.8	95.675

Table 32

Coating	**Nano Titania**	**Organo Silicones**	**l**	**a**	**b**	**de**
sc 1 (time 0)	0%	Yes	96.671	-0.822	1.286	
after 450 hours			95.317	-0.804	3.967	3.003
sc 2 (time 0)	0.5%	Yes	96.982	-0.822	1.373	
after 450 hours			96.138	-0.845	2.676	1.557
sc 3 (time 0)	1%	Yes	96.899	-0.772	1.266	
after 450 hours			95.149	-0.617	4.061	3.301
sc 4 (time 0)	0%	No	96.399	-0.906	1.428	
after 450 hours			95.564	-0.97	3.207	1.966
sc 5 (time 0)	0.5%	No	96.544	-0.884	1.551	
after 450 hours			96.018	-0.82	2.188	0.829
sc 6 (time 0)	1%	No	96.639	-0.889	1.602	
after 450 hours			95.887	-0.879	2.801	1.416

For all the paints there was negligible chalking indicating the binder was not getting affected. The DE value of 0.5% nTiO2 is lower for both the cases indicating enhanced durability with a low dosage of nano Titania. The DE value is higher with silicones which may be due to the enhancement of photocatalytic activity caused by the presence of organosilicones.

Example 49: Enhancement of photocatalytic activity with oragnosilicones (both hydrophilic and hydrophobic):

2 sets of paints were prepared each with 0%, 0.5% and 1% n TiO2 (p 25 from Evonik). One set contains 2 organosilicones (sc1, 2 and 3) whereas the other is without organosilicones (sc4, sc5, sc6) as shown in Table 31.

30% of the panels were dipped in a 100 microliter aqueous solution of methylene blue in a 500 mL glass beaker. The entire setup was irradiated with UV light with a wavelength of 365 nm. The decolorization of the methylene blue dye was quantified on a UV-2450, Shimadzu UV-vis spectrophotometer.

Simultaneously a control sample of methylene blue (without paint panel) was also exposed under UV for 8 hours. The table shows the reduction in the concentration of methylene blue after the test as measured by the UV visible spectrophotometer. All the 6 paints contained Rutile TiO_2 (0.405 microns particle size) R902 plus.

Table 33

	with organosilicones						
	Nano TiO_2 content in paint	initial reading	After 4 hours	% reduction	After 8 hours	% reduction	Total % reduction
Sc1	0%	0.15	0.12	20	0.098	18.33	34.67
Sc2	0.5%	0.15	0.09	40	0.044	51.11	70.67
Sc3	1%	0.15	0.08	46.7	0.036	55	76
	without organosilicones						
	Nano TiO_2 content in paint	initial reading	After 4 hours	% reduction	After 8 hours	% reduction	Total % reduction
	Control	0.156	0.128	17.95	0.12	6.25	23
Sc4	0%	0.156	0.111	28.85	0.099	10.81	36.54
Sc5	0.5%	0.156	0.108	30.77	0.097	10.19	37.82

Sc6	1%	0.156	0.103	33.94	0.089	13.6	42.95

The control sample shows that methylene blue is itself undergoing some degradation under UV (365 nm) i.e. (about 23% in 8 hours). Both paints Sc1 and sc4 with 0% nano TiO_2 show comparable degradation under UV (~35% in 8 hours), with sc4 showing a marginally higher value due to the presence of organosilicones. This may be due to the photocatalytic activity conferred by rutile TiO_2, DuPont R902 plus. In the paints sc2 to sc 6, increasing nano Titania is enhancing the activity and paints containing a combination of organosilicones is enhancing the degradation of methylene blue and hence the photocatalytic activity. With 0.5% nano TiO_2 increase in activity between without and with silicones is 87% whereas with 1% nano TiO2 the enhancement is 77%. The total degradation of methylene blue is 70.67% in 8 hours for sc2 which has a combination of organosilicones while it is 37.82% for sc5 which does not have the organosilicones. Single silicones (only hydrophobic or hydrophilic) may also be used to enhance the photocatalytic activity. However, according to the present invention a combination of hydrophobic and hydrophilic organosilicones/silanes is preferred.

Example 50

Paint without nano Titania using an alternate grade of rutile TiO_2

Table 34

Paint	initial reading	After 4 hours	% reduction	After 8 hours	% reduction	Total % reduction
Control	0.159	0.125	21	0.114	8.8	28.3
with silicones.	0.159	0.071	55	0.025	64.79	84.2
w/o silicones	0.159	0.097	39	0.038	59.79	76.1

Paint formulations are the same as shown in example 48. Organosilicone treatment according to the present invention is creating an enhancement of the photocatalytic activity of Rutile TiO_2 R931 from DuPont (particle size = 0.55 microns) by 10.64%.

Example 51: Photocatalytic activity of the coating under diffused sunlight

30% of the paint panels (6 inch x 3 inch) (sc1 to sc6 shown in Table 31) were immersed overnight in a 1000 microliter solution of methylene blue. Subsequently they were kept indoors away from the windows, receiving only diffused sunlight for a period of 7 days at room temperature (25 to 30 °C) and a relative humidity of 50 to 60%. The DE values of the stains were measured as shown in Table 37.

It was visually observed that the paints containing organosilicones (sc1, 2 and 3) stained less to start with compared with paints sc4, 5 and 6 which did not contain any organosilicones. Even after 48 hours in dispersed sunlight the stains of the paints sc1, 2 and 3 began to discolour at a faster rate than sc4, 5 and 6.

Table 35

	Time	**l**	**a**	**b**	**de**
sc 1	X (time zero)	96.671	-0.822	1.286	
	After 16 immersion in 1000 microliter MB solution (Y)	94.445	-4.976	-3.206	**6.615**
	After 7 days exposure to diffused sunlight (Z)	96.573	-0.988	1.391	**0.435**
sc 2	X	96.982	-0.822	1.373	
	Y	94.784	-5.336	-3.283	**6.847**
	Z	96.669	-0.945	1.428	**0.341**
sc 3	X	96.899	-0.772	1.266	
	Y	95.995	-3.195	-1.3	**3.643**
	Z	96.604	-0.913	1.525	**0.417**
sc 4	X	96.399	-0.906	1.428	
	Y	92.831	-8.08	-5.325	**10.479**
	Z	95.785	-1.326	1.179	**0.784**
sc 5	X	96.544	-0.884	1.551	
	Y	91.437	-10.257	-7.428	**13.952**
	Z	95.774	-1.507	1.063	**1.111**
sc 6	X	96.639	-0.889	1.602	
	Y	91.138	-10.134	-7.585	**14.147**
	Z	95.631	-1.48	1.105	**1.27**

Example 52: Rust resistance of the paints prepared according to the current invention

Different paints were prepared with 0, 0.5% and 3% nano Titania (p25 from Evonik). All the paints had the composition according to the present invention. These paints were applied on a vertical surface over an exterior primer immediately below a rusted iron bar. Observations were made over a period of 15 and 30 days during the monsoon season. For comparison 2 non stimuli responsive paints (one commercially available and one experimental, not in accordance with present invention) were applied which exhibit contact angles <90 degrees and show hydrophilicity when water is poured on their surface.

Table 36

Coating	Nano Titania	Rust marks after 15 days	Rust coverage on surface after 30 days
1	0%	No	<5%
2	0.50%	No	<10%
3	3%	No	<20%
4	0%	Yes	30-40%
5	0%	Yes	30-40%

After 15 days, the rust marks/ lines were visible only on coating 4 and 5. Coating 1, 2 and 3 show good water repellency which indicates that the water containing rust would roll off from the surface. The coatings according to the present invention have a reduced tendency of spreading of rust marks thereby leading to coatings which can maintain their aesthetic appeal for a longer time. Increased contents of nano Titania are leading to increased hydrophilicity and hence the coatings are showing increased spreading of the rust stains. The 2 non stimuli responsive hydrophilic paints taken for comparison (paint 4 and 5 in Table 36) showed inferior performance. Thus, a disadvantage of only hydrophilic surfaces is that corrosion/ rust stains tend to spread over large areas leading to loss of the aesthetic appeal of the surface. Hence it is desired to have a reversible switchable surface in accordance with the present invention.

Example 53: Paint film Water absorption

Table 37

Coating	% water absorption after 96 hours immersion in water
SC 4 (Table 31)	7.15%
SC 1 (Table 31)	3.60%

Example 54: Surface energy measurements of coating according to the invention after 7 days drying under ambient conditions (30 °C and a relative humidity of 50-60%).

