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(54) **DETERGENT COMPOSITIONS
COMPRISING RENEWABLY-BASED,
BIODEGRADABLE 1,3-PROPANEDIOL**

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(60) Provisional application No. 60/772,471, filed on Feb. 10, 2006. Provisional application No. 60/772,194, filed on Feb. 10, 2006. Provisional application No.

(57) **ABSTRACT**

Disclosed herein are detergent compositions comprising 1,3-propanediol, wherein the 1,3-propanediol in said detergent composition has a bio-based carbon content of about 1% to 100%. In addition, it is preferred that the 1,3-propanediol be biologically-derived, and wherein upon biodegradation, the biologically-derived 1,3-propanediol contributes no anthropogenic CO₂ emissions to the atmosphere.

FIGURE 1

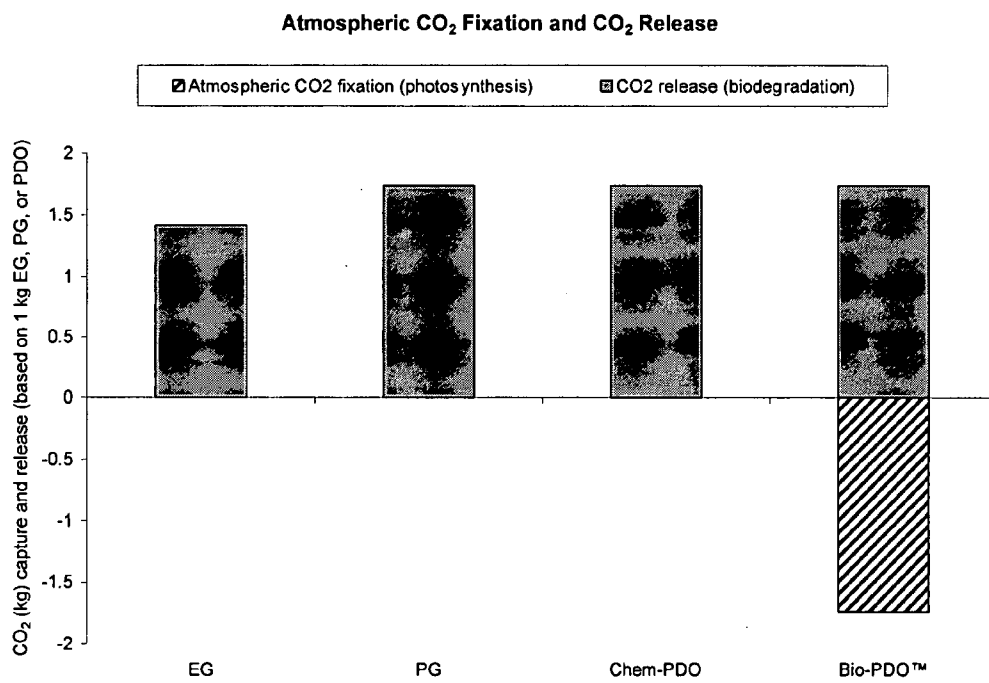


FIGURE 2

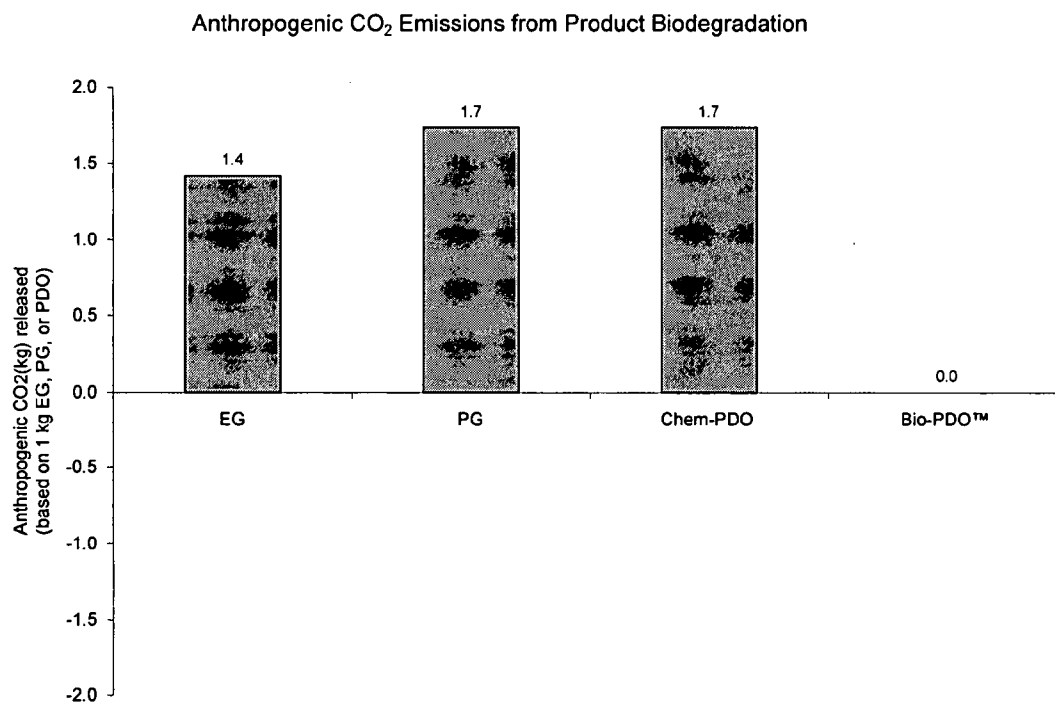


FIGURE 3

Product	Molecular weight	product	product	CO ₂ fixated	CO ₂ released	Anthropogenic emissions of CO ₂ from Product Biodegradation
	g/mol	kg	mol	mol	mol	kg
EG	62.068	1	16.1	0.0	32.2	1.4
PG	76.094	1	13.1	0.0	39.4	1.7
Chem-PDO	76.094	1	13.1	0.0	39.4	1.7
Bio-PDO™	76.094	1	13.1	39.4	39.4	0.0

**DETERGENT COMPOSITIONS COMPRISING
RENEWABLY-BASED, BIODEGRADABLE
1,3-PROPANEDIOL**

CROSS REFERENCE TO RELATED
APPLICATIONS

[0001] The present application claims the benefit of U.S. Provisional Application Ser. No. 60/772,471, filed Feb. 10, 2006; U.S. Provisional Application No. 60/772,194, filed Feb. 10, 2006, U.S. Provisional Application No. 60/772,193, filed Feb. 10, 2006, U.S. Provisional Application No. 60/772,111, filed Feb. 10, 2006, U.S. Provisional Application No. 60/772,120, filed Feb. 10, 2006, U.S. Provisional Application No. 60/772,110, filed Feb. 10, 2006, U.S. Provisional Application No. 60/772,112, filed Feb. 10, 2006, U.S. Provisional Application No. 60/846,948, filed Sep. 25, 2006, U.S. Provisional Application No. 60/853,920, filed Oct. 24, 2006, U.S. Provisional Application No. 60/859,264, filed Nov. 15, 2006, U.S. Provisional Application No. 60/872,705, filed Dec. 4, 2006 and U.S. Provisional Application No. 60/880,824, filed Jan. 17, 2007, the disclosures of which are expressly incorporated herein by reference in their entireties.

FIELD OF THE INVENTION

[0002] Disclosed herein are detergent compositions comprising 1,3-propanediol wherein the 1,3-propanediol in said detergent composition has a bio-based carbon content of about 1% to 100%. In addition, it is preferred that the 1,3-propanediol be biologically-derived, and wherein upon biodegradation, the biologically-derived 1,3-propanediol contributes no anthropogenic CO₂ emissions to the atmosphere.

BACKGROUND OF THE INVENTION

[0003] Consumers of detergents consider many factors in selecting products for use. Recently certain factors have been a focus of and have driven scientific study and product development. These driving factors include, product safety, environmental impact, the extent to which the components are natural, and the aesthetic quality of the overall product. Therefore, manufacturers have to be concerned with the environmental impact of their products. In fact, the effort towards environmental impact awareness is a universal concern, recognized by government agencies. The Kyoto Protocol amendment to the United Nations Framework Convention on Climate Change (UNFCCC) currently signed by 156 nations is one example of a global effort to favor safer environmental manufacturing over cost and efficiency. When applied to detergents, consumers are increasingly selective about the origins of the products they purchase. The 2004 Co-operative Bank's annual Ethical Consumerism Report (www.co-operativebank.co.uk) disclosed a 30.3% increase in consumer spending on ethical retail products (a general classification for environmental safe, organic and fair trade goods) between 2003 and 2004 while total consumer spending during the same period rose only 3.7%.

[0004] Glycols such as ethylene glycol, propylene glycol, 1,3-butylene glycol, and 2-methyl-1,3-propanediol are biodegradable compounds useful in compositions ranging from cosmetics and personal care formulations to detergents to heat transfer compositions. While biodegradability is an

important factor in protecting the environment, biodegradation of glycols derived from fossil-based sources has the unavoidable consequence of releasing previously fixed CO₂ into the atmosphere. Thus, while glycols in general are advantageous for their biodegradability, the resulting global warming potential of fossil-based glycols during biodegradation is significant. [OOS] Carbon dioxide is singled out as the largest component of the collection of greenhouse gases in the atmosphere. The level of atmospheric carbon dioxide has increased 50% in the last two hundred years. Recent reports indicate that the current level of atmospheric carbon dioxide is higher than the peak level in the late Pleistocene, the epoch before modern humans (Siegenthaler, U. et al. Stable Carbon Cycle-Climate Relationship During the Late Pleistocene, *Science*, Vol. 310, no. 5752 (Nov. 25, 2005), pp. 1313-1317). Therefore, any further addition of carbon dioxide to the atmosphere is thought to further shift the effect of greenhouse gases from stabilization of global temperatures to that of heating. Consumers and environmental protection groups alike have identified industrial release of carbon into the atmosphere as the source of carbon causing the greenhouse effect.

[0005] Greenhouse gas emission can occur at any point during the lifetime of a product. Consumers and environmental groups consider the full lifespan of a product when evaluating a product's environmental impact. Consumers look for products that do not contribute new carbon to the atmosphere considering the environmental impact of production, use and degradation. Only organic products composed of carbon molecules from plant sugars and starches and ultimately atmospheric carbon are considered to not further contribute to the greenhouse effect.

[0006] In addition to adding carbon dioxide to the atmosphere, current methods of industrial production of glycols produce contaminants and waste products that include among them sulfuric acid, hydrochloric acid, hydrofluoric acid, phosphoric acid, oxalic acid tartaric acid, acetic acids, Alkali metals, alkaline earth metals, transitional metals and heavy metals, including Iron, cobalt, nickel, copper, silver, molybdenum, tungsten, vanadium, chromium, rhodium, palladium, osmium, iridium, rubidium, and platinum (U.S. Pat. Nos. 2,434,110, 5,034,134, 5,334,778, and 5,10,036).

[0007] Also of concern to consumers, especially consumers of detergent products, is an individual's reaction to such a product. The rate of development of hypersensitivity has markedly increased in the US in the last two decades. Many of these reactions are attributed to trace amount of substances. Other reactions are of idiopathic origin. Consumers seek products that are composed of ingredients of a more purified source and/or of all natural composition.

SUMMARY OF THE INVENTION

[0008] The present invention is directed to a detergent composition comprising 1,3-propanediol and a surfactant, wherein said 1,3-propanediol has a bio-based carbon content of at least 1%.

[0009] The present invention is further directed to a detergent composition comprising 1,3-propanediol and a builder, wherein said 1,3-propanediol has a bio-based carbon content of at least 1%.

[0010] The present invention is also directed to a detergent composition comprising 1,3-propanediol wherein said 1,3-

propanediol has an ultraviolet absorption at 220 nm of less than about 0.200 and at 250 nm of less than about 0.075 and at 275 nm of less than about 0.075.

