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(54) Title: CLEANING COMPOSITIONS AND SOIL CAPTURE AGENT FOR CLEANING OBJECTS

(57) Abstract: A cleaning composition including a soil capture agent for cleaning objects.

CLEANING COMPOSITIONS AND SOIL CAPTURE AGENT FOR CLEANING OBJECTS

FIELD OF THE PRESENT INVENTION

The present disclosure generally relates to a cleaning composition having a soil capture agent used for cleaning objects.

BACKGROUND OF THE INVENTION

In the past, cleansing articles, such as paper towels, have been commonly utilized in combination with liquid cleaning compositions to clean windows, mirrors, countertops, and other hard surfaces. Known cleansing articles typically provide cleaning performance primarily by absorption of soil laden fluid, consequently, the cleaning performance of known cleansing articles is limited by the ability of the cleansing articles to absorb and retain the soil laden fluid.

Improved removal of soil from various surfaces continues to be a big consumer need. Formulators have attempted to enhance the soil removal properties of known cleansing articles by incorporating soil capture agents into liquid cleaning compositions. There are known liquid cleaning compositions, such as liquid spray cleaners, that comprise a soil capture agent, for example a Mirapol® polymer (a copolymer of an acrylic acid and a diquaternary ammonium compound) available from Rhodia and/or a polyacrylamide polymer, such as a Hyperfloc® polymer available from Hychem Inc. and/or a Lupasol® polymer (a polyethyleneimine) available from BASF Corporation, that are designed to aid in the removal of soil from various surfaces when applied to the surface in a liquid form.

One problem faced by formulators is that consumers desire improved soil adsorption properties from cleaning compositions compared to such properties from known cleaning composition.

However, there still exists a need for a cleaning composition including a soil capture agent that exhibit enhanced soil adsorption properties compared to known liquid cleaning solutions.

SUMMARY OF THE INVENTION

In accordance with one embodiment, a cleaning composition exhibits an average Soil Adsorption Value of about 38 mg or more as measured according to a Soil Adsorption Test Method described herein and comprises a soil capture agent. The soil capture agent comprises a polymer. The polymer comprises two or more monomeric units selected from the group consisting of nonionic monomeric units, anionic monomeric units, cationic monomeric units and zwitterionic monomeric units. The polymer comprises at least one monomeric unit selected from group a and at least one monomeric unit selected from groups b, c and d.

One solution to the problem identified above is to provide cleaning compositions that comprise a soil capture agent that improves the soil adsorption properties of the cleaning composition compared to known cleaning compositions.

In accordance with another embodiment, a cleaning composition comprises a soil capture agent. The soil capture agent comprises a polymer. The polymer comprises three or more monomeric units selected from the group consisting of nonionic monomeric units, anionic monomeric units, cationic monomeric units and zwitterionic monomeric units. The polymer comprises at least one monomeric unit selected from group a and at least two monomeric units selected from groups b, c and d. The at least two monomeric units are present in the polymer at a molar ratio of from about 3:1 to about 1:3.

In accordance with yet another embodiment, a cleaning composition comprises a soil capture agent. The soil capture agent comprises a polymer. The polymer comprises two or more monomeric units selected from the group consisting of nonionic monomeric units, anionic monomeric units, cationic monomeric units and zwitterionic monomeric units. The polymer comprises at least one monomeric unit selected from group a and at least one monomeric unit selected from groups b, c and d. The polymer comprises a number average molecular weight from about 500,000 g/mol to about 2,000,000 g/mol.

While the specification concludes with claims particularly pointing out and distinctly claiming the subject matter that is regarded as the present invention, it is believed that the invention will be more fully understood from the following description.

DETAILED DESCRIPTION OF THE INVENTION

I. Definitions

As used herein, the following terms shall have the meaning specified thereafter:

“Anionic monomer” as used herein means a monomer that exhibits a net negative charge at a pH of 7 and/or is identified as an anionic monomer herein. An anionic monomer is generally associated with one or more cations such as protons or cations of alkali metal or alkaline earth metal, for example sodium of cationic groups such as ammonium.

"Anionic monomeric unit" as used herein means a monomeric unit that exhibits a net negative charge at a pH of 7 and/or is identified as an anionic monomeric unit herein. An anionic monomeric unit may be derived from an anionic monomer. An anionic monomeric unit is generally associated with one or more cations such as protons or cations of alkali metal or alkaline earth metal, for example sodium of cationic groups such as ammonium.

"Article" as used herein means is any solid matter, such as a web, sponge, foam structure, co-form material, or particle. In one example, the article is a dry article.

"Basis Weight" as used herein is the weight per unit area of a sample reported in gsm and is measured according to the Basis Weight Test Method described herein.

"Cationic monomer" as used herein means a monomer that exhibits a net positive charge at a pH of 7 and/or is identified as a cationic monomer herein. A cationic monomer is generally associated with one or more anions such as a chloride ion, a bromide ion, a sulfonate group and/or a methyl sulfate group.

"Cationic monomeric unit" as used herein means a monomeric unit that exhibits a net positive charge at a pH of 7 and/or is identified as a cationic monomeric unit herein. A cationic monomeric unit is generally associated with one or more anions such as a chloride ion, a bromide ion, a sulfonate group and/or a methyl sulfate group.

"Dry article" as used herein means that the article includes less than about 30% and/or, less than about 20% and/or less than 10% and/or less than 5% and/or less than 3% and/or less than 2% and/or less than 1% and/or less than 0.5% by weight of moisture as measured according to the Moisture Content Test Method described herein.

"Fiber" and/or "Filament" as used herein means an elongate particulate having an apparent length greatly exceeding its apparent width, i.e. a length to diameter ratio of at least about 10. In one example, a "fiber" is an elongate particulate that exhibits a length of less than 5.08 cm (2 in.) and a "filament" is an elongate particulate that exhibits a length of greater than or equal to 5.08 cm (2 in.).

"Fibrous structure" as used herein means a structure that comprises one or more fibrous filaments and/or fibers. In one example, a fibrous structure according to the present invention means an orderly arrangement of filaments and/or fibers within a structure in order to perform a function. Non-limiting examples of fibrous structures can include paper, fabrics (including woven, knitted, and non-woven), and absorbent pads (for example for diapers or feminine hygiene products).

"Film" refers to a sheet-like material wherein the length and width of the material far exceed the thickness of the material.

“Hard surface" refers to any kind of surfaces typically found in and around houses like bathrooms, kitchens, basements and garages, e.g., floors, walls, tiles, windows, countertops, sinks, showers, shower plastified curtains, wash basins, WCs, dishes, fixtures and fittings and the like made of different materials like ceramic, enamel, painted and un-painted concrete, plaster, bricks, vinyl, no-wax vinyl, linoleum, melamine, Formica®, glass, any plastics, metals, chromed surface and the like. The term surfaces as used herein also include household appliances including, but not limited to, washing machines, automatic dryers, refrigerators, freezers, ovens, microwave ovens, dishwashers and so on.

“Monomeric unit” as used herein is a constituent unit (sometimes referred to as a structural unit) of a polymer.

“Nonionic monomer” as used herein means a monomer that exhibits no net charge at a pH of 7 and/or is identified as a nonionic monomer herein.

“Nonionic monomeric unit” as used herein means a monomeric unit that exhibits no net charge at a pH of 7 and/or is identified as a nonionic monomeric unit herein. A nonionic monomeric unit may be derived from nonionic monomer.

“Number average molecular weight” as used herein means the number average molecular weight M_n as determined using gel permeation chromatography according to the protocol found in Colloids and Surfaces A. Physico Chemical & Engineering Aspects, Vol. 162, 2000, pg. 107-121.

“Polydispersity Index” or “PDI” as used herein means the ratio of the weight average molecular weight to the number average molecular weight, M_w/M_n, as determined using gel permeation chromatography.

“Sanitary tissue product” as used herein means a soft, low density (i.e. < about 0.15 g/cm^3) web useful as a wiping implement for post-urinary and post-bowel movement cleaning (toilet tissue), for otorhinolaryngological discharges (facial tissue), and multi-functional absorbent and cleaning uses (absorbent towels), and folded sanitary tissue products such as napkins and/or facial tissues including folded sanitary tissue products dispensed from a container, such as a box. The sanitary tissue product may be convolutedly wound upon itself about a core or without a core to form a sanitary tissue product roll.

“Soil” refers to organic or inorganic material, often particulate in nature that may include dirt, clays, food particulates, sebum or greasy residue, soot, etc.

“Web” as used herein means a fibrous structure or a film.

"Weight average molecular weight" as used herein means the weight average molecular weight M_w as determined using gel permeation chromatography according to the protocol found in Colloids and Surfaces A. Physico Chemical & Engineering Aspects, Vol. 162, 2000, pg. 107-121.

"Zwitterionic monomer" as used herein means a monomer that exhibits both a negative charge and a positive charge on the same monomer at a pH of 7 and/or is identified as a zwitterionic monomer herein. A zwitterionic monomer is generally associated with one or more cations such as protons or cations of alkali metal or alkaline earth metal, for example sodium or cationic groups such as ammonium and one or more anions such as a chloride ion, a bromide ion, a sulfonate group and/or a methyl sulfate group.

"Zwitterionic monomeric unit" as used herein means a monomeric unit that exhibits both a negative charge and a positive charge on the same monomeric unit at a pH of 7 and/or is identified as a zwitterionic monomeric unit herein. A zwitterionic monomeric unit may be derived from a zwitterionic monomer. A zwitterionic monomeric unit is generally associated with one or more cations such as protons or cations of alkali metal or alkaline earth metal, for example sodium or cationic groups such as ammonium and one or more anions such as a chloride ion, a bromide ion, a sulfonate group and/or a methyl sulfate group.

II. Polymers and Soil Capture Agents

A soil capture agent as described herein provides enhanced benefits in capturing soil. Such soil capture agents can be used singularly or in combination with other components to form a cleaning composition (e.g., liquid cleansing solution). In certain embodiments, such soil capture agents can include polymers. Such polymers can include several monomeric units thus it can be referred to as a copolymer rather than a homopolymer, which consists of a single type of monomeric unit. The polymers of the present disclosure may be a terpolymer (3 different monomeric units). The polymers of the present disclosure may be a random copolymer. In one example, a polymer of the present disclosure may be water-soluble and/or water-dispersible, which means that the polymer does not, over at least a certain pH and concentration range, form a two-phase composition in water at 23°C ± 2.2°C and a relative humidity of 50% ± 10%.

In one example, the polymers of the present invention exhibit a Number Average Molecular Weight of less than 2,000,000 g/mol and/or less than 1,750,000 g/mol and/or less than 1,700,000 g/mol and/or less than 1,500,000 g/mol and/or greater than 500,000 g/mol and/or greater than 900,000 g/mol. In another example, the polymers exhibit a Number Average Molecular Weight of from about 500,000 to 2,000,000 g/mol and/or from about 900,000 to 1,700,000 g/mol and/or from about 1,000,000 to 1,500,000 g/mol.

In another example, the polymers of the present invention exhibit a Soil Adsorption Value of at least 38 mg and/or at least 40 mg and/or at least 42 mg and/or at least 45 mg and/or at least 47 mg and/or at least 50 mg and/or at least 53 mg and/or at least 55 mg and/or at least 57 mg and/or at least 60 mg and/or at least 62 mg as measured according to the Soil Adsorption Test Method described herein.