Table 38

Paint	**Details**	**surface energy (mN/m)**	**Water contact angle**		**Average water contact angle**	**Diodomethane contact angle**
sc1	0% nTiO2 with silicones	11.2	118.6	119.5	119.05	93.4
sc2	0.5%nTiO2 with silicones	11.5	118.4	119.1	118.75	92.3
sc3	1% nTiO2 with silicones	15.6	105.2	105.2	105.2	87.9
sc4	0% nTiO2 w/o silicones	9.6	126.8	127.4	127.1	100
sc5	0.5%nTiO2 w/o silicones	9.8	121.6	122.9	122.25	98.5
sc6	1% nTiO2 w/o silicones	13.8	124.6	126.8	125.7	88.2
sc1	with 3% nano TiO2 with silicones	8.5	121.8	121	121.4	100.5
Paint with 1% fluorinated binder	0% nTiO2 with silicones	10.8	113.5	115.7	114.6	95.9
Paint with Non fluorinated binder	0% nTiO2 with silicones	12	110	113.3	111.65	94.1
Paint with Emulsion 25	0% nTiO2 with silicones	11.7	115.1	115.5	115.3	92.5
Paint with Emulsion 44	0% nTiO2 with silicones	11.8	113.8	111.3	112.55	93.9
Paint with only hydrophilic silicone	sc7 (Table 31)	13.9	130	129.5	129.75	104.6
Paint with only hydrophilic silicone	sc 8 (Table 31)	6.5	127.7	130.5	129.1	107.3
Paints with treated particles**	With DuPont R105 and Aerosil R972	23.8	100.6	101.5	101.05	70.4

**Binder used is example 43 (1).

1- prepared 15%solution of R972 in IPA.

2- 60% solution of R105 in IPA.

3- added 1 part of R972 solution to 5 parts of R105 solution

4- mixed the above solution with binder in 1:2 ratios, i.e., 1 part of above solution to 2 parts of polymer dispersion

The paint formulas of sc1 to sc6 are given in Table 31.

Example 55: Contact angle hysteresis measurements of coating according to the present invention for the paints of example 54

The contact angle hysteresis is measured as the difference between advancing angle a1 and r1. Advancing angle for 10, 20 and 30 µL is measured (a1, a2 and a3 respectively) and receding angle is measured for 20 and 10 µL (r2 and r1 respectively). All measurements were carried out at 30 deg C. For the hydrophobic and hydrophilic organosilicones, their clear coats are applied on aerated cement blocks and the average value of CAH is taken as shown in Table 39.

Table 39

Contact angle hysteresis measured by dynamic sessile drop method

	Advancing angle a1	Receding angle r1	CAH 1	Advancing angle a2	Receding angle r2	CAH 2	Average CAH
sc 1	118.5	98.5	**20**	113.1	108.9	**4.2**	**12.1**
sc 2	123.5	97.9	**25.6**	122.7	118	**4.7**	**15.15**
sc 3	106.5	81.3	**25.2**	100	93.6	**6.4**	**15.8**
sc 4	119.1	107.2	**11.9**	119.9	116.1	**3.8**	**7.85**
sc 5	121.2	97.6	**23.6**	117.1	114.3	**2.8**	**13.2**
sc 6	121	97.5	**23.5**	116.4	109.2	**7.2**	**15.35**
Paint (of example 54) with 1% fluorinated binder	107.3	87.3	**20**	107.8	100.5	**7.3**	**13.65**
Paint with Non fluorinated binder	113.9	86.3	**27.6**	106.1	97	**9.1**	**18.35**
Paint with only hydrophilic silicone - (sc 7, Table 31)	129.4	115.3	**14.1**	127.3	125.3	**2**	**8.05**

Paint with only hydrophilic silicone (sc8, Table 31)	126.8	115.3	**11.5**	127.3	124.4	**2.9**	**7.2**
Paints with treated particles **	100.3	78.8	**21.5**	113.1	108.9	**4.2**	**12.85**
Hydro-phobic organo-silicone applied on aerated cement block	129.3	117.3	**12**	130.5	126.4	**4.1**	**8.05**
Hydrophilic organo-silicone applied on aerated cement block	122	102.9	**19.1**	124.5	118.7	**5.8**	**12.45**
Paint with Emulsion 25	122.6	95	**27.6**	109.7	104.7	5	13.5
Paint with Emulsion 44	118.1	94.2	**22**	112.3	107.3	**5**	**16.3**

Example 56: Paints prepared with different contents of wetting and dispersing agents showing the effect on accelerated storage stability (30 days at 55 C) in accordance with the present invention with varying contents of glycol

Table 40

Experiments with 1% Glycol					
	PBW	PBW	PBW	PBW	PBW
Mill base - 1	75.625	75.625	75.625	75.625	75.625

Polyoxyethylene (9) C12-C15 alcohol (HLB =13)		0.5	1	0.5	1
Anionic Dispersing agent		0.5	1	1	0.5
Hydrophilic organosilicones	4	4	4	4	4
Hydrophobic organosilicone	2.5	2.5	2.5	2.5	2.5
Polymeric Dispersion of example 43 (2)	16.875	16.875	16.875	16.875	16.875
Total	99	100	101	100.5	100.5
Initial Stormer Viscosity	Results	1060g	110g	300	180 g
Viscosity in 15 days		Gelled in 7days	510g	Gelled in 7days	520 g
Viscosity in 30days		Discontinued	Above 1000g	Discontinued	850 g
Experiments with 0.5% Glycol					
Mill base - 2		75.625	75.625	75.625	75.625
Polyoxyethylene (9) C12-C15 alcohol (HLB =13)		0.5	1	0.5	1

Anionic Dispersing agent		0.5	1	1	0.5
Hydrophilic organosilicones		4	4	4	4
Hydrophobic organosilicone		2.5	2.5	2.5	2.5
Polymeric Dispersion of example 43 (2)		16.875	16.875	16.875	16.875
		100	101	100.5	100.5
Initial Stormer Viscosity	Results	353	235	365	225 g
Viscosity in 15 days		Gelled in 7days	900	Gelled in 7days	650 g
Viscosity in 30days		Discontinued	Above 1090 g	Discontinued	925 g

The above data shows that a balance of the wetting agent (in this study Polyoxyethylene (9) C12-C15 alcohol (HLB =13) and the anionic dispersing agent are important to achieve accelerated storage stability (30 days at 55 deg C). This test indicates the shelf life of the paint; hence it is important to add suitable quantities of wetting and dispersing agents along with glycols to achieve storage stability.

Conventional paint systems based on latex polymers do not show such an observation of viscosity pickup on increase of dispersing agent. This was also the case when the emulsion of example 25 or example 44 was used in the paint formula; no viscosity pickup was observed on increase of the dispersing agent.

Hence according to the present invention it is also important to have a balance between the wetting agent and the dispersing agent in order to obtain a suitable shelf life and paint stability at 55□ for 30 days.

It is thus possible by way of the present advancement to provide for said aqueous coating composition that is oleophobic and has a water contact angle hysteresis of < 25° under certain environmental conditions with variations in at least one or more of temperature, humidity, pH, light which is reversibly switchable to a water contact angle hysteresis of >25° under said environmental conditions offering benefits of both superhydrophobic and superhydrophilic cleaning, good organic and inorganic dirt pickup resistance, resistance to dirt streaks, dirt lines, water spotting, water marks, good cleanability with water and forced air or wind, reduced chalking, good resistance to organic dirt and deposits such as bird droppings and oily stains, and reduced tendency for spreading of water containing rust with the additional benefits of better binding, durability .

We Claim:

1. Aqueous coating composition exhibiting reversible hydrophilic-hydrophobic switching under variable environmental conditions including variations in at least one or more of temperature, pH, humidity or other external stimuli including light comprising:
a) One or more oligomeric or polymeric dispersion/binder comprising acrylic, fluorinated and hydrophilic (acid/amine/ionic/non-ionic) backbone;
b) One or more hydrophobic organosilicone or silane (monomeric, oligomeric or polymeric);
c) One or more hydrophilic organosilicone or silane (monomeric, oligomeric or polymeric); and
d) At least partially surface treated particles with a mean particle size less than or equal to 100 microns, preferably less than or equal to 325 mesh (44 microns)
to selectively provide a balance of hydrophobicity and hydrophilicity such as to provide desired reversible hydrophilic-hydrophobic switching.

2. Aqueous coating composition as claimed in claim 1 that is oleophobic and has a water contact angle hysteresis of <25° under certain environmental conditions with variations in at least one or more of temperature, humidity, pH, light which is reversibly switchable to a water contact angle hysteresis of >25° under said environmental conditions offering benefits of both superhydrophobic and superhydrophilic cleaning, good organic and inorganic dirt pickup resistance, resistance to dirt streaks, dirt lines, water spotting, water marks, good cleanability with water and forced air or wind, reduced chalking, good resistance to organic dirt and deposits such as bird droppings and oily stains, and reduced tendency for spreading of water containing rust.