[0011] The present invention is additionally directed to a detergent composition comprising 1,3-propanediol wherein said 1,3-propanediol has a concentration of total organic impurities of less than about 400 ppm.

[0012] The present invention is even further directed to a detergent composition comprising 1,3-propanediol, wherein the 1,3-propanediol in said composition has an anthropogenic CO₂ emission profile of zero upon biodegradation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. 1 is a graph showing CO₂ emissions for CO₂ fixation from the atmosphere during photosynthesis for renewably based 1,3-propanediol (Bio-PDO™) (−1.7 kg CO₂/kg product) and CO₂ release to the atmosphere during biodegradation (kg CO₂/kg product) for ethylene glycol (EG) (+1.4 kg CO₂/kg product), propylene glycol (PG) (+1.7 kg CO₂/kg product), fossil-based 1,3-propanediol (Chem-PDO) (+1.7 kg CO₂/kg product), and fermentatively-derived 1,3-propanediol (Bio-PDO™) (+1.7 kg CO₂/kg product).

[0014] FIG. 2 is a graph showing that the net emissions of CO₂ to the atmosphere for renewably based 1,3-propanediol (Bio-PDO) is zero (0).

[0015] FIG. 3 is a table that shows the calculations for the data shown in FIGS. 1 and 2.

DETAILED DESCRIPTION OF THE INVENTION

[0016] Applicants specifically incorporate the entire content of all cited references in this disclosure. Further, when an amount, concentration, or other value or parameter is given as either a range, preferred range, or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

[0017] Compositions disclosed herein comprise 1,3-propanediol, having at least 1% bio-based carbon content, as greater as up to 100% of the glycol component of the composition. In one embodiment, the 1,3-propanediol comprises substantially all of the glycol component of the composition of the invention. In another embodiment, the 1,3-propanediol comprises all of the glycol component of the composition.

1,3-Propanediol

[0018] The terms “bio-PDO”, “biologically-derived, biodegradable 1,3-propanediol”, “biologically derived 1,3-propanediol”, “renewably-based 1,3-propanediol”, “renewably-based, biodegradable 1,3-propanediol”, “biosourced, and “biologically-produced 1,3-propanediol” and similar terms as used here in refer to 1,3-propanediol derived from micro-

organism metabolism of plant-derived sugars composed of carbon of atmospheric origin, and not composed of fossil-fuel carbon.

Anthropogenic CO₂ Emission Profile

[0019] Applicants' invention relates to detergent compositions comprising renewably-based, biodegradable 1,3-propanediol, in which said renewably-based, biodegradable 1,3-propanediol has an anthropogenic CO₂ emission profile of zero (0). An “anthropogenic emission profile” means anthropogenic CO₂ emissions that are contributed to the atmosphere upon biodegradation of a compound or composition.

[0020] “Biodegradable” or “Biodegradability” means the capacity of a compound to be broken down by living organisms to simple, stable compounds such as carbon dioxide and water.

[0021] Whereas photosynthesis is the process of creating growing matter through the conversion of carbon dioxide (CO₂) and water (H₂O) into plant material through the action of the sun, biodegradation is the process of converting organic material back into CO₂ and H₂O through the activity of living organisms.

[0022] There are many published test methods for measuring the biodegradability of organic chemicals such as glycols. One internationally recognized method is ASTM E1720-01, Standard Test Method for Determining Ready, Ultimate Biodegradability of Organic Chemicals in a Sealed Vessel CO₂ Production Test.

[0023] Chemicals that demonstrate 60% biodegradation or better in this test method will biodegrade in most aerobic environments and are classified as ready biodegradable. All of the glycols referred to in this document meet this criteria.

[0024] Calculations setting forth the finding that the 1,3-propanediol of the present invention provides no anthropogenic CO₂ emissions upon biodegradation is set forth below. A table in support of these calculations is provided in FIG. 3.

[0025] When one molecule of 1,3-propanediol degrades, three molecules of CO₂ are released into the atmosphere. Because all of these molecules of CO₂ released during degradation from “fermentatively-derived” 1,3-propanediol have an atmospheric origin, the net release of CO₂ to the atmosphere is thus zero. Comparatively, because a fossil fuel-derived propylene glycol and fossil-derived 1,3-propanediol contains three carbon atoms which originate from a fixed carbon source (i.e., the fossil fuel), degradation of one molecule of fossil fuel-derived propylene glycol or 1,3-propanediol results in a net release of three molecules of CO₂ into the atmosphere. Similarly, because fossil fuel-derived ethylene glycol contains two carbon atoms, which originate from a fixed carbon source, degradation of one molecule of fossil fuel-derived ethylene glycol results in a net release of two molecules of CO₂ into the atmosphere.

[0026] In order to quantify the CO₂ released for one kilogram of each ethylene glycol, propylene glycol, chemical 1,3-propanediol and “fermentatively-derived” 1,3 propanediol (Bio-PDO™), the product weight (1 kg) is divided by its molecular weight. For each carbon atom present in the molecule, one molecule of CO₂ is released. The molecules

of CO₂ are multiplied by the molecular weight of CO₂ (44 kg/kmole) to quantify the impact of CO₂ release (kg) per one unit (kg) of product.

Fossil-Fuel Based Carbon Feedstock Release

[0027] 1 kg of fossil fuel derived ethylene glycol*(1 kmol EG/62.068 kg)*(2 kmol CO₂/1 kmol EG)*(44 kg CO₂/kmol CO₂)=1.4 kg CO₂

[0028] 1 kg of fossil fuel derived propylene glycol*(1 kmol PG/76.094 kg)*(3 kmol CO₂/1 kmol PG)*(44 kg CO₂/kmol CO₂)=1.7 kg CO₂

[0029] 1 kg of fossil fuel derived 1,3-propanediol*(1 kmol chem-PDO/76.094 kg)*(3 kmol CO₂/1 kmol chem-PDO)*(44 kg CO₂/kmol CO₂)=1.7 kg CO₂

Bio-Based Carbon Feedstock Balance

[0030] Capture:

[0031] 1 kg of Bio-PDO™*(1 kmol Bio-PDO™/76.094 kg)*(-3 kmol CO₂/1 kmol Bio-PDO™)*(44 kg CO₂/kmol CO₂)=-1.7 kg CO₂

[0032] Release:

[0033] 1 kg of Bio-PDO™*(1 kmol Bio-PDO™/76.094 kg)*(3 kmol CO₂/1 kmol Bio-PDO™)*(44 kg CO₂/kmol CO₂)=1.7 kg CO₂

[0034] Net:

[0035] -1.7 kg+1.7 kg=0 kg

[0036] This Bio-based Carbon Feedstock Balance result demonstrates that there are no anthropogenic CO₂ emissions from the biodegradation of the renewably sourced Bio-PDO. The term “anthropogenic” means man-made or fossil-derived.

Bio-Based Carbon

[0037] “Carbon of atmospheric origin” as used herein refers to carbon atoms from carbon dioxide molecules that have recently, in the last few decades, been free in the earth’s atmosphere. Such carbons in mass are identifiable by the present of particular radioisotopes as described herein. “Green carbon”, “atmospheric carbon”, “environmentally friendly carbon”, “life-cycle carbon”, “non-fossil fuel based carbon”, “non-petroleum based carbon”, “carbon of atmospheric origin”, and “biobased carbon” are used synonymously herein.

[0038] “Carbon of fossil origin” as used herein refers to carbon of petrochemical origin. Such carbon has not been exposed to UV rays as atmospheric carbon has, therefore masses of carbon of fossil origin has few radioisotopes in their population. Carbon of fossil origin is identifiable by means described herein. “Fossil fuel carbon”, “fossil carbon”, “polluting carbon”, “petrochemical carbon”, “petrocarbon” and carbon of fossil origin are used synonymously herein.

[0039] The abbreviation “IRMS” refers to measurements of CO₂ by high precision stable isotope ratio mass spectrometry.

[0040] The term “carbon substrate” means any carbon source capable of being metabolized by a microorganism wherein the substrate contains at least one carbon atom.

[0041] “Renewably-based” denotes that the carbon content of the 1,3-propanediol is from a “new carbon” source as measured by ASTM test method D 6866-05 Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis, incorporated herein by reference. This test method measures the C-14/C-12 isotope ratio in a sample and compares it to the C-14/C-12 isotope ratio in a standard 100% biobased material to give percent biobased content of the sample. “Biobased materials” are organic materials in which the carbon comes from recently (on a human time scale) fixated CO₂ present in the atmosphere using sunlight energy (photosynthesis). On land, this CO₂ is captured or fixated by plant life (e.g., agricultural crops or forestry materials). In the oceans, the CO₂ is captured or fixated by photosynthesizing bacteria or phytoplankton. A biobased material has a C-14/C-12 isotope ratio in range of from 1:0 to greater than 0:1. Contrarily, a fossil-based material, has a C-14/C-12 isotope ratio of 0:1.

[0042] A small amount of the carbon dioxide in the atmosphere is radioactive. This ¹⁴C carbon dioxide is created when nitrogen is struck by an ultra-violet light produced neutron, causing the nitrogen to lose a proton and form carbon of molecular weight 14 which is immediately oxidized in carbon dioxide. This radioactive isotope represents a small but measurable fraction of atmospheric carbon. Atmospheric carbon dioxide is cycled by green plants to make organic molecules during the process known as photosynthesis. The cycle is completed when the green plants or other forms of life metabolize the organic molecules producing carbon dioxide which is released back to the atmosphere. Virtually all forms of life on Earth depend on this green plant production of organic molecule to produce the chemical energy that facilitates growth and reproduction. Therefore, the ¹⁴C that exists in the atmosphere becomes part of all life forms, and their biological products. These renewably based organic molecules that biodegrade to CO₂ do not contribute to global warming as there is no net increase of carbon emitted to the atmosphere. In contrast, fossil fuel based carbon does not have the signature radiocarbon ratio of atmospheric carbon dioxide.

[0043] Atmospheric origin and fixed carbon source as used herein are relative terms in that the time period of when CO₂ is of atmospheric or fixed origin relates to the life cycle of the 1,3-propanediol. Thus, while it is quite possible that, at one time, carbon from a fossil fuel was found in the atmosphere (and, as a corollary, that atmospheric CO₂ may one day be incorporated into a fixed carbon source), for purposes herein carbon is considered to be from a fixed carbon source until it is released into the atmosphere by degradation.

[0044] Assessment of the renewably based carbon in a material can be performed through standard test methods. Using radiocarbon and isotope ratio mass spectrometry analysis, the biobased content of materials can be determined. ASTM International, formally known as the American Society for Testing and Materials, has established a standard method for assessing the biobased content of materials. The ASTM method is designated ASTM-D6866.

[0045] The application of ASTM-D6866 to derive a “biobased content” is built on the same concepts as radiocarbon dating, but without use of the age equations. The analysis is

performed by deriving a ratio of the amount of radiocarbon (^{14}C) in an unknown sample to that of a modern reference standard. The ratio is reported as a percentage with the units “pMC” (percent modern carbon). If the material being analyzed is a mixture of present day radiocarbon and fossil carbon (containing no radiocarbon), then the pMC value obtained correlates directly to the amount of Biomass material present in the sample.

[0046] The modern reference standard used in radiocarbon dating is a NIST (National Institute of Standards and Technology) standard with a known radiocarbon content equivalent approximately to the year AD 1950. AD 1950 was chosen since it represented a time prior to thermo-nuclear weapons testing which introduced large amounts of excess radiocarbon into the atmosphere with each explosion (termed “bomb carbon”). The AD 1950 reference represents 100 pMC.