In yet another example, the polymers of the present invention exhibit a charge density (at pH 4.5) of from about -0.1 meq/g and/or from about -0.05 meq/g and/or from about -0.02 meq/g and/or from about 0 meq/g and/or to about +0.1 meq/g and/or to about +0.09 meq/g and/or to about +0.08 meq/g and/or to about +0.06 meq/g and/or to about +0.05 meq/g and/or to about +0.02 meq/g as measured according to the Charge Density Test Method described herein. In still another example, the polymers of the present invention exhibit a charge density of from about -0.1 meq/g to about +0.1 meq/g and/or from -0.05 meq/g to about +0.1 meq/g and/or from about 0 to less than +0.1 meq/g and/or to less than +0.09 meq/g and/or to less than +0.08 meq/g and/or to less than +0.06 meq/g and/or to less than +0.05 meq/g as measured according to the Charge Density Test Method described herein. In one example, the polymers of the present invention exhibit an excess charge (charge density) of from about 0 to about 0.1 meq/g. In another example, the polymers of the present invention exhibit an excess charge (charge density) of about 0.05 meq/g or less.

In another example, the polymers exhibit a Polydispersity Index of less than 2.5 and/or of less than 2.0 and/or less than 1.7 and/or less than 1.5 and/or less than 1.3.

In one example, a polymer of the present invention comprises two or more monomeric units selected from the group consisting of: a. nonionic monomeric units; b. anionic monomeric units; c. cationic monomeric units; d. zwitterionic monomeric units; and e. mixtures thereof.

The polymers of the present invention may exhibit a Soil Adsorption Value of at least 38 mg as measured according to the Soil Adsorption Test Method described herein.

a. Nonionic Monomeric Units

The nonionic monomeric units may be selected from the group consisting of: nonionic hydrophilic monomeric units, nonionic hydrophobic monomeric units, and mixtures thereof.

Non-limiting examples of nonionic hydrophilic monomeric units suitable for the present invention include nonionic hydrophilic monomeric units derived from nonionic hydrophilic monomers selected from the group consisting of: hydroxyalkyl esters of α,β-ethylenically unsaturated acids, such as hydroxyethyl or hydroxypropyl acrylates and methacrylates, glyceryl monomethacrylate, α,β-ethylenically unsaturated amides such as acrylamide, N,N-dimethylmethacrylamide, N-methylolacrylamide, α,β-ethylenically unsaturated monomers bearing a water-soluble polyoxyalkylene segment of the poly(ethylene oxide) type, such as poly(ethylene oxide) α-methacrylates (Bisomer S20W, S10W, etc., from Laporte) or α,ω-dimethacrylates, Sipomer BEM from Rhodia (ω-behenyl polyoxyethylene methacrylate), Sipomer SEM-25 from Rhodia (ω-tristyrylphenyl polyoxyethylene methacrylate), α,β-ethylenically unsaturated monomers which are precursors of hydrophilic units or segments, such as vinyl acetate, which, once polymerized, can be hydrolyzed in order to give rise to vinyl alcohol units or polyvinyl alcohol segments, vinylpyrrolidones, α,β-ethylenically unsaturated monomers of the ureido type, and in particular 2-imidazolidinone-ethyl methacrylamide (Sipomer WAM II from Rhodia), and mixtures thereof. In one example, the nonionic hydrophilic monomeric unit is derived from acrylamide.

Non-limiting examples of nonionic hydrophobic monomeric units suitable for the present invention include nonionic hydrophobic monomeric units derived from nonionic hydrophobic monomers selected from the group consisting of: vinylaromatic monomers such as styrene, alpha-methylstyrene, vinyltoluene, vinyl halides or vinylidene halides, such as vinyl chloride, vinylidene chloride, C_1-C_{12} alkylesters of α,β-monoethylenically unsaturated acids such as methyl, ethyl or butyl acrylates and methacrylates, 2-ethylhexyl acrylate, vinyl esters or allyl esters of saturated carboxylic acids, such as vinyl or allyl acetates, propionates, versatates, stearates, α,β-monoethylenically unsaturated nitriles containing from 3 to 12 carbon atoms, such as acrylonitrile, methacrylonitrile, α-olefins such as ethylene, conjugated dienes, such as butadiene, isoprene, chloroprene, and mixtures thereof.

b. Anionic Monomeric Units

Non-limiting examples of anionic monomeric units suitable for the present invention include anionic monomeric units derived from anionic monomers selected from the group consisting of: monomers having at least one carboxylic function, for instance α,β-ethylenically unsaturated carboxylic acids or the corresponding anhydrides, such as acrylic, methacrylic or maleic acids or anhydrides, fumaric acid, itaconic acid, N-methacroylalanine, N-acryloylglycine, and their water-soluble salts, monomers that are precursors of carboxylate functions, such as tert-butyl acrylate, which, after polymerization, give rise to carboxylic functions by hydrolysis, monomers having at least one sulfate or sulfonate function, such as 2-sulfooxyethyl methacrylate, vinylbenzene sulfonic acid, allyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), sulfoethyl acrylate or methacrylate, sulfopropyl acrylate or methacrylate, and their water-soluble salts, monomers having at least one phosphonate or phosphate function, such as vinylphosphonic acid, etc., the esters of ethylenically unsaturated phosphates, such as the phosphates derived from hydroxyethyl methacrylate (Empicryl 6835 from Rhodia) and those derived from polyoxyalkylene methacrylates, and their water-soluble salts, and 2-carboxyethyl acrylate (CEA), and mixtures thereof. In one example, the anionic monomeric unit is derived from an anionic monomer selected from the group consisting of: acrylic acid, AMPS, CEA, and mixtures thereof. In another example, the anionic monomeric unit is derived from acrylic acid.

c. Cationic Monomeric Units

Non-limiting examples of cationic monomeric units suitable for the present invention include cationic monomeric units derived from cationic monomers selected from the group consisting of: N,N-(dialkylamino-ω-alkyl)amides of α,β-monoethylenically unsaturated carboxylic acids, such as N,N-dimethylaminomethylacrylamide or -methacrylamide, 2-(N,N-dimethylamino)ethylacrylamide or -methacrylamide, 3-(N,N-dimethylamino)propylacrylamide or -methacrylamide, and 4-(N,N-dimethylamino)butylacrylamide or -methacrylamide, α,β-monoethylenically unsaturated amino esters such as 2-(dimethylamino)ethyl acrylate (DMAA), 2-(dimethylamino)ethyl methacrylate (DMAM), 3-(dimethylamino)propyl methacrylate, 2-(tert-butylamino)ethyl methacrylate, 2-(dipentylamino)ethyl methacrylate, and 2(diethylamino)ethyl methacrylate, vinylpyridines, vinylamine, vinylimidazolines, monomers that are precursors of amine functions such as N-vinylformamide, N-vinylacetamide, which give rise to primary amine functions by simple acid or base hydrolysis, acryloyl- or acryloyloxyammonium monomers such as trimethylammonium propyl methacrylate chloride, trimethylammonium ethylacrylamide or -methacrylamide chloride or bromide, trimethylammonium butylacrylamide or -methacrylamide methyl sulfate, trimethylammonium propylmethacrylamide methyl sulfate, (3-methacrylamidopropyl)trimethylammonium chloride (MAPTAC), (3-methacrylamidopropyl)trimethylammonium methyl sulphate (MAPTA-MES), (3-acrylamidopropyl)trimethylammonium chloride (APTAC), methacryloyloxyethyl-trimethylammonium chloride or methyl sulfate, and acryloyloxyethyltrimethylammonium chloride; 1-ethyl-2-vinylpyridinium or 1-ethyl-4-vinylpyridinium bromide, chloride or methyl sulfate; N,N-dialkyldiallylamine monomers such as N,N-dimethyldiallylammonium chloride (DADMAC); polyquaternary monomers such as dimethylaminopropylmethacrylamide chloride and N-(3-chloro-2-hydroxypropyl)trimethylammonium (DIQUAT or DQ) and 2-hydroxy-N^1-(3-(2((3-

methacrylamidopropyl)dimethylammino)-acetamido)propyl)-N^1, N^1, N^3, N^3, N^3 -pentamethylpropane-1,3-diaminium chloride (TRIQUAT or TQ), and mixtures thereof. In one example, the cationic monomeric unit comprises a quaternary ammonium monomeric unit, for example a monoquaternary ammonium monomeric unit, a diquaternary ammonium monomeric unit and a triquaternary monomeric unit. In one example, the cationic monomeric unit is derived from MAPTAC. In another example, the cationic monomeric unit is derived from DADMAC. In still another example, the cationic monomeric unit is derived from TQ.

In one example, the cationic monomeric units are derived from cationic monomers selected from the group consisting of: dimethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, di-tert-butylaminoethyl (meth)acrylate, dimethylaminomethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide, ethylenimine, vinylamine, 2-vinylpyridine, 4-vinylpyridine and vinyl imidazole, and mixtures thereof.

In another example, the cationic monomeric units are derived from cationic monomers selected from the group consisting of: trimethylammonium ethyl (meth)acrylate bromide, chloride or methyl sulfate, trimethylammonium ethyl (meth)acrylate bromide, chloride or methyl sulfate, trimethylammonium ethyl (meth)acrylate bromide, chloride or methyl sulfate, dimethylaminoethyl (meth)acrylate benzyl chloride, 4-benzoylbenzyl dimethylammoniumethyl (meth)acrylate bromide, chloride or methyl sulfate,, trimethylammonium ethyl (meth)acrylamido bromide, chloride, or methyl sulfate, trimethylammonium propyl (meth)acrylamido braomide, chloride, or methyl sulfate, vinyl benzyl trimethyl ammonium bromide, chloride or methyl sulfate, diallyldimethyl ammonium chloride, , 1-ethyl-2-vinylpyridinium bromide, chloride or methyl sulfate, 4-vinylpyridinium bromide, chloride or methyl sulfate, and mixtures thereof.

d. Zwitterionic Monomeric Units

Non-limiting examples of zwitterionic monomeric units suitable for the present invention include zwitterionic monomeric units derived from zwitterionic monomers selected from the group consisting of: sulfobetaine monomers, such as sulfopropyl dimethylammonium ethyl methacrylate (SPE from Raschig), sulfopropyldimethylammonium propylmethacrylamide (SPP from Raschig), and sulfopropyl-2-vinylpyridinium (SPV from Raschig), 3-((3-methacrylamidopropyl)dimethylammonio)propane-1-sulfonate (SZ), phosphobetaine monomers, such as phosphatoethyl trimethylammonium ethyl methacrylate, carboxybetaine monomers, N-(carboxymethyl)-3-methacrylamido-N,N-dimethlpropan-1-aminium chloride (CZ),. In one example, the zwitterionic monomeric unit is derived from CZ, SZ, and mixtures thereof.

In one example, a polymer of the present invention may comprise at least one monomeric unit selected from groups a (nonionic monomeric units) and b (anionic monomeric units) and at least one monomeric unit selected from groups c (cationic monomeric units) and d (zwitterionic monomeric units).