3. Aqueous coating composition as claimed in anyone of claims 1 or 2 that reversibly switches from superhydrophobic (contact angle hysteresis <25° and water droplet rolling effect) to superhydrophilic (contact angle hysteresis >25° and complete wetting) for at least 2000 hours of accelerated exterior exposure (Atlas and QUV testing), preferably the contact angle hysteresis values are <20°, more preferably <10° and most preferably <5° in one state and higher in the switched state for a deposited 0.02 mL water droplet, wherein preferably the contact angle exhibited in one state is $>100^\circ$ with water, more preferably $>120^\circ$, even more preferably superhydrophobic having contact angle >150° and contact angle <90° in the switched state for a deposited 0.02 mL droplet; and wherein said

switching takes place within a varying period of time from a few seconds to several minutes dependent on a particular stimuli.

4. Aqueous coating composition as claimed in anyone of the preceding claims having low surface energy of <40 mN/m and preferably <20 mN/m and most preferably <10 mN/m even with the second coat and hence recoatable to enhance film build-up to attain desired opacity/ translucency/ hiding/ whiteness.

5. Aqueous coating composition as claimed in anyone of the preceding claims comprising at least one or more wetting and dispersing agents, encapsulated or free antimicrobial agents selected from fungicide, algaecide, in-can preservative and optionally involving, one or more nanoparticles exhibiting photocatalytic activity

6. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprises dispersion polymers involving primary or secondary dispersion in water or in a water/ co-solvent mixture with or without emulsion/latex polymers.

7. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprises dispersion polymers with or without emulsion/ latex polymers that is preferably styrene free and is a free radical polymerization or controlled radical polymerization product of hydrophobic monomers C1-C8 straight, branched or cyclic esters of methacrylic acid/ acrylic acid selected from methyl methacrylate, ethyl methacrylate, butyl Methacrylate, isobutyl Methacrylate, tertiary butyl methacrylate, isobornyl methacrylate, 2-ethylhexyl methacrylate and various isomers and their corresponding acrylates also involving >C8 esters of methacrylic acid/ acrylic acid selected from lauryl acrylate, stearyl acrylate.

8. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprises dispersion polymers with or without emulsion/ latex polymers and has monomers selected such that the resulting polymer has an average octanol-water partition coefficient (log Kow) greater than 0.6, preferably greater than 1.5 and more preferably greater than 2.

9. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion including dispersion polymers with or without emulsion/ latex polymers in being styrene free involves styrene or alkylstyrene group as part of the polymer or as a part of additives including opacifiers in less than 15% of the film forming composition favouring reduced chalking of said composition on UV exposure.

10. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprising dispersion polymers and emulsion/ latex polymers is in the ratio range of dispersion to emulsion polymers of 95:5 to 5:95.

11. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprising dispersion polymers and emulsion/ latex polymers is preferably in the ratio range of 30:70.

12. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprising dispersion polymers includes primary or secondary dispersion in water or in a water/ co-solvent mixture involves co-solvent that is VOC exempt under Green Seal standard GS-11 with resulting coating VOC's in the range of 1 to 100 grams/liter.

13. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprising dispersion polymers with or without emulsion/ latex polymers includes polymers selected from natural polymer, a neoprene polymer, a nitrile polymer, a vinyl acrylic polymer, acrylic polymer; styrene acrylic polymer, styrene butadiene polymer, copolymer of vinyl acetate and butyl acrylate or veova monomers or ethylene/ propylene/ butylene, butadiene, isoprene involving crosslinkers selected from diacrylates, triacrylates, multifunctional acrylates, silane functional monomers, acetoacetate functional monomers, monomers with aziridine, hydrazine, carbodiimide or allylic functionality.

14. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprising dispersion polymers with or without emulsion/ latex polymers includes polymers of fluorinated monomers comprising 2 to 20 carbon atoms and polymeric fluorine content in the range of 0.1 to 50% on monomer solids and preferably in

the range of less than 5% on monomer solids resulting in economic benefits and a surface energy of <50 mN/m ,preferably <30 mN/m and more preferably <20 mN/m

15. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprising fluorinated backbone comprises fluorinated monomers including esters of acrylic or methacrylic acid with a linear or branched perfluoroalkyl functional group preferably involving 1-6 fluorinated carbons selected from trifluoroethyl meth(acrylate), pentafluoropropyl meth(acrylate), heptafluorobutyl meth(acrylate).

16. Aqueous coating composition as claimed in anyone of the preceding claims wherein said ionic or ionizable or non-ionic hydrophilic monomers are present within the range of 2 to 20% of polymer solids thus favoring reduction of water absorption of said composition to less than 15%, preferably less than 10% and even more preferably less than 5% after remaining immersed in water for 96 hours.

17. Aqueous coating composition as claimed in anyone of the preceding claims wherein said ionic or ionizable or non-ionic hydrophilic monomers are selected from acrylic acid, methacrylic acid and their aklali metal or quaternary ammonium ion salts; monoolefinic sulphonic acid compounds and their alkali metal salts including 2-acrylamido-2-methylpropanesulphonic acid; acrylates or methacrylates of aminoalcohols, acrylamides selected from N,N-dimethylaminopropylacrylamide or N, N-Dimethylaminoethylmethacrylate, polyalkylene oxide group containing monomers or a polymeric chain prepared by polymerizing a polyalkylene glycol (meth)acrylate, hydroxyl alkyl (ethyl, propyl or butyl) (meth)acrylates, wherein the hydrophilic component comprises at least one oxygen, sulfur, phosphorus and/or nitrogen atom.

18. An aqueous coating composition as claimed in anyone of the preceding claims wherein said acrylic, fluorinated and amine backbone or acrylic, fluorinated and acid backbone of the primary or secondary polymeric dispersion comprises sufficient content of acid or amine monomer including ionic or non-ionic external surfactants adapted for acid or amine value in the range 5 to 100 mg KOH/g.

19. Aqueous coating composition as claimed in anyone of the preceding claims wherein said particles comprising either micron sized particles or including particulate mixture of both

micron sized and nano sized particles and polymeric dispersion are present in selective ratios of 0.9 to 2.5 wherein higher ratios closer to 2 is preferred for a two coat application.

20. Aqueous coating composition as claimed in anyone of the preceding claims wherein said particles comprise either micron sized particles or includes particulate mixture of both micron sized and nano sized particles, and including particulate pigments wherein the pigment volume concentration (PVC) is in the range of about 40 to 90 % and preferably in the range of 60 to 80% for the coating and preferably the coating PVC is lower than the practical critical pigment volume concentration (CPVC).

21. An aqueous coating composition as claimed in anyone of the preceding claims wherein said particles comprising either micron sized particles or including particulate mixture of both micron sized and nano sized particles comprises micronized and nanosized particles present in selective ratios of 3.5 to 8 with ratios closer to 8 being preferred for a two coat application.

22. Aqueous coating composition as claimed in anyone of the preceding claims wherein said at least partially surface treated particles involve organic and/or inorganic particles having size ranging from 1 nm -100 microns includes surface treated nanometer sized organic and/or inorganic particles have size ranging from about 1 nm to 300 nm, and wherein said particles preferably has mean particle size less than 325 mesh (44 microns) and even more preferably less than 40 microns.

23. Aqueous coating composition as claimed in anyone of the preceding claims wherein the mass ratio of said hydrophobic organosilicone to hydrophilic organosilicone is in the range 10/90 to 60/40.

24. Aqueous coating composition as claimed in anyone of the preceding claims wherein said hydrophilic organosilicone/silane having a contact angle hysteresis of >10 degrees based on the average of readings for 10 and 20 μL of water when applied on an aerated cement block is present in the range of 10% to 90% by weight of dispersion solids in said composition.

25. Aqueous coating composition as claimed in anyone of the preceding claims wherein said hydrophobic organosilicone/silane having a contact angle hysteresis of <10 degrees based on the average of readings for 10 and 20 μL of water when applied on an aerated cement

block is present in the range of 5% to 80% by weight of dispersion solids in said composition.

26. Aqueous coating composition as claimed in anyone of the preceding claims wherein said hydrophobic and hydrophilic organosilicone content present as a part of the continuous phase in said composition is 10-90 % of the weight of the dispersion/binder.

27. Aqueous coating composition as claimed in anyone of the preceding claims wherein said wetting agent and dispersing agent is balanced by having said dispersing agent upto 1% and preferably in the range of 0.1 to 0.5% and the wetting agent upto 2% and preferably in the range of 0.2 to 1% by weight in said composition favouring accelerated storage stability for atleast 30 days at 55°C and a composition that passes at least 5 cycles of freeze thaw stability test (-15°C to 30°C).