[0047] “Bomb carbon” in the atmosphere reached almost twice normal levels in 1963 at the peak of testing and prior to the treaty halting the testing. Its distribution within the atmosphere has been approximated since its appearance, showing values that are greater than 100 pMC for plants and animals living since AD 1950. It’s gradually decreased over time with today’s value being near 107.5 pMC. This means that a fresh biomass material such as corn could give a radiocarbon signature near 107.5 pMC.

[0048] Combining fossil carbon with present day carbon into a material will result in a dilution of the present day pMC content. By presuming 107.5 pMC represents present day biomass materials and 0 pMC represents petroleum derivatives, the measured pMC value for that material will reflect the proportions of the two component types. A material derived 100% from present day soybeans would give a radiocarbon signature near 107.5 pMC. If that material was diluted with 50% petroleum derivatives, it would give a radiocarbon signature near 54 pMC.

[0049] A biomass content result is derived by assigning 100% equal to 107.5 pMC and 0% equal to 0 pMC. In this regard, a sample measuring 99 pMC will give an equivalent biobased content result of 93%.

[0050] A sample of “fermentatively-derived” 1,3-propanediol was submitted by DuPont to Iowa State University for biobased content analysis using ASTM method D 6866-05. The results received from Iowa State University demonstrated that the above sample was 100% bio-based content (ref: Norton, Glenn. Results of Radiocarbon Analyses on samples from DuPont Bio-Based Materials—reported Jul. 8, 2005).

[0051] Assessment of the materials described herein were done in accordance with ASTM-D6866. The mean values quoted in this report encompasses an absolute range of 6% (plus and minus 3% on either side of the biobased content value) to account for variations in end-component radiocarbon signatures. It is presumed that all materials are present day or fossil in origin and that the desired result is the amount of biobased component “present” in the material, not the amount of biobased material “used” in the manufacturing process.

[0052] Results of Radiocarbon Analyses on Samples from DuPont Bio-Based

[0053] Materials

[0054] Reported Jul. 8, 2005

PRODUCT	BIOBASED CONTENT (%)
1,3-Propanediol	100

[0055] There may be certain instances wherein a detergent composition of the invention may comprise a combination of a biologically-derived 1,3-propanediol and one or more non biologically-derived glycol components, such as, for example, chemically synthesized 1,3-propanediol. In such occasions, it may be difficult, if not impossible to determine which percentage of the glycol composition is biologically-derived, other than by calculating the bio-based carbon content of the glycol component. In this regard, in the detergent compositions of the invention, the glycol component, and in particular, the 1,3-propanediol, can comprise at least about 1% bio-based carbon content up to 100% bio-based carbon content, and any percentage therebetween.

Purity

[0056] “Substantially purified,” as used by applicants to describe the biologically-produced 1,3-propanediol produced by the process of the invention, denotes a composition comprising 1,3-propanediol having at least one of the following characteristics: 1) an ultraviolet absorption at 220 nm of less than about 0.200 and at 250 nm of less than about 0.075 and at 275 nm of less than about 0.075; or 2) a composition having $L^*a^*b^*$ “b*” color value of less than about 0.15 and an absorbance at 270 nm of less than about 0.075; or 3) a peroxide composition of less than about 10 ppm; or 4) a concentration of total organic impurities of less than about 400 ppm.

[0057] A “b*” value is the spectrophotometrically determined “Yellow Blue measurement as defined by the CIE $L^*a^*b^*$ measurement ASTM D6290.

[0058] The abbreviation “AMS” refers to accelerator mass spectrometry.

[0059] By the acronym “NMR” is meant nuclear magnetic resonance.

[0060] By the terms “color” and “color bodies” is meant the existence of visible color that can be quantified using a spectrophotometer in the range of visible light, using wavelengths of approximately 400-800 nm, and by comparison with pure water. Reaction conditions can have an important effect on the nature of color production. Examples of relevant conditions include the temperatures used, the catalyst and amount of catalyst. While not wishing to be bound by theory, we believe color precursors include trace amounts of impurities comprising olefinic bonds, acetals and other carbonyl compounds, peroxides, etc. At least some of these impurities may be detected by such methods as UV spectroscopy, or peroxide titration.

[0061] “Color index” refers to an analytic measure of the electromagnetic radiation-absorbing properties of a substance or compound.

[0062] Biologically-derived 1,3-propanediol useful in detergent compositions disclosed herein has at least one of the following characteristics: 1) an ultraviolet absorption at 220 nm of less than about 0.200 and at 250 nm of less than about 0.075 and at 275 nm of less than about 0.075; or 2) a composition having $L^*a^*b^*$ "b*" color value of less than about 0.15 and an absorbance at 270 nm of less than about 0.075; or 3) a peroxide composition of less than about 10 ppm; or 4) a concentration of total organic impurities of less than about 400 ppm. A "b*" value is the spectrophotometrically determined Yellow Blue measurement as defined by the CIE $L^*a^*b^*$ measurement ASTM D6290.

[0063] The level of 1,3-propanediol purity can be characterized in a number of different ways. For example, measuring the remaining levels of contaminating organic impurities is one useful measure. Biologically-derived 1,3-propanediol can have a purity level of less than about 400 ppm total organic contaminants; preferably less than about 300 ppm; and most preferably less than about 150 ppm. The term ppm total organic purity refers to parts per million levels of carbon-containing compounds (other than 1,3-propanediol) as measured by gas chromatography.

[0064] Biologically-derived 1,3-propanediol can also be characterized using a number of other parameters, such as ultraviolet light absorbance at varying wavelengths. The wavelengths 220 nm, 240 nm and 270 nm have been found to be useful in determining purity levels of the composition. Biologically-derived 1,3-propanediol can have a purity level wherein the UV absorption at 220 nm is less than about 0.200 and at 240 nm is less than about 0.075 and at 270 nm is less than about 0.075.

[0065] Biologically-derived 1,3-propanediol can have a b^* color value (CIE $L^*a^*b^*$) of less than about 0.15.

[0066] The purity of biologically-derived 1,3-propanediol compositions can also be assessed in a meaningful way by measuring levels of peroxide. Biologically-derived 1,3-propanediol can have a concentration of peroxide of less than about 10 ppm.

[0067] It is believed that the aforementioned purity level parameters for biologically-derived and purified 1,3-propanediol (using methods similar or comparable to those disclosed in U.S. Patent Application No. 2005/0069997) distinguishes such compositions from 1,3-propanediol compositions prepared from chemically purified 1,3-propanediol derived from petroleum sources, as per the prior art.

Fermentation

[0068] "Biologically produced" means organic compounds produced by one or more species or strains of living organisms, including particularly strains of bacteria, yeast, fungus and other microbes. "Bio-produced" and biologically produced are used synonymously herein. Such organic compounds are composed of carbon from atmospheric carbon dioxide converted to sugars and starches by green plants.

[0069] "Biologically-based" means that the organic compound is synthesized from biologically produced organic components. It is further contemplated that the synthesis process disclosed herein is capable of effectively synthesizing other monoesters and diesters from bio-produced alcohols other than 1,3-propanediol; particularly including ethylene glycol, diethylene glycol, triethylene glycol, 1,2-

propylene glycol, dipropylene diol, tripropylene diol, 2-methyl 1,3-propanediol, neopentyl glycol and bisphenol A. "Bio-based", and "bio-sourced"; "biologically derived"; and "bio-derived" are used synonymously herein.

[0070] "Fermentation" as used refers to the process of metabolizing simple sugars into other organic compounds. As used herein fermentation specifically refers to the metabolism of plant derived sugars, such sugar are composed of carbon of atmospheric origin.

[0071] Biologically-derived 1,3-propanediol can be obtained based upon use of the fermentation broth ("fermentatively-derived") generated by a genetically-engineered *Escherichia coli* (*E. coli*) previously disclosed in, for example, U.S. Pat. No. 5,686,276. However, other single organisms, or combinations of organisms, may be used to biologically produce 1,3-propanediol, using organisms that have been genetically-engineered according to methods known in the art. "Fermentation" refers to a system that catalyzes a reaction between substrate(s) and other nutrients to product(s) through use of a biocatalyst. The biocatalysts can be a whole organism, an isolated enzyme, or any combination or component thereof that is enzymatically active. Fermentation systems useful for producing and purifying biologically-derived 1,3-propanediol are disclosed in, for example, Published U.S. Patent Application No. 2005/0069997 incorporated herein by reference.

[0072] The biologically derived 1,3-propanediol (Bio-PDO) for use in the current invention, produced by the process described herein, contains carbon from the atmosphere incorporated by plants, which compose the feedstock for the production of Bio-PDO. In this way, the Bio-PDO used in the compositions of the invention contains only renewable carbon, and not fossil fuel based, or petroleum based carbon. Therefore the compositions of the invention have less impact on the environment as the propanediol used in the compositions does not deplete diminishing fossil fuels and, upon degradation releases carbon back to the atmosphere for use by plants once again. Thus, the present invention can be characterized as more natural and having less environmental impact than similar compositions comprising petroleum based glycols.

[0073] Moreover, as the purity of the Bio-PDO utilized in the compositions of the invention is higher than chemically synthesized 1,3-propanediol and other glycols, risk of introducing impurities that may cause irritation is reduced by its use over commonly used glycols, such as propylene glycol.

[0074] This 1,3-propanediol of the invention can be isolated from the fermentation broth and is incorporated into detergent compositions of the invention, by processes as are known to those of ordinary skill in the applicable art.

Detergent Compositions

[0075] As mentioned above, Bio-PDO can be incorporated in numerous concentrations as a glycol component. For example, Bio-PDO can be part of or the sole glycol component of detergent compositions.

[0076] It is contemplated herein that other renewably-based or biologically-derived glycols, such as ethylene glycol, diethylene glycol, triethylene glycol, 1,2 propylene glycol, dipropylene glycol, tripropylene glycol, neopentyl

glycol and bisphenol A, among others, can be used in the detergent compositions of the present invention.

[0077] In detergent compositions, the glycol component typically is an emulsifier and/or phase stabilizer a hydro-trope/solvent or an enzyme stabilizer.

Forms of the Composition

[0078] The composition of the invention can take a variety of physical forms including granular, gel, tablet, bar and liquid forms. These compositions include a so-called concentrated granular detergent composition adapted to be added to a washing machine by means of a dispensing device placed in the machine drum with the soiled fabric load.

[0079] Exemplary detergents include, but are not limited to, hand dish-washing detergents; machine dish-washing detergents, including solid block detergents; solid laundry detergents, liquid laundry including light-duty liquid detergents (LDLD) and heavy-duty liquid detergents (HDLD); organic or inorganic clothing softeners, laundry bar soaps and car wash detergent, among others.

[0080] The detergent compositions of the invention can comprise any form known or used in the art, such as powders, liquids, granules, gels, pastes, tablets, small bags, bars, and double-partitioned containers, sprays or foamed detergents and other homogenous or multi-phase daily detergent product forms. The products can be manually used or coated, and/or can be used in a constant or freely variable amount of use, or by automatic charge means, or can be used in electric products such as washing machines. These products can have a wide range of pH of, e.g., from 2 to 12 or more, and several tens gram-equivalent, per 100 g of the formulation, of NaOH may be added. These products can have a wide range of preliminary alkalinity. Both high suds and low suds detergents are included.

[0081] Light-Duty Liquid Detergents (LDLD) compositions include LDLD compositions containing magnesium ions for improving surface activity and/or organic diamines and/or various foam stabilizers and/or suds boosters, such as amine oxides and/or skin feeling improvers of surfactant and relaxing agents and/or enzyme types including protease, and/or sterilizers.

[0082] Heavy-Duty Liquid Detergents (HDLD) compositions include all of so-called "structured" or multi-phase and "non-structured" or isotropic liquid types, and generally include aqueous or non-aqueous bleaching agents, and/or enzymes, or do not include bleaching agents and/or enzymes.