In one example, the polymer comprises at least 69.9% wt and/or at least 70% wt and/or at least 75% wt and/or at least 80% wt and/or at least 85% wt and/or at least 90% wt and/or at least 95% wt and/or at least 98% wt and/or at least 99% wt and/or at least 99.5% wt of a monomeric unit from group a. The balance of the polymer (no more than 30.1% wt and/or no more than 30% wt and/or no more than 25% wt and/or no more than 20% wt and/or no more than 15% wt and/or no more than 10% wt and/or no more than 5% wt and/or no more than 2% wt and/or no more than 1% wt and/or no more than 0.5% wt total) comprises one or more monomeric units selected from groups b, c, and d. In one example, the polymer comprises from about 70% to about 99.5% wt of a monomeric unit from group a, from about 0.1% to about 10% wt of a monomeric unit from group b, and from about 0.3% to about 29% wt of a monomeric unit from group c. In still another example, the polymer comprises from about 70% to about 99.5% wt of a monomeric unit from group a, from about 0.5% to about 30% wt combined of monomeric units from groups b and c.

In one example, the polymer comprises at least 0.1% wt and/or at least 1% and/or at least 5% wt and/or at least 7% wt and/or at least 10% wt and/or to about 25% wt and/or to about 20% wt and/or to about 15% wt of a monomeric unit from group b.

In one example, polymer comprises at least 0.1% wt and/or at least 0.3% wt and/or at least 0.5% and/or at least 1% and/or at least 5% wt and/or at least 7% wt and/or at least 10% wt and/or to about 75% wt and/or to about 70% wt and/or to about 65% wt and/or to about 55% wt and/or to about 40% wt and/or to about 30% wt and/or to about 25% wt and/or to about 20% wt and/or to about 15% wt of a monomeric unit from group c.

In one example, polymer comprises at least 0.1% wt and/or at least 0.3% wt and/or at least 1% and/or at least 5% wt and/or at least 7% wt and/or at least 10% wt and/or to about 75% wt and/or to about 70% wt and/or to about 65% wt and/or to about 55% wt and/or to about 40% wt and/or to about 30% wt and/or to about 25% wt and/or to about 20% wt and/or to about 15% wt of a monomeric unit from group d.

In another example, the polymer comprises no more than 30.1% wt of a monomeric unit selected from the group consisting of: group b, group c, group d, and mixtures thereof.

In one example, the polymer may comprise a monomeric unit from group a and a monomeric unit from group b.

In one example, the polymer may comprise a monomeric unit from group a and a monomeric unit from group c.

In another example, the polymer of the present invention may comprise a monomeric unit from group a and a monomeric unit from group d.

In still another example, the polymer of the present invention may comprise a monomeric unit from group b and a monomeric unit from group c.

In still another example, the polymer of the present invention may comprise a monomeric unit from group b and a monomeric unit from group d.

In still another example, the polymer of the present invention may comprise a monomeric unit from group c and a monomeric unit from group d.

In yet another example, the polymer of the present invention may comprise a monomeric unit from group a, a monomeric unit from group b, and a monomeric unit from group c.

In even another example, the polymer of the present invention may comprise a monomeric unit from group a, a monomeric unit from group b, and a monomeric unit from group d.

In yet another example, the polymer of the present invention may comprise a monomeric unit from group a, a monomeric unit from group c, and a monomeric unit from group d.

In another example, the polymer of the present invention may comprise a monomeric unit from group b, a monomeric unit from group c, and a monomeric unit from group d.

In even yet another example, the polymer of the present invention may comprise a monomeric unit from group a, a monomeric unit from group b, a monomeric unit from group c and a monomeric unit from group d.

In one example, when present in the polymer, the monomeric unit from group b and the monomeric unit from group c are present in the polymer at a molar ratio of from about 3:1 to 1:3 and/or from about 2:1 to 1:2 and/or from about 1.3:1 to 1:1.3 and/or about 1:1 or less or about 1:1 or more.

In another example, when present in the polymer, the monomeric unit from group b and the monomeric unit from group d are present in the polymer at a molar ratio of from about 3:1 to 1:3 and/or from about 2:1 to 1:2 and/or from about 1.3:1 to 1:1.3 and/or about 1:1 or less or about 1:1 or more.

In another example, when present in the polymer, the monomeric unit from group c and the monomeric unit from group d are present in the polymer at a molar ratio of from about 3:1 to 1:3 and/or from about 2:1 to 1:2 and/or from about 1.3:1 to 1:1.3 and/or about 1:1 or less or about 1:1 or more.

In still another example, the polymer comprises a monomeric unit from group a and a monomeric unit from group c. For example, the polymer may comprise an acrylamide monomeric unit and a quaternary ammonium monomeric unit. The quaternary monomeric unit may be selected from the group consisting of: monoquaternary ammonium monomeric units, diquaternary ammonium monomeric units, and triquaternary ammonium monomeric units. In one example, the polymer may comprise at least 69.9% wt of the monomeric unit from group a and no more than 30.1% wt of the monomeric unit from group c.

In still another example, the polymer comprises a monomeric unit from group a and a monomeric unit from group b. For example, the polymer may comprise an acrylamide monomeric unit and an acrylic acid monomeric unit. In one example, the polymer may comprise at least 69.9% wt of the monomeric unit from group a and no more than 30.1% wt of the monomeric unit from group b.

In yet another example, the polymer comprises a monomeric unit from group b and a monomeric unit from group c. For example, the polymer may comprise an anionic monomeric unit derived from an anionic monomer selected from the group consisting of: acrylic acid, methacrylic acid, 2-acrylamido-2-methylpropane sulfonic acid, carboxyethyl acrylate, and mixtures thereof and a quaternary ammonium monomeric unit. The quaternary ammonium monomeric unit may be derived from a quaternary monomer selected from the group consisting of: monoquaternary ammonium monomeric units, diquaternary ammonium monomeric units, triquaternary ammonium monomeric units, and mixtures thereof. In one example, the polymer comprises an anionic monomeric unit derived from acrylic acid and a quaternary ammonium monomeric unit derived from MAPTAC. In one example, the polymer may comprise no more than 25% wt of the monomeric unit from group b and no more than 75% wt of the monomeric unit from group c.

In even yet another example, the polymer comprises a monomeric unit from group a and a monomeric unit from group b and a monomer unit from group c. For example, the polymer may comprise an acrylamide monomeric unit, and an anionic monomeric unit derived from an anionic monomer selected from the group consisting of: acrylic acid, methacrylic acid, 2-acrylamido-2-methylpropane sulfonic acid, carboxyethyl acrylate, and mixtures thereof and a quaternary ammonium monomeric unit. The quaternary ammonium monomeric unit may be derived from a quaternary monomer selected from the group consisting of: monoquaternary ammonium monomeric units, diquaternary ammonium monomeric units, triquaternary ammonium monomeric units, and mixtures thereof. In one example, the polymer comprises a nonionic monomeric unit derived from acrylamide, an anionic monomeric unit derived from acrylic acid, and a cationic monomeric unit derived from MAPTAC. In another example, the polymer comprises a nonionic monomeric unit derived from acrylamide, an anionic monomeric unit derived from acrylic acid, and a cationic monomeric unit derived from DADMAC. In still another example, the polymer comprises a nonionic monomeric unit derived from acrylamide, an anionic monomeric unit derived from acrylic acid, and a cationic monomeric unit derived from TQ. In another example, the polymer comprises a nonionic monomeric unit derived from acrylamide, an anionic monomeric unit derived from CEA, and a cationic monomeric unit derived from MAPTAC. In still another example, the polymer comprises a nonionic monomeric unit derived from acrylamide, an anionic monomeric unit derived from AMPS, and a cationic monomeric unit derived from MAPTAC. In one example, the polymer may comprise at least 69.9% wt of the monomeric unit from group a and no more than 30.1% wt combined of the monomeric units from groups b and c. In another example, the polymer may comprise from about 70% to about 99.5% wt of the monomeric unit from group a, from 0.1% to about 30% wt of the monomeric unit from group b, and from about 0.1% to about 30% wt of the monomeric unit from group c. In still another example, the polymer may comprise from about 70% to about 99.5% wt of the monomeric unit from group a and from about 0.5% to 30% wt combined of the monomeric units from groups b and c.

In even still yet another example, the polymer comprises a monomeric unit from group a and a monomeric unit from group c and a monomer unit from group d. For example, the polymer may comprise an acrylamide monomeric unit, a quaternary ammonium monomeric unit, and a zwitterionic monomeric unit selected from the group consisting of: CZ, SZ, and mixtures thereof. The quaternary ammonium monomeric unit may be derived from a quaternary monomer selected from the group consisting of: monoquaternary ammonium monomeric units, diquaternary ammonium monomeric units, triquaternary ammonium monomeric units, and mixtures thereof. In one example, the polymer comprises a nonionic monomeric unit derived from acrylamide, a cationic monomeric unit derived from MAPTAC, and a zwitterionic monomeric unit derived from CZ. In another example, the polymer comprises a nonionic monomeric unit derived from acrylamide, a cationic monomeric unit derived from MAPTAC, and a zwitterionic monomeric unit derived from

SZ. In one example, the polymer may comprise at least 69.9% wt of the monomeric unit from group a and no more than 30.1% wt combined of the monomeric units from groups c and d. In another example, the polymer may comprise from about 70% to about 99.5% wt of the monomeric unit from group a, from 0.1% to about 30% wt of the monomeric unit from group c, and from about 0.1% to about 30% wt of the monomeric unit from group d. In still another example, the polymer may comprise from about 70% to about 99.5% wt of the monomeric unit from group a and from about 0.5% to 30% wt combined of the monomeric units from groups c and d.

In even yet another example, the polymer comprises a monomeric unit from group a and a monomeric unit from group b and a monomer unit from group d. For example, the polymer may comprise an acrylamide monomeric unit, and an anionic monomeric unit derived from an anionic monomer selected from the group consisting of: acrylic acid, methacrylic acid, 2-acrylamido-2-methylpropane sulfonic acid, carboxyethyl acrylate, and mixtures thereof and a zwitterionic monomeric unit selected from the group consisting of: CZ, SZ, and mixtures thereof. In one example, the polymer comprises a nonionic monomeric unit derived from acrylamide, an anionic monomeric unit derived from acrylic acid, and zwitterionic monomeric unit derived from CZ. In another example, the polymer comprises a nonionic monomeric unit derived from acrylamide, an anionic monomeric unit derived from acrylic acid, and a zwitterionic monomeric unit derived from SZ. In one example, the polymer may comprise at least 69.9% wt of the monomeric unit from group a and no more than 30.1% wt combined of the monomeric units from groups b and d. In another example, the polymer may comprise from about 70% to about 99.5% wt of the monomeric unit from group a, from 0.1% to about 30% wt of the monomeric unit from group b, and from about 0.1% to about 30% wt of the monomeric unit from group d. In still another example, the polymer may comprise from about 70% to about 99.5% wt of the monomeric unit from group a and from about 0.5% to 30% wt combined of the monomeric units from groups b and d.

In even yet another example, the polymer comprises a monomeric unit from group a and a monomeric unit from group d. For example, the polymer may comprise an acrylamide monomeric unit, and a zwitterionic monomeric unit selected from the group consisting of: CZ, SZ, and mixtures thereof. In one example, the polymer comprises a nonionic monomeric unit derived from acrylamide and zwitterionic monomeric unit derived from CZ. In another example, the polymer comprises a nonionic monomeric unit derived from acrylamide and a zwitterionic monomeric unit derived from SZ. In one example, the polymer may comprise at least 69.9% wt of the monomeric unit from group a and no more than 30.1% wt of the monomeric unit from group d. In another example, the polymer may comprise from about 70% to about 99.5% wt of the monomeric unit from group a, from 0.5% to about 30% wt of the monomeric unit from group d.