28. Aqueous coating composition as claimed in anyone of the preceding claims including photocatalytically active agents comprising one or more nano particles exhibiting photocatalytic properties in amounts less than 1% and preferably less than 0.5% of total formulation especially for coatings containing particles more than or equal to 325 mesh, preferably comprise nano titania of the anatase or rutile grade in the range of 0.1 to 1% of the formulation with a particle size of 1 to 300 nm and more preferably comprise titania in anatase form adapted for enhancement of photocatalytic activity of said composition while maintaining its durability by even micron sized particles (>300 nm) of Titania (anatase or rutile) against organic pollutants of atleast >5%, more preferably >20% and most preferably >80% of the activity of the control.

29. Aqueous coating composition as claimed in anyone of the preceding claims wherein said at least partially surface treated particles are selected from substantially spherical particles, nodular particles, platy particles, cubical paraticles, various irregularly shaped particles, and mixtures thereof.

30. Aqueous coating composition as claimed in anyone of the preceding claims wherein said at least partially surface treated particles comprise at least one material selected from the group of silicates, doped silicates, minerals, metal oxides, silicas and metal powders and are selected from the group of aluminum oxides (alumina), titanium oxide, zirconium oxide, silver, nickel, nickel oxide, iron oxide, and alloys, polystyrene particles, (meth)acrylate

particles, PTFE particles, silica particles, polyolefin particles, polycarbonate particles, polysiloxane particles, silicone particles, polyester particles, polyamide particles, polyurethane particles, ethylenically unsaturated polymer particles, polyanhydride particles, biodegradable particles, polycaprolactone, nanofibers, nanotubes, nanowires, or combinations thereof that are preferably insoluble in organic solvents and water; and preferably comprise particles other than respirable crystalline silica wherein said silica is amorphous.

31. An aqueous coating composition as claimed in anyone of the preceding claims wherein said at least partially surface treated particles comprise particles that are surface treated with compounds selected from silanes (alkylsilanes, perfluoroalkylsilanes, and alkyldisilazanes), silicones and fluorinated compounds or fluorinated acrylics or other organic/ inorganic treatments to achieve a balance between hydrophobicity and hydrophilicity.

32. An aqueous coating composition as claimed in anyone of the preceding claims wherein said at least partially surface treated particles comprise preferably externally surface treated particles with selective hydrophobic and hydrophilic balance and are obtained of sol-gel treatment to prevent any colour change or graying of white particles present in said coating composition, especially where fluorosilanes or fluorosilicones are used for treatment or is alternatively in-situ treated while preparation of the coating with said mixture of hydrophobic and hydrophilic silicones/silanes.

33. Aqueous coating composition as claimed in anyone of the preceding claims wherein said coating composition is flowable comprising at least one organic diluent or solvent, wherein the solvent is selected from the group comprising of water, an alcohol, an ether, a ketone, an ester, a glycol, a glycol ether, an alkylene carbonate, a C_5 - C_{18} aliphatic hydrocarbon, a C_6 - C_{18} aromatic hydrocarbon, various polar/non-polar solvents and mixtures thereof.

34. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprises thermoplastic or thermosetting polymers including a single polymer or a blend of more than one polymer or self crosslinking polymers selected from acrylics, polyesters, polyurethanes, polycarbonates, polyolefins, alkyds, epoxies, polyamides, fluoropolymers, silicone polymers and their hybrids, wherein said fluoropolymers include polyperfluoropolyethers, and a polymer having one or more

monomer repeat units selected from the group consisting of ethylene, propylene, styrene, tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene, perfluoro(methyl vinyl ether), perfluoro(ethyl vinyl ether), and perfluoro(propyl vinyl ether) and/ or includes a colloid, a latex, or a suspension of a fluoropolymer selected from a group comprising of polytetrafluoroethylene; perfluoroalkoxy polymer resin; copolymer of tetrafluoroethylene and hexafluoropropylene; copolymers of hexafluoropropylene and vinylidene fluoride; terpolymers of tetrafluoroethylene, vinylidene fluoride, and hexafluoropropylene.

35. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprising polymers have a Tg of -30 to 100 deg C or preferably Tg in the range of 0 to 50°C.

36. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprising polymers have surface energy of <50 mN/m and preferably less than 30 mN/m and more preferably <20 mN/m.

37. An aqueous coating composition as claimed in anyone of the preceding claims comprising components that are multifunctional or having individual functions selected from thickeners, biocides, wetting and dispersing agents, fluorosurfactants, defoamers, opacifying polymers, cosolvents, coalescents, plasticizers, pigments, special effect pigments, extenders, colorants, freeze thaw stabilizers, buffers, fire retardants, uv absorbers, organic fiber material, and inorganic fiber materials, flow and levelling agents, adhesion promoters, oil and water repellents and other components known to be provided in paint formulations.

38. An aqueous coating composition as claimed in anyone of the preceding claims that is ambient curing including air curing, infra-red curing and thermal curing.

39. An aqueous coating composition as claimed in anyone of the preceding claims wherein a dry film of said coating has a dry film thickness of 1 to 200 microns and preferably 40 to 120 microns and withstands at least 30 to 1000 cycles and preferably 100 to 3000 cycles in a wet scrub resistance test with a scrub brush and a 0.45 kg load.

40. An aqueous coating composition as claimed in anyone of the preceding claims adapted for applications comprising self cleaning, easy cleaning, anti-graffiti, stain resistant, soil-

degrading, deodorizing, air-cleaning, antifouling, antimicrobial, water-cleaning, superhydrophobicizing, superhydrophilicizing and/or antifogging effects.

41. A process for the preparation of aqueous coating composition as claimed in anyone of the preceding claims 1-40 comprising the steps of:
a) providing at least partially surface treated organic or inorganic particles to selectively provide a balance of hydrophobicity and hydrophilicity that is either micron sized or includes a particulate mixture of micron sized and nanometer sized particles;
b) providing for one or more oligomeric or polymeric dispersion/binder comprising acrylic, fluorinated and hydrophilic (acid/amine/ionic/non-ionic) backbone;
c) providing for one or more hydrophobic organosilicone or silane (monomeric, oligomeric or polymeric) and one or more hydrophilic organosilicone or silane (monomeric, oligomeric or polymeric);
d) mixing said particles with said polymeric dispersion and silane; to obtain said aqueous coating composition therefrom having desired reversible hydrophilic-hydrophobic switching adapted for coating various types of substrates by brush, spray or roller type applications and also dipping, padding, doctor blade, wipe, wet-on-wet procedure or spin coating type applications.

42. A process for the preparation of aqueous coating composition as claimed in claim 41 wherein said at least partially surface treated organic or inorganic particles is provided by subjecting the particles to sol-gel treatment with compounds selected from silicones, fluorinated compounds to prevent color change of the particles.

43. A process for the preparation of aqueous coating composition as claimed in anyone of claims 41 or 42 wherein said step (a) of providing treated organic or inorganic particles that is either micron sized has a mean particle size of less than or equal to 100 microns, preferably less than or equal to 325 mesh (44 microns) or providing a particulate mixture of micron and nanometer sized particles involves providing micro and nanosized particles in selective ratios of 3.5 to 8, and are externally or in-situ treated particles with a balance of hydrophobicity and hydrophilicity;
wherein said step (d) comprising mixing said particles preferably in a slurry form in a water miscible co-solvent to the polymer dispersion including organosilicone or silane is mixed in selective ratios of 0.9 to 2.5.

44. A process for the preparation of aqueous coating composition as claimed in anyone of claims 41-43 adapted for substrates selected from masonary, concrete, cementitious, plaster, baked clay tiles, cellulosic, wood, one or more polymer, dry or damp surfaces, brick, tile, stone, grout, mortar, composite materials, gypsum board, , porous and non porous surfaces, interior surfaces or surfaces exposed to weathering on at least one surface of the substrate, which surface is preferably pretreated for better adhesion of the aqueous coating composition with various types of surface treatments.

45. A commercial or industrial material, a structure or building or a substrate comprising aqueous coating reversible switchable composition of claims 1-40 exhibiting reversible hydrophilic-hydrophobic switching under variable environmental conditions including variations in at least one or more of temperature, pH, humidity or other external stimuli including light.

46. A method of producing reversible switchable coated commercial or industrial material, structure or building or substrate comprising

selectively applying the aqueous coating of said reversible switchable composition of claims 1-40 to atleast a portion of commercial or industrial material, a structure or building or a substrate requiring said reversible coating characteristic such as to exhibit reversible hydrophilic-hydrophobic switching under variable environmental conditions including variations in at least one or more of temperature, pH, humidity or other external stimuli including light.