[0083] Heavy-duty granular detergents (HDGD) compositions include both of a so-called "compact" or coagulated, or non-spray dried type and a so-called "floculated" or spray dried type. These compositions include both of a phosphate addition type and a phosphate non-addition type. Such detergents can include a type comprising a more general anionic surfactant as a substrate, or may be a so-called "highly nonionic surfactant" type comprising a generally nonionic surfactant held on an absorbent, for example, in or on the surface of a zeolites or other porous inorganic salt.

[0084] Softener (STW) compositions include various types of granular or liquid products that are softened by

laundry, and can generally include organic (such as quaternary) or inorganic (such as clay) softeners.

[0085] Bar Soap (BS & HW) compositions include laundry bars and include both of a type comprising a synthetic detergent and a soap as substrates and a type containing a softener. Such compositions include compositions manufactured by general soap manufacture techniques, such as pressure molding, or techniques that are not so general, such as casting and absorption of surfactant into a porous support. Other hand wash detergents are also included.

[0086] Fabric softeners (FS) include both of the conventional liquid and concentrated liquid types and kinds to be added by dryers or supported by a substrate. Other fabric softeners include those that are solid.

[0087] Special purpose cleaners (SPC) including the following products are also considered detergents for purposes of this invention: house-hold dry detergent modes, pre-treatment products of laundry bleaching agents, pre-treatment products for fabric protection, liquid higher fabric detergent types, especially high suds products, liquid bleaching agents including both of chlorine type and oxygen bleaching agent type, disinfectants, detergent aids, pre-treatment types including, for example, bleaching additives and "stain-stick" or special sudsing type cleaners, and anti-fading treatment by sunlight.

[0088] Specialty household cleanser (SHC) including the following products are also considered detergents for the purposes of this invention: all purpose cleansing in the form of creams, gels, liquids, and floor cleaners; all-purpose sprays such as for cleaning glass surfaces; wipes including all-purpose wipes, glass cleaners, floor cleaners and disinfectants; bathroom, shower and toilet cleaners; mildew cleaners and bleach.

[0089] The renewably-based, biodegradable 1,3-propanediol of the present invention is present in the aforementioned detergent compositions in amounts well known to those of ordinary skill in the appropriate art, typically up to about 25% by weight based on the weight of the total composition.

[0090] A typical nonspecific detergent formulation may include, but is not limited to, the following components by weight percent: 0.01-50.0% renewably-based, biodegradable 1,3-propanediol, 5.0-40.0% fatty acid and lower carbon number carboxylic acid esters, or mono and/or di-esters (a surfactant), and 1.0 to 70.0% of other surfactants or surfactant blends. Additionally, up to 5.0% by weight of the following components may be included: suds stabilizer/booster (preferred 1-10%), pH buffer (preferred 2-8%), enzymes, chelating agent, perfumes, builders, antioxidants, adjuvants, deteratives.

[0091] A basic formula embodiment for a Light Duty Liquid Detergent (LDLD) product may include 0.1-70% of a surfactant, 0.1-20% of Bio-PDO and q.s. to 100% water. LDLDs are commonly used in dishwashing applications, including automatic, manual, dishwasher rinses, plastic stain removers, pots & pans cleaners, pre-treatments and water softeners.

[0092] A basic formula embodiment for a Heavy Duty Liquid Detergent (HDLD) product may include 0.1-50% of a surfactant, 0.1-20% of Bio-PDO and q.s. to 100% water.

HDLs are commonly used in laundry applications, including laundry products containing bleach, hypo-allergenic, phosphate-free materials, dry cleaning materials, fabric conditioners, fabric enhancers, fabric finishes, fabric sizing, fabric softeners, pre-washes, stain removers and starches.

[0093] A basic formula embodiment for a Liquid Automatic Dishwasher Detergent (LADD) product may include 0.1-30% of a builder, 0.1-17% of a caustic/Bleach, 0.1-20% of Bio-PDO and q.s. to 100% of water. Applications include dishwash, liquid Pre-spotters, rinse aids, phosphate-free materials, hypochlorite-free materials and enzymes.

[0094] A basic formula embodiment for a specialty household cleanser (SHC) may include 0.1-70% of a surfactant, 0.1-50% of Bio-PDO, and q.s. to 100% water. Specific applications include, all purpose cleansing in the form of creams, gels, liquids, and floor cleaners; all-purpose sprays such as for cleaning glass surfaces; wipes including all-purpose wipes, glass cleaners, floor cleaners and disinfectants; bathroom, shower and toilet cleaners; mildew cleaners and bleach.

Detergent Components

[0095] Detergent compositions of the invention can contain from 0.01 to 99% by weight of one or more of any of the following general auxiliary components: builders, surfactants, enzymes, polymers, bleaching agents, bleach surfactants, catalyst components, various active components or special components such as dispersant polymers, color speckles, silver protecting agents, anti-fogging agents and/or corrosion inhibitors, dyes, fillers, sterilizers, alkaline agents, hydrotropic agents, antioxidants, enzyme stabilizers, perfumes, fragrances, plasticizers, carriers, processing aids, pigments, and solvents for liquid formulations.

[0096] In general, detergent components are included for converting a composition containing only the minimum essential components into a composition useful for the desired detergent purpose. It is recognized that those skilled in the art can readily determine which detergent components are required for desired detergent applications.

[0097] The precise nature of these additional components, and levels of incorporation thereof, will vary depending upon the physical form of the composition and the nature of the cleaning operation for which it is to be used.

Detergent Surfactants

[0098] The detergent compositions of the invention may contain any known detergent surfactant, and such surfactants are well known to those having skill in the art. Specifically, detergent surfactants of the invention can include anionic, nonionic, zwitter-ionic or amphoteric, betaine, and diamine are, surfactants that are known to be useful in detergent applications.

[0099] In all of the detergent surfactants, the chain length of the hydrophobic moiety is typically in the general range of from C8 to C20, and especially in the case of laundering with cold water, the chain length is often preferably in the range of from C8 to C18.

Detergent Enzymes

[0100] The detergent composition of the invention may use enzymes for various purposes such as removal of protein-based, carbohydrate-based, or triglyceride-based

soils from substrates, transfer inhibition of refugee dyes in fabric laundering, and fabric restoration. "Detergent enzymes" as used herein mean all enzymes having advantageous effects in washing, soil removal, and others in laundering.

Builders

[0101] Builder compositions are preferably those that control the hardness of minerals in washing water, especially Ca and/or Mg, thus simplifying the removal and/or dispersal of granular soils from the surface, while also optionally imparting an alkaline agent and/or buffering action. In granular or powder detergents, the builder may function as an absorbent for the surfactant. Alternatively, some compositions can be formulated in a completely water-soluble form, which may be either organic or inorganic, depending on the intended utility.

[0102] Suitable silicate builders include water-soluble types and hydrated solid types, and include other kinds such as those having a chain, layer or steric structure, amorphous solid silicates, and those as prepared such that they are used as not particularly structured liquid detergents.

[0103] Aluminosilicate builders, so-called zeolites, are particularly useful in granular detergents, but can be incorporated into pastes or gels. The aluminosilicates may be crystalline or amorphous, or may be natural or synthetic.

[0104] For the purpose of making it easy to control the hardness of minerals in the washing water, especially Ca and/or Mg, or of making it easy to remove granular solids from the surface, the composition of the invention may optionally contain detergent builders in place of or in addition to the foregoing silicates and aluminosilicates. The builders can be made to function in various mechanisms so as to form soluble or insoluble complexes with mineral ions by ion exchange or by providing mineral ions with the surface more adherent than the surface of the material to be cleaned. The amount of the builder can be varied widely depending on the final utility and physical form of the composition.

[0105] Here, suitable builders can be selected from the group consisting of phosphates and polyphosphates, especially sodium salts, carbonates, bicarbonates, sodium carbonate, organic mono-, di-, tri-, and tetracarboxylates, especially water-soluble non-surfactant carboxylates in acid, sodium, potassium or alkanolammonium forms, and aliphatic and aromatic type-containing oligomers or water-soluble low-molecular polymer carboxylates. For example, for the purpose of pH buffer, these builders can be complemented by all of fillers or carriers that are important in the techniques of detergent compositions including borates or sulfates, especially sodium sulfate, and other stabilized surfactants and/or builders.

[0106] In the invention, builder mixtures can be used. In general, the builder mixture optionally comprises two or more usual builders, and is complemented by a chelating agent, a pH buffer, or a filler.

[0107] Examples of phosphorus-containing builders include polyphosphates, represented by tripolyphosphates, pyrophosphates, and glassy polymer metaphosphates, of alkali metals and ammonium and alkanolammoniums, and phosphonates.

[0108] Suitable carbonate builders include carbonates of an alkaline earth metal or an alkali metal, inclusive of carbonate minerals such as sodium bicarbonate and sodium carbonate, complex salts of sodium carbonate or potassium carbonate, and calcium carbonate.

[0109] As described herein, the “organic detergent builders” suitable for the use along with the alkylaryl sulfonate surfactant include polycarboxylate compounds including water-soluble non-surfactant dicarboxylates and tricarboxylates. More generally, the builder polycarboxylate has plural carboxylate groups, preferably at least three carboxylates. The carboxylate builder can be incorporated in an acidic or partially neutral, neutral or excessively basic form. In the case of the salt form, salts of alkali metals such as sodium, potassium, and lithium, or alkanolammonium salts are preferred. The polycarboxylate builder includes ether polycarboxylates.

[0110] Nitrogen containing builders including amino acids such as lysine, or lower alcohol amines like mono, di-, and tri-ethanolamine, try(hydroxymethyl)amino methane, 2-amino-2-methylpropanol, and disodium glutamate.

[0111] Citric acid salts such as citric acid and soluble salts thereof are a polycarboxylate builder important for, for example, heavy-duty liquid detergents (HDL) because they are available from resources that can be regenerated and are biodegradable. The citric acid salts can also be used in granular compositions especially in combination of zeolites and/or layered silicates. Oxydisuccinic acid salts are especially useful in such compositions and combinations.

[0112] In the detergent composition of the invention, any builders known in this field can be incorporated generally in an amount of from about 0.1 to about 50% by weight, more preferably 0.5 to 30% by weight and most preferably 1 to 25% by weight.

Oxygen Bleaching Agents

[0113] In one embodiment, the invention comprises an “oxygen bleaching agent” as a part or whole of the detergent composition. Any known oxidizing agents can be used. Alternatively, oxidizing agent bleaching agents such as systems of generating hydrogen peroxide by oxygen or an enzyme, or hypohalogenic acid salts, for example, chlorine bleaching agents such as hyposulfites, can also be used.

[0114] Examples of peroxide-based general oxygen bleaching agents include hydrogen peroxide, inorganic peroxohydrates, organic peroxohydrates, and organic peroxy acids including hydrophilic or hydrophobic mono- or diperoxy acids. These components may be peroxycarboxylic acids, peroxyimide acids, amidoperoxycarboxylic acids, or salts thereof including their calcium, magnesium or mixed cationic salts. Various kinds of peracids can be used in a liberated form or as precursor materials called “bleach surfactant” or “bleach promoters”, which release peracids corresponding to hydrolysis in the case of a combination with a supply source of hydrogen peroxide.

[0115] Inorganic peroxides, suproxides, organic hydroperoxides such as cumene hydroperoxide and t-butyl hydroperoxide, and inorganic peroxy acids and salts thereof, such as peroxosulfates, are also useful as the oxygen bleaching agent.

[0116] Mixed oxygen bleaching agent systems are generally effective as in mixtures of oxygen bleaching agents with known bleach surfactant, organic catalysts, enzyme catalysts, or mixtures thereof. Further, these mixtures can further contain brighteners, light bleaching agents, and dye transfer inhibitors of types that are well known in this field.