In one example, the polymer of the present invention comprises a nonionic hydrophilic monomeric unit. Non-limiting examples of suitable hydrophilic monomeric units are derived from nonionic hydrophilic monomers selected from the group consisting of: hydroxyalkyl esters of α,β-ethylenically unsaturated acids, α,β-ethylenically unsaturated amides, α,β-ethylenically unsaturated monoalkyl amides, α,β-ethylenically unsaturated dialkyl amides, α,β-ethylenically unsaturated monomers bearing a water-soluble polyoxyalkylene segment of the poly(ethylene oxide) type, α,β-ethylenically unsaturated monomers which are precursors of hydrophilic units or segments, vinylpyrrolidones, α,β-ethylenically unsaturated monomers of the ureido type, and mixtures thereof. In one example, the nonionic hydrophilic monomeric unit is derived from acrylamide.

In another example, the polymer of the present invention comprises a nonionic hydrophobic monomeric unit. Non-limiting examples of suitable nonionic hydrophobic monomeric units are derived from nonionic hydrophobic monomers selected from the group consisting of: vinylaromatic monomers, vinyl halides, vinylidene halides, C_1-C_{12} alkylesters of α,β-monoethylenically unsaturated acids, vinyl esters of saturated carboxylic acids, allyl esters of saturated carboxylic acids, α,β-monoethylenically unsaturated nitriles containing from 3 to 12 carbon atoms, α-olefins, conjugated dienes, and mixtures thereof.

In one example, the polymer comprises an anionic monomeric unit. Non-limiting examples of suitable anionic monomeric units are derived from anionic monomers selected from the group consisting of: monomers having at least one carboxylic function, for instance α,β-ethylenically unsaturated carboxylic acids or the corresponding anhydrides, monomers that are precursors of carboxylate functions, monomers having at least one sulfate or sulfonate function, monomers having at least one phosphonate or phosphate function, esters of ethylenically unsaturated phosphates, and mixtures thereof. In one example, the anionic monomeric unit is derived from an anionic monomer selected from the group consisting of: acrylic acid, methacrylic acid, 2-acrylamido-2-methylpropane sulfonic acid, carboxyethyl acrylate, and mixtures thereof.

In one example, the polymer comprises a cationic monomeric unit. Non-limiting examples of suitable cationic monomeric units are derived from cationic monomers selected from the group consisting of: acryloyl- or acryloyloxyammonium monomers, 1-ethyl-2-vinylpyridinium or 1-ethyl-4-vinylpyridinium bromide, chloride or methyl sulfate, N,N-dialkyldiallylamine monomers, polyquaternary monomers, N,N-(dialkylamino-ω-alkyl)amides of α,β-monoethylenically unsaturated carboxylic acids, α,β-monoethylenically unsaturated amino esters, vinylpyridines, vinylamine, vinylimidazolines, monomers that are precursors of amine functions which give rise to primary amine functions by simple acid or base hydrolysis, and mixtures thereof. In one example, the cationic monomeric unit is derived from MAPTAC. In another example, the cationic monomeric unit is derived from DADMAC. In still another example, the cationic monomeric unit is derived from 2-hydroxy-N^1-(3-(2((3- methacrylamidopropyl)dimethylammino)-acetamido)propyl)-N^1, N^1, N^3, N^3, N^3 -pentamethylpropane-1,3-diaminium chloride.

In one example, the polymers of the present invention are water-soluble.

Process for Making Polymers

The polymers of the present invention may be made by any suitable process known in the art. For example, the polymer may be made by radical polymerization.

The polymers of the present invention can be made by a wide variety of techniques, including bulk, solution, emulsion, or suspension polymerization. Polymerization methods and techniques for polymerization are described generally in Encyclopedia of Polymer Science and Technology, Interscience Publishers (New York), Vol. 7, pp. 361-431 (1967), and Kirk-Othmer Encyclopedia of Chemical Technology, 3rd edition, Vol 18, pp. 740-744, John Wiley & Sons (New York), 1982, both incorporated by reference herein. See also Sorenson, W. P. and Campbell, T. W., Preparative Methods of Polymer Chemistry. 2nd edition, Interscience Publishers (New York), 1968, pp. 248-251, incorporated by reference herein, for general reaction techniques suitable for the present invention. In one example, the polymers are made by free radical copolymerization, using water soluble initiators. Suitable free radical initiators include, but are not limited to, thermal initiators, redox couples, and photochemical initiators. Redox and photochemical initiators may be used for polymerization processes initiated at temperatures below about 30°C (86°F). Such initiators are described generally in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd edition, John Wiley & Sons (New York), Vol. 13, pp. 355- 373 (1981), incorporated by reference herein. Typical water soluble initiators that can provide radicals at 30°C or below include redox couples, such as potassium persulfate/silver nitrate, and ascorbic acid/hydrogen peroxide. In one example, the method utilizes thermal initiators in polymerization processes conducted above 40°C (104°F). Water soluble initiators that can provide radicals at 40°C (104°F) or higher can be used. These include, but are not limited to, hydrogen peroxide, ammonium persulfate, and 2,2'-azobis(2-amidinopropane) dihydrochloride. In one example, water soluble starting monomers are polymerized in an aqueous alcohol solvent at 60°C (140°F) using 2,2'-azobis(2-amidinopropane) dihydrochloride as the initiator. The solvent should typically contain at least about 10% by volume, of alcohol in order to prevent the polymerization reaction medium from gelling. Suitable alcohols for use in such reaction include low molecular weight alcohols such as, but not limited to, methanol, ethanol, isopropanol, and butanol.

Another technique is a solution polymerization as described in U.S. Pat. No. 3,317,370, Kekish, issued May 2, 1967 and U.S. Pat. No. 3,410,828, Kekish, issued Nov. 12, 1968, both incorporated herein by reference. According to such process, the acrolein, or other aldehydic monomer, is copolymerized with a non-nucleophilic, water soluble, nitrogen-heterocyclic polymerizable monomer and a redox initiator system. The copolymer is then made cationic by reacting the copolymer with a water soluble amine or amine quaternary. Amines, including amine quaternaries, that are useful include, but are not limited to, primary, secondary, and tertiary amines such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, or partial or fully quaternized derivatives of any of the foregoing, hydrazides and quaternaries thereof such as betaine hydrazide chloride, N-N-dimethylglycine hydrazide, unsymmetrical dimethyl hydrazides, polymers, such as those formed by reaction of urea and polyalkylene polyamines, guanidines, biguanides, guanylureas, mono and polyhydroxy polyamines and quaternaries thereof, etc. When using this emulsion copolymerization technique, it will be necessary to control molecular weight to within the ranges provided herein.

In one example, a method for making a polymer according to the present invention comprises the steps of:

i. providing two or more monomeric units selected from the group consisting of:
   a. nonionic monomeric units;
   b. anionic monomeric units;
   c. cationic monomeric units;
   d. zwitterionic monomeric units; and
   e. mixtures thereof; and

ii. polymerizing the two or more monomeric units such that a polymer that exhibits a Soil Adsorption Value of at least 38 mg as measured according to the Soil Adsorption Test Method described herein is produced. In one example, the step of polymerizing comprises the step of mixing the two or more monomeric units or the monomers from which they are derived with water to form a monomer solution. The monomer solution may be deoxygenated. In addition, the monomer solution may be subjected (heated) to a temperature of at least 25°C, such as 60°C. The temperatures used to make the polymer may be any suitable temperature so long as a polymer according to the present invention is produced. The polymer may be subject to such temperature for a time sufficient to polymerize the monomeric units into a polymer, for example at least 10 minutes, and/or at least 18 hours depending on the reaction conditions. An initiator, such as a free-radical initiator, may be added to the monomer solution to polymerize the monomeric units (monomers) within the monomer solution to produce a polymer of the present invention. The levels of free radical initiator(s) used to make the polymer may be any suitable level so long as a polymer according to the present invention is produced. The levels of the various monomeric units (monomers) used to make the polymer may be any suitable level so long as a polymer according to the present invention is produced.

Non-limiting Synthesis Examples

Sample Preparation

Initiator Solution Preparation

10ml of water is added to a flask along with 1 gram of 2,2'-azobis(2-methylpropionamidine) dihydrochloride (available from Wako Chemicals), herein called V-50. This solution is sparged with argon gas to remove oxygen.

Monomer Preparation

Synthesis of 2-Hydroxy-N^1-(3-(2-((3-Methacrylamidopropyl)Dimethylammonio)-Acetamido)Propyl)-N^1,N^1,N^3,N^3,N^3-Pentamethylpropane-1,3-Diaminium Chloride (Herein Called TQ)

To a jacketed round bottom flask equipped with mechanical stirrer, gas inlet, condenser and thermometer is added 340.6 grams of dimethylamino propyl methacrylamide (DMAPMA, available from Sigma-Aldrich), 238.8 grams of methyl chloroacetate (available from Sigma-Aldrich), 0.5 g 4-methoxy phenol (available from Sigma-Aldrich), and 423 grams of methanol (available from Sigma-Aldrich). The round bottom flask is heated at 70 °C for 5 hours. This reaction is cooled to room temperature and then 0.5 grams of 4-methoxy phenol (available from Sigma-Aldrich) and 225 grams of dimethylaminoipropylamine (available from Sigma-Aldrich) is added evenly over a 2 hour period. After 2 hours the reaction is heated to 65 °C for 2 hours after which methanol is distilled out at 50 °C under vacuum. To this is added 690 grams of (3-chloro-2-hydroxypropyl)trimethylammonium chloride (available as a 60% aqueous solution from Sigma-Aldrich). The temperature is maintained at 65-70 °C for 2 hours. During these 2 hours methanol is stripped out and water is added to make a 55% solution in water based on weight. The reaction is continued in water at 65-70 °C for another hour to yield the TQ monomer.

Synthesis of 3-((3-Methacrylamidopropyl)Dimethylammonio)Propane-1-Sulfonate (Herein Called SZ)

Into a round bottom flask is added 26.4 grams of anhydrous acetonitrile (available from Sigma-Aldrich) and 15.5 grams of propane sultone (available from Sigma-Aldrich), and this is stirred for 30 minutes. After the 30 minutes, a solution of 25.6 grams of DMAPMA in 56.5 grams of acetonitrile is added. The mixture is stirred and warmed to 35 °C. A white precipitate quickly forms. Once the white precipitate takes up the bulk of the volume, the liquid is decanted. The solid is washed once with acetonitrile and again the liquid is removed by decanting. The solids are then washed in 2x volume diethyl ether. They are then filtered via funnel and washed with copious amounts (via filtration) of diethyl ether. The NMR structure is consistent with the structure of the target molecule SZ.

Synthesis of N-(Carboxymethyl)-3-Methacrylamido-N,N-Dimethylpropan-1-Aminium Chloride (Herein Called CZ)

To a round bottom flask is added 16.5 grams of methyl bromoacetate (available from Sigma-Aldrich), 74 grams of tetrahydrofuran (THF, available from Sigma-Aldrich), and 16.5 grams of DMAPMA. The solution is stirred for 16 hours at 25 °C, and then the stirring is discontinued. After settling, the top layer of THF is discarded. The lower layer is washed with 50 mL of hexanes (available from Sigma-Aldrich) twice and becomes a viscous material. The material is then dissolved in 15 mL of methanol (available from Sigma-Aldrich) and precipitated into 150 mL of diethyl ether (available from Sigma-Aldrich). The precipitate is washed several times with diethylether until it becomes a viscous semi-solid. It is then dried overnight under high vacuum at room temperature. A small portion is taken for NMR analysis. The remainder of the intermediate is placed in a glass desiccator containing calcium chloride until the next step.