AMENDED CLAIMS

received by the International Bureau on 16 April 2014 (16.04.2014)

1. Aqueous coating composition exhibiting reversible hydrophilic-hydrophobic switching under variable environmental conditions including variations in at least one or more of temperature, pH, humidity or other external stimuli including light comprising:

a) An emulsifier free aqueous dispersion of fluorinated acrylic copolymer with a Tg of 0-50 deg C comprising C1 to C8 esters of acrylic and/or methacrylic acid, perfluorinated monomers, and a hydrophilic ionic and or non-ionic monomer ;

b) Mixture of hydrophobic and hydrophilic organoilicones and/or silanes with alkyl and or aryl functionality with alkoxy groups and or silanol groups, the mass ratio of said hydrophobic organosilicones/silane to hydrophilic organosilicones/silane being in the range 10/90 to 60/40;
and

c) At least partially surface treated particles with a mean particle size less than 44 microns, said surface treated particles comprising particles treated with a mixture of said hydrophobic and hydrophilic organosilicones and/or silanes to which said particles are physically or chemically attached, said particles comprising either micron sized particles or a particulate mixture of both micron sized/ nano sized particles and is present in selective ratios of 0.9 to 2.5 with said polymeric dispersion wherein higher ratios closer to 2 is preferred for a two coat application;
to selectively provide a balance of hydrophobicity and hydrophilicity such as to provide desired reversible hydrophilic-hydrophobic switching.

2. Aqueous coating composition as claimed in claim 1 wherein said hydrophobic organosilicone/silane has a contact angle hysteresis of <10 degrees based on the average of readings for 10 and 20 μL of water when applied on an aerated cement block is present in the range of 5% to 80% by weight of dispersion solids in said composition, and wherein said hydrophilic organosilicone/silane having a contact angle hysteresis of >10 degrees based on the average of readings for 10 and 20 μL of water when applied on an aerated cement block is present in the range of 10% to 90% by weight of dispersion solids in said composition.

3. Aqueous coating composition as claimed in anyone of claims 1 or 2 including photocatalytically active agents comprising one or more nano particles exhibiting photocatalytic properties in amounts less than 1% and preferably less than 0.5% of total formulation, preferably comprise nano titania of the anatase or rutile grade in the range of 0.1 to 1% of the formulation with a particle size of 1 to 300 nm and more preferably comprise titania in anatase form adapted for enhancement of photocatalytic activity of said composition while maintaining its durability by even micron sized particles (>300 nm) of Titania (anatase or rutile) against organic pollutants of atleast >5%, more preferably >20% and most preferably >80% of the activity of the control.

4. Aqueous coating composition as claimed in anyone of the preceding claims that is oleophobic and has a water contact angle hysteresis of <25° under certain environmental conditions with variations in at least one or more of temperature, humidity, pH, light which is reversibly switchable to a water contact angle hysteresis of >25° under said environmental conditions offering benefits of both superhydrophobic and superhydrophilic cleaning, good organic and inorganic dirt pickup resistance, resistance to dirt streaks, dirt lines, water spotting, water marks, good cleanability with water and forced air or wind, reduced chalking, good resistance to organic dirt and deposits such as bird droppings and oily stains, and reduced tendency for spreading of water containing rust.

5. Aqueous coating composition as claimed in anyone of the preceding claims that reversibly switches from superhydrophobic (contact angle hysteresis <25° and water droplet rolling effect) to superhydrophilic (contact angle hysteresis >25° and complete wetting) for at least 2000 hours of accelerated exterior exposure (Atlas and QUV testing), preferably the contact angle hysteresis values are <20°, more preferably <10° and most preferably <5° in one state and higher in the switched state for a deposited 0.02 mL water droplet, wherein preferably the contact angle exhibited in one state is >100° with water, more preferably >120°, even more preferably superhydrophobic having contact angle >150° and contact angle <90° in the switched state for a deposited 0.02 mL droplet; and wherein said switching takes place within a varying period of time from a few seconds to several minutes dependent on a particular stimuli.

6. Aqueous coating composition as claimed in anyone of the preceding claims having low surface energy of <40 mN/m and preferably <20 mN/m and most preferably <10 mN/m

even with the second coat and hence recoatable to enhance film build-up to attain desired opacity/ translucency/ hiding/ whiteness.

7. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprising dispersion polymers involving primary or secondary dispersion in water or in a water/ co-solvent mixture with or without emulsion/ latex polymers wherein the ratio range of dispersion to emulsion/latex polymers is of 95:5 to 5:95.

8. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprises dispersion polymers with or without emulsion/ latex polymers that is preferably styrene free and is a free radical polymerization or controlled radical polymerization product of hydrophobic monomers C1-C8 straight, branched or cyclic esters of methacrylic acid/ acrylic acid selected from methyl methacrylate, ethyl methacrylate, butyl Methacrylate, isobutyl Methacrylate, tertiary butyl methacrylate, isobornyl methacrylate, 2-ethylhexyl methacrylate and various isomers and their corresponding acrylates also involving >C8 esters of methacrylic acid/ acrylic acid selected from lauryl acrylate, stearyl acrylate.

9. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprises dispersion polymers with or without emulsion/ latex polymers and has monomers selected such that the resulting polymer has an average octanol-water partition coefficient (log Kow) greater than 0.6, preferably greater than 1.5 and more preferably greater than 2.

10. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion including dispersion polymers with or without emulsion/ latex polymers in being styrene free involves styrene or alkylstyrene group as part of the polymer or as a part of additives including opacifiers in less than 15% of the film forming composition favouring reduced chalking of said composition on UV exposure.

11. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprising dispersion polymers with or without emulsion/ latex polymers includes polymers selected from natural polymer, a neoprene polymer, a nitrile polymer, a vinyl acrylic polymer, acrylic polymer; styrene acrylic polymer, styrene

butadiene polymer, copolymer of vinyl acetate and butyl acrylate or veova monomers or ethylene/ propylene/ butylene, butadiene, isoprene involving crosslinkers selected from diacrylates, triacrylates, multifunctional acrylates, silane functional monomers, acetoacetate functional monomers, monomers with aziridine, hydrazine, carbodiimide or allylic functionality.

12. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprising dispersion polymers with or without emulsion/ latex polymers includes polymers of fluorinated monomers comprising 2 to 20 carbon atoms and polymeric fluorine content in the range of 0.1 to 50% on monomer solids and preferably in the range of less than 5% on monomer solids resulting in a surface energy of <50 mN/m, preferably <30 mN/m and more preferably <20 mN/m.

13. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprising fluorinated backbone comprises fluorinated monomers including esters of acrylic or methacrylic acid with a linear or branched perfluoroalkyl functional group preferably involving 1-6 fluorinated carbons selected from trifluoroethyl meth(acrylate), pentafluoropropyl meth(acrylate), heptafluorobutyl meth(acrylate).

14. Aqueous coating composition as claimed in anyone of the preceding claims wherein said ionic or ionizable or non-ionic hydrophilic monomers are present within the range of 2 to 20% of polymer solids thus favoring reduction of water absorption of said composition to less than 15%, preferably less than 10% and even more preferably less than 5% after remaining immersed in water for 96 hours.

15. Aqueous coating composition as claimed in anyone of the preceding claims wherein said ionic or ionizable or non-ionic hydrophilic monomers are selected from acrylic acid, methacrylic acid and their aklali metal or quaternary ammonium ion salts; monoolefinic sulphonic acid compounds and their alkali metal salts including 2-acrylamido-2-methylpropanesulphonic acid; acrylates or methacrylates of aminoalcohols, acrylamides selected from N,N-dimethylaminopropylacrylamide or N, N-Dimethylaminoethylmethacrylate, polyalkylene oxide group containing monomers or a polymeric chain prepared by polymerizing a polyalkylene glycol (meth)acrylate, hydroxyl alkyl (ethyl, propyl or butyl) (meth)acrylates, wherein the hydrophilic component comprises at least one oxygen, sulfur, phosphorus and/or nitrogen atom.

16. Aqueous coating composition as claimed in anyone of the preceding claims wherein said at least partially surface treated particles are selected from substantially spherical particles, nodular particles, platy particles, cubical particles, various irregularly shaped particles, and mixtures thereof.