[0117] Hydroperoxides and peroxohydrates are organic salts, or more generally, inorganic salts that can readily release hydrogen peroxide. The peroxohydrates are a general example of a “hydrogen peroxide source” and include perborates, percarbonates, perphosphates, and persulfates. Preferred peroxohydrates include all of sodium carbonate hydroperoxide and equivalent commercially available “percarbonate” bleaching agents, and so-called sodium perborate hydrates, and sodium pyrophosphate hydroperoxide can also be used. Urea hydroperoxides are also useful as the peroxohydrate.

[0118] There are included inorganic peroxohydrates, organic peroxohydrates, hydrophilic or hydrophobic mono- or diperacids, organic peracids including peroxycarboxylic acids, peroxyimide acids, and amidoperoxycarboxylic acids, salts of calcium, magnesium, or mixed cationic salts.

[0119] In the detergent composition of the invention, any oxygen bleaching agents are added in such formulations preferably in ranges from about 0 to 15%, and most preferably from about 0.2 to 12%

[0120] Bleach Surfactant can be used as well. Examples of useful bleach surfactants include amides, imides, esters, and acid anhydrides. Generally, in such bleach surfactants, there is present at least one substituted or unsubstituted acyl moiety having a leaving group in the structure, R—C(O)—L. One alternative method of use comprises a combination of the bleach surfactant with a hydrogen peroxide supply source such as perborates and percarbonates. One or more peracid-forming moieties or leaving groups can be present. Mixtures of bleach surfactants can be also used.

[0121] The bleach surfactant can be used in an amount of up to 20% by weight, and preferably from 0.1 to 10% by weight of the composition. For the form of highly concentrated bleaching agent additive products or the form in which the bleach surfactant is used in an automatic charge device, it can be used in an amount of 40% by weight or more.

[0122] Transition Metal Bleaching Agent Catalysts can also be used in the invention. For example, manganese compounds can be optionally used as the bleaching compound to have a catalytic action. As useful cobalt bleaching catalysts, ones that are known may be used.

[0123] In addition to the above-enumerated bleach surfactant, Enzyme-Based Supply Sources of Hydrogen Peroxide. For instance, suitable hydrogen peroxide generating mechanisms include combinations of C1 to C4 alkanol oxidases and C1 to C4 alkanols, especially a combination of methanol oxidase (MOX) and ethanol. Bleaching-related other enzymatic materials such as peroxidases, haloperoxidases, and oxidases, superoxide molecular displacement enzymes, catalases, and their reinforcing agents, or more generally, inhibitors can be optionally used in the composition.

Oxygen Transfer Agents and Precursors

[0124] All known organic bleaching agent catalysts, oxygen transfer agents, or precursors thereof are also useful herein. These materials include their compounds themselves and/or precursors thereof, such as all of ketones suitable for manufacture of dioxiranes, and and/or dioxirane precursors or all different atom-containing analogues of dioxiranes. As preferred examples of such components, are especially included hydrophilic or hydrophobic ketones that manufacture the dioxiranes on the spot, along with monoperoxysulfate. Examples of such oxygen bleaching agents that are preferably used along with the oxygen transfer agent or precursor include percarboxylic acids and salts, percarbonic acids and salts, peroxy monosulfuric acid and salts, and mixtures thereof.

Polymeric Soil Releasing Agents

[0125] The composition of the invention can optionally comprise one or more soil releasing agents. The polymeric soil releasing agent is characterized by having hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of the laundry cycle to function as an anchor for the hydrophilic segments. This can enable stains occurring sequent to treatment with the soil releasing agent to be more easily cleaned in later washing procedures.

[0126] In the case of the use, the soil releasing agent generally accounts for from about 0.01 to about 10% by weight of the composition.

Clay Soil Removal/Anti-Redeposition Agents

[0127] The composition of the invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and anti-redeposition properties. Granular detergent compositions containing these compounds typically contain from about 0.01% to about 10.0% by weight of the water-soluble ethoxylated amines, and liquid detergent compositions typically contain about 0.01% to about 5% by weight of the water-soluble ethoxylated amines.

[0128] Preferred soil release and anti-redeposition agents are ethoxylated tetraethylenepentamine. Other preferred soil release removal/anti-redeposition agents are ethoxylated amine polymers, zwitter-ionic polymers, and amine oxides. Other soil release removal and/or anti-redeposition agents that are known in this field can also be used in the composition of the invention. Another type of the preferred anti-redeposition agent includes carboxy methyl cellulose (CMC)-based components.

Polymeric Dispersing Agents

[0129] Polymeric dispersing agents can be effectively used in an amount of from about 0.01 to about 10% by weight of the composition of the invention especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release, peptization, and anti-redeposition.

[0130] Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid forms. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid, and methylenemalonamic acid.

[0131] Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers that are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 1,000 to 500,000, more preferably from about 2,000 to 250,000, and most preferably from about 3,000 to 100,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts.

[0132] Acrylic acid/maleic acid-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 3,000 to 80,000, and most preferably from about 4,000 to 70,000. The ratio of acrylate to maleate segments in such copolymers generally ranges from about 9:1 to about 1:9, and more preferably from about 8:2 to 3:7. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts.

[0133] Copolymers of acrylic acid and/or maleic acid and a polyalkylene glycol can also be used as a preferred component of the dispersing/anti-redeposition agent. The copolymers are preferably graft polymers of acrylic acid and/or maleic acid and a polyalkylene glycol, copolymers of acrylic acid and/or maleic acid and an alkylene oxide adduct of allyl alcohol or isoprenol, and copolymers of acrylic acid and/or maleic acid and a polyalkylene glycol acrylate or methacrylate, and more preferably graft polymers of acrylic acid and/or maleic acid and a polyalkylene glycol and copolymers of acrylic acid and/or maleic acid and an alkylene oxide adduct of allyl alcohol or isoprenol.

[0134] The average molecular weight of the copolymers preferably ranges from about 2,000 to 100,000, more preferably from about 3,000 to 80,000, and most preferably from about 4,000 to 70,000.

[0135] Acrylic acid/acrylamide based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. The average molecular weight of such copolymers in the acid form preferably ranges from about 3,000 to 100,000, more preferably from about 4,000 to 20,000, and most preferably from about 4,000 to 10,000. The acrylamide content in such copolymers generally is less than about 50%, preferably less than about 20%, and most preferably about 1 to about 15%, by weight of the polymer.

[0136] Another polymeric component that can be incorporated is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal/anti-redeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about

100,000, preferably from about 1,000 to about 50,000, and more preferably from about 1,500 to about 10,000.

[0137] Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolites builders. Dispersing agents such as polyaspartate preferably have a (weight average) molecular weight of about 10,000.

[0138] In the detergent composition of the invention, Polymeric Dispersing Agents known in this field can be incorporated generally in an amount of from about 0.01 to about 15%, more preferably from 0.05 to 10%, then most preferably 0.1 to 5%.

Brighteners

[0139] In the detergent composition of the invention, any optical brighteners or other brightening or whitening agents known in this field can be incorporated generally in an amount of from about 0.01 to about 1.2% by weight. Such optical brighteners are often used in the case where the detergent is designed for fabric washing or processing applications.

Polymeric Dye Transfer Inhibiting Agents

[0140] The composition of the invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinylpyrrolidone polymers, polyamide N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents generally comprise from about 0.01 to about 10% by weight, preferably from about 0.01 to about 5% by weight, and more preferably from about 0.05 to about 2% by weight of the composition.

[0141] The optical brightener selected for use in the invention exhibits especially effective dye transfer inhibition performance benefits when used in combination with the polymeric dye transfer inhibiting agent. The combination of such selected polymeric materials with such selected optical brightener provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone.

Chelating Agents

[0142] The detergent composition of the invention may also optionally contain one or more chelating agents, especially chelating agents for transition metal coming from others. The transition metals generally seen in washing solutions include water-soluble, colloidal or granular iron and/or manganese and may sometimes associate as oxides or hydroxides. Preferred chelating agents are chelating agents that effectively inhibit such transition metals, especially inhibit such transition metals or their compounds to adhere to fabrics, and/or inhibit non-preferred redox reaction occurred in the washing medium and/or on the interface of the fabric or hard surface. The general chelating agents can be selected from the group consisting of amino carboxylates, amino phosphates, polyfunctionally-substituted aromatic chelating agents, and mixtures thereof.

[0143] The composition of the invention may also contain water-soluble methyl glycine diacetic acid salts as a chelat-

ing agent that can effectively be used together with insoluble builders such as zeolites and layered silicates.

[0144] If utilized, the chelating agent generally accounts for from about 0.1 to about 15% by weight of the composition. More preferably, if utilized, the chelating agent accounts for from about 0.1 to about 3.0% by weight.

Suds Suppressors

[0145] In the case where washing is required in intended utilities, especially washing by washing machines, compounds for reducing or suppressing the formation of suds can be incorporated into the composition of the invention. For other compositions, for example, compositions as designed for hand washing, high sudsing may be desired, and such components can be omitted. Suds suppression can be of particularly importance in the so-called "high concentration cleaning process" and in front-loading European-style washing machines (so-called drum type washing machines).

[0146] A very wide variety of materials may be used as suds suppressors. The composition of the invention generally comprises from 0% by weight to about 10% by weight of suds suppressors.

Fabric Softeners

[0147] Various through-the-wash fabric softeners can optionally be used in an amount of from about 0.5 to about 10% by weight to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners. Further, in the cleaning process of the invention, known fabric softeners including those of biodegradation type can be used in modes including the pre-treatment, main cleaning, post-laundry, and addition into washing machines and dryers.

Perfumes

[0148] Perfumes and perfumery ingredients useful in the compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, and esters. Also, included are various natural extracts and essences that can comprise complex mixtures of ingredients such as orange oil, lemon, oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, and cedar. Finished perfumes typically comprise from about 0.01 to about 2% by weight of the detergent composition, and individual perfumery ingredients can comprise from about 0.0001 to about 90% by weight of a finished perfume composition.

Esters

[0149] Esters can function as many of the above noted ingredients. While those in those having skill in the art can readily determine which esters are most appropriate to provide a particularly desired function, applications specifically note that esters used in this invention may include the esters produced, including all the appropriate conjugate mono and diesters, from biologically-derived 1,3 propanediol using organic carboxylic acids. Some esters in particular that are produced include propanediol distearate and monostearate, propanediol dilaurate and monolaurate, propanediol dioleate and monooleate, propanediol divalerate and monovalerate, propanediol dicaprylate and monocaprylate, propanediol dimyristate and monomyristate, pro-

panediol dipalmitate and monopalmitate, propanediol dibehenate and monobehenate, propanediol adipate, propanediol maleate, propanediol dioxalate, propanediol dibenzoate, propanediol diacetate, and all mixtures thereof.

Other Components

[0150] A wide variety of other ingredients useful in detergent compositions can be included in the composition, including other ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, and soil fillers for bar compositions. If high sudsing is desired, suds boosters such as C10 to C16 alkanolamides can be incorporated into the composition, typically in an amount of from 1% by weight to 10% by weight. C10 to C14 monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjuvant surfactants such as the amine oxides, betaines and sultanines noted above is also advantageous. If desired, water-soluble magnesium and/or calcium salts can be added typically in an amount of from 0.1% by weight to 2% by weight, to provide additional suds.

[0151] Various detergent ingredients employed in the composition can optionally be further stabilized by absorbing the ingredients onto a porous hydrophobic substrate, then coating the substrate with a hydrophobic coating. Preferably, the detergent ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the detergent ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended detergent function.