3.3 grams of the intermediate from above is dissolved in 10 mL of deionized water and run through a column consisting of 50 mL of Dowex Marathon A hydroxide exchange resin (available from VWR Scientific) in a glass column of 2.5 cm diameter at 2.7 mL/min. The effluent is collected and 13 mL of 1N hydrochloric acid (available from Sigma-Aldrich) is added. The water is dried off under vacuum at room temperature. The sample is then dried overnight under high vacuum at room temperature. The material is removed from the vacuum and a small portion is taken for NMR analysis. 2.71 g of deionized water is added to the material to form the finished product CZ which is stored as a solution in water.

Polymer Preparation

Into a reaction vessel are added the monomers in the amounts listed for the examples in Table 1 below and 456 g of water. The monomers, acrylamide (herein called AAM), acrylic acid (herein called AA), diallyldimethylammonium chloride (herein called DADMAC), 2-carboxy ethyl acrylate (herein called CEA), 2-acrylamido-2-methylpropane sulfonic acid (herein called AMPS) and [3-(methyacryloylamino)propyl] trimethylammonium chloride (herein called MAPTAC), are all available from Sigma Aldrich. MAPTAC is used as a 50% w/w solution. TQ, SZ and CZ are used as prepared above. The reaction vessel is sparged with nitrogen to remove oxygen from the system and a nitrogen atmosphere is maintained in the vessel. The reaction vessel and contents are heated to a temperature of 60 °C.

Once the contents have reached 60 °C, the initiator solution 1 mL of the V-50 as prepared above is added as a 10% solution (except for Example 1.17 which used 0.0562 g of V-50 neat). The reaction is kept at 60 °C for 48 hours.

The following tables set forth non-limiting examples of polymers of the present invention that were made.

Table 1. Examples: Polymer Construction Data

Ex.	AAM (g)	AA (g)	MAPTAC (g)	DADMAC (g)	TQ (g)	CEA (g)	AMPS (g)	SZ (g)	CZ (g)
1.1	21.60	0.00	2.40	0.00	0.00	0.00	0.00	0.00	0.00
1.2	21.60	0.31	2.09	0.00	0.00	0.00	0.00	0.00	0.00
1.3	21.60	0.60	1.81	0.00	0.00	0.00	0.00	0.00	0.00
1.4	21.60	1.20	1.21	0.00	0.00	0.00	0.00	0.00	0.00
1.5	21.60	1.80	0.61	0.00	0.00	0.00	0.00	0.00	0.00
1.6	21.59	2.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.7	0.00	6.00	18.00	0.00	0.00	0.00	0.00	0.00	0.00
1.8	2.41	5.40	16.20	0.00	0.00	0.00	0.00	0.00	0.00
1.9	7.20	4.20	12.60	0.00	0.00	0.00	0.00	0.00	0.00
1.10	12.00	3.00	9.00	0.00	0.00	0.00	0.00	0.00	0.00
1.11	16.79	1.81	5.42	0.00	0.00	0.00	0.00	0.00	0.00
1.12	19.22	1.20	3.60	0.00	0.00	0.00	0.00	0.00	0.00
1.13	20.41	0.90	2.70	0.00	0.00	0.00	0.00	0.00	0.00
1.14	21.61	0.60	1.80	0.00	0.00	0.00	0.00	0.00	0.00

1.15	22.81	0.31	0.92	0.00	0.00	0.00	0.00	0.00	0.00
1.16	23.51	0.12	0.36	0.00	0.00	0.00	0.00	0.00	0.00
1.17	23.75	0.06	0.18	0.00	0.00	0.00	0.00	0.00	0.00
1.18	23.76	0.06	0.18	0.00	0.00	0.00	0.00	0.00	0.00
1.19	23.87	0.03	0.10	0.00	0.00	0.00	0.00	0.00	0.00
1.20	24.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1.21	23.76	0.07	0.00	0.17	0.00	0.00	0.00	0.00	0.00
1.22	23.77	0.0285	0.00	0.00	0.212	0.00	0.00	0.00	0.00
1.23	23.76	0.00	0.145	0.00	0.00	0.0939	0.00	0.00	0.00
1.24	23.76	0.00	0.13	0.00	0.00	0.00	0.12	0.00	0.00
1.25	23.77	0.00	0.00	0.00	0.00	0.00	0.00	0.252	0.00
1.26	23.76	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.240
1.27	23.52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.479
1.28	23.76	0.00	0.003	0.00	0.00	0.00	0.00	0.00	0.240
1.29	23.76	0.002	0.00	0.00	0.00	0.00	0.00	0.00	0.240

Table 2. Examples: Polymer Solution Data (with Water as the Diluent)

Ex.	Mass Composition of Monomers	Solids (%)	Polymer Solution (g)	Polymer Solution + Water (g)	Conc. (%)
2.1	90% AAM, 10% MAPTAC	5.44	0.4253	115.68	0.02
2.2	90% AAM, 1.3% AA, 8.7% MAPTAC	5.41	0.3927	106.24	0.02
2.3	90% AAM, 2.5% AA, 7.5% MAPTAC	5.45	0.4013	109.34	0.02
2.4	90% AAM, 5% AA, 5% MAPTAC	5.43	0.3974	107.89	0.02
2.5	90% AAM, 7.5% AA, 2.5% MAPTAC	5.42	0.7522	203.84	0.02
2.6	90% AAM, 10% AA	5.42	0.3985	108.00	0.02
2.7	25% AA, 75% MAPTAC	5.25	0.3823	100.36	0.02
2.8	10% AAM, 22.5% AA, 67.5% MAPTAC	5.24	0.3788	99.27	0.02
2.9	30% AAM, 17.5% AA, 52.5% MAPTAC	5.26	0.3979	104.64	0.02
2.10	50% AAM, 12.5% AA, 37.5% MAPTAC	5.36	0.3692	98.95	0.02
2.11	69.9% AAM, 7.5% AA, 22.6% MAPTAC	5.30	0.3810	100.97	0.02
2.12	80% AAM, 5% AA,15 % MAPTAC	5.31	0.3899	103.53	0.02
2.13	85% AAM, 3.7% AA,11.3 % MAPTAC	5.30	0.4403	116.69	0.02
2.14	90% AAM, 2.5% AA, 7.5% MAPTAC	5.26	0.3800	99.93	0.02
2.15	94.9% AAM, 1.3% AA, 3.8% MAPTAC	5.34	0.3982	106.34	0.02
2.16	98% AAM, 0.5% AA, 1.5% MAPTAC	2.54	0.7969	101.21	0.02

2.17	99% AAM, 0.25% AA, 0.75% MAPTAC	2.56	0.7944	101.68	0.02
2.18	99% AAM, 0.25% AA, 0.75% MAPTAC	5.32	0.3751	100.49	0.02
2.19	99.5% AAM, 0.125% AA, 0.375% MAPTAC	2.57	0.7850	100.89	0.02
2.20	100% AAM (Comparative Example)	5.23	0.3979	104.02	0.02
2.21	99% AAM, 0.3% AA, 0.7% DADMAC	5.40	0.3876	104.70	0.02
2.22	99% AAM, 0.12% AA, 0.88% TQ	5.16	3.8100	980.46	0.02
2.23	99.01% AAM, 0.39% CEA, 0.6% MAPTAC	5.27	0.3914	103.13	0.02
2.24	99% AAM, 0.5% AMPS, 0.5% MAPTAC	5.40	0.3823	103.22	0.02
2.25	98.95% AAM, 1.05% SZ	5.29	0.3791	100.25	0.02
2.26	99% AAM, 1% CZ	5.28	0.4004	105.73	0.02
2.27	98% AAM, 2% CZ	5.13	0.4055	104.15	0.02
2.28	98.99% AAM, 0.01% MAPTAC, 1% CZ	5.15	0.5177	133.36	0.02
2.29	98.99% AAM, 0.01% AA, 1% CZ	5.14	0.5941	152.90	0.02
2.30	Mirapol® HSC300 (Comparative Example)	20.81	0.1378	143.38	0.02
2.31	Deionized Water (Control)				

Table 3. Test Results (Soil Adsorption Test of Polymers Done using Handsheet as the Substrate)

Ex.	Mass Composition of Monomers	Mn	PDI	Soil Adsorption Value (mg)	St Dev (mg)	% Soil Retained$_{avg}$ (%)	St Dev (%)
3.1	90% AAM, 10% MAPTAC	1,211,000	1.240	41	1	23	1
3.2	90% AAM, 1.3% AA, 8.7% MAPTAC	948,200	1.239	42	6	24	3
3.3	90% AAM, 2.5% AA, 7.5% MAPTAC	852,500	1.351	47	2	26	1
3.4	90% AAM, 5% AA, 5% MAPTAC	753,500	1.402	40	3	23	2
3.5	90% AAM, 7.5% AA, 2.5% MAPTAC	970,300	1.271	43	3	24	2
3.6	90% AAM, 10% AA	1,021,000	1.222	46	1	26	0
3.7	25% AA, 75% MAPTAC	201,500	1.823	44	3	24	2
3.8	10% AAM, 22.5% AA, 67.5% MAPTAC	226,400	1.712	32	1	18	1
3.9	30% AAM, 17.5% AA, 52.5% MAPTAC	311,800	1.604	32	2	18	1
3.10	50% AAM, 12.5% AA, 37.5% MAPTAC	583,800	1.406	34	3	19	2
3.11	69.9% AAM, 7.5% AA, 22.6% MAPTAC			38	1	21	1
3.12	80% AAM, 5% AA, 15% MAPTAC	821,000	1.269	40	1	23	1
3.13	85% AAM, 3.7% AA, 11.3% MAPTAC	865,600	1.241	44	3	25	2
3.14	90% AAM, 2.5% AA, 7.5% MAPTAC			45	0	25	0

3.15	94.9% AAM, 1.3% AA, 3.8% MAPTAC	927,100	1.222	53	3	30	1
3.16	98% AAM, 0.5% AA, 1.5% MAPTAC			55	3	31	2
3.17	99% AAM, 0.25% AA, 0.75% MAPTAC	858,100	1.302	57	3	32	2
3.18	99% AAM, 0.25% AA, 0.75% MAPTAC	814,200	1.293	57	5	32	3
3.19	99.5% AAM, 0.125% AA, 0.375% MAPTAC	1,212,000	1.285	65	3	36	2
3.20	100% AAM (Comparative Example)	1,116,600	1.204	40	3	22	2
3.21	99% AAM, 0.3% AA, 0.7% DADMAC	520,400	1.432	53	4	30	2
3.22	99% AAM, 0.12% AA, 0.88% TQ	1,050,000	1.165	54	2	30	1
3.23	99.01% AAM, 0.39% CEA, 0.6% MAPTAC	791,200	1.219	61	4	34	2
3.24	99% AAM, 0.5% AMPS, 0.5% MAPTAC	644,400	1.579	59	2	33	1
3.25	98.95% AAM, 1.05% SZ	542,800	1.566	54	4	30	2
3.26	99% AAM, 1% CZ	862,700	1.269	57	3	32	1
3.27	98% AAM, 2% CZ			62	2	35	1
3.28	98.99% AAM, 0.01% MAPTAC, 1% CZ			60	4	33	2
3.29	98.99% AAM, 0.01% AA, 1% CZ			60	2	33	1
3.30	Mirapol® HSC300* (Comparative Example)			34	3	19	1
3.31	Deionized Water (Control)			20	4	11	2
3.32	Swiffer WetJet			23	3	13	1

Table 4. Examples: Polymer Solution Data (with Swiffer WetJet as the Diluent)

Ex.	Mass Composition of Monomers	Cleaning Solution	Solids (%)	Polymer Solution (g)	Polymer Solution + Water (g)	Conc. (%)
4.18	99% AAM, 0.25% AA, 0.75% MAPTAC	Swiffer WetJet	5.32	0.39	103.74	0.02
4.22	99% AAM, 0.12% AA, 0.88% TQ	Swiffer WetJet	5.16	0.37	95.46	0.02
4.20	100% AAM (Comparative Example)	Swiffer WetJet	5.23	0.37	96.76	0.02
4.30	Mirapol HSC300* (Comparative Example)	Swiffer WetJet	20.81	0.15	156.08	0.02

* Mirapol® HSC 300 was obtained from Rhodia S. A. (Paris, France).