17. Aqueous coating composition as claimed in anyone of the preceding claims wherein said at least partially surface treated particles comprise at least one material selected from the group of silicates, doped silicates, minerals, metal oxides, silicas and metal powders and are selected from the group of aluminum oxides (alumina), titanium oxide, zirconium oxide, silver, nickel, nickel oxide, iron oxide, and alloys, polystyrene particles, (meth)acrylate particles, PTFE particles, silica particles, polyolefin particles, polycarbonate particles, polysiloxane particles, silicone particles, polyester particles, polyamide particles, polyurethane particles, ethylenically unsaturated polymer particles, polyanhydride particles, biodegradable particles, polycaprolactone, nanofibers, nanotubes, nanowires, or combinations thereof that are preferably insoluble in organic solvents and water; and preferably comprise particles other than respirable crystalline silica wherein said silica is amorphous.

18. Aqueous coating composition as claimed in anyone of the preceding claims wherein said at least partially surface treated particles involve organic and/or inorganic particles having size ranging from 1 nm-44 microns includes surface treated nanometer sized organic and/or inorganic particles have size ranging from about 1 nm to 300 nm, and wherein said particles preferably has mean particle size less than 40 microns and even more preferably less than 20 microns.

19. An aqueous coating composition as claimed in anyone of the preceding claims wherein said particles comprising either micron sized particles or including particulate mixture of both micron sized and nano sized particles comprises micronized and nanosized particles present in selective ratios of 3.5 to 8 with ratios closer to 8 being preferred for a two coat application.

20. Aqueous coating composition as claimed in anyone of the preceding claims wherein said particles comprise either micron sized particles or includes particulate mixture of both micron sized and nano sized particles, and including particulate pigments wherein the pigment volume concentration (PVC) is in the range of about 30 to 80 % and preferably in

the range of 40 to 75% for the coating and preferably the coating PVC is lower than the practical critical pigment volume concentration (CPVC).

21. An aqueous coating composition as claimed in anyone of the preceding claims wherein said at least partially surface treated particles comprise particles that are surface treated with compounds selected from silanes (alkylsilanes, perfluoroalkylsilanes, and alkyldisilazanes), silicones and fluorinated compounds or fluorinated acrylics or other organic/ inorganic treatments to achieve a balance between hydrophobicity and hydrophilicity.

22. An aqueous coating composition as claimed in anyone of the preceding claims wherein said at least partially surface treated particles comprise preferably externally surface treated particles with selective hydrophobic and hydrophilic balance and are obtained of sol-gel treatment to prevent any colour change or graying of white particles present in said coating composition, especially where fluorosilanes or fluorosilicones are used for treatment or is alternatively in-situ treated while preparation of the coating with said mixture of hydrophobic and hydrophilic silicones/silanes.

23. Aqueous coating composition as claimed in anyone of the preceding claims wherein said hydrophobic and hydrophilic organosilicone content present as a part of the continuous phase in said composition is 10-90 % of the weight of the dispersion/binder.

24. Aqueous coating composition as claimed in anyone of the preceding claims comprising at least one or more wetting and dispersing agents, encapsulated or free antimicrobial agents selected from fungicide, algaecide, in-can preservative and optionally involving, one or more nanoparticles exhibiting photocatalytic activity.

25. Aqueous coating composition as claimed in anyone of the preceding claims wherein said coating composition is flowable comprising at least one organic diluent or solvent, wherein the solvent is selected from the group comprising of water, an alcohol, an ether, a ketone, an ester, a glycol, a glycol ether, an alkylene carbonate, a C_5 - C_{18} aliphatic hydrocarbon, a C_6 - C_{18} aromatic hydrocarbon, various polar/non-polar solvents and mixtures thereof.

26. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprising dispersion polymers includes primary or secondary

dispersion in water or in a water/ co-solvent mixture involves co-solvent that is VOC exempt under Green Seal standard GS-11 with resulting coating VOC's in the range of 1 to 100 grams/liter.

27. Aqueous coating composition as claimed in anyone of the preceding claims wherein said polymeric dispersion comprises thermoplastic or thermosetting polymers including a single polymer or a blend of more than one polymer or self crosslinking polymers selected from acrylics, polyesters, polyurethanes, polycarbonates, polyolefins, alkyds, epoxies, polyamides, fluoropolymers, silicone polymers and their hybrids, wherein said fluoropolymers include polyperfluoropolyethers, and a polymer having one or more monomer repeat units selected from the group consisting of ethylene, propylene, styrene, tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene, perfluoro(methyl vinyl ether), perfluoro(ethyl vinyl ether), and perfluoro(propyl vinyl ether) and/ or includes a colloid, a latex, or a suspension of a fluoropolymer selected from a group comprising of polytetrafluoroethylene; perfluoroalkoxy polymer resin; copolymer of tetrafluoroethylene and hexafluoropropylene; copolymers of hexafluoropropylene and vinylidene fluoride; terpolymers of tetrafluoroethylene, vinylidene fluoride, and hexafluoropropylene.

28. An aqueous coating composition as claimed in anyone of the preceding claims comprising components that are multifunctional or having individual functions selected from thickeners, biocides, wetting and dispersing agents, fluorosurfactants, defoamers, opacifying polymers, cosolvents, coalescents, plasticizers, pigments, special effect pigments, extenders, colorants, freeze thaw stabilizers, buffers, fire retardants, uv absorbers, organic fiber material, and inorganic fiber materials, flow and levelling agents, adhesion promoters, oil and water repellents and other components known to be provided in paint formulations.

29. An aqueous coating composition as claimed in anyone of the preceding claims that is ambient curing including air curing, infra-red curing and thermal curing.

30. An aqueous coating composition as claimed in anyone of the preceding claims wherein a dry film of said coating has a dry film thickness of 1 to 200 microns and preferably 40 to 120 microns and withstands at least 30 to 1000 cycles and preferably 100 to 3000 cycles in a wet scrub resistance test with a scrub brush and a 0.45 kg load.

31. An aqueous coating composition as claimed in anyone of the preceding claims adapted for applications comprising self cleaning, easy cleaning, anti-graffiti, stain resistant, soil-degrading, deodorizing, air-cleaning, antifouling, antimicrobial, water-cleaning, superhydrophobicizing, superhydrophilicizing and/or antifogging effects.

32. A process for the preparation of aqueous coating composition as claimed in anyone of the preceding claims 1-31comprising the steps of:

a) providing at least partially surface treated particles with a mean particle size less than 44 microns, said surface treated particles comprising particles treated with a mixture of said hydrophobic and hydrophilic organosilicones and/or silanes to which said particles are physically or chemically attached, said particles comprising either micron sized particles or a particulate mixture of both micron sized/ nano sized particles and is present in selective ratios of 0.9 to 2.5 with said polymeric dispersion wherein higher ratios closer to 2 is preferred for a two coat application;

b) providing for an emulsifier free aqueous dispersion of fluorinated acrylic copolymer with a Tg of 0-50 deg C comprising C1 to C8 esters of acrylic and/or methacrylic acid, perfluorinated monomers, and a hydrophilic ionic and or non-ionic monomer;

c) providing for a mixture of hydrophobic and hydrophilic organoilicones and/or silanes with alkyl and or aryl functionality with alkoxy groups and or silanol groups, the mass ratio of said hydrophobic organosilicones/silane to hydrophilic organosilicones/silane being in the range 10/90 to 60/40;

d) mixing said particles with said polymeric dispersion and silane; to obtain said aqueous coating composition therefrom having desired reversible hydrophilic-hydrophobic switching adapted for coating various types of substrates by brush, spray or roller type applications and also dipping, padding, doctor blade, wipe, wet-on-wet procedure or spin coating type applications.

33. A process for the preparation of aqueous coating composition as claimed in claim 32 wherein said at least partially surface treated particles including organic or inorganic particles is provided by subjecting the particles to sol-gel treatment with compounds selected from silicones, fluorinated compounds to prevent color change of the particles.

34. A process for the preparation of aqueous coating composition as claimed in anyone of claims 32 or 33 wherein said step (a) of providing treated organic or inorganic particles that is either micron sized has a mean particle size of less than or equal to 44 microns or providing a particulate mixture of micron and nanometer sized particles involves providing micro and nanosized particles in selective ratios of 3.5 to 8, and are externally or in-situ treated particles with a balance of hydrophobicity and hydrophilicity;
wherein said step (d) comprising mixing said particles preferably in a slurry form in a water miscible co-solvent to the polymer dispersion including organosilicone or silane is mixed in selective ratios of 0.9 to 2.5.

35. A process for the preparation of aqueous coating composition as claimed in anyone of claims 32-34 adapted for substrates selected from masonary, concrete, cementitious, plaster, baked clay tiles, cellulosic, wood, one or more polymer, dry or damp surfaces, brick, tile, stone, grout, mortar, composite materials, gypsum board, porous and non porous surfaces, interior surfaces or surfaces exposed to weathering on at least one surface of the substrate, which surface is preferably pretreated for better adhesion of the aqueous coating composition with various types of surface treatments.