[0152] The liquid detergent composition can contain water and other solvents as diluents. Low-molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for stabilizing the surfactant, but polyols such as those having from 2 to about 6 carbon atoms and from 2 to about 6 hydroxyl groups (such as 1,3-propanediol, ethylene glycol, glycerin, and propylene glycol) can also be used. The composition can contain such diluents in an amount of from 5% by weight to 90% by weight, and preferably from 10% by weight to 50% by weight.

[0153] The detergent composition is preferably formulated such that, during use in aqueous cleaning operations, the wash water has a pH of from about 6.5 to about 12.5, preferably from 7 to 12, and more preferably from about 7.0 to about 11. Laundry products are typically at a pH of from 9 to 11. Techniques for controlling the pH at recommended usage levels include the use of buffers, alkalis, acids, etc.

[0154] The detergent compositions of the invention can contain any natural ingredients where appropriate. Natural ingredients include any natural or nature-derived ingredients similar in composition or in function to any of the ingredients listed above.

Liquid Laundry Detergents

[0155] While the following listing of ingredients is particularly suited for liquid laundry detergents, it is clearly within the scope of one having skill in the art to determine whether such ingredients may be useful for other detergent applications.

[0156] Bio-PDO is preferably provided in liquid laundry detergents at concentration ranges of about 0.1% to about 25%, more preferably about 0.5% to about 20% and most preferably about 1% to about 15%

Thickeners

[0157] The physical stability of the liquid product may be improved and the thickness of the liquid product may be altered by the addition of a cross linking polyacrylate thickener to the liquid detergent product as a thixotropic thickener.

PH Adjusting Components

[0158] The above liquid detergent product is preferably low foaming, readily soluble in the washing medium and most effective at pH values best conducive to improved cleaning performance, such as in a range of desirably from about pH 6.5 to about pH 12.5, and preferably from about pH 7.0 to about pH 12.0, more preferably from about pH 8.0 to about pH 12.0, and most preferably, less than about 9.0 pH. The pH adjusting components are desirably selected from sodium or potassium hydroxide, sodium or potassium carbonate or sesquicarbonate, sodium or potassium silicate, boric acid, sodium or potassium bicarbonate, sodium or potassium borate, and mixtures thereof. NaOH or KOH are the preferred ingredients for increasing the pH to within the above ranges. Other preferred pH adjusting ingredients are sodium carbonate, potassium carbonate, and mixtures thereof.

Low Foaming Surfactant

[0159] The liquid nonionic surfactant detergents that can be used to practice the present invention are preferably alkyl ethoxylates in non-chlorine bleach liquid ADW compositions. One example of a non-chlorine bleach stable surfactant is SLF18.®, manufactured by BASF Corporation. Alternatively, in chlorine bleach containing liquid ADW compositions, chlorine bleach stable low foaming surfactants are preferred and such surfactants are present in a range of from about 0.1% to about 10% by weight of the liquid composition. Such surfactants are generally known to one skilled in the art and need not be elaborated here, for purposes of brevity. An example of a chlorine bleach stable surfactant is Dowfax.®, anionic surfactant available from the Dow Chemical Company.

[0160] Examples of the nonionic surfactant include polyoxyalkylene alkyl ethers, polyoxyalkylene fatty acid esters, polyoxyalkylene sorbitan esters, polyoxyalkylene sorbitan fatty acid esters, polyoxyalkylene sorbitol fatty acid esters, polyoxyalkylene glycerin fatty acid esters, monoglycerides, sorbitan fatty acid esters, fatty acid monoethanolamides, fatty acid diethanolamides and alkyl polyglucosides.

[0161] Examples of the amphoteric surfactants include acetic acid betaines, amidoacetic acid betaines, sulfobetaines, amidosulfobetaines, phosphobetaines, alkylamine oxides, and amidoamine oxides. Of these, fatty acid amidopropylbetaines such as cocamidopropyl betaine and lauramidopropyl betaine are preferred. Include imidazoline derived amphoteric: disodium cocoa amphodipropionate.

[0162] Two or more of these surfactants may be used in combination. The surfactant is preferably contained in an amount of from 5 to 50 wt. %, more preferably from 10 to 30 wt. %, even more preferably from 10 to 20 wt. % based

on the detergent composition of the present invention, from the viewpoints of foaming property, liquid properties during use and detergency.

Silicones

[0163] The detergent composition of the present invention may contain silicones for further improvement in the conditioning effects. The silicones include dimethylpolysiloxanes (viscosity: 5 mm.sup.2/s to 20 million mm.sup.2/s), amino-modified silicones, polyether-modified silicones, methylphenylpolysiloxanes, fatty acid-modified silicones, alcohol-modified silicones, alkoxy-modified silicones, epoxy-modified silicones, fluorine-modified silicones, cyclic silicones and alkyl -modified silicones, of which dimethylpolysiloxanes are preferred. The content of the silicone in the detergent composition of the present invention is preferably from 0.01 to 10 wt. %. The detergent composition of the present invention may contain other conditioning components such as a cationic polymer (cationic cellulose, cationic guar gum, or the like). Their content in the detergent composition of the present invention is preferably from 0.1 to 5 wt. %.

General Liquid Components

[0164] The detergent composition of the present invention may contain, in addition, components employed ordinarily for detergent compositions according to the intended use. Examples of such components include humectants such as propylene glycol, glycerin, diethylene glycol monoethyl ether, sorbitol and panthenol; colorants such as dyes and pigments; viscosity regulators such as methyl cellulose, polyethylene glycol and ethanol; plant extracts; antiseptics; bactericides; chelating agents; vitamin preparations; anti-inflammatory agents; perfumes; ultraviolet absorbers; and antioxidants.

Solid and Semi-Solid Laundry Detergents

[0165] While the following listing of ingredients is particularly suited for solid laundry detergents, it is clearly within the scope of one having skill in the art to determine whether such ingredients may be useful for other detergent applications.

[0166] The solid laundry detergent compositions of the invention comprises a ratio of Bio-PDO to binder portion in the range of 1:20 to 20:1, by weight percentage; preferably in the range of from 1:5 to 5:1, and most preferably from 1:2 to 2:1 therefore 0.1 to 25%, 0.5 to 15%, 1 to 10% from about 0.001 wt % to about 0.5 wt %, more preferably from about 0.1 wt % to about 0.25 wt %, and most preferably from about 0.25 wt % to about 0.1 wt % bio-PDO.

[0167] Preferably, the detergent composition has a particle size distribution such that no more than 10 wt % by weight of the composition, has a particle size greater than 850 micrometers, and no more than 10 wt % by weight of the composition, has a particle size less than 250 micrometers.

[0168] The composition optionally comprises one or more adjunct components. The adjunct components are typically selected from the group consisting of other anionic surfactants, cationic surfactants, non-ionic surfactants, zwitterionic surfactants, other builders, polymeric co-builders such as polymeric polycarboxylates, bleach, other hydrotropes, chelants, enzymes, anti-redeposition polymers, soil-release polymers, polymeric soil-dispersing and/or soil-suspending

agents, dye-transfer inhibitors, fabric-integrity agents, fluorescent whitening agents, suds suppressors, fabric-softeners, flocculants, cationic fabric-softening components, perfumes and combinations thereof.

[0169] A suitable adjunct component may be an anionic surfactant other than the alkyl alkoxyated sulphate surfactant and the linear alkyl benzene sulphonate surfactant. Suitable other anionic surfactants are branched or linear C.sub.8-C.sub.18 alkyl sulphate surfactants. An especially suitable other anionic surfactants are methyl branched C.sub.8-C.sub.18 alkyl sulphate surfactants.

[0170] A suitable adjunct component may be an anionic surfactant other than the alkyl alkoxyated sulphate surfactant and the linear alkyl benzene sulphonate surfactant. Suitable other anionic surfactants are branched or linear C.sub.8-C.sub.18 alkyl sulphate surfactants. An especially suitable other anionic surfactants are methyl branched C.sub.8-C.sub.18 alkyl sulphate surfactants.

[0171] A suitable adjunct component may be a hydrotrope other than the alkoxyated alkyl alcohol. Suitable hydrotropes include sodium cumene sulphate, sodium toluene sulphate and sodium xylene sulphate.

Gel Detergents

[0172] While the following listing of ingredients is particularly suited for gel detergents, it is clearly within the scope of one having skill in the art to determine whether such ingredients may be useful for other detergent applications. Auto-dish washing formulations are most commonly used in gel form.

[0173] Bio-PDO is preferably provided in liquid laundry detergents at concentration ranges of about 0.1% to about 25%, more preferably about 0.5% to about 20% and most preferably about 1% to about 15%.

[0174] Preferably, the lamellar-phase gel laundry composition of the invention comprises from 1 to 8%, more preferably from 3 to 6%, by weight of a gelling agent.

[0175] Such a gelling agent may suitably be a fatty alcohol having the formula R.sub.1-(CHOH)-R.sub.2, wherein R.sub.1, R.sub.2 are independently selected from hydrogen and saturated or unsaturated, linear or branched, C.sub.1-C.sub.16 alkyl groups, whereby the total number of carbon atoms in the fatty alcohol is between 8 and 17.

[0176] Preferably a fatty alcohol gelling agent is used that has the above formula, wherein R.sub.1 is hydrogen and R.sub.2 is selected from saturated or unsaturated, linear or branched C.sub.9-C.sub.13 alkyl groups. Favorable results could generally be obtained when applying as gelling agent a fatty alcohol in which the total chain length is similar to the average chain length of the surfactants present in the formulation. Such a gelling agent is preferably selected from the group consisting of 1-decanol, 1-dodecanol, 2-decanol, 2-dodecanol, 2-methyl-1-decanol, 2-methyl-1-dodecanol, 2-ethyl-1-decanol, and mixtures thereof. Commercially available materials that are particularly suitable for use as gelling agent include Neodol 23 or Neodol 25 produced by Shell Chemical Co., Exxal 12 or Exxal 13 produced by Exxonmobil Chemical Co. and Isalchem 123 or Lialchem 123 produced by Sasol Chemical Co.

[0177] The gelling agent may also suitably be a non-neutralised fatty acid having the formula R₃-(COOH)—

R_4 , wherein R_3 and R_4 are independently selected from hydrogen and saturated or unsaturated, linear or branched C_1 - C_{22} alkyl groups, whereby the total number of carbon atoms in the fatty acid is between 10 and 23. Such a fatty acid gelling agent is preferably selected from oleic acid, lauric acid, myristic acid, palmitic acid, stearic acid, linoleic acid, linolenic acid and mixtures thereof.

[0178] Furthermore, the gelling agent may suitably be a naturally obtainable fatty acid selected from tallow, coconut, and pal kernel fatty acids.

Anionic Surfactant

[0179] The anionic surfactant that may be present in the gel composition of the invention is preferably selected from the group consisting of linear alkyl benzene sulphonates, alkyl sulphonates, alkylpolyether sulphates, alkyl sulphates and mixtures thereof.

Nonionic Surfactant

[0180] The surfactant system in the gel composition of the invention may also contain a nonionic surfactant.

[0181] Nonionic detergent surfactants are well-known in the art. They normally consist of a water-solubilizing polyalkoxyethylene or a mono- or di-alkanolamide group in chemical combination with an organic hydrophobic group derived, for example, from alkylphenols in which the alkyl group contains from about 6 to about 12 carbon atoms, dialkylphenols in which primary, secondary or tertiary aliphatic alcohols (or alkyl-capped derivatives thereof), preferably having from 8 to 20 carbon atoms, monocarboxylic acids having from 10 to about 24 carbon atoms in the alkyl group and polyoxypropylene. Also common are fatty acid mono- and di-alkanolamides in which the alkyl group of the fatty acid radical contains from 10 to about 20 carbon atoms and the alkylol group having from 1 to 3 carbon atoms. In any of the mono- and di-alkanolamide derivatives, optionally, there may be a polyoxyalkylene moiety joining the latter groups and the hydrophobic part of the molecule.