Table 5. Test Results

Ex.	Mass Composition of Monomers	Cleaning Solution	Soil Adsorption Value (mg)	St Dev (mg)	% Soil Retained$_{avg}$ (%)	St Dev (%)	% Change
5.18	99% AAM, 0.25% AA, 0.75% MAPTAC	Swiffer WetJet	56	5	31	3	146
5.22	99% AAM, 0.12% AA, 0.88% TQ	Swiffer WetJet	88	14	49	8	285
5.20	100% AAM (Comparative Example)	Swiffer WetJet	19	1	10	1	-18
5.30A	Mirapol HSC300* (Comparative Example)	Swiffer WetJet	33	3	18	2	44

* Mirapol® HSC 300 was obtained from Rhodia S. A. (Paris, France).

Test Methods

Determination of Percent Solids

An empty weigh pan (VWR disposable aluminum crinkle dishes with tabs, VWR Catalog #25433-010; or equivalent pan) is weighed to within ± 0.1 mg ($Weight_{Pan}$). An aliquot of a polymer solution, for example a polymer solution as prepared above, 2.5 ± 0.5 grams, is placed into the pan and weighed to within ± 0.1 mg ($Weight_{Pan + Polymer Solution}$). The pan and the polymer solution are placed in an 80 °C ventilated oven, uncovered for 12 hours. After cooling to room temperature, the pan and the polymer solids are then weighed to within ± 0.1 mg ($Weight_{Pan + Polymer Solid}$). The percent solids is calculated as follows:

$$PercentSolids(\%) = \left(\frac{Weight_{Pan+PolymerSolid} - Weight_{Pan}}{Weight_{Pan+PolymerSolution} - Weight_{Pan}} \right) * 100\%$$

Preparation of 0.02% Polymer Solution

Using the amounts listed in Table 2 and 4, respectively, the polymer solutions prepared above need to be diluted to 0.02% percent solids with deionized water for soil adsorption testing of the polymer alone or with a commercial cleaning solution (see below for description) for soil adsorption testing of the cleaning composition containing the polymer. If the cleaning composition already contains a polymer to be tested at a level of greater than 0.02% percent solids it needs to be diluted with more deionized water to get the polymer level to 0.02% percent solids using the following equation:

$$\frac{Weight_{PolymerSolution}}{Weight_{PolymerSolution+Water}} = \frac{0.02\%}{PercentSolids(\%)}$$

If the polymer solution or cleaning composition containing the polymer contains less than 0.02% percent solids of the polymer, then no dilution is necessary. (It will be appreciated that the cleaning composition does not have to be the Swiffer Wetjet solution* provided below, but can include any cleaning composition in question when applying this method)

A receiving vessel large enough to hold the diluted solution is tared. The desired amount of the original polymer solution is added to the receiving vessel and the weight (of the solution only) recorded to within ± 0.01 g ($\text{Weight}_{\text{Polymer Solution}}$). The 0.02% percent solids polymer solution or commercial cleaning composition weights are recorded to within ± 0.01 g ($\text{Weight}_{\text{Polymer Solution + Cleaning Composition}}$). The polymer solution or cleaning composition is then capped and allowed to sit for 24 hours with occasional agitation prior to use to ensure polymer dissolution. The concentration is calculated as follows:

$$Concentration(\%) = \frac{Weight_{PolymerSolution} * PercentSolids(\%)}{Weight_{PolymerSolution+Water}}$$

*Swiffer WetJet Multipurpose Cleaner Refill, produced by Procter & Gamble, Cincinnati, Ohio (Open Window Fresh scent, 42.2 fluid ounces, available at Walmart)

Polymer Molecular Weight Determination

Polymer molecular mass is determined by GPC SEC/MALS. The HPLC is a Waters Alliance 2695 HPLC with an auto injector equipped with a bank of two linear μStyragel HT columns at room temperature. The flow rate is 1.0 mL/min and the mobile phase is dimethyl sulfoxide (DMSO) with 0.1% (weight/volume) LiBr. The detectors are Wyatt Dawn EOS Light scattering detector calibrated with toluene and normalized using 25K dextran in mobile phase and a Wyatt Optilab rEX refractive index detector at 30 °C.

Samples for analysis are prepared at a known concentration in the range of 1 to 5 mg/mL. Samples are filtered using 0.2 μm polypropylene membrane filters. The injection volume is 100 μL. The data are collected and analyzed using ASTRA 5.3.4.14. Values for dn/dc are calculated from the RI trace assuming 100% mass recovery. Number average molecular weight and polydispersity index are calculated and reported.

Preparation of Treated Article

A rectilinear 3.00 inch x 4.00 inch piece of a handsheet prepared and treated as set forth below is cut, if necessary, using a 3 inch x 4 inch die cutter to provide a sample portion having a basis weight of from 19 g/m^2 to 33 g/m^2 (sample portions outside this range are discarded). All specimens are obtained from a portion of the test material at least 0.5 inches from any edges. The handsheet is labeled with the specimen name using a ball-point pen or equivalent marker. After the handsheet has been conditioned in the conditioned room at 70°F ± 2°F and a relative humidity of 50% ± 2% for at least 2 hours (preferably overnight), the handsheet is weighed to within ± 10 mg ($\text{Weight}_{\text{Substrate}}$) while still maintaining the conditioning conditions. The remainder of the work is done in a laboratory at a temperature of 73 °F ± 3.5 °F and a relative humidity < 70%. The handsheet is then placed on a lattice (23.75" x 47.75" polystyrene light panel manufactured by Plaskolite, Inc., Columbus, Ohio, available from Home Depot as model #1425005A; or equivalent lattice). Each handsheet is then treated with a total of 3.8 mL (in 1-4 aliquots to avoid oversaturation if necessary) of the 0.02% percent solids polymer solution or cleaning composition prepared as described above or if the polymer solution or cleaning composition being tested is less than 0.02% percent solids, then the total amount of the polymer solution or cleaning composition to be added to each handsheet (in 1-4 aliquots to avoid oversaturation if necessary) is determined by the following equation:

$$AmountAdded(mL) = \frac{3.8mL * 0.02\%}{PercentSolids(\%)}$$

The polymer solution or cleaning composition is applied to the upper (treated) side of the handsheet only. At least 1.5 hours between aliquots is given to allow the handsheet to at least partially dry. After application of all the polymer solution or cleaning composition, the handsheet are left to air dry for at least 4 hours on the lattice.

Soil Solution Preparation

A centrifuge tube (VWR brand 50 mL superclear ultra high performance freestanding centrifuge tube with flat cap, VWR Catalog #82018-052; or equivalent tube) is labeled with the specimen name and weighed to within ± 1 mg ($\text{Weight}_{\text{Vial + Cap}}$). Next 0.1784 g ± 0.0005 g of a model soil (Black Todd Clay available from Empirical Manufacturing Co., 7616 Reinhold Drive, Cincinnati, Ohio 45237-3208) is weighed ($\text{Weight}_{\text{Added Soil}}$) and then placed into the centrifuge tube. Deionized water, 25.0 mL ± 0.2 mL, is added slowly to the centrifuge tube using a suitable dispenser. The deionized water is poured carefully into the centrifuge tube to avoid causing a plume of dust from the model soil. If a plume of dust occurs, the tube is discarded and a new tube is prepared. The tube is then re-weighed to within ± 1 mg ($\text{Weight}_{\text{Vial + Cap + Dispersion}}$).

A Petri dish (VWR sterile Petri dish, Simport plastics, 60 mm x 15 mm, 28 mL volume, VWR Catalog #60872-306; or equivalent) is labeled with the specimen name and weighed to within ± 1 mg ($\text{Weight}_{\text{Dish}}$).

<u>Soil Adsorption Test Method</u>

The 3 inch x 4 inch specimen is folded in half with the treated side facing in so that it is 1.5 inch long x 4 inch wide. An accordion style (paper fan) folding technique is then used to fold the specimen 5 times, to produce a sample that contains 6 segments each about ⅔ of an inch in width. The capped centrifuge tube containing the model soil and water is agitated / shaken to disperse the soil in the water to form a soil dispersion. The centrifuge tube is then uncapped permitting the folded specimen to be fully immersed into the dispersion of model soil and water in the centrifuge tube so that the folds run parallel to the length of the centrifuge tube. The tube is immediately re-capped and shaken in a WS 180 degree shaker for 60 ± 1 seconds. The WS 180 degree shaker (Glas-Col #099AWS18012; or equivalent shaker) is set (50% speed) so that it inverts the specimen 160-170 degrees every 1 second.

After shaking, the folded specimen is carefully removed over the Petri dish using laboratory tweezers. Care must be taken to ensure that all of the dispersion is kept either in the original centrifuge tube or corresponding Petri dish. The dispersion is wrung from the specimen using a "wringing" motion and collected in the Petri dish (≥85% of the dirt dispersion should be collected). Once the dispersion has been removed from the specimen, the specimen is discarded. The remaining dispersion is poured from the centrifuge tube into the Petri dish after swirling the mixture to re-disperse the model soil into the water, thereby ensuring that no model soil is inadvertently left behind in the centrifuge tube. The Petri dish containing the model soil / water mixture is weighed to within ± 1 mg ($\text{Weight}_{\text{Dish+Effluent}}$). The Petri dish is then placed into a vented laboratory drying oven at 60 °C until the sample is dry, preferably overnight.

Once the specimen is dry, it is removed from the oven and allowed to cool to room temperature 73 °F ± 3.5 °F. The Petri dish containing the dried model soil is re-weighed to within ± 1 mg ($\text{Weight}_{\text{Dish+DriedSoil}}$).

Preparation of Handsheet - In order to test the soil adsorption properties of a material, such as a polymer, a handsheet is prepared as follows and is then used in the Soil Adsorption Test Method described above.