36. A commercial or industrial material, a structure or building or a substrate comprising aqueous coating reversible switchable composition of claims 1-31 exhibiting reversible hydrophilic-hydrophobic switching under variable environmental conditions including variations in at least one or more of temperature, pH, humidity or other external stimuli including light.

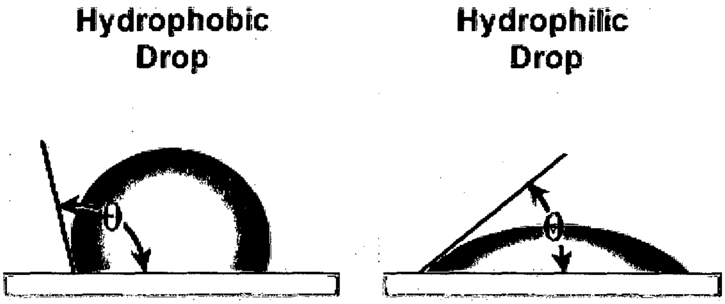
37. A method of producing reversible switchable coated commercial or industrial material, structure or building or substrate comprising
selectively applying the aqueous coating of said reversible switchable composition of claims 1-31 to atleast a portion of commercial or industrial material, a structure or building or a substrate requiring said reversible coating characteristic such as to exhibit reversible hydrophilic-hydrophobic switching under variable environmental conditions including variations in at least one or more of temperature, pH, humidity or other external stimuli including light.

STATEMENT UNDER ARTICLE 19 OF PCT

Amended claims are directed to further clarify, qualify and indicate the advancement residing in the aqueous coating composition, and provides clarity to the necessary technical features of the ingredients required to achieve the desired attributes of reversible hydrophobic-hydrophilic switching under variable environmental conditions including variations in at least one or more of temperature, pH, humidity or other external stimuli including light and is yet advantageously ambient curing, either translucent or opaque and free of any dirt streaks and water marks.

The aqueous coating composition involving the dispersion has been made more definitive by qualifying with the specific copolymers comprising the specific monomers, the mixture of hydrophobic and hydrophilic organoilicones and/or silanes qualified by their mass ratio in which it is present in the composition, the particles comprising either micron sized particles or a particulate mixture of both micron sized/ nano sized particles qualified with the selective ratio that it bears with the dispersion that is also further qualified to comprise particles treated with a mixture of said hydrophobic and hydrophilic organosilicones and/or silanes that are physically or chemically attached and have also been qualified with the type of functionalities on the silanes; which together demonstrate surprisingly and unexpectedly said desired end attributes as exemplified in the PCT original disclosure.

The amendments in the claims are thus solely directed to qualify the claimed invention and do not extend beyond the disclosure and directions in the international application as filed.



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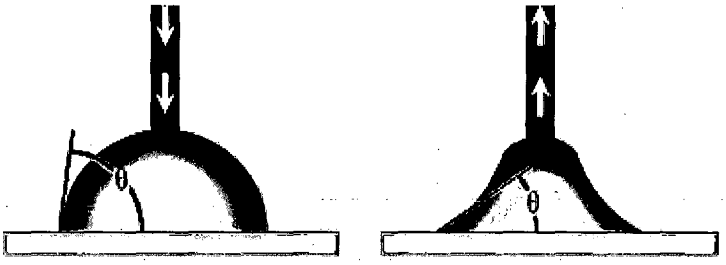


advancing angle receding angle

Figure 2

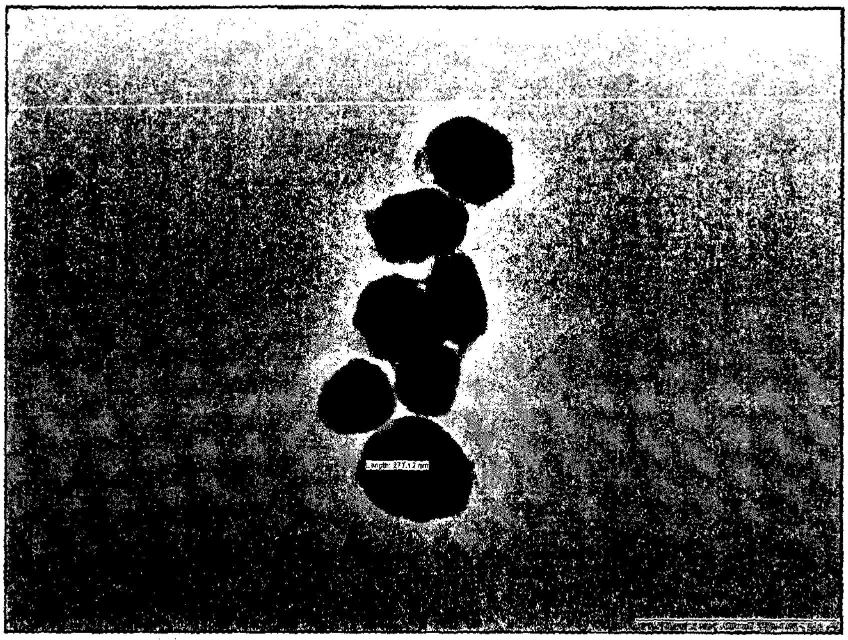
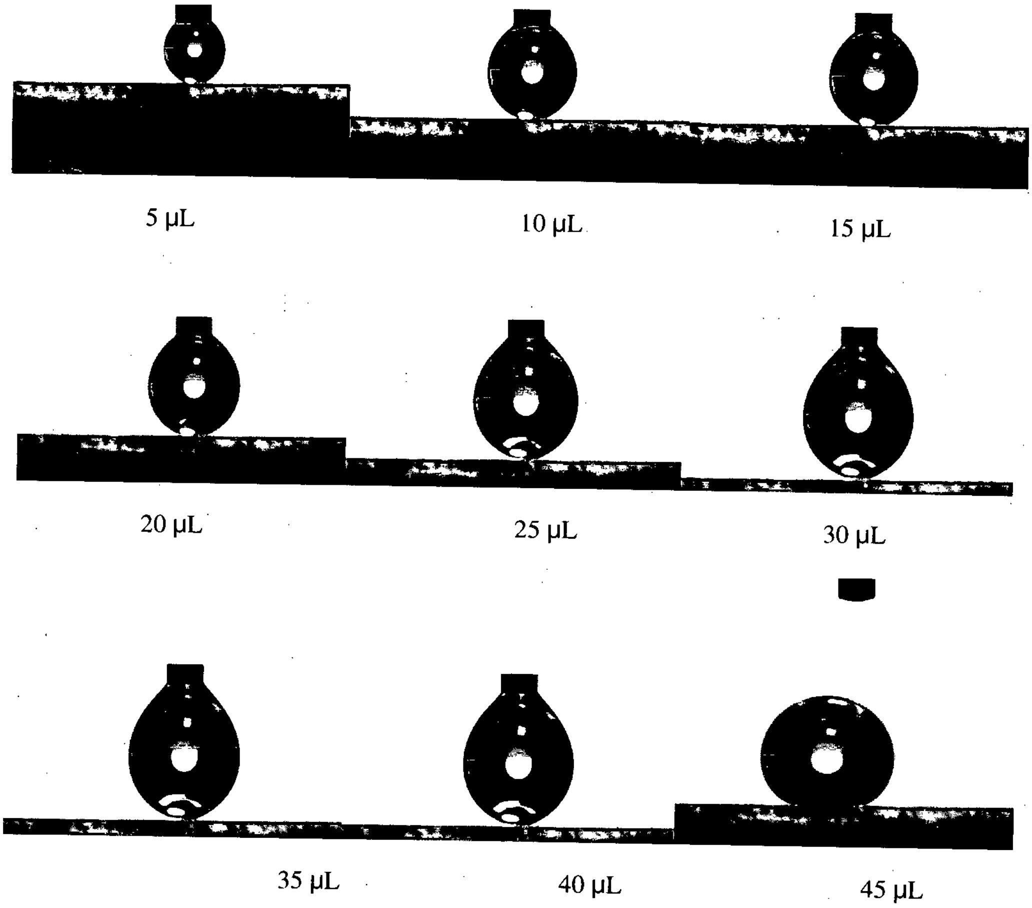