Builders

[0182] Builders in this embodiment that may be used according to the present invention include conventional alkaline detergent builders, inorganic or organic, which can be used at levels of from 0% to 50% by weight of the gel composition, preferably from 1% to 35% by weight.

[0183] Examples of suitable inorganic detergency builders that may be used are water soluble alkali metal phosphates, polyphosphates, borates, silicates, and also carbonates and bicarbonates. Specific examples of such builders are sodium and potassium triphosphates, pyrophosphates, orthophosphates, hexametaphosphates, tetraborates, silicates, and carbonates.

[0184] Examples of suitable organic detergency builders are: (1) water-soluble amino polycarboxylates, e.g. sodium and potassium ethylenediaminetetraacetates, nitrilotriacetates and N-(2 hydroxyethyl)-nitrilotriacetates; (2) water-soluble salts of phytic acid, e.g. sodium and potassium phytates; (3) water-soluble polyphosphonates, including specifically sodium and potassium salts of ethane-1,1-diphosphonic acid; sodium and potassium salts of methylene diphosphonic acid; sodium and potassium salts of

ethylene diphosphonic acid; and sodium and potassium salts of ethane-1,1,2-triphosphonic acid.

[0185] In addition, polycarboxylate builders can be used satisfactorily, including water-soluble salts of mellitic acid, citric acid, and carboxymethylsuccinic acid, salts of polymers of itaconic acid and maleic acid, tartrate monosuccinate, and tartrate disuccinate.

[0186] Desirably, the detergency builder is selected from the group consisting of carboxylates, polycarboxylates, aminocarboxylates, carbonates, bicarbonates, phosphates, phosphonates, silicates, borates and mixtures thereof.

[0187] Alkalimetal (i.e. sodium or potassium) citrate is most preferred builder material for use in the invention.

[0188] Amorphous and crystalline zeolites or aluminosilicates can also be suitably used as detergency builder in the gel composition of the invention.

Enzymes

[0189] Suitable enzymes for use in the present embodiment of the invention include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof, of any suitable origin, such as vegetable, animal bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity, thermostability, and stability to active bleach detergents, builders and the like. In this respect bacterial and fungal enzymes are preferred such as bacterial proteases and fungal cellulases.

[0190] Enzymes are normally incorporated into detergent composition at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, or freshness improving effect on the treated substrate. In practical terms for normal commercial operations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of detergent composition. Stated otherwise, the composition of the invention may typically comprise from 0.001 to 5%, preferably from 0.01 to 1% by weight of a commercial enzyme preparation.

[0191] Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Higher active levels may be desirable in highly concentrated detergent formulations.

[0192] Suitable examples of proteases are the subtilisins that are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH-range of 8-12, developed and sold as ESPERASE® by Novozymes of Industries A/S of Denmark.

[0193] Other suitable proteases include ALCALASE®, EVERLASE®, LIQUANASE®, and SAVINASE®, and POLARZYME® from Novozymes, from PURAFECT®, and PROPERASE®, from Genencor International and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands.

[0194] Suitable lipase enzymes for use in the composition of the invention include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB-1,372,034. A very suitable

lipase enzyme is the lipase derived from *humicola lanuginosa* and available from Novozymes, Denmark Nordisk under the tradename LIPOLEASE®. Other suitable lipase enzymes are LIPEX®. from Novozymes.

[0195] Suitable cellulose enzymes for use in the composition of the invention include those produced by microorganism of the *Aspergillus* sp. Suitable cellulose enzymes are available under tradename CAREZYME®, CELLUZYME®, from Novozymes, PURADAX®, AND PRIMAFAST®LUNA from Genencor International.

[0196] Alpha-amylase enzymes can be produced by microorganism of *Bacillus* sp. and are available under the tradename as TERMAMYL®, STAINZYME®, DURAMYL®, from Novozymes, Denmark. Alpha-amylase enzyme is available as PURASTAR®. from Genencor International.

[0197] Mannanase enzymes are available under tradename MANNAWAY®, from Novozymes, Denmark and PURABRITE® from Genencor International.

[0198] Mixtures or blends of enzymes for use in the compositions of the invention are available under tradename as T-BLEND EVERLASE/DURAMYL/LIPEX®, T-BLEND SAVINASE/CAREZYME®, T-BLEND SAVINASE/LIPEX®, T-BLEND SAVINASE/LIPOLEASE®, T-BLEND SAVINASE/STAINZYME®, T-BLEND SAVINASE/TERMAMYL®, T-BLEND SAVINASE/TERMAMYL/CELLUZYME®, from Novozymes, Denmark.

Other Optional Components

[0199] In addition to the anionic and nonionic surfactants described above, the surfactant system of the invention may optionally contain a cationic surfactant.

[0200] Furthermore, alkaline buffers may be added to the compositions of the invention, including monethanolamine, triethanolamine, borax, and the like.

[0201] As another optional ingredient, an organic solvent may suitably be present in the gel composition of the invention, preferably at a concentration of up to 10% by weight.

[0202] There may also be included in the formulation, minor amounts of soil suspending or anti-redeposition agents, e.g. polyvinyl alcohol, fatty amides, sodium carboxymethyl cellulose or hydroxy-propyl methyl cellulose.

[0203] Optical brighteners for cotton, polyamide and polyester fabrics, and anti-foam agents such as silicone oils and silicone oil emulsions may also be used.

[0204] Other optional ingredients which may be added in minor amounts, are soil release polymers, dye transfer inhibitors, polymeric dispersing agents, suds suppressors, dyes, perfumes, colourants, filler salts, antifading agents and mixtures thereof.

Liquid Hand Dishwashing Detergents

[0205] While the following listing of ingredients is particularly suited for liquid hand dishwashing detergents, it is clearly within the scope of one having skill in the art to determine whether such ingredients may be useful for other detergent applications.

[0206] The concentration of the polyethylene glycol in the instant composition is 0.5 to 10 wt. %, more preferably 0.75 wt. % to 6 wt. %.

Anionic Surfactants

[0207] Anionic sulfonate surfactants suitable for use herein include the salts of C.sub.5-C.sub.20 linear alkylbenzene sulfonates, alkyl ester sulfonates, C.sub.6-C.sub.22 primary or secondary alkane sulfonates, C.sub.6-C.sub.24 olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

[0208] Anionic sulfate surfactants suitable for use in the compositions of the invention include linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, and alkyl phenol ethylene oxide ether sulfates.

[0209] Suitable anionic carboxylate surfactants include alkyl ethoxy carboxylates, alkyl polyethoxy polycarboxylate surfactants and soaps ("alkyl carboxyls").

[0210] An example of a preferred anionic surfactant (sulfonates & sulfates) would be the sodium salt of secondary alkane sulfonate commercially available under the tradename of Hostapur®. SAS (Clariant Corporation, Charlotte, N.C.).

[0211] Sulfonates: linear alkylbenzene sulfonate (LAS), alpha-olefin sulfonate (AOS), paraffin sulfonate (PS).

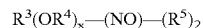
[0212] Sulfates: sodium lauryl sulfate (SLS), sodium lauryl ethoxy sulfate (SLES).

Water

[0213] The final ingredient in the inventive compositions is water. The proportion of water in the compositions generally is in the range of 35% to 85%, preferably 50% to 80% by weight of the usual composition.

Amine Oxide

[0214] Amine oxides useful in the present invention include long-chain alkyl amine oxides, ie., those compounds having the formula:



[0215] wherein R³ is selected from an alkyl, hydroxyalkyl, acylamidopropyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms, preferably 8 to 16 carbon atoms; R⁴ is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, preferably 2 carbon atoms, or mixtures thereof; x is from 0 to 3, preferably 0; and each R⁵ is an alkyl or hydroxyalkyl group containing from 1 to 3, preferably from 1 to 2 carbon atoms, or a polyethylene oxide group containing from 1 to 3, preferably 1, ethylene oxide groups. The R³ groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

[0216] These amine oxide surfactants in particular include C₁₀-C₁₈ alkyl dimethyl amine oxides and C₈-C₁₂ alkoxy ethyl dihydroxyethyl amine oxides and alkyl amido propyl amine oxide. Examples of such materials include dimethyloctylamine oxide, diethyldecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, dimethyldodecylamine oxide, dodecylamidopropyl dimethylamine oxide and dim-

ethyl-2-hydroxyoctadecylamine oxide. Preferred are C₁₀-C₁₈ alkyl dimethylamine oxide, and C₁₀-C₁₈ acylamidodimethylamine oxide.

Betaine

[0217] The betaines useful in the present invention are those compounds having the formula $R(R^1)_2N^+R^2COO^-$ wherein R is a C₆-C₁₈ hydrocarbyl group, preferably C₁₀-C₁₆ alkyl group, each R¹ is typically C₁-C₃, alkyl, preferably methyl, and R² is a C₁-C₅ hydrocarbyl group, preferably a C₁-C₅ alkylene group, more preferably a C₁-C₂ alkylene group. Examples of suitable betaines include coconut acylamidopropylbetaine; hexadecyl dimethyl betaine; C₁₂-C₁₄ acylamidopropylbetaine; C₁₂-C₁₈ acylamidohexyldiethyl betaine; 4-[C₁₄-C₁₆ acylmethylamidodiethylammonio]-1-carboxybutane; C₁₆-C₁₈ acylamidodimethylbetaine; C₁₂-C₁₆ acylamidopentanedithylbetaine; C₁₂-C₁₆ acylmethylamidodimethylbetaine, and coco amidopropyl betaine. Preferred betaines are C₁₂-C₁₈ dimethylammoniohexanoate and the C₁₀-C₁₈ acylamidopropane (or ethane)dimethyl (or diethyl)betaines. Also included are sulfobetaines (sultaines) of formula $R(R_1)_2N^+R_2SO_3^-$, wherein R is a C₆-C₁₈ Hydrocarbyl group, preferably a C₁₀-C₁₆ alkyl group, more preferably a C₁₂-C₁₃ alkyl group; each R₁ is typically C₁-C₃ alkyl, preferably methyl and R₂ is a C₁-C₆ hydrocarbyl group, preferably a C₁-C₃ alkylene or, preferably, hydroxyalkylene group. Examples of suitable sultaines are C₁₂-C₁₄ dihydroxyethylammonio propane sulfonate, and C₁₆-C₁₈ dimethylammonio hexane sulfonate, with C₁₂-C₁₄ amido propyl ammonio-2-hydroxypropyl sultaine being preferred.

Alkanolamide Compounds

[0218] The present formulation can include an alkanolamide compound such as an alkyl monoalkanol amide, an alkyl dialkanol amide, and mixtures thereof.

[0219] The formulation of the present invention can include a hydrotrope selected from the group consisting of ethanol, isopropanol, sodium xylene sulfonate, propylene glycol, sodium cumene sulfonate, urea, polyethylene glycol and mixtures thereof.

Solvents

[0220] The formulation of the present invention can include a solvent selected from the group consisting of alcohols (ethanol, isopropanol) glycols (propylene glycol, polyethylene glycol) polyols and polyethers (dipropylene glycol, dipropylene glycol methyl ether) and mixtures thereof. A variety of other water-miscible liquids such as lower alkanols, diols, other polyols, ethers, amines, and the like may be used in the present invention. Preferred are the C₁-C₄ alkanols. When present the composition will preferably contain at least about 0.01%, more preferably at least about 0.5%, even more preferably still, at least about 1% by weight of the composition of solvent. The composition will also preferably contain no more than about 20%, more preferably no more than about 10%, even more preferably, no more than about 8% by weight of the composition of solvent.