A handsheet is a hand made specimen of a fibrous structure. Handsheets are prepared at target basis weight of 26.8 g/m^2, but no less than 19 g/m^2 and no more than 33 g/m^2 using the following procedure.

a. Pulp Preparation - A pulp slurry of Northern Softwood Kraft (NSK) pulp is made as follows. Using an analytical balance capable of weighing to ±0.0002 g, weigh out 30 g of NSK dry lap (pulp). Record the weight of the NSK dry lap. Record the percent bone-dry pulp or consistency for this pulp. Put 500 mL of 23°C ± 2°C of City of Cincinnati, Ohio Water (or equivalent having the following properties: Total Hardness = 155 mg/L as $CaCO_3$; Calcium content = 33.2 mg/L; Magnesium content = 17.5 mg/L; Phosphate content = 0.0462) into a 2000 mL polypropylene beaker. Add the weighed NSK dry lap to the water in the beaker immediately following the addition of the water to the beaker. After the NSK dry lap is completely wetted (about 50-60 seconds), remove the wetted NSK dry lap and manually tear into small pieces of wetted NSK dry lap, approximately 2 cm^2 or less pieces. Add the small pieces of wetted NSK dry lap back into the water in the beaker. Let the wetted NSK dry lap soak in the water for at least 1 hour, typically 1-2 hours. At the end of the soaking period, transfer the contents of the beaker (water and pulp) to a disintegrator tank of a pulp disintegrator commercially available from Testing Machines, Inc. under the tradename 73-18 Pulp Disintegrator or its equivalent. Follow the manufacturer's instructions for maintaining, calibrating, and cleaning the disintegrator, as needed. The disintegrator must meet TAPPI Standard T-205. Using more of the City of Cincinnati, Ohio water (or equivalent water as described above) delivered by a polyethylene wash bottle, wash and remove any remaining pulp adhering to the beaker into the disintegrator tank. Additional City of Cincinnati, Ohio water (or equivalent water as described above) is added to the disintegrator tank to result in a total of 1500 mL of total volume in the disintegrator tank.

Next, place the disintegrator tank containing the pulp and City of Cincinnati, Ohio water (or equivalent water as described above) (23°C ± 2°C) on the distintegrator's platform and position it under the shaft and impeller blade of the disintegrator. Clamp the disintegrator tank firmly in place on the disintegrator's platform. Lower the impeller blade into position and lock in place according to the manufacturer's instructions. Put the disintegrator tank's lid in place on the disintegrator tank. Set an interval timer with timed switch outlet for exactly 10 minutes. Turn the disintegrator on and start the timer with the alarm on the timer turned on such that the alarm sounds and the disintegrator turns off automatically after exactly 10 minutes of operation. Turn the alarm off. Use the pulp slurry (pulp plus City of Cincinnati, Ohio water (or equivalent water as described above)) in the disintegrator within an hour after the completion of the 10 minutes of operation. Do not let the pulp slurry stand idle for more than an hour before using it to make the handsheets.

b. Proportioning of Pulp - After the pulp slurry is prepared in the disintegrator tank as described above, the pulp slurry is then proportioned in a proportioner, such as a Noble and Wood Handsheet Forming Machine or a proportioner and handsheet forming machine, which is commercially available from Adirondack Machine Corporation as follows.

To a proportioner having a 19-21 L stainless steel tank, City of Cincinnati, Ohio water (or equivalent water as described above) is added to fill the tank to about half full (about 9-10 L). The agitator of the proportioner is turned on and the speed of the agitator is adjusted to 23 rpm ± 2 rpm to provide good mixing once the pulp slurry is added. Good mixing can be determined by seeing that the pulp slurry is evenly mixing with the City of Cincinnati, Ohio water (or equivalent water as described above) that is added to the tank. Next, add the equivalent of 30 g of bone-dry pulp of the pulp slurry produced above to the tank. After addition of the pulp slurry to the tank, set the volume scale of the proportioner to the 19 L mark. Add additional City of Cincinnati, Ohio water (or equivalent water as described above) to make the liquid level approximately even with the top of the hook on the solution indicator pointer of the proportioner.

c. Forming Handsheet - A handsheet is made from the pulp slurry present in the proportioner, described above, as follows.

The handsheet is made using a 12" x 12" stainless steel sheet mold commercially available from Adirondack Machine Corporation. First, open the drain valve on the deckle box of the sheet mold and completely drain the deckle box. The deckle box needs to be clean and free of contaminants. Close the drain valve and open the deckle box. Turn on the water supply, City of Cincinnati, Ohio water (or equivalent water as described above) and allow the deckle box to overflow. Place a clean forming wire (84M 14" x 14" polyester monofilament plastic cloth, commercially available from Appleton Wire Co.), on the coarse deckle box wire so as not to entrap any air bubbles under the forming wire. If air bubbles persist, eliminate by rubbing the wire gently with hands before closing the deckle box. Air bubbles under the forming wire, if not removed, will cause holes in the handsheet and makes the handsheet unacceptable for use in the tests described herein.

After the forming wire has been thoroughly wetted by the water, close and lock the deckle box and allow the water to rise to 8 ½" from the forming wire in the deckle box. A mark on the inside of the deckle box should be used to permanently indicate this volume. Add 2543 mL of the pulp slurry from the proportioner to the water in the deckle box using the proportioner sample container. Using the perforated metal deckle box plunger, distribute the pulp slurry uniformly by moving the plunger from near the top of the pulp slurry to the bottom of the pulp slurry within the deckle box and back for three complete up and down cycles. Do not touch the forming wire on the downward strokes. After the third cycle, bring the plunger up and pause for two seconds holding the plunger plate just beneath the pulp slurry surface (to eliminate wave action) and then withdraw slowly. Make sure that the pulp slurry is undisturbed in the deckle box.

Depress the switch to activate the timed opening of the drop valve of the deckle box. The drop valve will close automatically after the deckle box is completely drained. Most units completely drain in about 20-25 seconds. After the drop valve closes, open the deckle box and carefully remove the forming wire with fiber mat side up from the deckle box. Immediately place the forming wire with fiber mat side up on a vacuum box's surface (a vacuum box table) having a surface at a vacuum slot (13" x 1/16" 90° flare) over which the forming wire with fiber mat passes. Keep the edge of the forming wire which is next to the operator in the same relative position during this transfer from the deckle box to the vacuum box table.

The vacuum box table's vacuum valves are set such that the low level of vacuum (pre-vacuum) peaks at 4.0 ± 0.5" Hg and the high level vacuum peaks at 10.0 ± 0.5" Hg according to an Ashcroft Vacuum Gauge Model 1189, range 0-15" Hg commercially available from Ashcroft Inc.

Turn on the vacuum pump (a Nash H4 Pump with a draw of 106 cfm Motor-10 HP, 1745 rpm, 3 Ph, 60 Hz available from ECM Inc.) associated with the vacuum box table. Engage the low level vacuum (pre-vacuum). Position the forming wire with the fiber mat side up on the vacuum box table so that the front edge of the forming wire (edge next to the operator) extends over the vacuum slot about ¼" – ½". Pull the forming wire with fiber mat across the vacuum slot in 1 ± 0.3 seconds at a uniform rate. The vacuum gauge should peak at 4.0 ± 0.5" Hg. This step is referred to as the Pre-vacuum Step.

Next, turn the low level vacuum and open the high level side of the vacuum system. Place the knubby side up of a transfer wire (44M 16" x 14" polyester monofilament plastic cloth commercially available from Appleton Wire Co. with the knobby side, which is the sheet side, marked with an arrow indicating the machine direction) on the vacuum box table behind the vacuum slot. The transfer wire is placed on the vacuum box table such that the 16" length is perpendicular to the vacuum slot. Carefully turn the forming wire with the fiber mat over keeping the edge of the forming wire, which has been next to the operator, in the same relative position. Gently place the forming wire with fiber mat onto the center of the transfer wire, forming a "sandwich" so that the front edge of the transfer wire (edge next to the operator) extends over the vacuum slot about ¼" – ½". The direction of travel of the fiber mat over the vacuum slot must be identical to the direction of travel of the forming wire with fiber mat during the Pre-vacuum Step described above. The "sandwich" is pulled across the vacuum slot in 1 ± 0.3 seconds at a uniform rate. The vacuum gauge should peak at 10.0 ± 0.5" Hg. This step, which transfers the fiber mat from the forming wire to the transfer wire, is called the Transfer Vacuum Step.

Close the high level vacuum and turn off the entire vacuum system. By this time the fiber mat has become a handsheet. Next, place the "sandwich" on the vacuum box table. Separate the forming wire from the handsheet and the transfer wire by gently lifting one corner of the forming wire and removing it, leaving the handsheet attached to the transfer wire. Keep the edge of the fabric next to the operator in the same relative position as the handsheet as it was during the Transfer Vacuum Step. Make an arrow with an indelible pencil (a water color pencil commercially available from Dick Blick Art Supplies) on a corner of the handsheet to indicate the direction of travel across the vacuum slot. This identifies the handsheet's machine direction.

Next, pass the transfer wire with the handsheet attached through an E-100 Drum Dryer commercially available from Adirondack Machine Corporation with the transfer wire next to the drum dryer and with the edge that was kept next to the operator going into the drum dryer last. Pass the transfer wire with the handsheet attached through the drum dryer a second time with the handsheet next to the drum dryer.

The handsheet is removed immediately after exiting the dryer drum the second time while it is still warm.

The handsheet formed must be at a target basis weight of 26.8 g/m^2, but no less than 19 g/m^2 and no more than 33 g/m^2 suitable for testing. If the basis weight is less than 19 g/m^2 or greater than 33 g/m^2 then either the amount of pulp is too small or too large and the process needs to be adjusted accordingly to produce a handsheet with a target basis weight of 26.8 g/m^2, but no less than 19 g/m^2 and no more than 33 g/m^2.

Calculations

To calculate the amount of residual model soil ($\text{Mass}_{\text{Residual Soil}}$) left in the Petri dish, the following equation is used:

$$Mass_{\mathrm{Re}\,sidualSoil} = Weight_{Dish+DriedSoil} - Weight_{Dish}$$

Residual model soil is reported in mg.

To calculate the amount of soil adsorbed (Soil Retained) in the specimen, the following calculation is used:

$$Soil\,\mathrm{Re}\,tained = Weight_{AddedSoil} - Mass_{\mathrm{Re}\,sidualSoil}$$

The amount of soil adsorbed is reported in mg.

To calculate the percent of soil retained (% Soil Retained), the following calculation is used:

$$\%Soil\,\mathrm{Re}\,tained = \left[\frac{Soil\,\mathrm{Re}\,tained}{Weight_{AddedSoil}}\right] * 100\%$$

The test is performed on four replicates and the average amount of soil adsorbed (also known as the Soil Adsorption Value) and the average percent of soil retained ($\%\text{Soil Retained}_{\text{avg}}$) are calculated for the article.

Charge Density Test Method

The charge density of a polymer, such as a soil adsorption polymer, can be determined by using a Mutek PCD-04 Particle Charge Detector available from BTG, or equivalent instrument. The following guidelines provided by BTG are used.

Start with a 0.1% solution (0.1 g polymer + 99.9 g deionized water) (sample). Depending on the titrant consumption increase or decrease polymer content if needed. Solution pH is adjusted prior to final dilution as charge density of many polymers and/or additives is dependent upon solution pH. A pH of 4.5 is used here.

1. Place 20 mL of sample in the PCD measuring cell and insert piston.
2. Put the measuring cell with piston and sample in the PCD, the electrodes are facing the rear. Slide the cell along the guide until it touches the rear.

3. Pull piston upwards and turn it counter-clock-wise to lock the piston in place.

4. Switch on the motor. The streaming potential is shown on the touch panel. Wait 2 minutes until the signal is stable.

5. Use an oppositely charged titrant (for example for a cationic sample having a positive streaming potential: use an anionic titrant). Titrants are available from BTG consisting of 0.001N PVSK or 0.001N PolyDADMAC.