Figure 3

Figure 4



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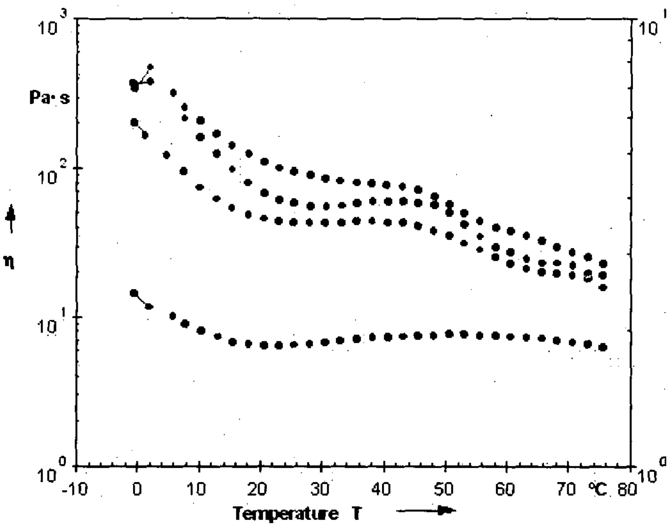

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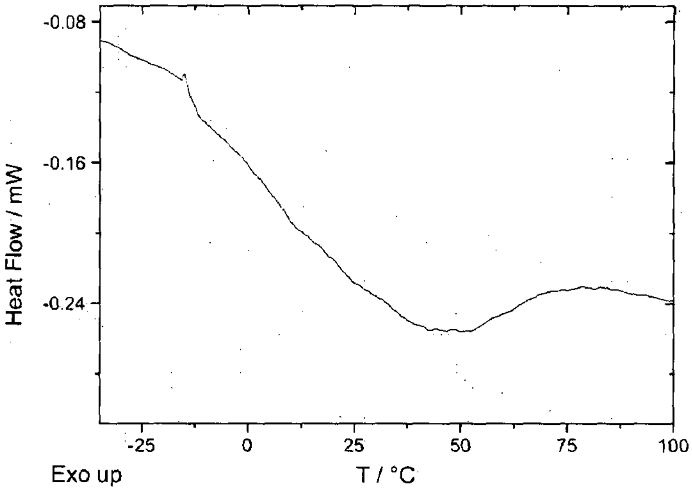

Figure 7

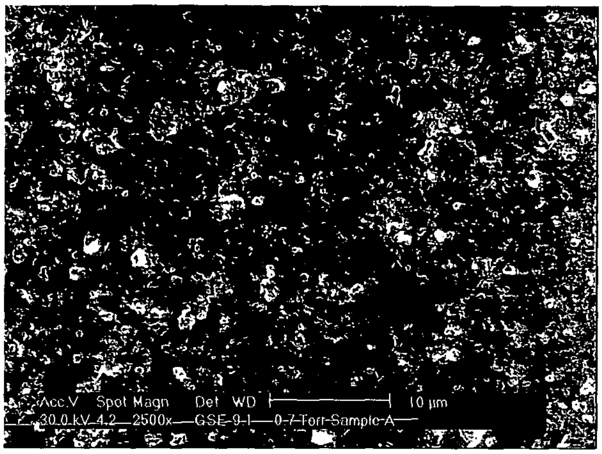

Figure 8

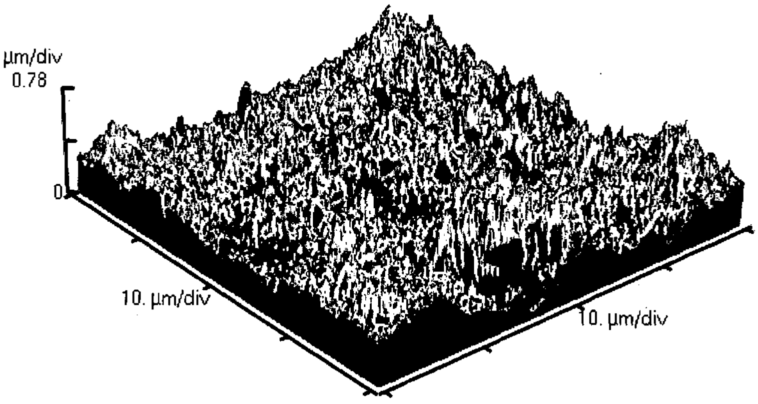

Figure 9

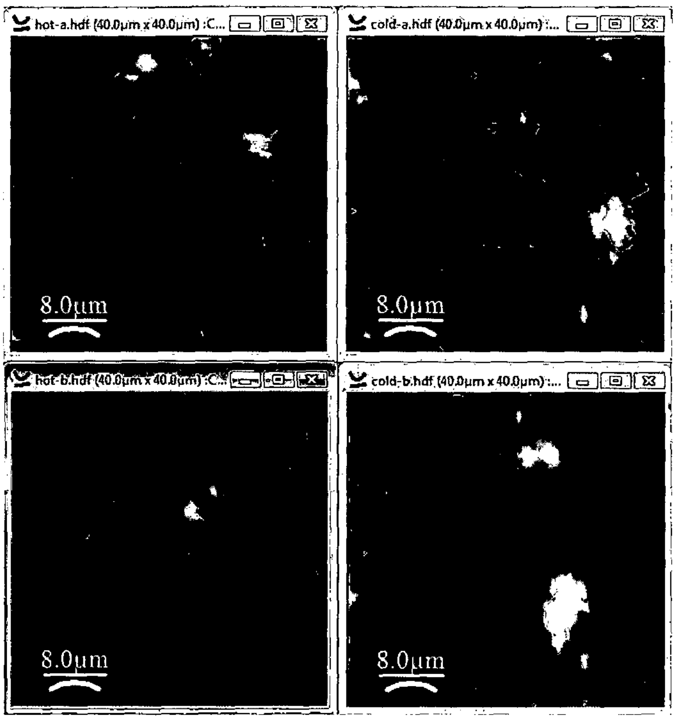

Figure 10

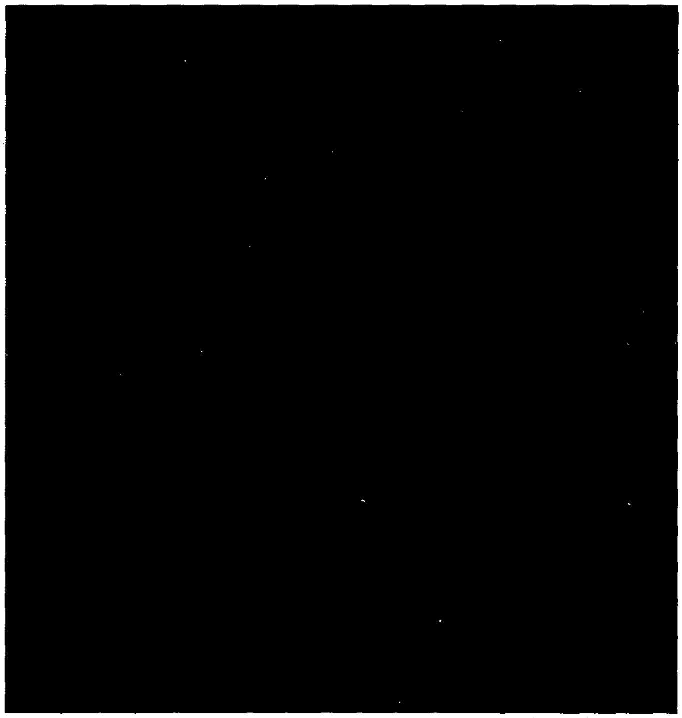

Figure 11

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2013/000101

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/00
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)
C09D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/067638 A2 (AMO GRONINGEN BV [NL]; LIU YAN [SE]; HILBORN JONS GUNNAR [SE]; HAITJEM) 29 June 2006 (2006-06-29) page 3, line 21 - line 32 page 4, line 19 - page 6, line 4 page 6, line 20 - page 7, line 14 abstract; claims 1-7, 12-16, 18-23; figures 1-3; example 1 -----	1-46
X	US 2006/029808 A1 (ZHAI LEI [US] ET AL) 9 February 2006 (2006-02-09) paragraph [0004] - paragraph [0016] paragraph [0027] - paragraph [0032] abstract; claims 1, 3-5, 9-21, 25-37, 45 -----	1-46
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☒ 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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 6 August 2013	Date of mailing of the international search report 19/08/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Glomm, Bernhard

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2013/000101

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 2012/107612 A1 (CONSEJO SUPERIOR INVESTIGACION [ES]; VECIANA MIRO JAUME [ES]; ROVIRA A) 16 August 2012 (2012-08-16) the whole document -----	1-46
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X	EP 2 159 573 A1 (KONINKL PHILIPS ELECTRONICS NV [NL]) 3 March 2010 (2010-03-03) paragraph [0015] - paragraph [0032] paragraph [0034] - paragraph [0038] paragraph [0064] - paragraph [0066] abstract; claims 1-5, 10-13, 15-18; figures 1-7; example 1 -----	1-46

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IN2013/000101

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