Inorganic Salt

[0221] The formulation of the present invention can include an inorganic or organic salt or oxide of a multivalent cation, particularly Mg.sup.++ which has phase stabilization properties. The multivalent cation salt or oxide provides

several benefits including improved cleaning performance in dilute usage, particularly in soft water areas, and minimized amounts of perfume required to obtain the microemulsion state. Magnesium sulfate, either anhydrous or hydrated (e.g., heptahydrate), is preferred as the magnesium salt. Good results also have been reported with magnesium oxide, magnesium chloride, magnesium acetate, magnesium propionate and magnesium hydroxide. These magnesium salts can be used with formulations at neutral or acidic pH since magnesium hydroxide will not precipitate at these pH levels.

[0222] Although magnesium is a preferred multivalent cation from which the salts (inclusive of the oxide and hydroxide) are formed, other polyvalent metal ions also can be used provided that their salts are nontoxic and are soluble in the aqueous phase of the system at the desired pH level.

Other Components

[0223] The liquid cleaning composition of this invention may, if desired, also contain other optional components either to provide additional effect or to make the product more attractive to the consumer. The following are mentioned by way of example: Colorants or dyes in amounts up to 0.5% by weight; preservatives or antioxidantizing agents, such as formalin, 5-bromo-5-nitro-dioxan-1,3; 5-chloro-2-methyl-4-isothiazolin--3-one, 2,6-di-tert.butyl-p-cresol, etc., in amounts up to 2% by weight; and pH adjusting agents, such as sulfuric acid or sodium hydroxide, as needed. Furthermore, if opaque compositions are desired, up to 4% by weight of an opacifier may be added. Preferably, the optional ingredients are selected from the group consisting of hydrotropes, perfumes, colorants, pH adjusting agents, preservatives, biocidal agents, inorganic salts, opacifiers, viscosity modifiers, and mixtures thereof

Specialty Household Cleansers (SHC)

[0224] Specialty household cleaners of the invention comprise Bio-PDO and one or more of the typical detergent ingredients set forth in the above sections. Those having skill in the art can readily determine appropriate ingredients to combine with the Bio-PDO in order to obtain a desired specialty household cleaner.

Viscosity

[0225] Some detergent compositions containing Bio-PDO may require approximately 30% less salt to adjust the viscosity than other compositions containing comparable glycols such as propylene glycol, butylene glycol, 2-methyl-1,3 propanediol etc. In other compositions, Bio-PDO may help maintain and build viscosity.

[0226] All of the compositions and methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of the present disclosure have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions and methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit, and scope of the invention. More specifically, it will be apparent that certain agents, which are chemically related, may be substituted for the agents described herein while the same or similar results would be achieved. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be

within the spirit, scope, and concept of the invention as defined by the appended claims.

EXAMPLES

[0227] The present invention is further defined in the following Examples. It should be understood that these Examples, while indicating preferred embodiments of the invention, are given by way of illustration only. From the above discussion and these Examples, one skilled in the art can ascertain the preferred features of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various uses and conditions.

Example 1

[0228]

<u>Liquid Automatic Dishwashing Detergent</u>	
Ingredients:	Wt. %
Water	54.30
Citric Acid	5.93
Bio-PDO	6.92
Carbopol™ 934	2.18
NaOH (50%)	5.74
Sodium Borate	0.99
Sodium Citrate	3.96
Sodium Formate	1.98
CaCl	0.10
Sodium Xylene Sulfanate (40%)	4.95
EO/PO Block Copolymer	1.98
Sodium Polyacrylate Mn1200 (45%)	9.89
Protease	0.69
Amylase	0.20
Lemon Essential Oil	0.20
Total	100.0

[0229] Procedure: Combine and stir water H₂O, citric acid and Bio-PDO™. Add Carbopol™ to mixture and stir until dissolved. Slowly add sodium hydroxide, and thereafter add remaining ingredients.

Example 2

[0230]

<u>Liquid Laundry Detergent</u>	
Ingredients:	Wt. %
Linear Dodecyl Benzene Sulfonate	6.93
Coconut Fatty Acid (C12-C18)	7.52
Tergitol 15-S-7	16.83
Triethanolamine	7.52
Bio-PDO	10.89
Citric Acid (50%)	6.33
KOH (45%)	9.30
Water	33.65
Protease	0.69
Amylase	0.20

-continued

<u>Liquid Laundry Detergent</u>	
Ingredients:	Wt. %
Lavendar Essential Oil	0.10
FD&C Blue 1	0.03
FD&C Red 40	0.01
Total	100.0

[0231] Procedure: Combine Linear Dodecyl Benzene Sulfonate, H₂O, Triethanolamine and Bio-PDO™, and stir mixture at 70° C. Add Tergitol. Melt the fatty acids and add to the mix. Slowly add KOH, then slowly add the citric acid. Cool mixture below 30° C. Add the enzymes, fragrance and dye.

Example 3

[0232]

<u>Liquid Laundry Detergent</u>	
Ingredients:	Wt. %
C12-C13 Linear Alcohol EO-7	4.0
Linear Dodecyl Benzene Sulfonate (60%)	14.0
Sodium Laureth Sulfate (60%)	5.0
Sodium Citrate	4.0
Sodium Borate	4.0
Bio-PDO	3.0
Tinopal CBS-X	0.1
Protease	0.7
Amylase	0.2
Monethanolamine	0.5
Coconut Fatty Acid (C12-C18)	2.0
Water	62.5
Total	100.0

[0233] Procedure: Ingredients were combined in the following order, allowing each to dissolve/disperse completely before adding the next ingredient: water, Tinopal CBS-X, sodium citrate, sodium borate, monoethanolamine, coconut fatty acid, C12-C13 linear alcohol EO-7, linear dodecyl benzene sulfonate (60%), sodium laureth sulfate (60%), protease, amylase, and Bio-PDOTM.

Example 4

[0234]

<u>Hand Dishwashing Liquid</u>	
Ingredients:	Wt. %
Bio-PDO	15.35
Linear Dodecyl Benzene Sulfonate	19.95
Triethanolamine	6.14
Cocamide DEA	10.74
Tergitol 15-S-7	4.60
Sodium Laureth-3EO Sulfate (28%)	4.60
Coco Amido Propyl Betaine	7.67
Polyquaternium-6 (20%)	3.07

-continued

<u>Hand Dishwashing Liquid</u>	
Ingredients:	Wt. %
NaCl (25%)	1.53
Sodium Xylene Sulfanate (40%)	6.55
Water	19.19
Lemon Essential Oil	0.58
FD&C Yellow 5	0.03
FD&C Red 40	0.01
Total	100.0

[0235] Procedure: Combine all liquid ingredients and stir mixture at 70° C. Gradually add Linear Dodecyl Benzene Sulfonate and stir until dissolved in mixture and mixture is clear. Cool mixture below 30° C and add fragrance and coloring.

Example 5

[0236]

<u>Hand Dishwashing Liquid</u>	
Ingredients:	Wt. %
Bio-PDO	15.56
Linear Dodecyl Benzene Sulfonate	20.23
Triethanolamine	6.22
Cocamide DEA	10.89
Tergitol 15-S-7	4.67
Sodium Lauryl Sulfate	4.67
Coco Amido Propyl Betaine	7.78
Polyquaternium-6 (20%)	3.11
NaCl (25%)	3.11
Sodium Xylene Sulfanate (40%)	3.50
Water	19.45
Lemon Essential Oil	0.78
FD&C Yellow 5	0.04
Total	100.0

[0237] Procedure: Combine all liquid ingredients and stir mixture at 70° C. Gradually add Sodium Lauryl Sulfate and stir until dissolved and liquid mixture is clear. Gradually add Linear Dodecyl Benzene Sulfonate and stir until dissolved and liquid mixture is clear. Cool mixture below 30° C. and add fragrance and coloring.

What is claimed:

1. A detergent composition comprising 1,3-propanediol and a surfactant, wherein said 1,3-propanediol has a bio-based carbon content of at least 1%.
2. The detergent composition of claim 1 further comprising a builder.
3. The detergent composition of claim 1 further comprising water.
4. The detergent composition of claim 1 wherein the 1,3-propanediol has at least 5% biobased carbon.
5. The detergent composition of claim 1 wherein the 1,3-propanediol has at least 10% biobased carbon.
6. The detergent composition of claim 1 wherein the 1,3-propanediol has at least 25% biobased carbon.

7. The detergent composition of claim 1 wherein the 1,3-propanediol has at least 50% biobased carbon.

8. The detergent composition of claim 1 wherein the 1,3-propanediol has at least 75% biobased carbon.

9. The detergent composition of claim 1 wherein the 1,3-propanediol has at least 90% biobased carbon.

10. The detergent composition of claim 1 wherein the 1,3-propanediol has at least 99% biobased carbon.

11. The detergent composition of claim 1 wherein the 1,3-propanediol has 100% biobased carbon.

12. The detergent composition of claim 1 wherein the 1,3-propanediol is biologically-derived.

13. The detergent composition of claim 12 wherein the biologically-derived 1,3-propanediol is biologically produced through a fermentation process.

14. A detergent composition comprising 1,3-propanediol and a builder, wherein said 1,3-propanediol has a bio-based carbon content of at least 1%.

15. The detergent composition of claim 14 further comprising water.

16. The detergent composition of claim 14 wherein the 1,3-propanediol has at least 5% biobased carbon.

17. The detergent composition of claim 14 wherein the 1,3-propanediol has at least 10% biobased carbon.

18. The detergent composition of claim 14 wherein the 1,3-propanediol has at least 25% biobased carbon.

19. The detergent composition of claim 14 wherein the 1,3-propanediol has at least 50% biobased carbon.

20. The detergent composition of claim 14 wherein the 1,3-propanediol has at least 75% biobased carbon.

21. The detergent composition of claim 14 wherein the 1,3-propanediol has at least 90% biobased carbon.

22. The detergent composition of claim 14 wherein the 1,3-propanediol has at least 99% biobased carbon.

23. The detergent composition of claim 14 wherein the 1,3-propanediol has 100% biobased carbon.

24. The detergent composition of claim 14 wherein the 1,3-propanediol is biologically-derived.

25. The detergent composition of claim 24 wherein the biologically-derived 1,3-propanediol is biologically produced through a fermentation process.

26. A detergent composition comprising 1,3-propanediol wherein said 1,3-propanediol has an ultraviolet absorption at 220 nm of less than about 0.200 and at 250 nm of less than about 0.075 and at 275 nm of less than about 0.075.

27. The detergent composition of claim 26 wherein said 1,3-propanediol has a "b" color value of less than about 0.15 and an absorbance at 275 nm of less than about 0.050.

28. The detergent composition of claim 26 wherein said 1,3-propanediol has a peroxide concentration of less than about 10 ppm.

29. The detergent composition of claim 26 wherein said 1,3-propanediol has a concentration of total organic impurities in said composition of less than about 400 ppm.

30. The detergent composition of claim 26 wherein said 1,3-propanediol has a concentration of total organic impurities of less than about 300 ppm.

31. The detergent composition of claim 26 wherein said 1,3-propanediol has a concentration of total organic impurities of less than about 150 ppm.

32. A detergent composition comprising 1,3-propanediol wherein said 1,3-propanediol has a concentration of total organic impurities of less than about 400 ppm.

33. The detergent composition claim 32 wherein said 1,3-propanediol has a concentration of total organic impurities of less than about 300 ppm.

34. The detergent composition claim 32 wherein said 1,3-propanediol has a concentration of total organic impurities of less than about 150 ppm.

35. The detergent composition claim 32 wherein said 1,3-propanediol has a concentration of peroxides of less than about 10 ppm.

36. The detergent composition claim 32 wherein said 1,3-propanediol has a concentration of carbonyl groups of less than about 10 ppm.

37. A detergent composition comprising 1,3-propanediol, wherein the 1,3-propanediol in said composition has an anthropogenic CO₂ emission profile of zero upon biodegradation.

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