6. An automatic titrator available from BTG is utilized. After selecting the proper titrant, set the titrator to rinse the tubing by dispensing 10 mL insuring that all air bubbles have been purged.

7. Place tubing tip below the surface of the sample and start titration. The automatic titrator is set to stop automatically when the potential reaches 0 mV.

8. Record consumption of titrant, ideally, the consumption of titrant should be 0.2 mL to 10 mL; otherwise decrease or increase polymer content.

9. Repeat titration of a second 20 mL aliquot of the polymer sample.

10. Calculate charge demand (solution) or charge demand (solids);

$$\text{Charge demand (eq/L)} = \frac{\text{V titrant used(L) x Conc. of titrant in Normality (eq/L)}}{\text{Volume of sample titrated (L)}}$$

$$\text{Charge demand (eq/g)} = \frac{\text{V titrant used(L) x Conc. of titrant in Normality (eq/L)}}{\text{Wt. solids of the sample or its active substance (g)}}$$

The charge demand (charge density) of a polymer is reported in meq/g units.

Basis Weight Test Method

The rectilinear 3.00 inch x 4.00 inch piece of specimen cut as above in the soil adsorption test method is conditioned in a conditioned room at 70 °F ± 2 °F and a relative humidity of 50% ± 2% for at least 2 hours, typically overnight. The specimen is weighed to within ±10 mg ($\text{Weight}_{\text{Substrate}}$) while still maintaining the conditioning conditions. The Basis Weight of the specimen is then calculated as follows:

$$BasisWeight(gsm) = \left(\frac{Weight_{Substrate}(g)}{3inchx4inch}\right) * \left(\frac{inch}{2.54cm}\right)^2 * \left(\frac{100cm}{m}\right)^2$$

Moisture Content Test Method

The moisture content present in an article is measured using the following Moisture Content Test Method.

An article or portion thereof ("sample") is placed in a conditioned room at a temperature of 73°F ± 4°F (about 23°C ± 2.2°C) and a relative humidity of 50% ± 10% for at least 24 hours prior to testing. The weight of the sample is recorded when no further weight change is detected for at least a 5 minute period. Record this weight as the "equilibrium weight" of the sample. Next, place the sample in a drying oven for 24 hours at 70°C with a relative humidity of about 4% to dry the sample. After the 24 hours of drying, remove the sample from the drying oven and immediately weigh the sample. Record this weight as the "dry weight" of the sample. The moisture content of the sample is calculated as follows:

$$\%\ \text{Moisture in sample} = 100\% \times \frac{(\text{Equilibrium weight of sample} - \text{Dry weight of sample})}{\text{Dry weight of sample}}$$

The % Moisture in sample for 3 replicates is averaged to give the reported % Moisture in sample.

III. Cleaning Compositions

The present disclosure further relates to having a soil capture agent (as described herein) included in a cleaning composition for cleaning surfaces and objects (e.g., hard surfaces).

In certain embodiments, a soil capture agent may be present in a cleaning composition at a level of greater than 0.005% and/or greater than 0.01% and/or greater than 0.05% and/or greater than 0.1% and/or greater than 0.15% and/or greater than 0.2% and/or to about 50% and/or to about 25% and/or to about 10% and/or to about 5% and/or to about 3% and/or to about 2% and/or to about 1% by weight of the cleaning composition. In one example, the soil capture agent is present in a cleaning composition at a level of from about 0.005% to about 1% by weight of the cleaning composition.

Such cleaning compositions can be aqueous. For example, such cleaning compositions can have from about 70% to about 99% by weight of the cleaning composition of water, in certain embodiments from about 75% to about 95% water, and in certain embodiments from about 80% to about 95% water. In other suitable embodiments, a cleaning composition may include other non-water based solutions, including for example, alcohol-based solutions.

Cleaning compositions have a pH, and in certain embodiments have a pH from about 2.0 to about 10.0, in certain embodiments have a pH from about 2.5 to about 7.5, and in certain embodiments from about 2.5 to about 5.0, and in certain embodiments from about 2.8 to about 4.0.

Cleaning compositions can have a water-like viscosity. By "water-like viscosity" it is meant herein a viscosity that is close to that of water. Such cleaning compositions can have a viscosity of about 50cps or less at 60rpm, in certain embodiments from 0 cps to about 30 cps, in certain embodiments from 0 cps to about 20 cps, and in certain embodiments from 0 cps to about 10 cps at 60rpm and 20°C when measured with a Brookfield digital viscometer model DV II, with spindle 2.

In alternative embodiments, a cleaning composition can be thickened. Thus, such cleaning compositions can have a viscosity of from about 50 cps to about 5000 cps at 20 s^{-1}, in certain embodiments from about 50 cps to about 2000 cps, in certain embodiments from about 50 cps to about 1000 cps, and in certain embodiments from about 50 cps to about 500 cps at 20 s^{-1} and 20°C when measured with a Rheometer, model AR 1000 (Supplied by TA Instruments) with a 4 cm conic spindle in stainless steal, 2° angle (linear increment from 0.1 to 100 sec^{-1} in max. 8 minutes). Such thickened cleaning compositions can be shear-thinning compositions, whereby the compositions can include a thickening agent (e.g., polysaccharide polymer). Such thickening agents are described in PCT Application No. PCT/US2011/042644.

Cleaning compositions as described herein can exhibit improved average Soil Adsorption Values as measured according to the Soil Adsorption Test Method described herein compared to known compositions using other soil capture agents. In certain embodiments, a cleansing solution may exhibit an average Soil Adsorption Value of about 40 mg or more; in certain embodiments about 55 mg or more; in certain embodiments about 80 mg or more; in certain embodiments about 90 mg or more; and in certain embodiments about 100 mg or more as measured according to the Soil Adsorption Test Method described herein.

A cleaning composition, in addition to the soil capture agent, can include a variety of other ingredients. Such optional ingredients can be selected based on the technical benefit aimed for and the type of surfaces being treated. Suitable optional ingredients for use herein include acids (e.g., formic acid, acetic acid, lactic acid, citric acid), chelating agents, anionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants, vinylpyrrolidone homopolymer or copolymer, polysaccharide polymer, radical scavengers, perfumes, surface-modifying polymers other than vinylpyrrolidone homo- or copolymers and polysaccharide polymers, solvents, other surfactants, builders, buffers, bactericides, hydrotropes, colorants, stabilizers, bleaches, bleach activators, suds controlling agents like fatty acids, enzymes, soil suspenders, brighteners, anti dusting agents, dispersants, pigments, and dyes. Examples of each of these optional ingredients are described in U.S. Patent Application Publication No. 2010/0154823A1 and PCT Application No. PCT/US2011/042644.

During use, such cleaning compositions may be used in combination with a cleansing article. Such cleansing articles can be wet articles or dry articles. The cleansing articles can include a web. A web can include one or more of a nonwoven web and a woven web, or a combination thereof. In certain embodiments, a web can include a plurality of pulp fibers. In certain embodiments, a web can include a fibrous structure. The fibrous structures in certain embodiments may be co-formed fibrous structures. Such suitable examples of co-form fibrous structures are described in U.S. Patent No. 4,100,324.

In still another embodiment, an article may comprise a foam structure or a sponge. Suitable foam structures or sponges are described in U.S. Patent Nos. 4,638,017, 4,738,992, and 4,957,810; and U.S. Patent Application Publication Nos. 2007/0061991 A1, 2007/0161533 A1, and 2009/0163598 A1.

The cleansing article can have the cleaning composition applied to the article prior to use or applied to the surface prior to applying the article. For example, the cleaning composition can be pre-applied (e.g., embedded) onto a surface of the article prior to using it to clean a surface of an object. In alternative embodiments, a cleaning composition may be applied to a surface to be cleaned (e.g., table top) and then the article is placed into contact with the surface to remove the soil.

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 mm” is intended to mean “about 40 mm.”

For clarity purposes, the total “% wt” values do not exceed 100% wt.

All documents cited in the Detailed Description are, in relevant part, incorporated herein by reference; the citation of any document is not to be construed as an admission that it is prior art with respect to the present invention. To the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

CLAIMS

1. A cleaning composition exhibiting a Soil Adsorption Value of 38 mg or more as measured according to a Soil Adsorption Test Method described herein and comprising a soil capture agent, wherein the soil capture agent comprises a polymer, the polymer comprising two or more monomeric units selected from the group consisting of:

    a. nonionic monomeric units;
    b. anionic monomeric units;
    c. cationic monomeric units; and
    d. zwitterionic monomeric units;

    wherein the polymer comprises at least one monomeric unit from group a and at least one monomeric unit selected from groups b, c and d.

2. The cleaning composition of claim 1, wherein the cleaning composition exhibits a Soil Adsorption Value of 55 mg or more as measured according to the Soil Adsorption Test Method.

3. The cleaning composition of any preceding claims, wherein the nonionic monomeric units comprise a nonionic hydrophilic monomeric unit.

4. The cleaning composition of any preceding claims, wherein the anionic monomeric unit is derived from acrylic acid.

5. The cleaning composition of any preceding claims, wherein the cationic monomeric unit is derived from MAPTAC.

6. The cleaning composition according to any preceding claims, wherein the polymer comprises at least 69.9% wt of a monomeric unit from group a, preferably wherein the polymer comprises no more than 30.1% wt of a monomeric unit selected from the group consisting of: group b, group c, group d, and mixtures thereof.

7. The cleaning composition of any preceding claims, wherein the polymer comprises at least 69.9% wt of the monomeric unit from group a and no more than 30.1% wt of the monomeric unit from group b.

8. The cleaning composition of any preceding claims, wherein the polymer comprises at least 69.9% wt of the monomeric unit from group a, no more than 30.1% wt of the monomeric unit from group b and no more than 30.1% wt of the monomeric unit from group c.

9. The cleaning composition of any preceding claims, wherein the polymer comprises from 70% to 99.5% wt of the monomeric unit from group a, from 0.1% to 10% wt of the monomeric unit from group b, and from 0.3% to 29% wt of the monomeric unit from group c.

10. The cleaning composition of any preceding claims, wherein the polymer comprises from 70% to 99.5% wt of the monomeric unit from group a and from 0.5% to 30% wt combined of the monomeric unit from group b and the monomeric unit from group c.

11. The cleaning composition of any preceding claims, wherein the polymer exhibits a Polydispersity Index of less than 2.5.

12. The cleaning composition of any preceding claims, wherein the polymer is water-soluble.

13. The cleaning composition of any preceding claims, comprising from 0.005% to 50% wt of the soil capture agent.

14. The cleaning composition of any preceding claims, wherein the cleaning composition is applied to a cleansing article prior to cleaning a surface.

15. The cleaning composition of any preceding claims, wherein the cleaning composition is applied to a surface to be cleaned prior to contact with a cleansing article.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/053071

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/37 C11D17/04
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)
C11D

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P L	WO 2012/031063 A1 (PROCTER & GAMBLE [US]; NEAL CHARLES WILLIAM [US]; REDD CHARLES ALLEN [] 8 March 2012 (2012-03-08) page 1, lines 5-10; claims 1-15; figures 1-8; tables 5-7 page 58, line 1 - page 60, line 15 -----	1-15
X	US 2010/190679 A1 (VANPACHTENBEKE TIM ROGER MICHEL [BE] ET AL) 29 July 2010 (2010-07-29) paragraphs [0003], [0006], [0007]; claims 1-20; examples I-VIII -----	1-14
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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

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"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

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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 Klier, Erich

2

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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2

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Information on patent family members

International application No
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